

Mechanical behavior of glass-filled epoxy resins: experiments, homogenization methods for syntactic foams, and applications

Tesi presentata per il
conseguimento del titolo di Dottore di Ricerca

Dottorato in Materiali per l'Ingegneria — XIII Ciclo
Università degli Studi di Brescia
Dipartimento di Ingegneria Civile

di

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Dicembre 2000

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Acknowledgments

Thanks are due to Professor Ezio Tempesti, formerly of the Department of Chemistry and Physics for Engineering and for Materials of the University of Brescia, for allowing access to the Applied Chemistry Laboratory and for providing the raw materials for experiments; to Professors Roberto Contro and Riccardo Pietrabissa for granting the use of the Laboratory of Biological Structure Mechanics of the Politecnico di Milano; to Professor Giorgio Donzella for allowing access to the Laboratory for Tests on Materials of the Department of Mechanical Engineering of the University of Brescia.

The author is indebted to Professor Francesco Genna for his invaluable guidance.

Dr. Michel Palumbo is gratefully acknowledged for his fundamental help in what concerned the material production.

Dr. Maria Prandini deserves my gratitude for her irreplaceable work in the parameter identification of the epoxy resin model.

Acknowledgments to Mr. Luca Martinelli, Dr. Virginio Quaglini, and Mr. Modestino Savoia for their assistance in the experimental work, to Mr. Leonardo Lauri for his help with the Scanning Electron Microscope, and to Mr. Gianmarco Calò, Mr. Alessandro Gamba, Mr. Ivan Guizzetti, Mr. Sergio Marini, and Mr. Gabriele Samuelli, who were involved in the present research during the preparation of their Laurea theses ([33], [49], and [103]).

Furthermore, the author wishes to thank anyone else who somehow helped to accomplish this work (and anybody tells you they helped, probably did).

The Finite Element code ABAQUS has been run at the Department of Civil Engineering, University of Brescia, Italy, under an academic license.

Finally, since some things are better left unsaid, let me just deeply thank anyone who supported this work through either love or friendship.

Sommario

Questa tesi si occupa principalmente dello studio del comportamento meccanico di materiali eterogenei costituiti da un aggregato in sfere cave di vetro (*filler*) disperso in una matrice in resina epossidica (*binder*). Questa morfologia è caratteristica di compositi chiamati *schiume sintattiche*, i cui singoli componenti omogenei (*fasi*), in genere, possono essere costituiti da qualsiasi materiale che soddisfi certi requisiti tecnologici. L'uso di un filler in vetro e una matrice in resina epossidica è comunque la scelta più comune, in quanto permette sia di ottenere schiume sintattiche con buone proprietà (macroscopiche) finali, sia di soddisfare al meglio i requisiti tecnologici per la produzione di tali compositi.

L'obiettivo di questa ricerca è lo sviluppo strumenti analitici in grado di predire il comportamento meccanico di schiume sintattiche, materiali sempre più utilizzati nella pratica ingegneristica, ma che a tutt'oggi vengono ancora progettati in base all'esperienza o a regole empiriche.

Al fine di ottenere modelli dipendenti dalle caratteristiche meccaniche e geometriche delle varie fasi, si è scelto di seguire un approccio micromeccanico basato sulla teoria dell'omogeneizzazione. Tale approccio, se da un lato permette di ottenere strumenti utili alla progettazione di materiali compositi, dall'altro, per essere seguito, richiede la conoscenza del legame costitutivo di ciascuna fase. In questa ricerca, il comportamento meccanico del vetro è stato sempre assunto elastico lineare fino a rottura, mentre si è appositamente sviluppato un legame costitutivo per descrivere il comportamento meccanico di resine epossidiche, per le quali non sembrano essere disponibili strumenti di calcolo adeguati per predirne il comportamento meccanico, nonostante si tratti materiali vastamente impiegati nell'ingegneria.

I principali argomenti trattati nella presente tesi possono essere riassunti

1. in una parte sperimentale, consistente nella produzione di provini sia di resine epossidiche che di schiume sintattiche e nelle prove meccaniche degli stessi;
2. nello sviluppo di una tecnica di omogeneizzazione capace di stimare accuratamente i moduli elastici di schiume sintattiche per un ampio spettro di parametri caratterizzanti le fasi costituenti;
3. nella validazione di questa tecnica di omogeneizzazione e nella sua applicazione alla progettazione di materiali compositi;
4. nello sviluppo di un legame costitutivo per resine epossidiche;
5. nell'analisi micromeccanica di schiume sintattiche in regime non lineare e anelastico.

Il primo punto costituisce la prima parte della tesi, in cui è inclusa la descrizione di come i materiali testati per questa ricerca sono stati prodotti. I punti 2 e 3 sono trattati nella seconda parte di questa dissertazione, dedicata all'omogeneizzazione in campo elastico lineare. Infine, la terza parte della tesi si occupa degli ultimi due argomenti, essendo rivolta allo studio del comportamento oltre il campo elastico e lineare dei materiali studiati.

La tecnica di omogeneizzazione in campo elastico lineare è stata sviluppata in modo tale da essere in grado di predire accuratamente le costanti elastiche di schiume sintattiche (i) costituite da fasi isotrope, (ii) il cui filler sia composto da sfere cave di diverse dimensioni, densità ed eventualmente materiale e (iii) in cui siano restaste imprigionate bolle d'aria nella matrice a causa delle modalità di produzione.

Come esempio di applicazione a un problema ingegneristico, tale tecnica di omogeneizzazione è stata utilizzata per la progettazione ottima di pannelli sandwich non convenzionali, impiegati nell'industria navale per la fabbricazione di scafi. Tali sandwich sono costituiti da lastre di resina fibrorinforzata tra loro interconnesse e suddivise da un cuore in schiuma sintattica. L'obiettivo della progettazione è consistito nell'ottenere, sotto vincoli dettati da considerazioni tecnologiche, il sandwich più leggero che soddisfasse un ulteriore vincolo sulla sua rigidità globale.

Il legame costitutivo per le resine epossidiche è stato sviluppato con il fine di descriverne il comportamento meccanico, sia ciclico che viscoso, nello stato vetroso e prima che la loro resistenza massima sia raggiunta. Le prove meccaniche hanno dimostrato che in tale regime deformativo le resine epossidiche esibiscono un comportamento prevalentemente viscoelastico non lineare. Tale modello è stato impiegato per studiare, attraverso simulazioni numeriche agli Elementi Finiti, il comportamento meccanico oltre il limite elastico lineare di schiume sintattiche.

L'omogeneizzazione analitica del comportamento meccanico di schiume sintattiche in regime non lineare e anelastico è stata basata su un legame semplificato per le resine epossidiche e sull'approntata tecnica di omogeneizzazione dei moduli elastici. L'estensione di tale tecnica al campo non lineare e anelastico è stata condotta sia tramite metodi noti di letteratura, sia attraverso lo sviluppo di un nuovo metodo di omogeneizzazione specificatamente sviluppato per schiume sintattiche.

I risultati ottenuti in questa ricerca sono stati parzialmente pubblicati, in forma generalmente più compatta, in [12], [13], [11], [9], [10], [15], [14], [98] e [16].

Summary

This thesis is mainly concerned with the investigation of the mechanical behavior of heterogeneous materials made up of glassy hollow spheres dispersed into an epoxy resin matrix. This peculiar composite morphology characterizes the so-called syntactic foams, whose phases can in general be constituted by any homogeneous material which meets proper technological specifications. However, the use of both glassy fillers and epoxy binders is the most common because this choice allows one to both obtain good properties for the final composite and best satisfy the technological requirements in the manufacturing stage.

The key goal of this research consists of providing analytical tools able to predict the mechanical behavior of such composites, which are being increasingly employed in the engineering practice, but still designed by means of rules of thumb. A micromechanical approach based on the homogenization theory has been followed, in order to obtain constitutive laws based on both geometrical and mechanical data of the phases.

Since the homogenization approach requires the knowledge of the constitutive laws of all the phases, the mechanical behavior of epoxy resins, interesting engineering materials in themselves and apparently not much studied in their glassy state, has been investigated as well.

The research herein reported involves the following steps:

1. performing experimental tests on both epoxy resins and syntactic foams in order to both get an insight into their mechanical behaviors and make results available to validate the analytical models;
2. the development of a linear elastic homogenization procedure able to accurately estimate the elastic moduli of syntactic foams for a wide range of constituent parameters;
3. the verification of the capability of such a homogenization method to design syntactic foams in the linear elastic range;
4. the development of a constitutive law for epoxy resins;
5. the micromechanical analysis of the syntactic foams behavior beyond the linear elastic range.

The first point is embodied in the first part of the thesis which also includes the description of the production modalities of both the epoxy resins and the syntactic foams tested for this research. Both the second and third points are treated in the second part of this dissertation, concerned with the homogenization methods in the linear elastic range. Finally, the third part of this thesis deals with the last two points and, in general, with the analysis of nonlinear and inelastic effects on the studied materials.

The linear elastic homogenization procedure has been developed to be suitable for syntactic foams (i) made up of isotropic phases, (ii) whose filler can be constituted by graded hollow spheres, possibly of different (isotropic) materials, and (iii) in which the imperfect vacuum manufacturing has left adventitious air bubbles entrapped in the matrix.

As an engineering application example, this model has been employed for the optimum elastic design of syntactic foamed sandwich panels used in the naval industry.

The constitutive law for epoxy resins has been developed in order to describe their behavior before the material strength is reached, which has been shown, through the experimental tests, to be mainly nonlinear viscoelastic. Such a constitutive model is needed to investigate the nonlinear and inelastic behavior of syntactic foams constituted by glassy fillers into epoxy matrixes, by means of a numerical homogenization based on Finite Element analyses.

The analytical homogenization of the syntactic foam behavior beyond the linear elastic range has been based on both the here developed linear elastic homogenization procedure and a simplified constitutive law for epoxy resins. The nonlinear and inelastic effects have been accounted for by both exploiting suitable literature theories and developing an ad hoc nonlinear homogenization scheme.

Part of the results obtained in this research has been published in a usually more compact form in [12], [13], [11], [9], [10], [15], [14], [98], and [16].

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Notation

An indicial notation will be adopted to indicate tensors with the following exceptions, for which boldface letters will be used: (i) the case in which tensors are used as implicit independent variables of a function (e.g., $\sigma_{ij} = f_{ij}(\boldsymbol{\varepsilon})$), (ii) the formalism needed to express the appurtenance of a tensor to a set (e.g., $\boldsymbol{x} \in \Gamma$), and (iii) when tensors are used to indicate independent functions in variational problems (e.g., $u(\boldsymbol{\sigma}) = \sup_{\boldsymbol{\varepsilon}} \{ \sigma_{ij} \varepsilon_{ij} - w(\boldsymbol{\varepsilon}) \}$).

We shall adopt lower case letters to indicate vectors and second-order tensors if they are referred to microscopic quantities, otherwise (i.e., for any tensor indicating macroscopic quantities and for higher order tensors) capital letters will be employed.

Chapter 1

Introduction

Syntactic foams (the first term coming from the Greek meaning “the placing of parts in a certain order”) are heterogeneous materials classifiable as *particulate composites*. This class of composites consists of materials made up of an aggregate, constituted by discrete particles approximately spherically shaped, embedded into a continuous phase, the so-called matrix or binder. From the morphological viewpoint, these heterogeneous materials are distinguished from the *fiber-reinforced composites* (in which the presence of fibers aligned along preferential directions usually gives high mechanical properties in those directions), from the *interpenetrating network composites*, made by two or more continuous phases, and from the *granular composites*, such as polycrystals, in which a continuous phase does not exist.

Syntactic foams are obtained by filling a polymeric matrix with a gas-filled aggregate usually consisting of hollow spherical inclusions. In most of the applications the matrix is made by an epoxy resin, that gives to the composite good temperature resistance since it maintains high stiffness at elevated temperatures, and the aggregate is constituted by glass, that contributes to the dimensional stability of these materials (i.e., they have low coefficient of thermal expansion over a wide temperature range).

In recent years, syntactic foams have been employed in many engineering applications, ranging from aerospace plug manufacturing to ablative heat shields for re-entry vehicles, underwater buoyancy aids, and, more recently, structural components such as hulls and bulkheads of ships and submarines; in these last cases syntactic foams have been employed also as the core materials of sandwiches. Besides, syntactic foams are also used as putties for fixing hydraulic structures and in the naval industry.

These applications often exploit several features typical of syntactic foams, beside the high *specific mechanical properties* (defined by the ratios between the values of the mechanical properties and the material density), such as the low dielectric constant value, the good ablation behavior, the good match to acoustic impedance of water (for sonar applications), and the good thermal and water insulation properties. One of the most exploited specific mechanical properties in naval engineering is the capability of withstanding considerable hydrostatic pressure. Moreover, the hollow filler allows the final material to have lower residual stresses than particulate composites filled with solid particles [104].

The use of syntactic materials as plug assist tooling, replacing conventional materials such as aluminum, wood, or felt, has become increasingly popular in the thermoforming industry; indeed, the low thermal conductivity and the low specific heat translate to

lower heat transfer which reduces warmup time and virtually eliminates material sticking to the plug. Typical applications in this field are on sheet-fed, rotary, or in-line machines; syntactic foams may be used with most commonly thermoformed materials, as well as some of the most exotic materials available today.

Furthermore, there is interest in employing syntactic foams for biomedical applications such as the core of artificial limbs or prostheses.

Syntactic foams are preferred to standard foams (containing blown gas bubbles only) when high specific mechanical properties are required, rather than just low density. Moreover, standard foams have the voids completely, or at least partly, connected to each other (reason for which they are often considered as interpenetrating network composites), feature that makes them difficult to use for underwater applications; on the contrary, syntactic foams show very low water absorption. Standard foams may become preferable because they can be produced at very low densities, unlike syntactic foams for which densities less than 0.1 g/cm^3 are almost impossible to achieve, assuming the absence of adventitious air bubbles entrapped in the matrix (vacuum manufacturing).

A comprehensive review of the technological research on syntactic foams until the mid eighties can be found in Shutov [104], where, by the way, many papers are quoted about the use of syntactic foams in naval, industrial, aerospace, and civil engineering.

For an optimal structural design, there is the need, for instance to allow numerical simulations on Finite Element codes, of developing constitutive models able to describe the material behavior of syntactic foams.

If such models are developed by means of a suitable micromechanical approach, they result, unlike the macroscopic phenomenological models, to be functions of the mechanical and geometrical data of the composite phases. This desirable feature allows one to even design the best composite for a given engineering application. Without the knowledge of such a constitutive model, the composite design may be a very expensive trial and error procedure which may even not lead to the best possible result. For instance, in the case of syntactic foams, after having decided the materials to be employed as matrix and hollow spheres, it is important to choose both the filler volume fraction and its gas content (which affects the *particle density*).

As far as we know, the constitutive modeling of syntactic foams is a rather unexplored area (see, for instance, the methods reviewed in [104], mostly either heuristic or based on unreal assumptions). Even the computation of the so-called *effective* (i.e., macroscopic) elastic moduli of such composites can be difficult if standard *homogenization techniques* (i.e., methods developed in order to link the microscopic and macroscopic composite behaviors) are employed; indeed, the presence of a void phase causes a poor behavior of methods which cannot properly take the connectedness of the matrix into account. Such a problem directly translates into the nonlinear range, whose description is even made more difficult by the dependence of the syntactic foam behavior on the constitutive laws of the phases. In fact, owing to the polymeric nature of the matrix, the prediction of the binder behavior itself may constitute a problem.

In this thesis, we shall focus on syntactic foams whose matrixes are made up of epoxy resins, which are known to be the best binders for syntactic foams [104] and are by themselves interesting materials for engineering.

Epoxy resins are being widely employed for structural applications, mostly when there is the need of connecting structural elements made up of different materials; for instance,

they are used to anchor steel bars into concrete (concrete joints) or timber (composite beams).

The use of epoxy resins as matrixes of both particulate and fiber-reinforced composite materials is anyway one of the most important applications in engineering; one meaningful and interesting instance is that already cited of sandwich panels filled with syntactic foam, in which the skins consist of fiber-reinforced epoxy resins. These sandwiches are being employed with increasing frequency in naval engineering applications when weight, water absorption, and strength are critical issues.

In all the above mentioned applications, epoxy resins are subjected to high stress gradients. To design such kinds of (micro)structures it is then definitely necessary to be able to predict how the stress and strain fields develop over these materials.

The subject of this dissertation is the development of constitutive models for epoxy resins and syntactic foams.

These materials have shown in laboratory tests to have very limited ductility at room temperature. In particular, syntactic foams filled with high volume fractions of glass hollow spheres, which are the most interesting for engineering applications, have exhibited a behavior nearly elastic-brittle and failed in compression at a deformation of the order of 5%. Therefore, all the studied models have been developed under the assumption of small strains.

The first step of this work has consisted in the preparation, instrumentation, and mechanical testing of a reasonably wide range of both epoxy resins and syntactic foams. Such a step has been necessary to get an insight into the mechanical behavior of these materials, whose experimental behavior, specially for the composites, is quite scarcely documented in the literature. Furthermore, the industrial nature of the epoxy resin batches makes different batches have slightly different properties. Therefore, it has been judged essential to produce and test also the plain epoxy resins used as matrixes for the syntactic foams.

In this thesis, we shall furnish an homogenization technique able to accurately predict the elastic constants of any syntactic foam whose final density, filler gradation, and filler volume fraction are known beside the elastic moduli of the phases.

As an example of engineering application of such a model, we shall make ready an optimum design procedure for syntactic foamed sandwiches in the linear elastic range; the goal of this optimization is of designing, under some technological constraints, the lightest sandwich whose stiffness is prescribed. To this purpose, we shall also propose an approximate but accurate method to evaluate the shear stiffness of sandwich beams.

For what the behavior beyond the linear elastic range is concerned, we shall both derive a model able to describe the nonlinear viscoelastic behavior of epoxy resins in the glassy state and propose models to estimate the nonlinear and inelastic behavior of syntactic foams, again by means of a homogenization approach.

The predictions of all the proposed models will be compared (i) with reference experimental results, (ii) with the new experimental results obtained in the course of this work, and (iii) with the results of numerical simulations.

Part I

Experimental results

Chapter 2

Material preparation

In this chapter, we report the production modalities of the specimens tested by us together with the description of how the mechanical behavior of different syntactic foams has been experimentally characterized.

Two different epoxy resins have been employed as matrixes for making different syntactic foams. Specimens of plain epoxy resins were also tested to characterize the matrix behavior.

The specimens were produced at both the Applied Chemistry Laboratory and the Mechanical Engineering Laboratory of the Faculty of Engineering of the University of Brescia.

Part of this chapter has already been published in [9].

2.1 Production of epoxy resin and syntactic foam

To obtain a syntactic foam there is the need of mixing two components: the matrix (also called binder) and the hollow spheres (i.e., the filler). For the syntactic foams produced by us, the matrix has always been constituted by an epoxy resin and the filler by hollow microspheres (i.e., hollow spheres whose outer radius is less than $100\ \mu m$). The binder is in turn constituted by a pure resin (epoxy prepolymer) and a hardener (or curing agent), which allows chemical bonds to arise among the molecules of the prepolymer in the so-called “curing” process. Different types of pure epoxy resins and curing agents have been mixed obtaining different matrixes and then different types of syntactic foams. The prepolymers employed in this research are:

- epoxy resin DGEBA (diglycidyl ether of bisphenol A), produced by Dow Chemicals under the name DER 332;
- epoxy resin SP Ampreg 20TM, produced by SP Systems, Montecatini Advanced Materials,

and the curing agents are:

- hardener DDM 32950, produced by Fluka (always used to cure the epoxy resin DGEBA DER 332);

- hardener Laromin C252, produced by BASF (used only once, in conjunction with the epoxy resin DGEBA DER 332, to make a syntactic foam: see section 4.2);
- curing agent “UltraSlow Hardener”, produced by SP Systems, Montecatini Advanced Materials (always employed to harden the epoxy resin SP Ampreg 20TM).

Since all these components are usually preserved in a state incompatible with the mixing operation, they need a preparation to be mixed.

At room conditions the hardener DDM 32950 is in a granular state; since its melting temperature is 92.5°C (Celsius degrees), we had to warm it up to 120°C on an electric plate (see figure 2.1) to make it liquid as fast as possible without getting into oxidization problems.

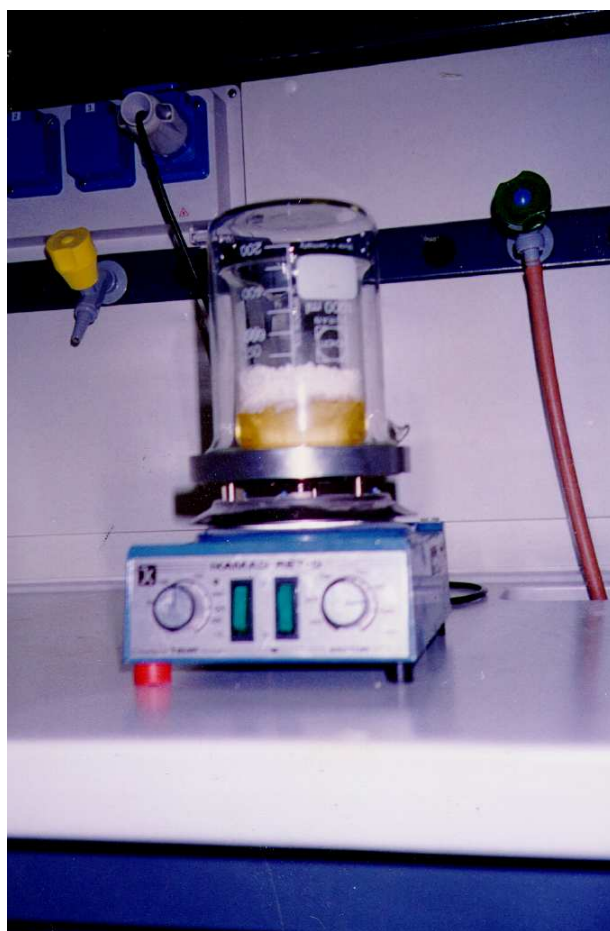


Figure 2.1: *The hardener melting*

The prepolymer DGEBA DER 332 is instead preserved at the temperature of -18°C to avoid secondary polymerization reactions; at this temperature it is in a crystallized state. To make it possible to mix it with the curing agent it is necessary to warm also the pure resin up to the temperature of 60°C .

The preparation of both the resin SP Ampreg 20TM and the UltraSlow Hardener is instead trivial, because at the room temperature both of them are in a liquid state.

When both the curing agent and the epoxy prepolymer are liquid, the stoichiometric amount of the former has to be transferred in the beaker containing the latter, which in turn is laid on a technical balance to check the amount of hardener decanted. This last expedient is essential because the amount of hardener to be melted before the decanting must be more than that strictly stoichiometric; indeed, in the decanting process an amount of curing agent that can not be quantified gets lost for crystallization in the contact with the top of the beaker, cooler than its bottom (which has a temperature of $\approx 120^{\circ}\text{C}$). This operation has then to be done as fast as possible, to avoid to lose too much hardener, and carefully, to be sure to transfer the right amount of curing agent into the beaker containing the pure resin (see figure 2.2).

The obtained mixture has to be stirred by hand with a glass rod until the filaments visible to the naked eye, due to the contact of hardener and prepolymer, disappear; usually this last process takes more or less 5 minutes. The glass rod is in turn warmed up at 60°C to avoid thermal shocks that would inhibit the curing. If just plain epoxy resin specimens



Figure 2.2: *The decanting operation*

have to be produced, at this point one can decant the mixture in the moulds. The moulds have to be internally spreaded with silicone to allow the specimens extraction after the material hardens. After the dies are filled with the resin, they must be left in an oven to allow the curing process, for a time and at a temperature dependent upon the resin itself. The epoxy resin DGEBA DER 332, cured with the hardener DDM 32950, needs to be kept in the oven for 24 hours at the temperature of 60°C ; instead, to cure the

epoxy resin SP Ampreg 20TM with UltraSlow Hardener there is the need to leave it in the oven for 24 hours at the temperature of 30°C, then for 16 more hours at the temperature of 50°C. These long times can be explained by considering that the curing process is highly exothermic; indeed, the stabilized glass transition temperature, T_g , of the epoxy resin DGEBA DER 332 hardened with the DDM 32950, is of about $T_g \approx 170^\circ\text{C}$ and its curing reaction easily brings the temperature of the specimens to more than 200°C: this means that the specimens have to be kept in the oven for a long time to cool them down (at 60°C) to avoid thermal shocks when they are removed from the oven. This last observation makes it clear that the choice between different prepolymers and hardeners is also dependent upon the easiness of keeping the exothermy of the curing process under control, in particular when operating with large amounts of material. Furthermore, the moulds have to be designed in such a way as to allow the resin to maintain its highest curing temperature for the longest possible time: this allows the resin to reach an actual glass transition temperature close to its stabilized value. To this purpose the moulds should be designed large enough to contain an amount of resin such that it can stay as warm as possible for a long time; the whole process of finding the conditions for having an efficient curing stage is empiric and the quality of the obtained resin can be a posteriori checked by measuring its actual glass transition temperature by means of a Differential Stream Calorimeter (DSC). Note that the resin SP Ampreg 20TM needs a two step curing process, because the hardener UltraSlow is actually a mixture of different curing agents which react at different temperatures.

We produced two, in principle different, kinds of epoxy resins, both made by the prepolymer DGEBA DER 332 cured with the hardener DDM 32950. This is because a few specimens of this epoxy resin have also been postcured at 180°C to be sure to stabilize their glass transition temperature, i.e., to build the maximum number of crosslinks between the prepolymer and the curing agent, number dependent upon the stoichiometry and the random topology of the mixture; indeed, although the epoxy prepolymer and the hardener are stoichiometrically mixed, it is not obvious at all that all the molecules get the chance to build all the chemical bonds they theoretically could, because of the random relative position between the prepolymer and the curing agent molecules (Oleinik, [92]).

Independently upon the constituents, any resin has to be degassed in the first half hour of the curing process; to do that the oven is connected with a vacuum pump.

To produce syntactic foam specimens, the filler has to be added to the not yet hardened epoxy resin. This operation is not trivial at all, by the way being dependent upon the wanted volume fraction of filler f in the composite. If the filler volume fraction is less than $\approx 50\%$ there is the need to use a “traditional” technique, characterized by mixing at various stages, by hand and mechanically, the binder and the filler; on the contrary, if the maximum content of filler compatible with its granulometry is the goal, one can not use the “traditional” technique owing to the high viscosity that the slurry would have, but it is necessary to employ the so-called “injection” technique, in which the binder is directly injected under vacuum in a die filled with hollow microspheres packed as tightly as possible by means of a vibrator. This last technique (Tempesti, [114]) does not allow the filler volume fraction to be known in advance before weighing the final specimen; furthermore, with the “injection” method it is quite difficult to avoid the presence in the composite of adventitious air bubbles entrapped in the matrix (in the following called “unwanted” voids, even if in some cases they are on purpose blown in the matrix in order

to lighten the composite).

Let us now go into more details about the two mixing techniques. The **“traditional” technique** consists of mixing the epoxy resin with the filler by transferring the former in the beaker containing the latter, placed on a technical balance. This decanting process has to be done very slowly to avoid turbulence which could disperse a significant amount of microspheres in the air because of their very low density. Note that also the hollow microspheres need to be warmed up at 60°C in order both to avoid thermal shocks in the resin when mixing them together and to make the slurry as fluid as possible; this is important because an excessive slurry viscosity could give rise to problems in the mixing process, with the result of producing a macroscopically inhomogeneous syntactic foam containing also a large amount of “unwanted” voids.

After mixing by hand with a glassy rod for a few minutes, the slurry becomes homogeneous enough to be put on a reactor thermostated at $T_r = 45^{\circ}\text{C}$, where the foam is degassed under vacuum and is continuously shaken mechanically (see figure 2.3). The

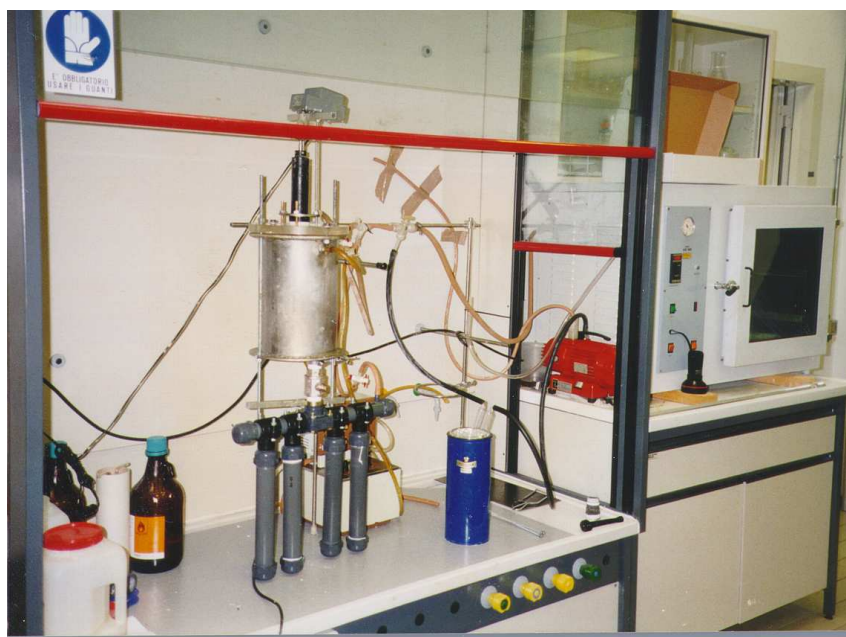


Figure 2.3: The devices employed with the “traditional” technique: the reactor, the dies, the vacuum pump, and the oven

temperature T_r must be set coming to an arrangement between the necessity of having a slurry fluid enough to be mixed and the need of slowing down the curing process as long as the slurry is not in the dies yet. This phase, lasting at least 90 minutes, needs to be accomplished very carefully; indeed, because of the large amount of air entrapped in the syntactic foam during the first shaking process made by hand, the degassing causes the slurry to inflate owing to the ascensional motion of the air bubbles. This phenomenon could cause an excessive volumetric increment of the mix which would give rise to the adhesion of a large amount of foam to the top of the reactor, making this portion of material

unavailable for the subsequent transferring in the dies because of the high viscosity of the slurry. To avoid this problem it is necessary to connect and to disconnect alternately the vacuum pump to the reactor, allowing the slurry to go back to the bottom of the reactor when the pump is disconnected after some swelling has been observed. To check the behavior of the slurry under vacuum, a reactor with a plexiglas top, much more capacious than the amount of the produced syntactic foam, has been designed and used.

Finally, the syntactic foam can be decanted in the moulds, which are also kept under vacuum until all the slurry is correctly placed into them. The moulds must be internally spreaded with silicone to allow the specimens extraction after their hardening.

With the **“injection” technique** the die, in which the filler is placed, must be thermostated like the reactor in the “traditional” technique, to allow the epoxy resin, injected using a piston system, to fill as much as possible the space left by the hollow microspheres in the mould; to obtain the best performance in this process the filler can be treated with plasma, which reduces the filler surface tension. Furthermore, the filler can be silanized (i.e., subjected to a surface treatment with chemical agents, [114]), in order to build chemical bonds between the glass of the filler and the epoxy resin. All these techniques, designed both to improve the adhesion between the filler and the matrix and to make the volume fraction of “unwanted” voids as small as possible, are still under study; the improvement of the adhesion between glass and epoxy resin should have effects on the nonlinear behavior of syntactic foams, whereas the presence of “unwanted” voids affects, as it will be shown in the second part of this thesis, the linear elastic behavior too.

After placing the syntactic foam into the dies, independently on the technique used to do that, the dies must be left in an oven set at a temperature and for a time dependent upon the resin employed, as above explained.

2.2 Geometry and instrumentation of the specimens

The Young modulus, the Poisson ratio, and the shear modulus were measured in compressive, tensile, torsional, and cyclic uniaxial tests, for both epoxy resins and syntactic foams; furthermore, biaxial tests were performed on specimens subjected to combined torsion and tension or compression to determine, under plane stress conditions, the failure envelope in its part where the principal stresses have opposite sign. Finally, uniaxial compressive creep tests were carried out to characterize the epoxy resin viscous behavior.

We produced specimens of different geometries depending on the various testing machines employed. Moreover, the production modalities affected the specimen size.

The compressive tests were accomplished on cylindrical specimens. The “traditional” technique allowed us to make cylindrical specimens of height $h = 100 \text{ mm}$ and base diameter $\phi = 30 \text{ mm}$; this type of specimen will be in the following labeled as CYL1; by employing the “injection” technique it was possible to produce specimens of diameter $\phi \approx 20 \text{ mm}$ and height h such that $h \approx 3.3\phi$ (CYL2): this smaller specimen was sometimes employed when the “traditional” technique was adopted also (see section 4.4). All the compressive tests on the plain epoxy resins were carried out on cylindrical specimens CYL1, with the exception of the creep tests, for which the height of the specimens was $h = 75 \text{ mm}$ instead of 100 mm ; this shorter cylinder will be labeled as CYL3.

In the compressive test the barrelling was prevented by inserting thin sheets of Teflon

between the loading platens and the specimen bases in such a way as to reduce the friction.

In the case in which the composite was made by the “traditional” technique, the tensile and cyclic tests were performed on dog-bone specimens (later indicated by the label DB1) whose dimensions are reported on figure 2.4; the dog-bone specimens made

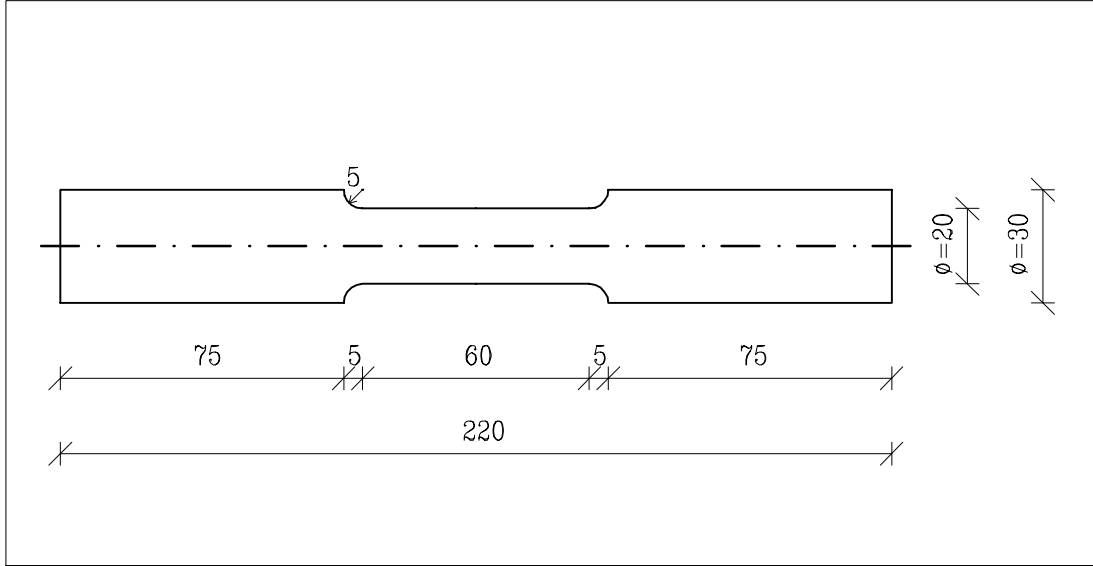


Figure 2.4: DB1 dog-bone specimen geometry (dimensions in mm)

by means of the “injection” are substantially different only in their parts which had to be gripped, that were turned at a diameter $\phi_s \approx 25 \text{ mm}$ instead of 30 mm . The specimen geometry reported in figure 2.4 was adopted also for the tensile and cyclic tests carried out on the plain epoxy resin DGEBA DER 332 cured with DDM 32950, whereas for the same type of tests on the epoxy resin SP Ampreg 20TM cured with UltraSlow Hardener smaller specimens were employed, characterized by a diameter $R_s = 17 \text{ mm}$ in the middle part, where the deformations were measured; they will be in the following called “small dog-bone” specimens and labeled as DB2.

Finally, for all the tests in which the samples were twisted, dog-bone specimens with grips of square section were employed, as reported in figure 2.5; we needed this geometry to make the specimens fit into the torsional testing machine. These specimens, which will be later denoted by the label DB3, were also adopted to carry out some uniaxial test; this is because in the last stage of the laboratory experience we tried to get a few failure envelope points and, for this purpose, we wanted to keep the same specimen geometry for any stress state (uniaxial or biaxial). The torsional testing machine was the only one available which allowed us to subject the specimens to a biaxial stress state by twisting and stretching them simultaneously.

Both the strain gauges and the adhesive used to instrument the specimens are produced by Hottinger Baldwin Messtechnik.

The syntactic foam specimens were instrumented with strain gauges of the type 1 – LY13 – 6/120, which can accurately measure a maximum strain of 5% in both tension and compression and have measuring grid of dimensions $6 \text{ mm} \times 2.8 \text{ mm}$, nominal resistance

equal to $120\ \Omega$, and a gauge factor of about 2.10 (the precise value of this last datum is dependent upon the batch). The specimens of plain epoxy resins subjected to tensile or compressive tests were instrumented with strain gauges of the type 1 – $LD20 - 6/120$, which are similar to the strain gauges 1 – $LY13 - 6/120$ but can measure strains up to 10% in both tension and compression. For the torsion tests the strain gauges type 1 – $XY21 - 1.5/120$ were employed; they can measure a maximum deformation of 5% and have measuring grid of dimensions $1.5\text{ mm} \times 2.5\text{ mm}$, nominal resistance equal to $120\ \Omega$, and a gauge factor of about 1.90. All the strain gauges were applied to the specimens by means of the one-component adhesive Z70.

For each elastic parameter measured, two strain gauges were applied on diametrically opposite positions on the specimens: this allows us, in the linear elastic range, to compensate measure errors due to the not perfectly centered load application, if it is the case. In

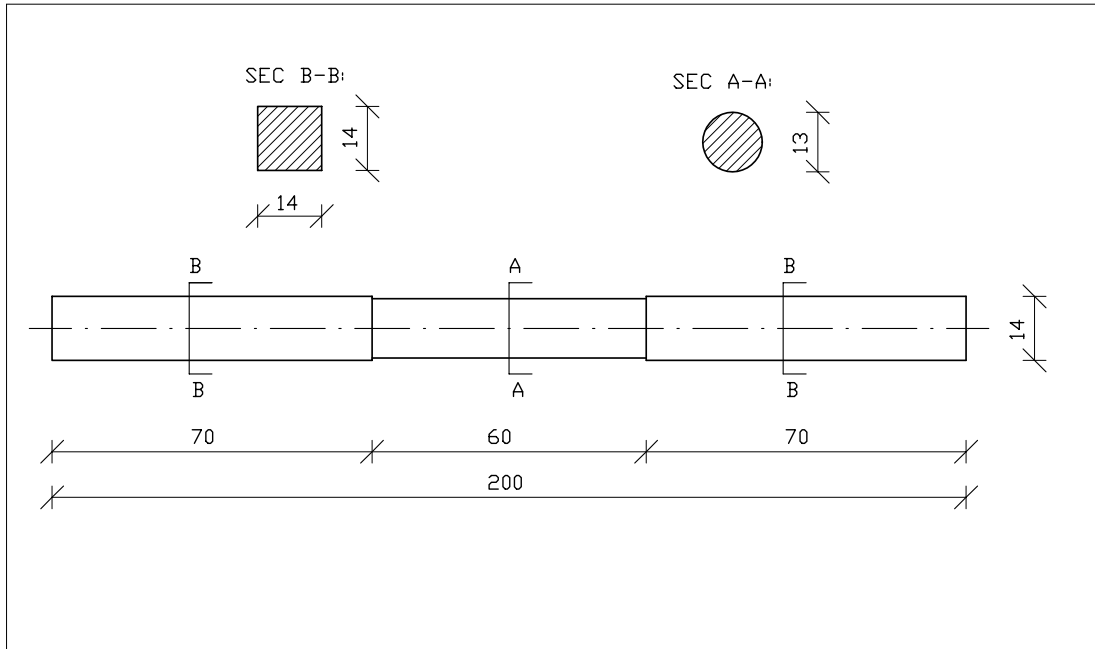


Figure 2.5: DB3 dog-bone specimen geometry (dimensions in mm)

the case of a uniaxial test, the normal Cauchy stress σ_n has been computed by means of the relation:

$$\sigma_n = \frac{P}{\pi r_0^2 (1 + \varepsilon_t)^2} \quad (2.2.1)$$

in which P is the axial force and r_0 is the nominal radius at the point where the transversal strain ε_t is recorded.

All the tests were performed at room temperature ($\approx 23^\circ\text{C}$) and, with the exception of the torsion tests and most of those carried out on the small dog-bone specimens, were performed by means of an Instron testing machine (model 1274) at the Laboratory for Tests on Materials “Pietro Pisa” of the Department of Civil Engineering, University of Brescia. The load, the displacement, and the strains were usually recorded at a frequency of 3 Hz

by a data acquisition system implemented by means of the “LabWindows” program. To check the measures, the applied displacement was recorded twice, using, beside the Instron internal measurement device, a linear voltage displacement transducer (LVDT); for the compressive tests the force acquisition was checked also, by means of a 10 *kN* load cell. All the uniaxial tests were done at a crosshead constant displacement rate variable from 0.2 *mm/min* to 10 *mm/min*; anyway, most of them were performed imposing a displacement rate of 1 *mm/min*. The elastic moduli dependence on the displacement rate will be discussed in chapter 3. Exception was made for the cyclic tests, in which different cycles were often done at different rates. The dog-bone specimens were gripped using oil pressure controlled tensile grip fixtures. The only tests accomplished by controlling the load instead of the displacement were the creep tests.

The Instron testing machine model 8501 of the Laboratory for Tests on Materials of the Department of Mechanical Engineering, University of Brescia, was used to perform tests on small dog-bone specimens.

The tests involving torsion were carried out on the MTS testing machine models 319.10.S and 858 Mini Bionix at the Laboratory of Biological Structure Mechanics of the Politecnico of Milano.

The elastic constants were computed by linear regressions on the set of data and computed values (e.g., the Cauchy stress) referred to the relevant longitudinal or shear strain data ranging from 0 to 0.004, regardless of the sign. In the rest of this first, experimental, part of the thesis, the term “elastic moduli” (referred for instance to the Young modulus and the Poisson ratio) will mean the measure by linear regression of the stress-strain slope in the range just defined, taken a priori as linear elastic range. This assumption will be discussed with respect to phenomena like viscoelasticity which can affect our measures, in order to try to correctly evaluate the *linear elastic constants*.

Chapter 3

Epoxy resins: experimental results

3.1 Introduction

This chapter is devoted to reporting the results obtained from the experiments carried out on specimens of plain epoxy resins. These results have partly been published, in a more compact form, in [11].

The mechanical characterization of the matrix employed to make a syntactic foam is obviously a fundamental step in predicting, by means of any kind of microscale approach (e.g., either theoretical or numerical), the macroscopic behavior of syntactic foams. Even when syntactic foams are filled with high volume fractions of hollow spheres, there is the need of having an accurate constitutive law describing the epoxy resin behavior to understand, for instance, the failure modalities, dependent upon the interaction between the matrix and the filler. Anyway, for any volume fraction of filler, the determination of the elastic moduli of the matrix is indispensable for applying any homogenization technique even in the linear elastic range.

Here, we are first of all interested in determining the elastic moduli. Other material parameters and features of the epoxy resin behavior, like strength, ductility, hysteretic behavior, viscosity, and fracture toughness, will be partly investigated by means of uniaxial tests only, with the exception of a few torsion and Charpy tests. It would obviously be interesting to investigate the temperature dependence of the mechanical behavior, but this is beyond the scope of the present work.

The mechanical behavior of several epoxy resins has been characterized, for instance, in [77] and [82]. These works, however, were mostly concerned with the study of plastic deformations, which, at least in uniaxial compression, are usually assumed to develop after the stress-strain curve flattens or reaches a maximum (corresponding to the material strength which is then assumed to be coincident to the yield stress) [82]. Instead, the tests here described will most of all focus on the behavior before yielding.

Yamini and Young [135] measured both the Young modulus and the strength of the epoxy resin DGEBA Epikote 828 produced by Shell cured with various amounts of triethylene tetramine (TETA), in order to find the dependence of measured material parameters on the resin composition. They found that for given testing conditions (i.e., temperature and testing rate), both the Young modulus and the strength decrease as the amount of hardener or the curing temperature are increased. Furthermore, they established that for a

given resin composition, both the Young modulus and the yield stress are increasing functions of the testing rate and decreasing functions of the temperature (below T_g). However, we shall not discuss the effects of both the curing agent amount and the temperature on the mechanical properties of the epoxy resins produced by us (as it may appear obvious owing to what reported in chapter 2).

Note that the industrial nature of the epoxy resin batches causes different batches to have slightly different properties. This fact, together with the randomness of the curing process (see section 2.1), made the material parameters of the tested epoxy resins difficult to be precisely determined.

First (section 3.2), we shall describe the tests on the epoxy resin made by the prepolymer DGEBA DER 332 cured with the hardener DDM 32950 (section 3.2), then (section 3.3) we shall report the experimental results concerning the epoxy resin SP Ampreg 20TM cured with UltraSlow Hardener (section 3.3).

The matrix of the syntactic foams produced by us (see chapter 4) has always been chosen between these two kinds of epoxy resins, with one exception only (see section 4.2) in which the prepolymer DGEBA DER 332 has been cured with the hardener Laromin C252. We did not test this plain epoxy resin, but it is known that the use of different hardeners affects the molecular weight between crosslinks and it is typical of thermoset polymers, as epoxy resins are, that the elastic moduli do not depend upon it (see, for instance, [92] and [80]). It is instead expected that the viscoelastic behavior and, most of all, the glass transition temperature T_g are affected from the hardener choice; for instance, Lee and McKenna, [78], using exactly the same prepolymer but the curing agent Jeffamine produced by Texaco Chemical Co., found $T_g = 42.4^\circ\text{C}$, sensibly less than the value found for the epoxy here described, $T_g \approx 170^\circ\text{C}$.

3.2 Epoxy resin DGEBA DER 332 cured with the hardener DDM 32950

This section is concerned with both the regular and the postcured epoxy resin made by the prepolymer DGEBA DER 332 cured with the hardener DDM 32950 (see section 2.1). The comparison between the mechanical behavior of the postcured samples and that of the regular ones will give an idea about the most convenient way of producing this epoxy resin and, then, syntactic foams made up of it.

Moreover, the aging of this epoxy resin was partly investigated by testing a few specimens one year after their production.

Figures 3.1–3.17 show the results obtained from 26 of the 30 tests carried out on this resin. Table 3.1 collects all the elastic constants computed from those tests.

In Table 3.1, as well as in the following Table 3.2, the symbol (*) means that the relevant elastic moduli were measured by a regression over a set of data whose corresponding maximum absolute value of the longitudinal strain was lower than 0.4%, whereas the ending *ng* in four sample labels in Table 3.1 means that those tests have not been plotted here owing to the low accuracy of the recorded data, which, anyway, were as many as needed to assure nice linear regressions for the elastic constant evaluation. The first column refers to the shape of the employed specimens (see section 2.2).

Unlike for the tests performed on the epoxy resin SP Ampreg 20TM (which will be

Sample	E [MPa]	ν	Rate [mm/min]	Aging [years]	Stress State	Cycle #	Postcuring
1 DB1	2856	-	0.2	0	tens	1	no
1ng DB1	2886	-	0.1	0	tens	1 (*)	no
2 CYL1	2814	0.408	0.2	0	comp	1	no
3 CYL1	2924	0.407	1	0	comp	1	no
5 CYL1	2836	0.404	1	0	comp	1	no
6 CYL1	2809	0.417	1	1	comp	1	no
7 CYL1	2992	0.416	1	1	comp	1	no
8 CYL1	2857	0.413	1	0	comp	1	no
9 DB1	2895	-	1	0	comp	1	no
9 DB1	2576	-	0.25	0	tens	2	no
10 DB1	2927	-	1	0	comp	1	no
10 DB1	2550	-	0.25	0	tens	2	no
11 DB1	2767	-	0.25	0	tens	1	no
11 DB1	2675	-	1	0	comp	2	no
12 DB1	2884	-	0.25	0	tens	1	no
12 DB1	2894	-	1	0	comp	2	no
14 DB1	2871	0.394	0.25	1	tens	1	no
14 DB1	2849	0.402	1	1	comp	2	no
20 CYL1	3231	0.464	10	1	comp	1	yes
21 CYL1	2513	0.434	10	1	comp	1	yes
22 DB1	2882	0.405	0.2	0	tens	1	yes
23 DB1	2826	-	0.25	0	tens	1	yes
23 DB1	2760	-	1	0	comp	2	yes
2ng DB1	2898	-	0.5	0	comp	1	yes
2ng DB1	2851	-	0.125	0	tens	2	yes
3ng DB1	2863	-	0.5	0	comp	1	yes
3ng DB1	2754	-	0.125	0	tens	2	yes
24 DB1	2808	-	1	0	comp	1	yes
24 DB1	2556	-	0.25	0	tens	2	yes
25 DB1	2826	-	0.25	0	tens	1	yes
25 DB1	2596	-	1	0	comp	2	yes
26 CYL1	2802	0.409	0.1	0	comp	1 (*)	yes
4ng DB1	3017	-	0.25	0	tens	1 (*)	yes

Table 3.1: Elastic moduli computed from displacement-controlled uniaxial tests on epoxy resin DGEBA DER 332 cured with DDM 32950

reported in section 3.3), we could not record enough data in the initial load ramp of the creep tests on the epoxy resin DGEBA DER 332 to be able to compute meaningful elastic constants; therefore, in Table 3.1, samples 15–19 are skipped and, then, only results from displacement-controlled tests are reported.

From Table 3.1, it is possible to compute the following Young modulus average values:

- compressive Young modulus on the regular (i.e., non-postcured) specimens: $E_c = 2861 \text{ MPa}$;
- compressive Young modulus on the postcured specimens: $E_c = 2809 \text{ MPa}$;
- tensile Young modulus on the regular specimens: $E_t = 2770 \text{ MPa}$;
- tensile Young modulus on the postcured specimens: $E_t = 2816 \text{ MPa}$.

We do not have enough data to discriminate between regular and postcured material in computing the Poisson ratio; its average value is $\nu_t = 0.400$ in tension (but we computed it by averaging of two data only) and $\nu_c = 0.410$ in compression, without accounting for the values given by samples 20 and 21, which would make the average value for the compressive tests equal to $\nu_c = 0.417$.

Most likely, the large deviation from the average values of both the Young modulus and the Poisson ratio of samples 20 and 21 is due to the too low frequency at which we could record the data in those tests; unfortunately, the recorded data have been even found to be highly scattered. This, together with the high rate of application of the load (10 mm/min), caused the linear regressions to furnish bad elastic moduli values. This problem in the data acquisition results in hiding the possible differences between these “fast tests” and the slower ones which might be affected by viscous effects, even in the elastic moduli measurement.

Note that the rate, the cycle number, and the aging have not been taken into account as parameters affecting the elastic moduli measurement in averaging the elastic constant values collected in Table 3.1; their influence has been neglected for the following reasons. We could check only a small range of rates; the loading rate does indeed influence the overall epoxy behavior, but Table 3.1 shows that it does not clearly affect it for uniaxial longitudinal strains lower than 0.4%. The cycles accounted for in Table 3.1 are just the first and, for the cyclic tests, the second one; since the first cycle in cyclic tests has always been carried out at a low strain level, damage should not affect the second cycle. This is not evident from the data of Table 3.1, in which a few Young modulus values computed in the second cycle are significantly lower than those computed in the first cycle of the same test (samples 9, 10, 24, and 25); in a moment, we shall give more insight about damage and we shall show that damage does not play a fundamental role in the epoxy behavior. The 1 year aging effect is a cause which neither makes the epoxy behavior appreciably stiffer nor strengthens it; this can be evicted from figure 3.5, in which the compression tests on the regular samples are compared.

Since the force–displacement plot shows that, most likely, sample 3 had some flaw, it results that the main discriminant variable on the epoxy behavior is the prescribed displacement rate and not the sample age, even if from these tests it is not easy to make it clear how much these two variables influence the epoxy behavior. Anyway, as said,

appreciable differences do not concern the strain range employed to define the elastic constants.

Even the postcuring (samples 20–26 in figures 3.14–3.17) does not clearly affect the linear elastic behavior, but, again, it seems to have some influence on the ultimate behavior, giving more ductility and a higher strength to the material. Since the postcuring does not strongly affect the molecule packing, but, if it is the case, the crosslink distribution, it should not influence the elastic moduli ([92], [80]). In particular, the postcuring should in case produce a stronger chemical network, thus increasing the physical sources of resistance to flowing, consisting both of the fact that molecules can not freely rotate and, then, of the so-called orientational hardening ([54], [28], and [134] — for more details see chapter 16).

In summary, it is reasonable to assume the epoxy resin DGEBA DER 332 cured with DDM 32950 as a material whose linear elastic behavior is symmetric in tension and compression, characterized by $E = 2800 \text{ MPa}$ and $\nu = 0.41$.

Table 3.2 reports the elastic constant values as functions of the cycle number and the cycle amplitudes for the cyclic test on sample 26. As one can evict from that Table,

Cycle #	E_{comp} [MPa]	ν_{comp} [–]	Rate [mm/min]	u_{max} [mm]	σ_{max} [MPa]
1 (*)	2802	0.4088	0.1	0.3	6
2 (*)	2835	0.4128	0.2	0.4	8
3	2858	0.4133	0.2	0.5	11
4	2824	0.4149	0.3	0.6	13
5	2765	0.4144	0.5	0.7	16
6	2878	0.4134	0.5	0.8	18
7	2832	0.4137	0.5	0.9	20
8	2850	0.4136	0.5	1	22
9	2775	0.4153	1	2	42
10	2736	0.4096	1	3	57
11	2602	0.4129	2	4	72
12	2457	0.4144	3	5	82
13	2206	0.4118	4	7	98
14	2274	0.4136	5	>10	107

Table 3.2: Elastic moduli of a specimen (sample 26) of postcured epoxy resin DGEBA DER 332 cured with DDM 32950 subjected to cyclic, displacement-controlled uniaxial compression

damage starts affecting the DGEBA epoxy resin behavior for a uniaxial stress roughly equal to and greater than 60 MPa , which corresponds to a strain of about 2.5%. After fourteen cycles the Young modulus decreases of about the 20%, whereas the Poisson ratio stays more or less constant. Note that the interpretation of Table 3.2 is made difficult by the fact that the crosshead displacement rate increases together with the cycle number.

The most interesting feature (and one which will prove the toughest to be described analytically) of the DGEBA DER 332 behavior can be appreciated by means of the cyclic tests: upon unloading, the stress–strain curve shows a flex and plastic deformations do not

develop in a significative amount. This observation agrees with the assumption that the yield stress and the strength are coincident ([135] and [77]). A similar cyclic behavior has been found in [17] for a different epoxy resin. In chapter 16, we shall propose a constitutive law to model this behavior.

With the relaxation test on sample 13 and with the creep tests reported in figures 3.10–3.13, we looked into the time-dependent behavior. From the relaxation test on sample 13 we can just evict that viscoelasticity strongly affects the epoxy behavior: after more or less 16 hours the load, needed to keep the imposed shortening displacement of 5 mm on a specimen type CYL1, decreases of about 20%. Figure 3.12 shows, as a function of the time, the relaxation modulus, defined as the ratio between the constant longitudinal stress and the increasing longitudinal strain in a creep test; from this figure one can evict that this viscoelasticity is nonlinear, the relaxation modulus being a decreasing function of the constant stress level, by the way even for low stress levels. The opposite of the ratio between the transversal strain and the constant longitudinal strain (i.e., the Poisson ratio if linear elasticity holds) has been plotted in figure 3.13; it is quite evident that it is an increasing function of both the stress, when the stress is high enough, and the time. The time dependence becomes very mild after a short time.

The compressive strength of this epoxy resin is more or less equal to 100 MPa for the regular samples and it is greater than 105 MPa for the postcured samples; both these values correspond to a longitudinal strain of about 10%.

In most of the monotonic compressive tests, long after the maximum in the force–displacement curve has been reached, it is possible to observe that the curve has a flat minimum and then its slope becomes positive again. Unfortunately, the strain gauges could not measure deformations greater than 10% and, therefore, it is not possible to confirm this behavior through material point measurements. In order to understand whether this behavior is the true material behavior, there would be the need of both performing plane strain compression tests, that do not suffer from buckling of the specimens, and somehow checking whether localization (shear banding) occurs [82]. This kind of behavior, even if really more emphasized, characterizes the orientational hardening of some thermoplastic materials (which, unlike epoxy resins, do not have a strong chemical network which links their macromolecules — see chapter 16 for more details) ([54] and [28]).

The tensile strength is expected to be affected by a size effect due to fracture propagation, for each of the resins that we tested. This means that more tests on specimens of different sizes should be carefully carried out to understand what kind of size effect law can describe the tensile failure of epoxy resins as a function of the specimen size. The main point is to individualize the minimum size for which Linear Elastic Fracture Mechanics (LEFM) is accurate enough to fit the experimental data. When the size range is known in which LEFM holds, it is then possible to carry out tests with the purpose of determining, for instance, the epoxy resin fracture toughness. Without that knowledge it is therefore not possible to assume the tensile strength, here determined by means of tests on one size only, to characterize the epoxy resin, e.g., in the simulations of syntactic foam failure. To try to avoid the microcrack propagation effect on the apparent strength, one should carry out tests on small not turned specimens; this, anyway, would make it difficult both to compute the stresses and to acquire the strains.

The epoxy resin DGEBA DER 332 behavior is modestly ductile in compression whereas it is very brittle in tension, but this is definitely dependent upon the specimen size. The

strong brittleness in tension prevented us from performing tests whose stress level was greater than about 50 MPa in tension; this is the reason why we could not investigate whether the hysteresis in tension is similar to that in compression.

3.3 Epoxy resin SP Ampreg 20TM cured with UltraSlow Hardener

In figures 3.18–3.28, the results have been plotted of the 18 tests carried out on the epoxy resin SP Ampreg 20TM cured with UltraSlow Hardener. Table 3.3 collects all the elastic constants computed from those tests.

Note that the shear stress in the torsion tests is referred to the external specimen surface and has been computed by exploiting the linear elastic relation for circular cross sections, which should overestimate the shear stress in the nonlinear range. Unfortunately, we had not the chance to prepare hollow cylindrical specimens suitable for torsional tests. The following average values have been computed from the data of Table 3.3:

Sample	E [MPa]	ν	G [MPa]	Rate	Stress State	Cycle #
1 CYL1	3612	0.386	-	1 mm/min	comp	1
2 CYL1	3723	0.383	-	2 mm/min	comp	1
3 CYL1	3826	0.385	-	5 mm/min	comp	1
4 CYL1	3951	0.395	-	10 mm/min	comp	1
5 DB2	3446	-	-	10 mm/min	tens	1
6 DB2	3522	-	-	10 mm/min	tens	1
7 DB3	-	-	1277	1 deg/min	tors	1
8 DB3	-	-	1374	10 deg/min	tors	1
9 DB3	-	-	1272	10 deg/min	tors	1
10 DB3	-	-	1318	2 deg/min	tors	1
11 CYL3	3296	0.379	-	2.5 kN/sec	comp	1
12 CYL3	3472	0.402	-	2.5 kN/sec	comp	1
13 CYL3	3394	0.383	-	2.8 kN/sec	comp	1
14 CYL3	3464	0.397	-	3.0 kN/sec	comp	1
15 CYL3	3322	0.394	-	3.2 kN/sec	comp	1
16 DB2	4264	-	-	5 mm/min	comp	1
17 DB2	3882	-	-	8 mm/min	comp	1
18 DB2	3407	-	-	0.25 mm/min	tens	1
18 DB2	3472	-	-	0.5 mm/min	comp	2

Table 3.3: Elastic moduli computed from uniaxial and torsion tests on epoxy resin SP Ampreg 20TM cured with UltraSlow Hardener

- compressive Young modulus: $E_c = 3640$ MPa;
- tensile Young modulus: $E_t = 3458$ MPa;

- Poisson ratio (measured in compression only): $\nu_c = 0.389$;
- shear modulus: $G = 1310 \text{ MPa}$.

The first four tests show that the Young modulus is dependent on the crosshead displacement rate (see also figure 3.20). In principle, the elastic moduli should be taken from the fastest tests, to avoid viscous effects as much as possible. For the creep tests, done on samples 11–15 by controlling the load, it is easy to see, by means of the specimen geometrical data (see section 2.2), that the load rates applied to the specimen to reach the chosen constant load are more or less equivalent to a crosshead displacement rate equal to 5 mm/min ; accounting for the fact that the creep specimens are shorter than those employed for the compressive tests on samples 1–4, the rate value increases to about 7 mm/min , to be compared with those related to the tests on samples 1–4. In spite of this high rate, the Young modulus values computed from the creep tests are appreciably lower than those evaluated from the tests on samples 1–4. This observation, compared with the Young modulus value obtained from the test on sample 16, is a little confusing. Most likely, the reason for this disagreement is that we have produced samples 1–4 and samples 11–15 several days apart from each other, and the first ones may have cured differently from the second ones.

Anyway, it is possible to check the surprisingly good consistency among the average values $E_c = 3640 \text{ MPa}$, $\nu_c = 0.389$, and $G = 1310 \text{ MPa}$. Moreover, the Young modulus in tension is found to be lower of about 5% than that in compression. In spite of this, owing to all the sources of uncertainty related to making and testing these materials, we find it sensible to assume the linear elastic behavior of this epoxy resin to be symmetric, characterized by the constants $E = 3640 \text{ MPa}$, $\nu = 0.39$.

The cyclic tests carried out on the epoxy resin SP Ampreg 20TM (samples 16, 17, and 18) can be commented as follows:

- the cyclic test on sample 16 does not show either damage or Mullins effect (i.e., stress-softening occurring at the very first cycle). 41 cycles have been carried out in compression at a maximum stress level of $\approx 50 \text{ MPa}$. The Young modulus varies from a minimum of 4246 MPa related to the second cycle to a maximum of 4481 MPa reached in the thirteenth cycle; these values are anyway higher of about 20% than the average Young modulus, showing once more the high scattering in the elastic constants of this epoxy resin;
- the cyclic test on sample 17 (see Table 3.4) shows some damage occurring for cycles carried out at a stress level of almost 100 MPa . The strain gauges could measure the deformation of the first 12 cycles only, after which the Young modulus has decreased of about 10%; all the Young modulus values related to this test are reported in Table 3.4. Table 3.5 collects the measured Young modulus values for the test on sample 18; before failure (ninth cycle), the Young modulus has decreased in tension only and still of about 10%. From these data, we evict that the damage effect does not constitute a main feature of this resin;
- the hysteresis shown in the cyclic tests is not as marked as for the resin DGEBA DER 332; anyway, according to the assumption that yielding occurs after the strength has

been reached ([135] and [77]), plastic deformations are still trifling and the flex in the unloading stress–strain curve is still there (see figure 3.28).

Cycle #	E_c [MPa]
1	3941
2	3837
3	3824
4	3750
5	3699
6	3712
7	3709
8	3676
9	3668
10	3661
11	3637
12	3603

Table 3.4: *Elastic moduli of a specimen (sample 17) of epoxy resin SP Ampreg 20TM cured with UltraSlow Hardener subjected to cyclic uniaxial compression; constant displacement rate equal to 8 mm/min*

Cycle #	E_c [MPa]	Rate [mm/min]	Stress State
1	3407	0.25	tens
2	3472	0.5	comp
3	3371	0.5	tens
4	3440	1.	comp
5	3320	0.75	tens
6	3410	1.5	comp
7	3285	1.	tens
8	3312	2.	comp
9	3096	1.25	tens

Table 3.5: *Elastic moduli of a specimen (sample 18) of epoxy resin SP Ampreg 20TM cured with UltraSlow Hardener subjected to cyclic uniaxial tension and compression*

The time-dependent behavior of this epoxy resin is still nonlinear, but the nonlinearity is not as strong as for the resin DGEBA DER 332. For low stress levels, the viscoelasticity is nearly linear (see figures 3.25–3.26). At the highest stress level we tested (sample 15), we got a very high flow rate which soon led the specimen to the tertiary creep stage and caused failure after a couple of minutes only.

The compressive strength of this epoxy resin is, as for the DGEBA DER 332 resin, approximately equal to 100 MPa and it is reached at a longitudinal strain lower than

3.5%, i.e., about a third of the strain at which the epoxy resin DGEBA DER 332 shows its peak.

As for the DGEBA DER 332, the same arguments hold for this resin: it is not possible to determine the tensile strength by means of the tests here available only.

The SP Ampreg 20 behavior is stiffer and brittler than that of the resin DGEBA DER 332, and even shows some pronounced softening.

Finally, a Charpy test allowed the tentative evaluation of the fracture toughness K_{IC} for this epoxy resin. Having measured an energy dissipation of 1.89 J on a rectangular notch section of 13 $mm \times 15 mm$, and using $E = 3640 MPa$, we found $K_{IC} \approx 6 MN/m^{3/2}$. Of course, this datum should be confirmed by performing more tests. To accomplish the Charpy test, we employed the Charpy pendulum 6545/00 for plastic materials produced by CEAS; it furnishes an energy of 15 J and it digitally records the energy dissipation. We made the test at the Applied Chemistry Laboratory of the Faculty of Engineering of the University of Brescia.

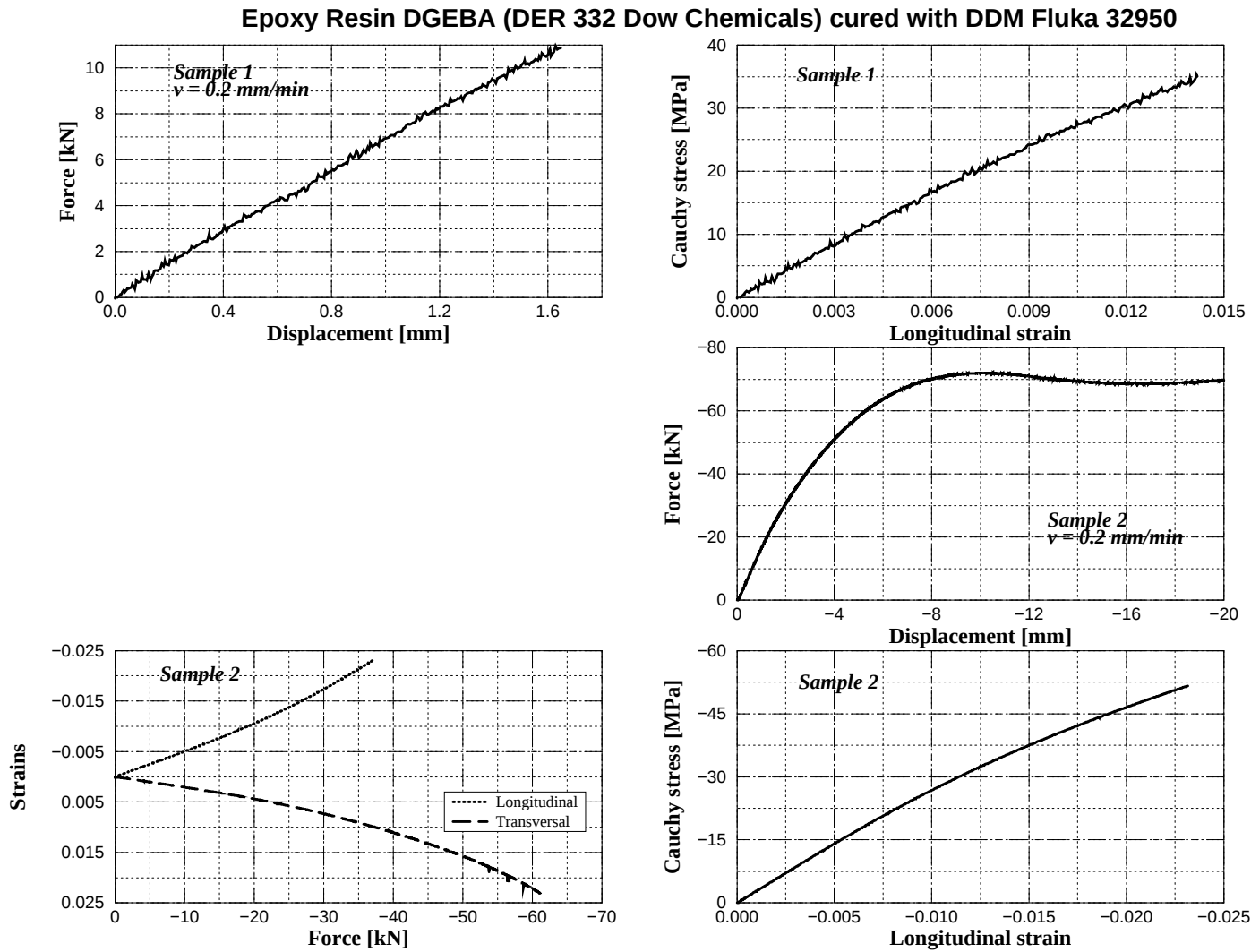


Figure 3.1: Monotonic compressive tests: load–displacement, strain–load, and stress–strain curves

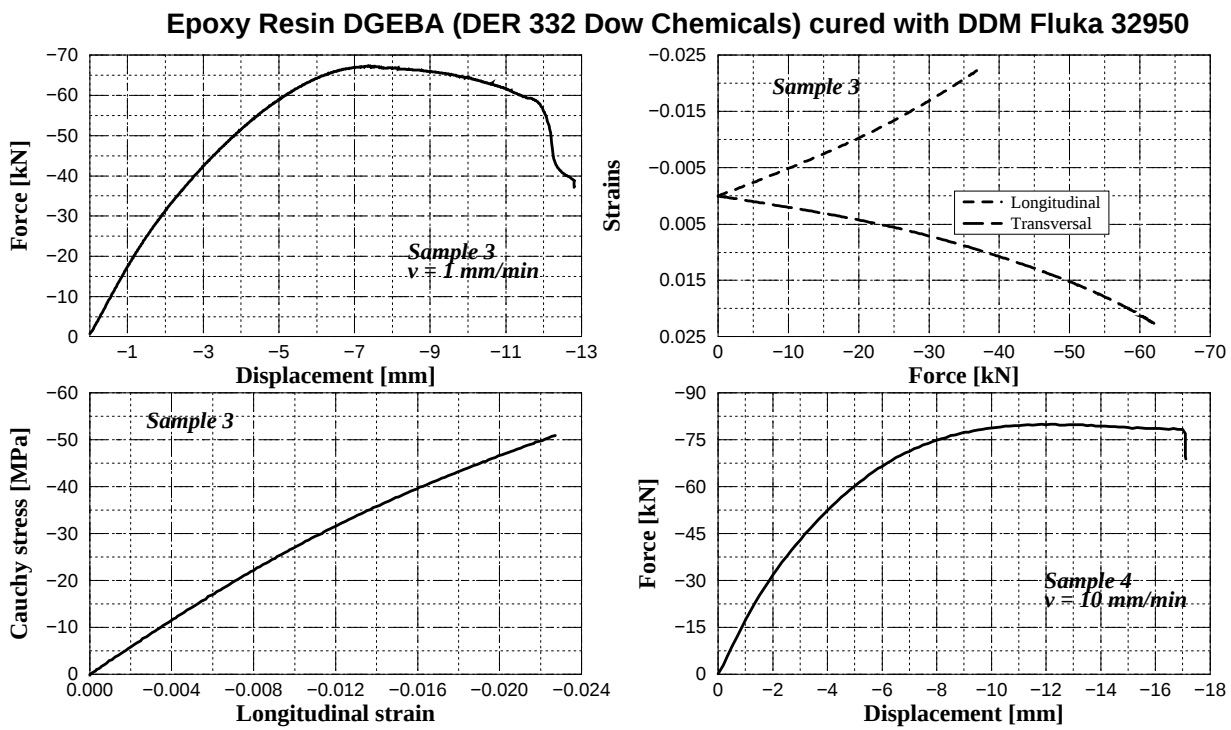


Figure 3.2: Monotonic compressive tests: load–displacement, strain–load, and stress–strain curves

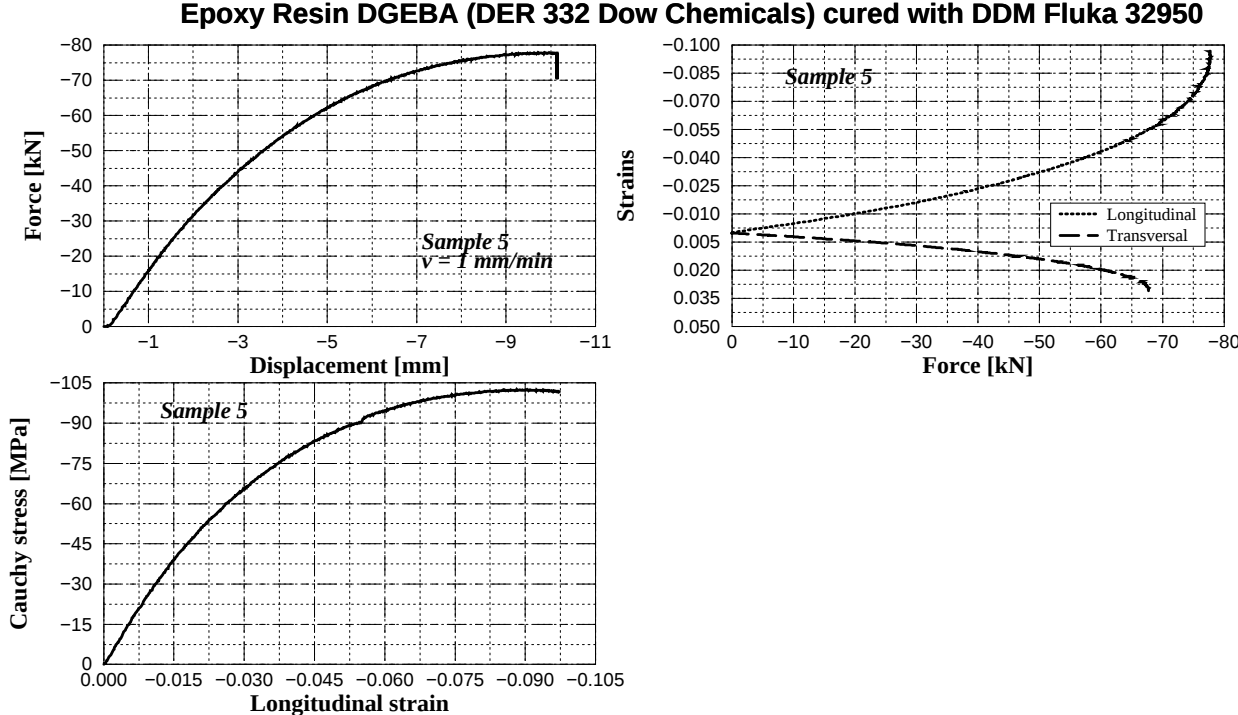


Figure 3.3: Experiments on the epoxy resin DGEBA DER 332 cured with the hardener DDM 32950

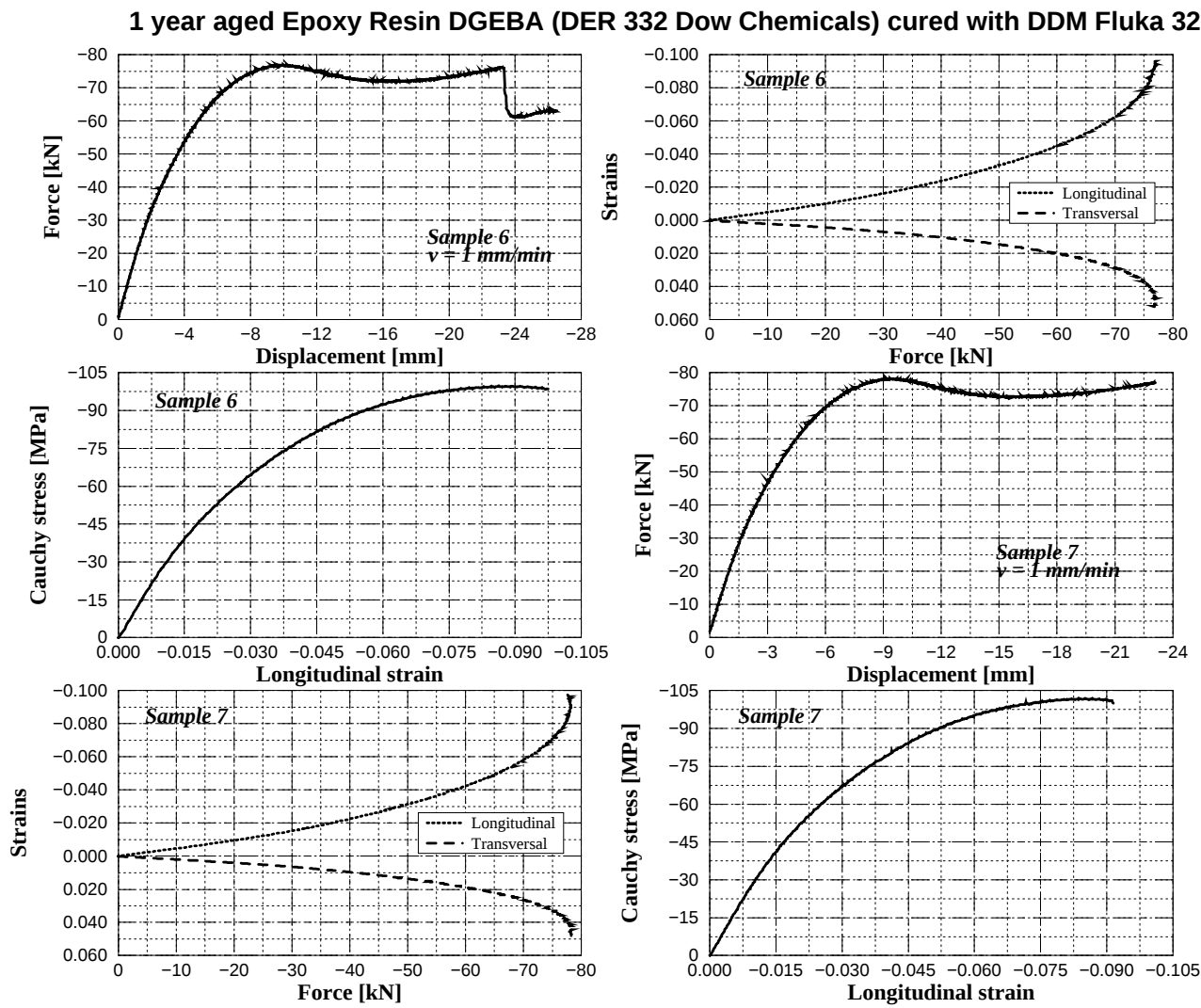


Figure 3.4: Monotonic compressive tests: load–displacement, strain–load, and stress–strain curves

Epoxy Resin DGEBA (DER 332 Dow Chemicals) cured with DDM Fluka 32950

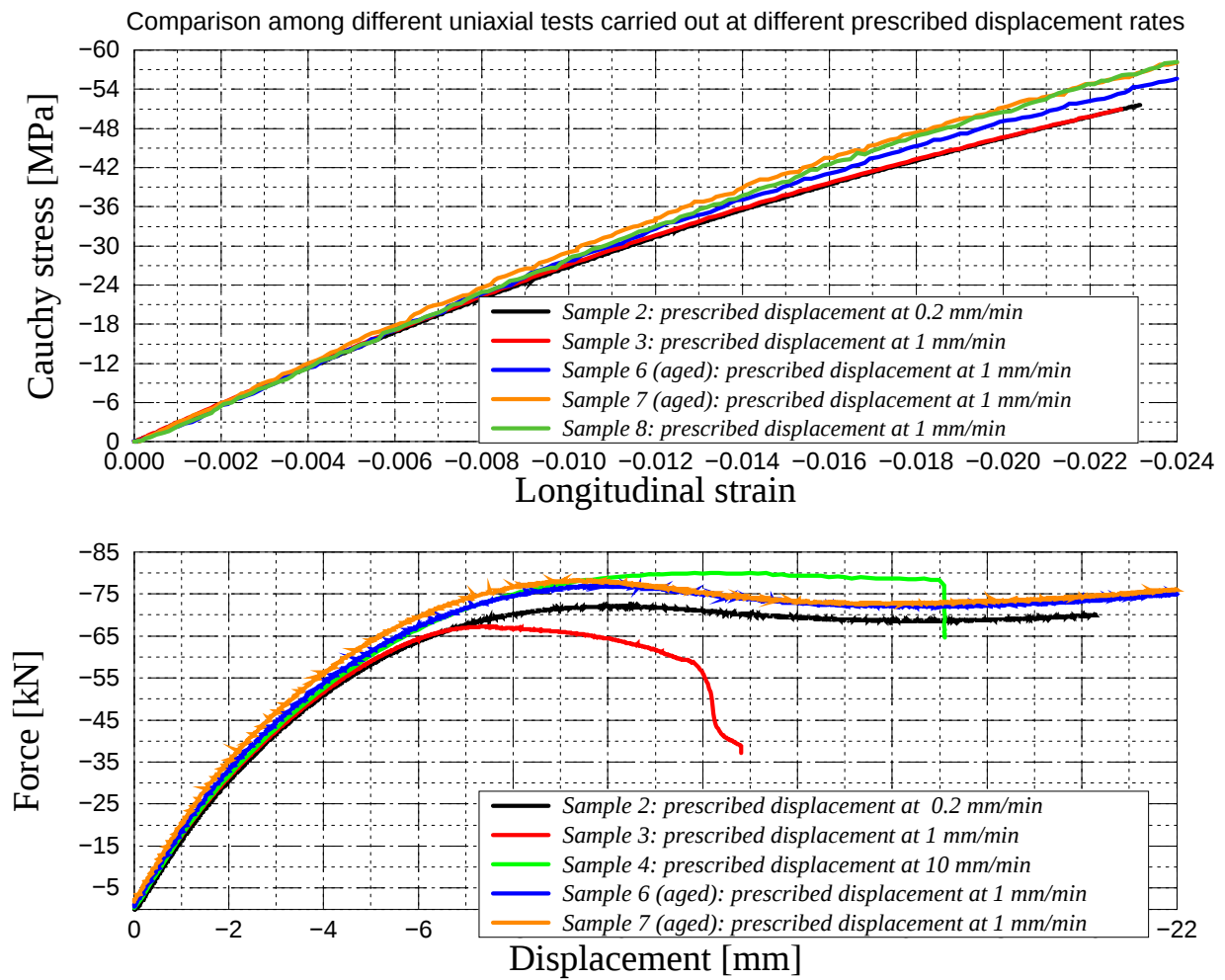


Figure 3.5: Monotonic compressive tests: comparison among results obtained at different loading rates

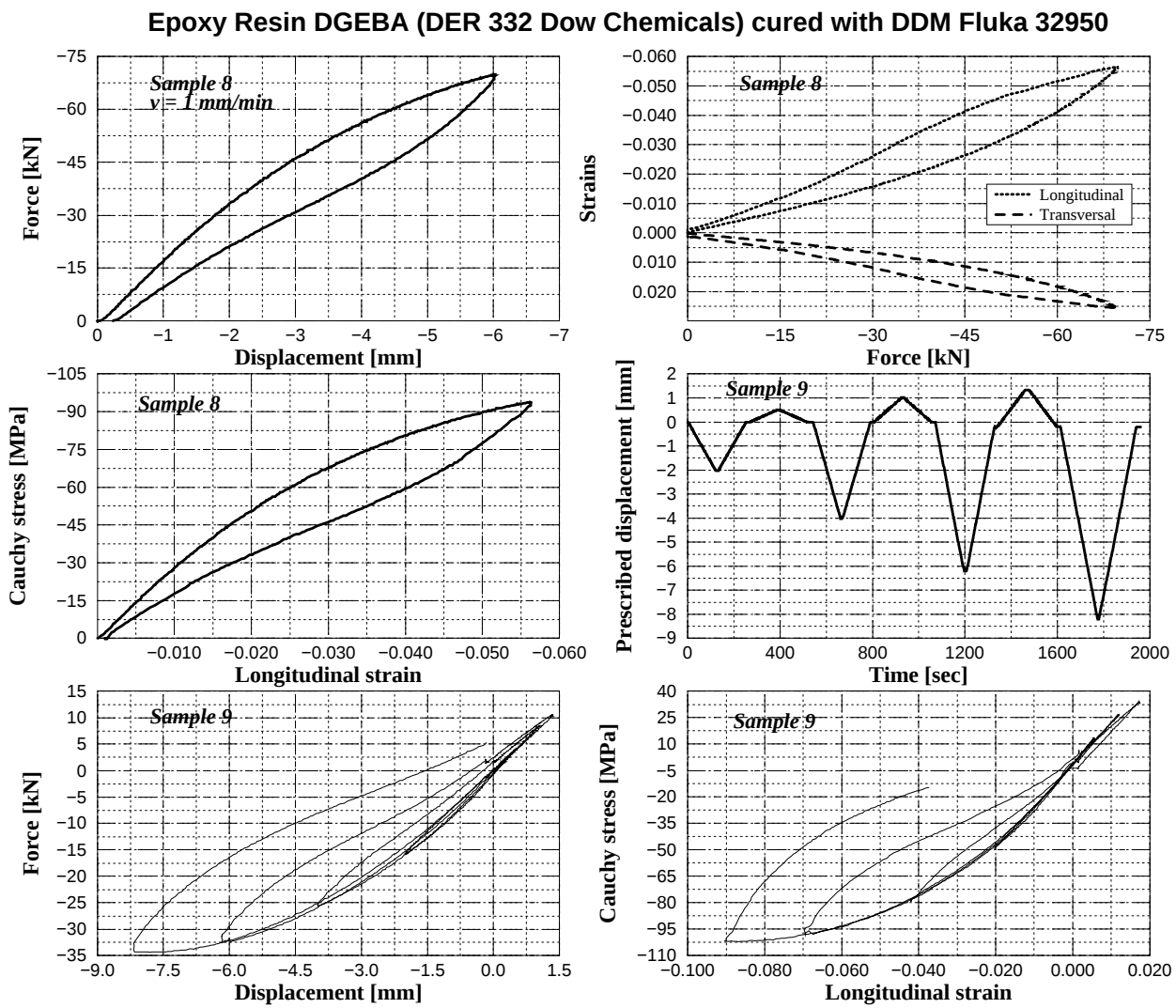


Figure 3.6: Cyclic tests: displacement–time, load–displacement, strain–load, and stress–strain curves

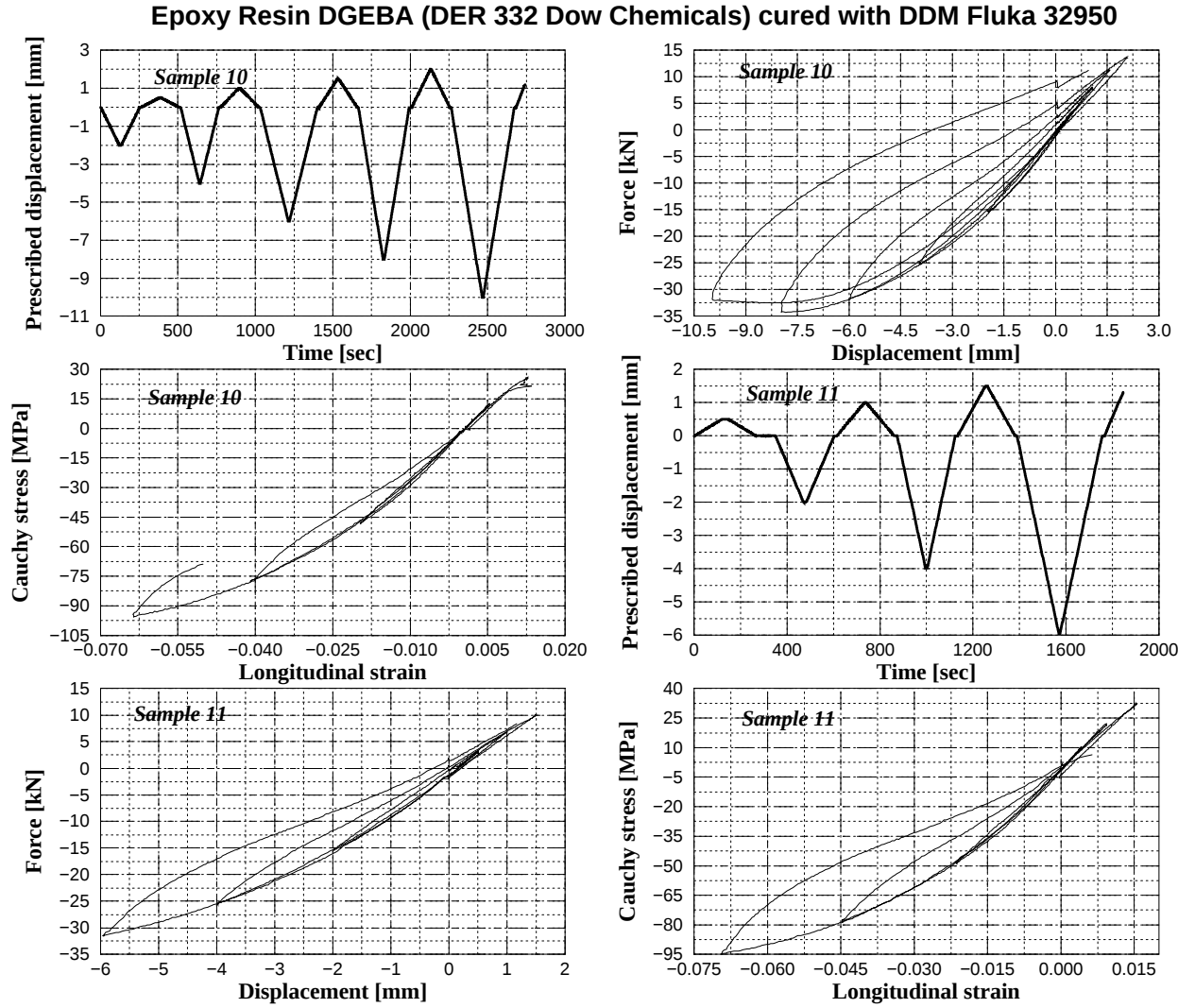


Figure 3.7: Cyclic tests: displacement–time, load–displacement, and stress–strain curves

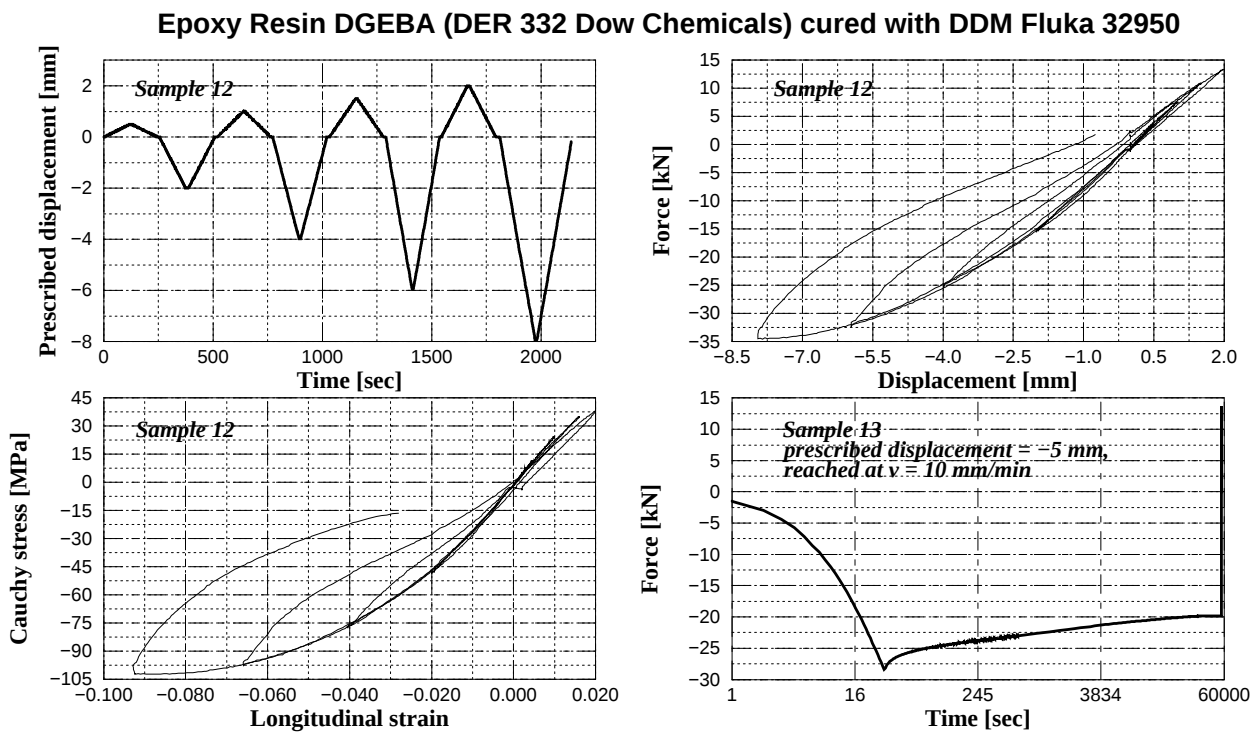


Figure 3.8: Experiments on the epoxy resin DGEBA DER 332 cured with the hardener DDM 32950

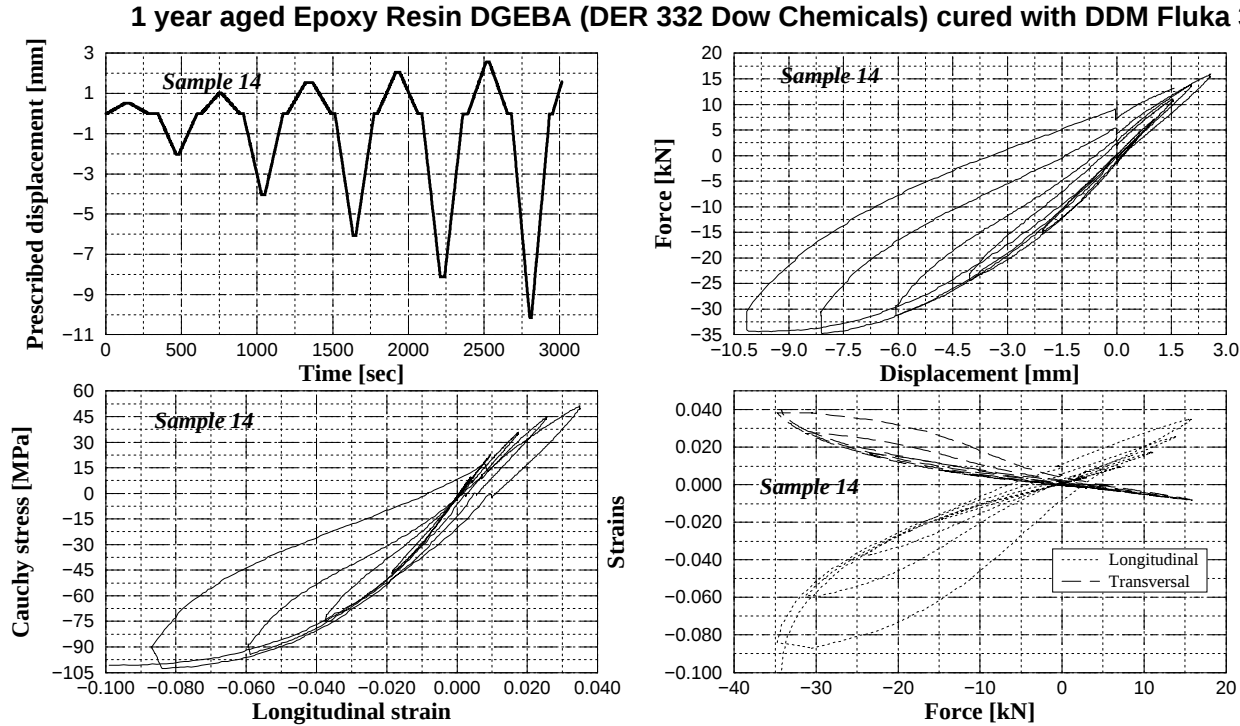


Figure 3.9: Cyclic tests: displacement–time, load–displacement, strain–load, and stress–strain curves

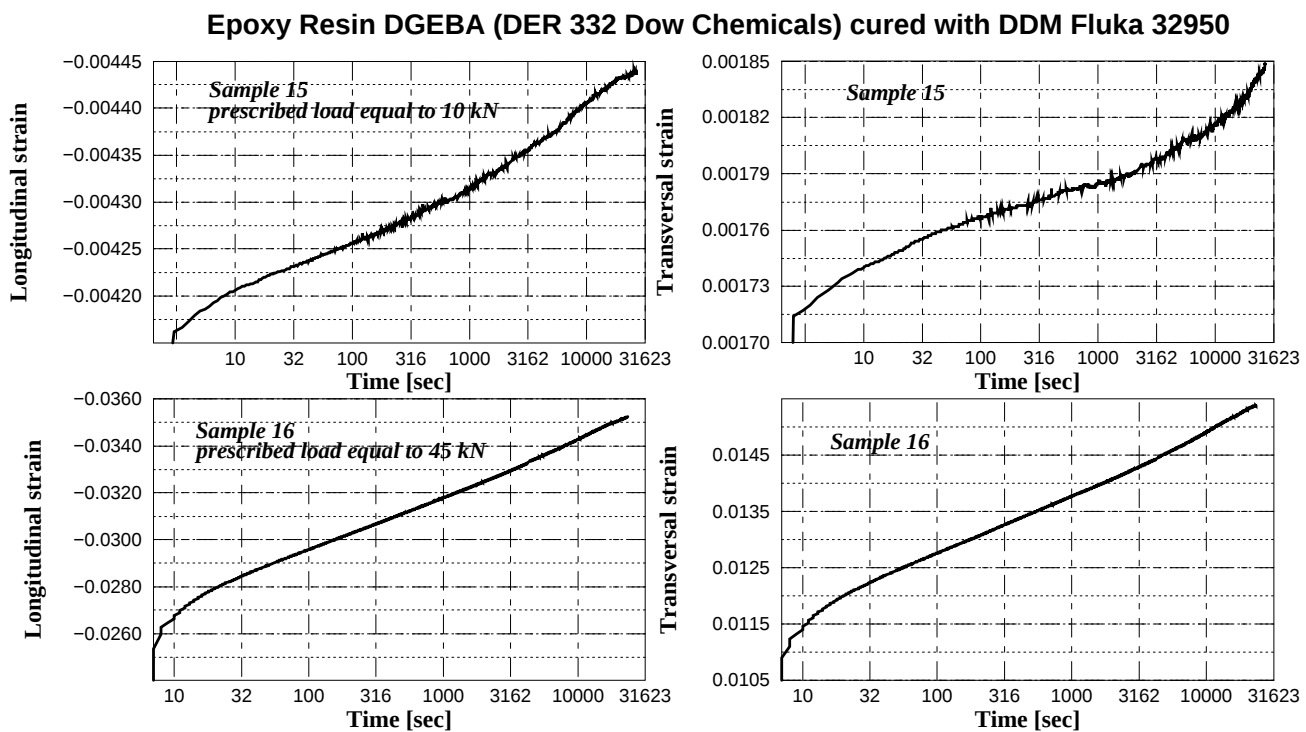


Figure 3.10: Creep tests: strain–time curves

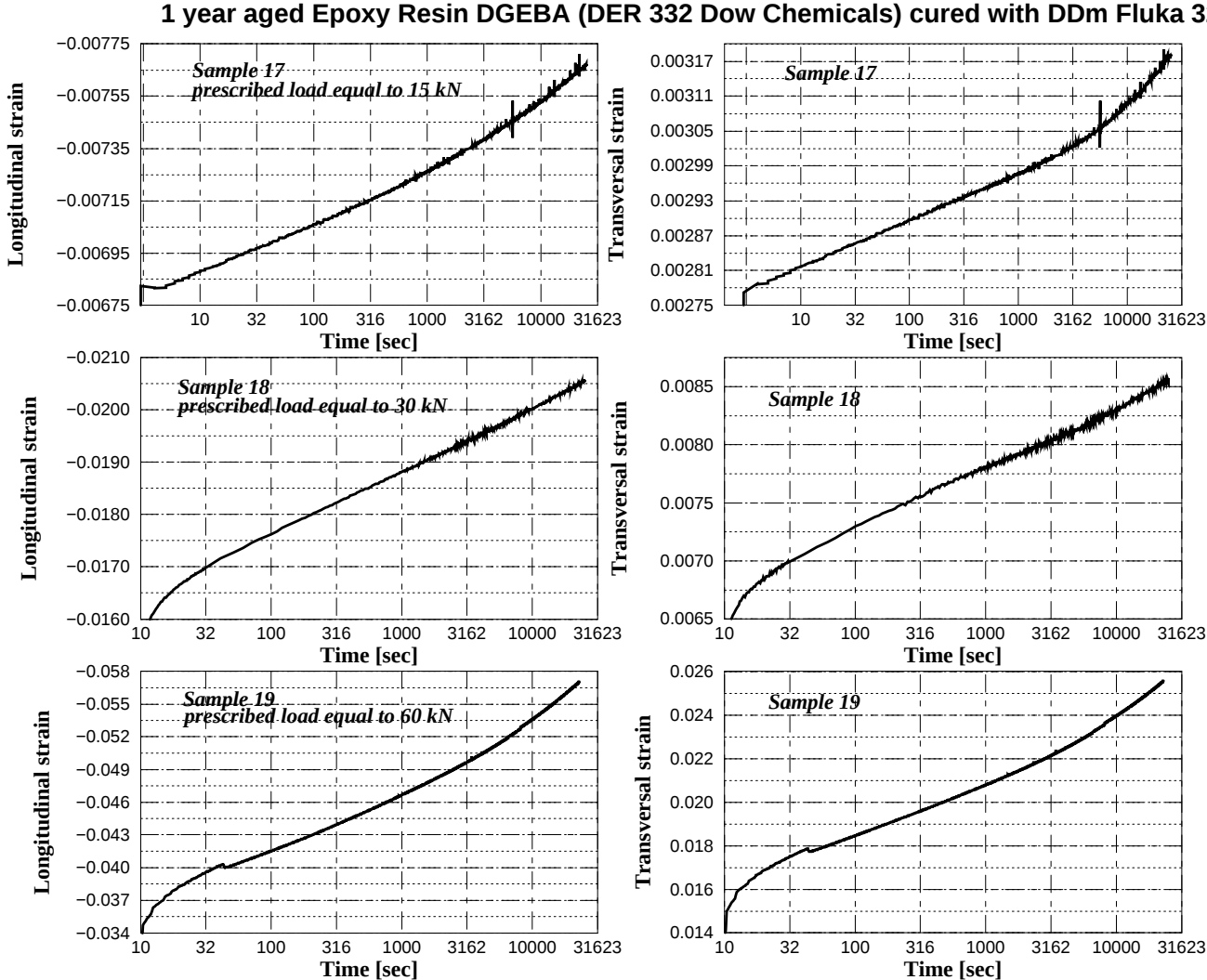


Figure 3.11: Creep tests: strain-time curves

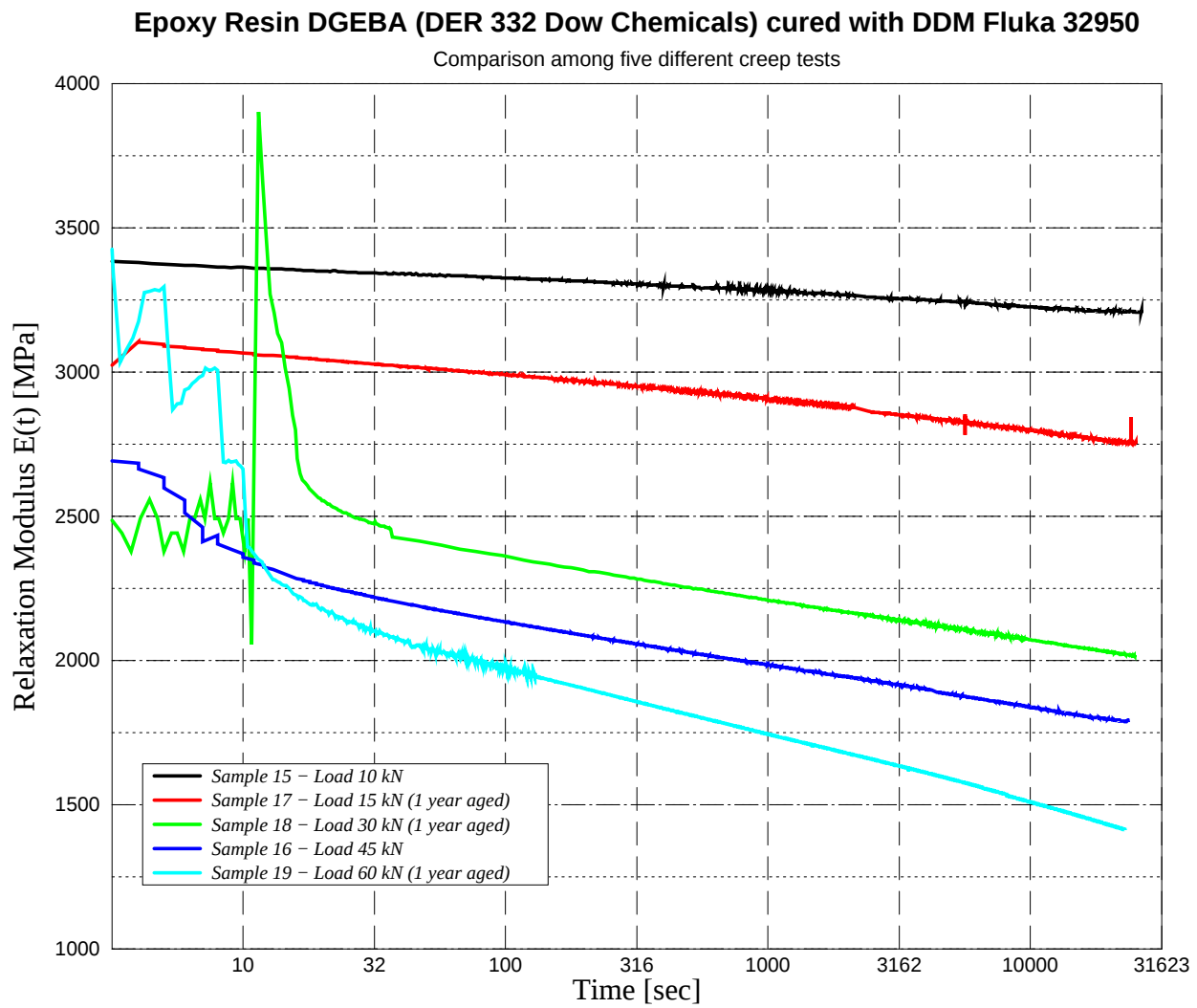


Figure 3.12: Creep tests: relaxation modulus–time curves at different instantaneous stress level

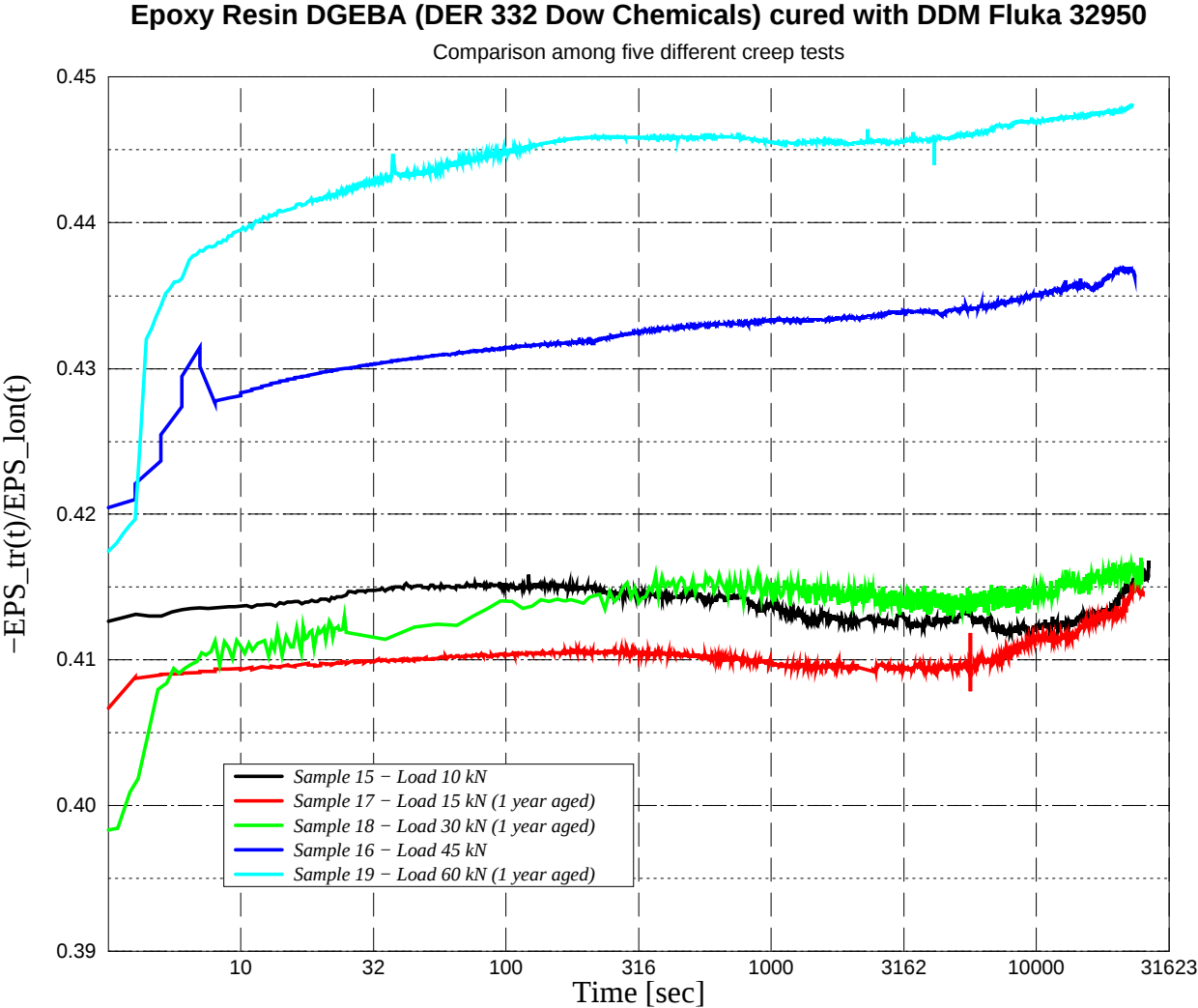


Figure 3.13: Creep tests: strain ratio-time curves at different instantaneous stress level

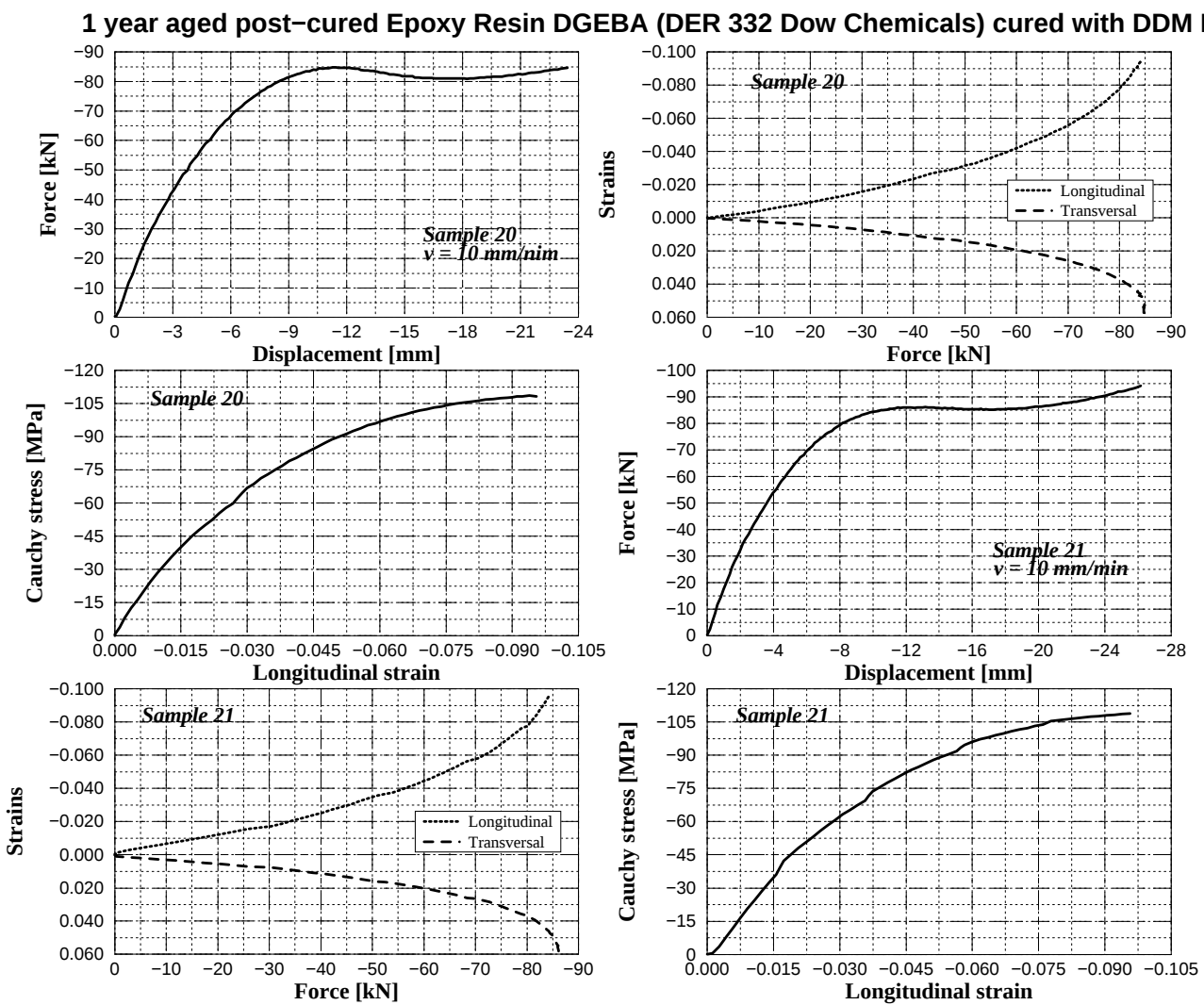


Figure 3.14: Monotonic compressive tests: load–displacement, strain–load, and stress–strain curves

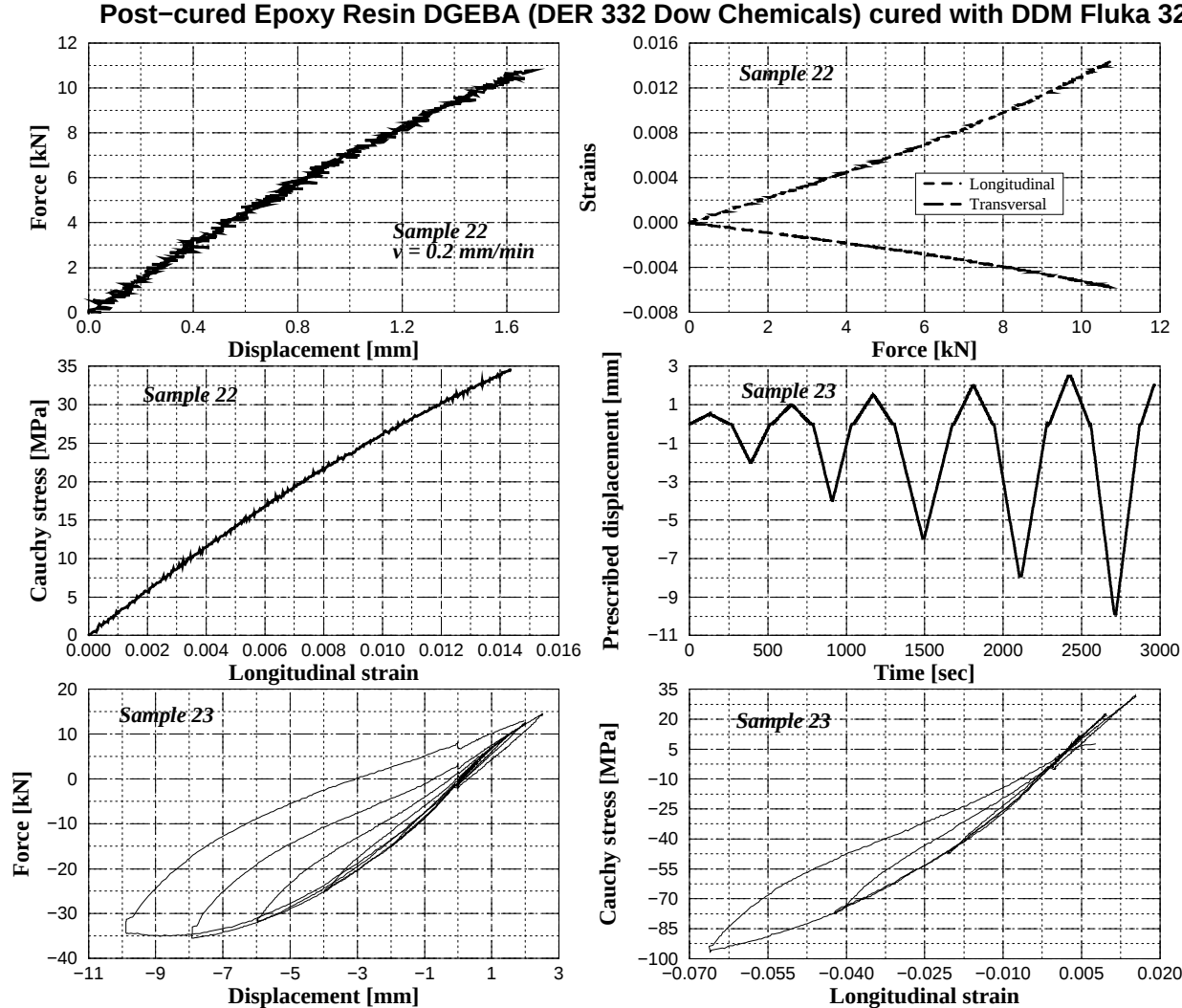


Figure 3.15: Monotonic tensile and cyclic tests: load–displacement, strain–load, stress–strain, and displacement–time curves

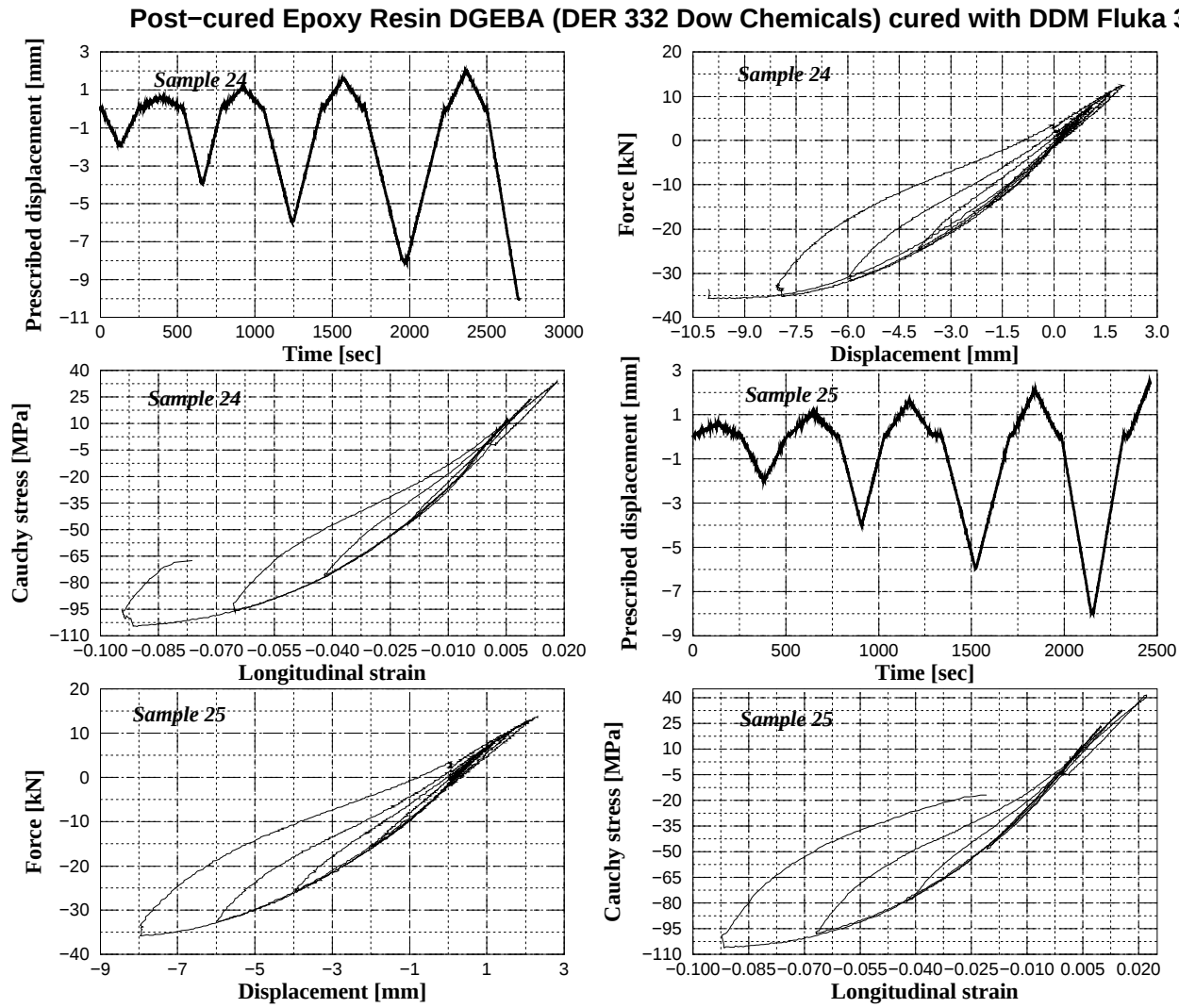


Figure 3.16: Cyclic tests: displacement–time, load–displacement, and stress–strain curves

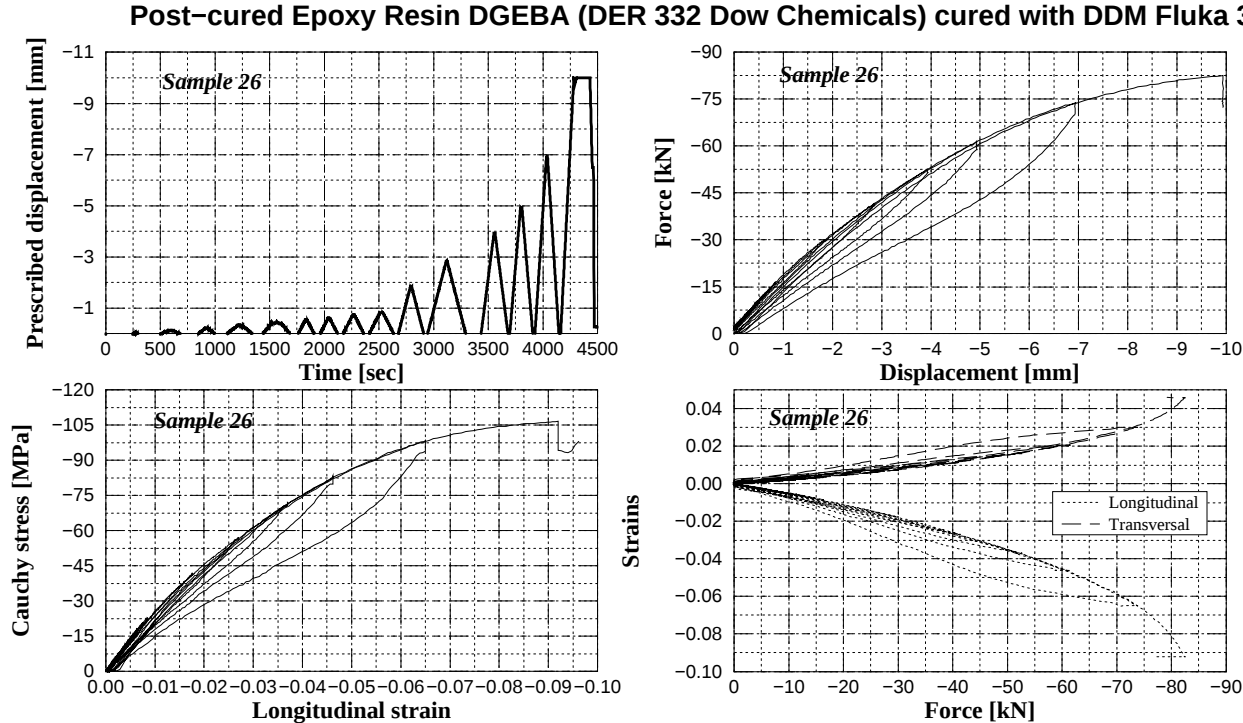


Figure 3.17: Cyclic tests: displacement–time, load–displacement, strain–load, and stress–strain curves

Epoxy Resin SP Ampreg 20 cured with UltraSlow Hardener (SP Systems, Montecatini Advanced Materials)

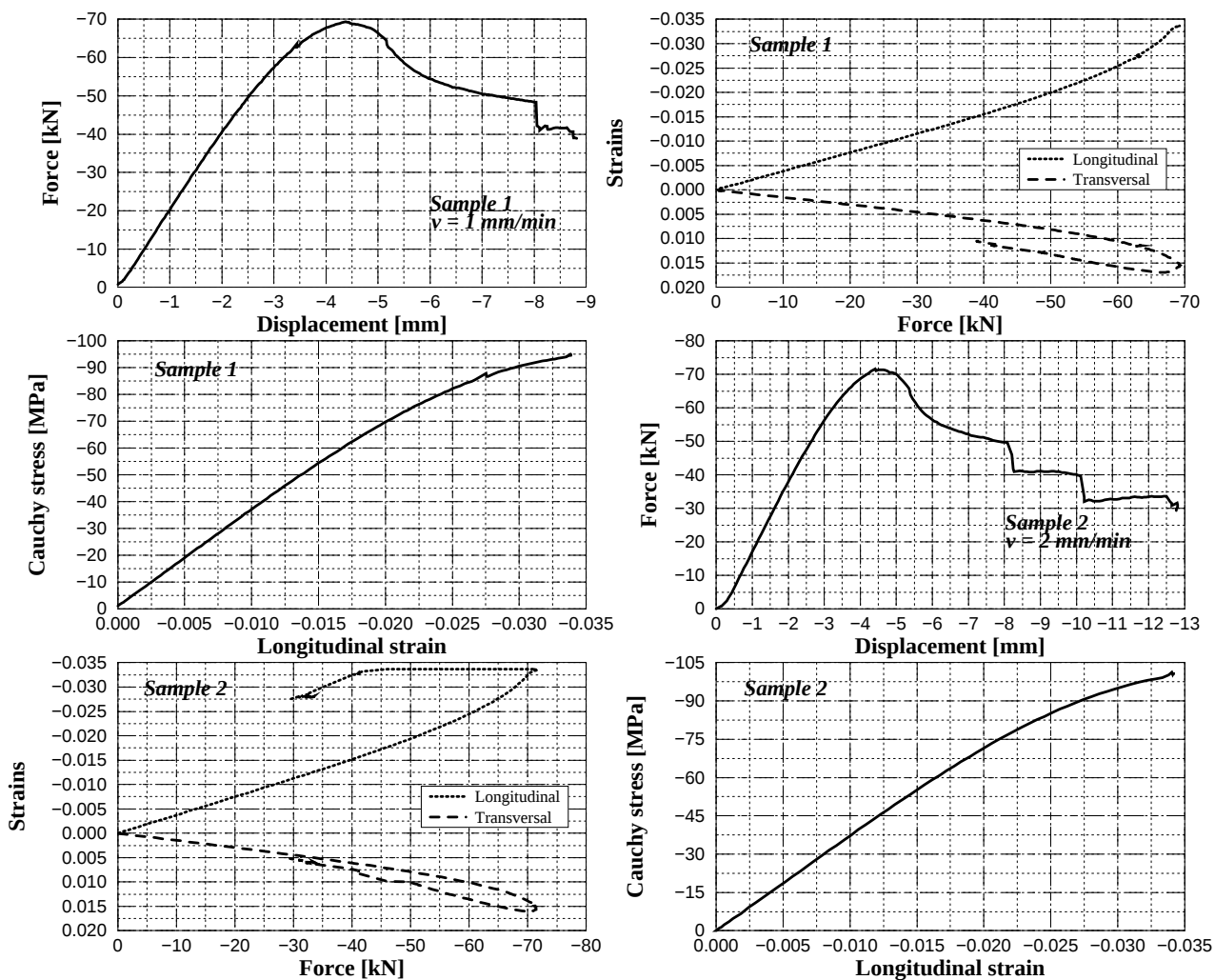


Figure 3.18: Monotonic compressive tests: load–displacement, strain–load, and stress–strain curves

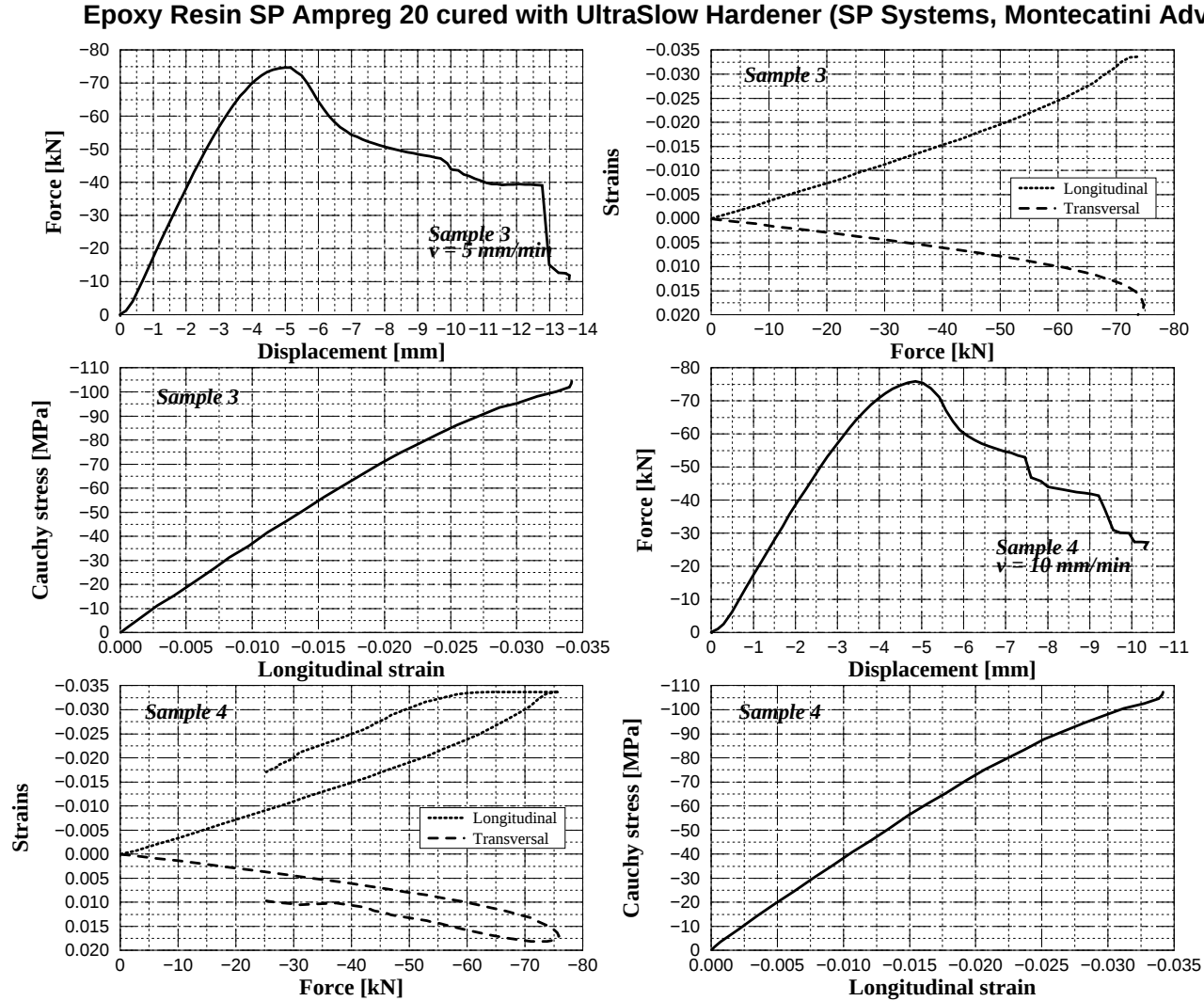


Figure 3.19: Monotonic compressive tests: load–displacement, strain–load, and stress–strain curves

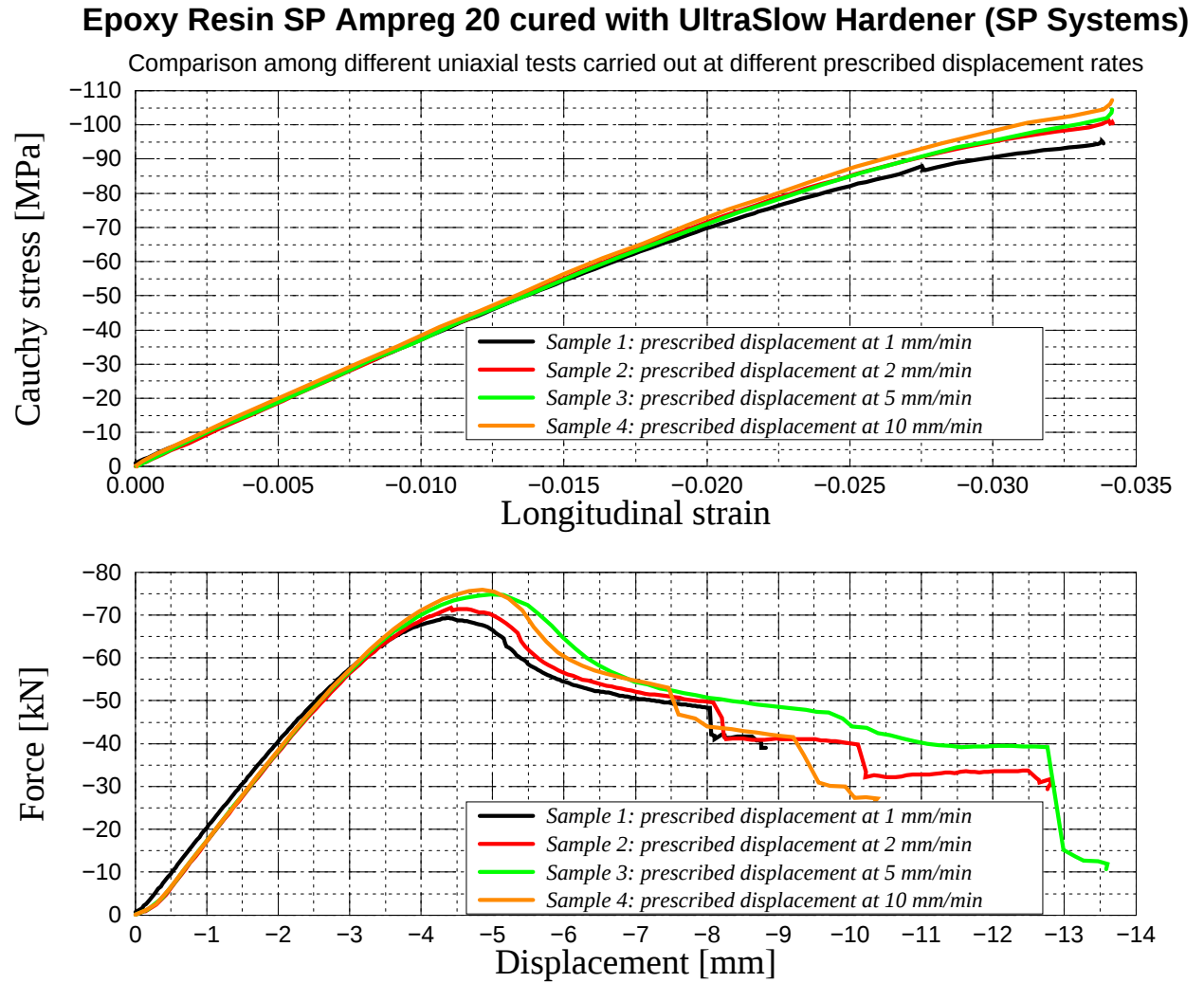


Figure 3.20: Monotonic compressive tests: comparison among results obtained at different loading rates

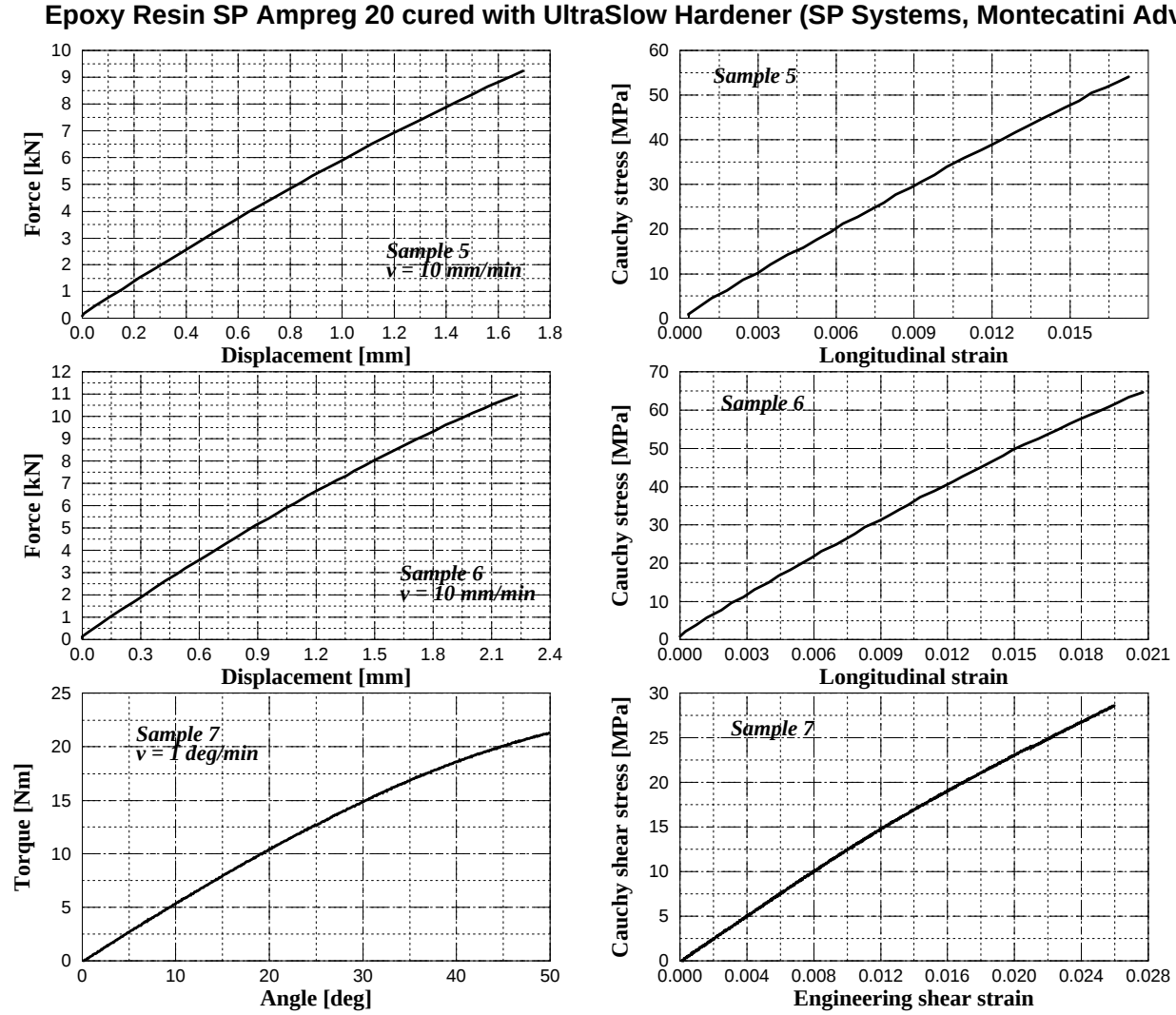


Figure 3.21: Monotonic tensile tests: load-displacement and stress-strain curves

Epoxy Resin SP Ampreg 20 cured with UltraSlow Hardener (SP Systems, Montecatini Advanced Materials)

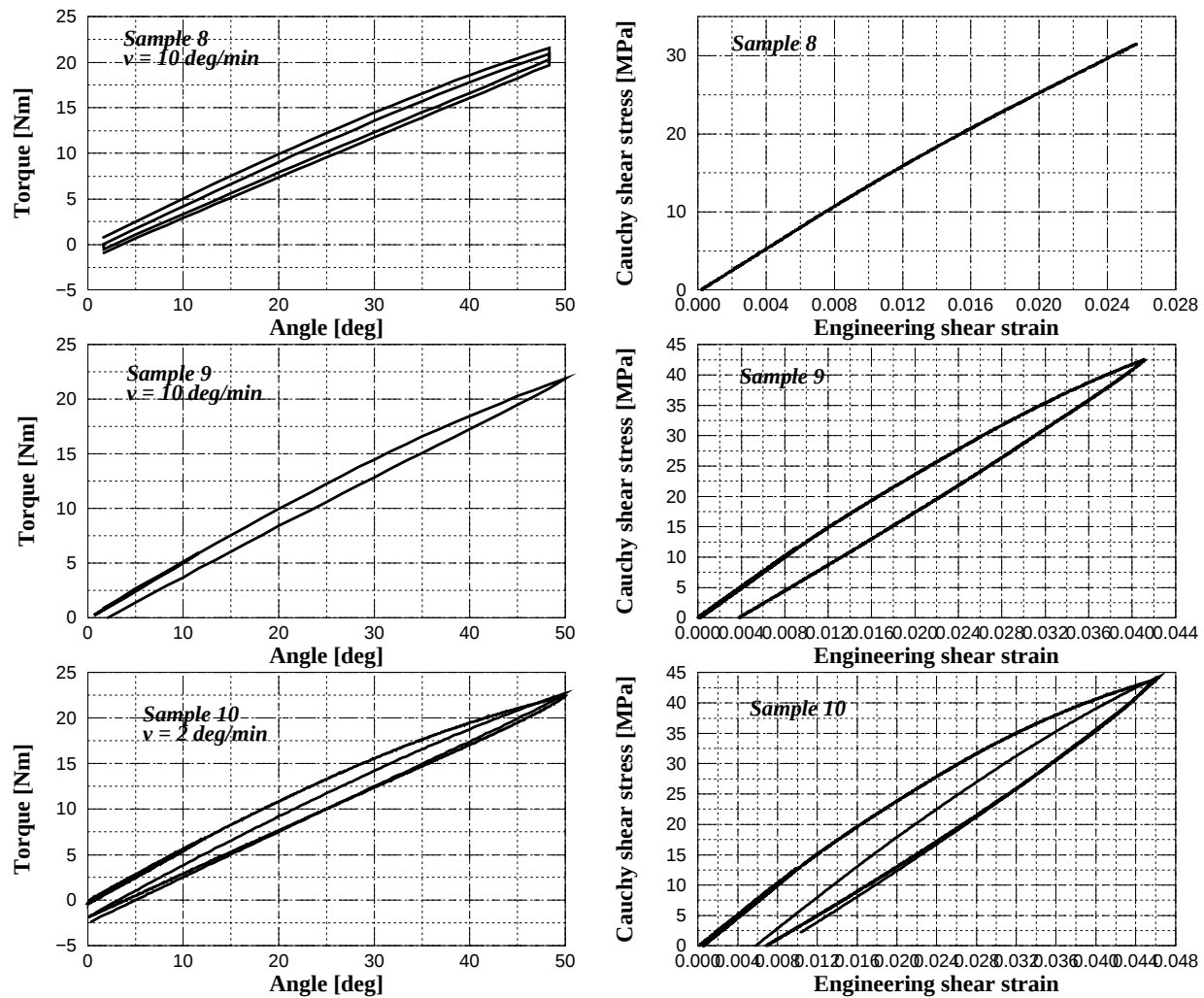


Figure 3.22: Torsion tests: torque–angle and shear stress–engineering shear strain curves

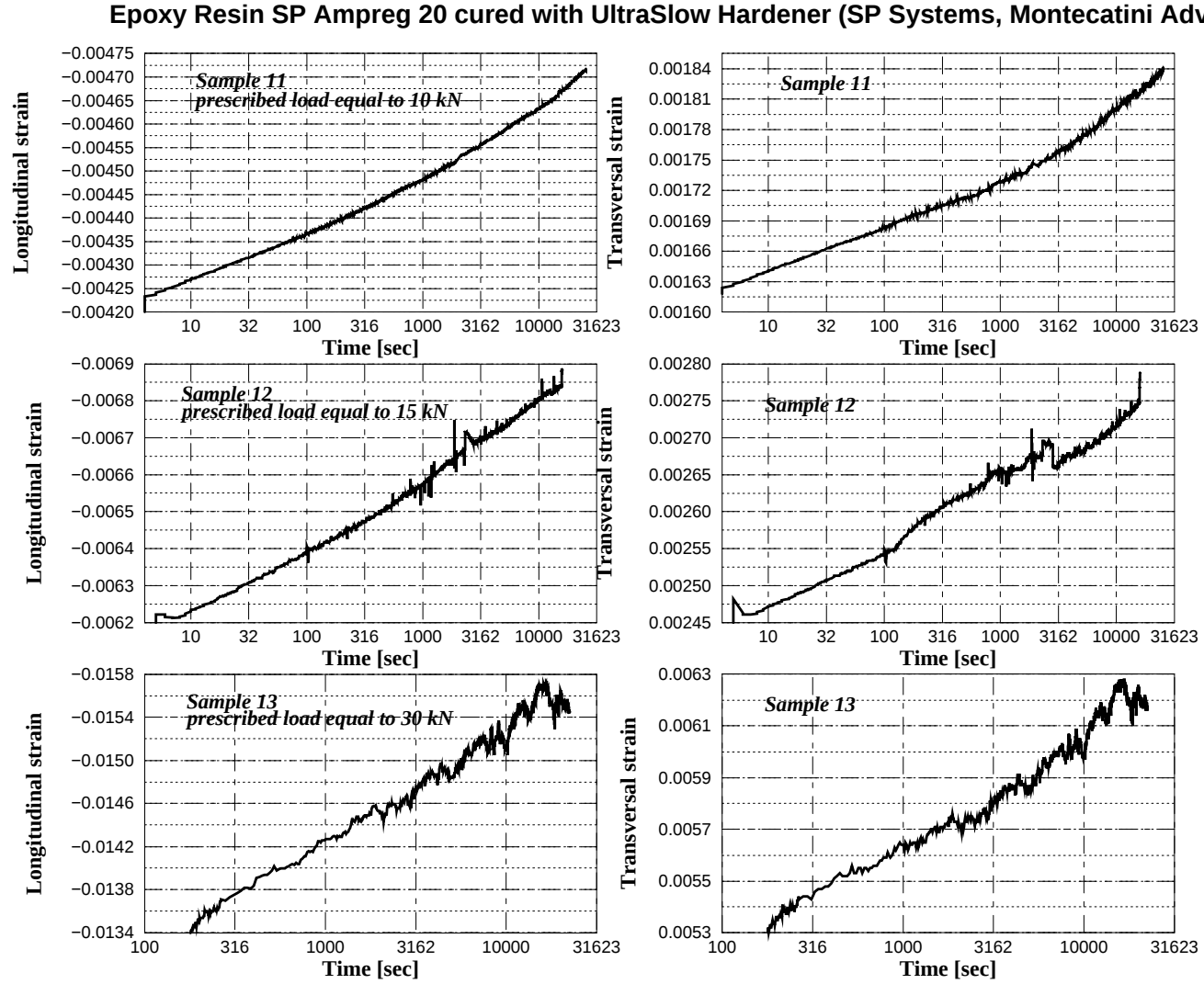


Figure 3.23: Creep tests: strain-time curves

Epoxy Resin SP Ampreg 20 cured with UltraSlow Hardener (SP Systems, Montecatini Advanced Materials)

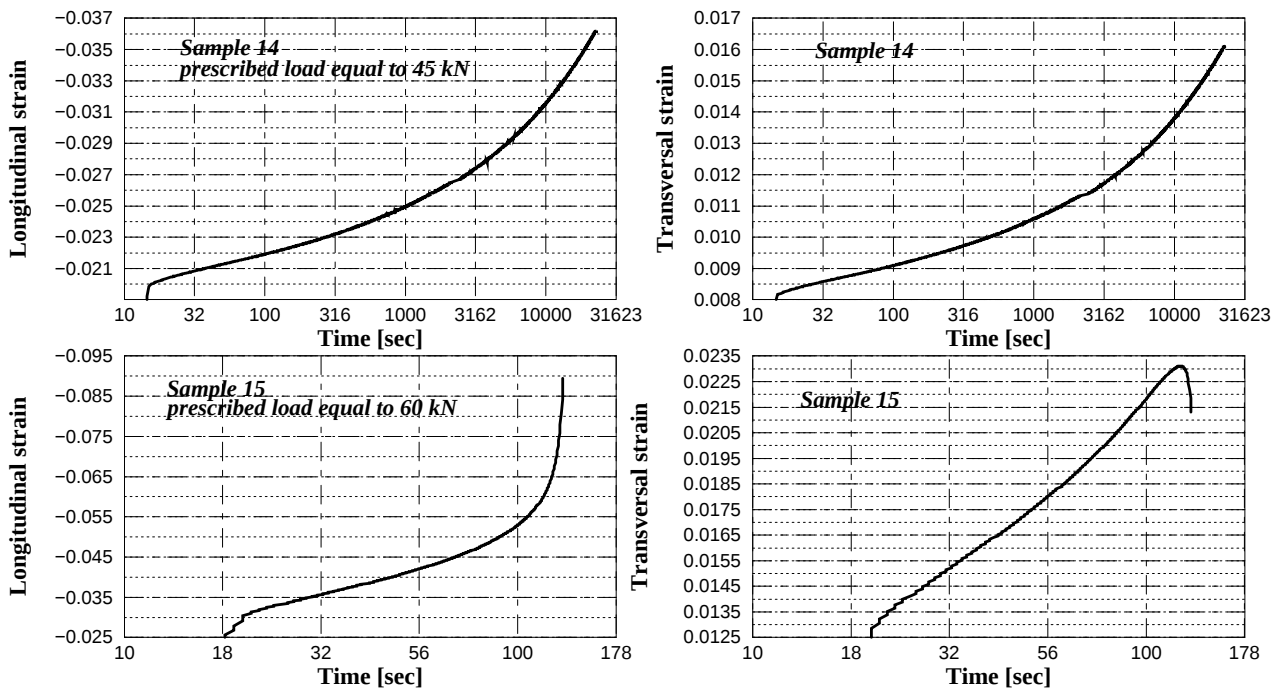


Figure 3.24: Creep tests: strain–time curves

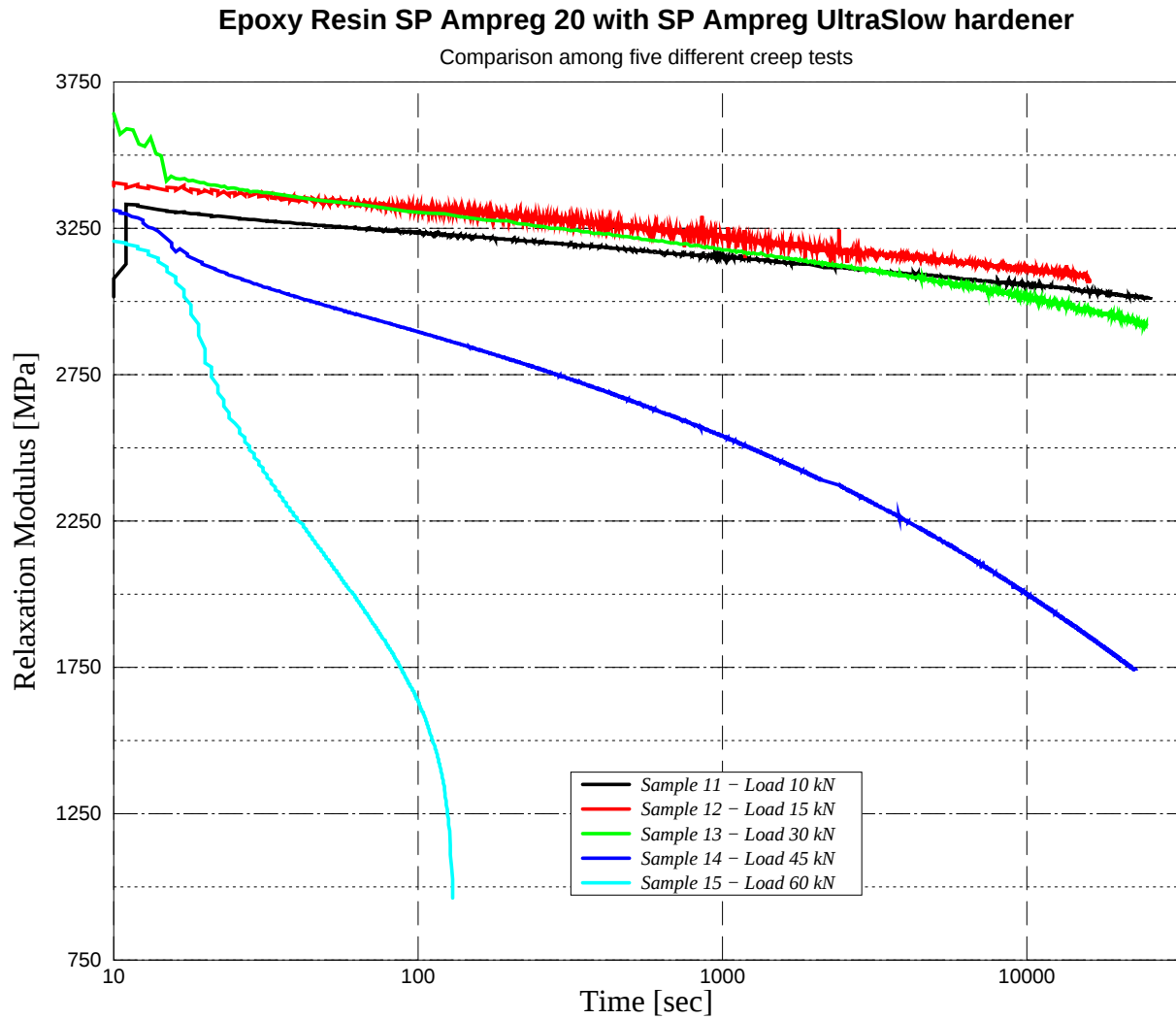


Figure 3.25: Creep tests: relaxation modulus–time curves at different instantaneous stress level

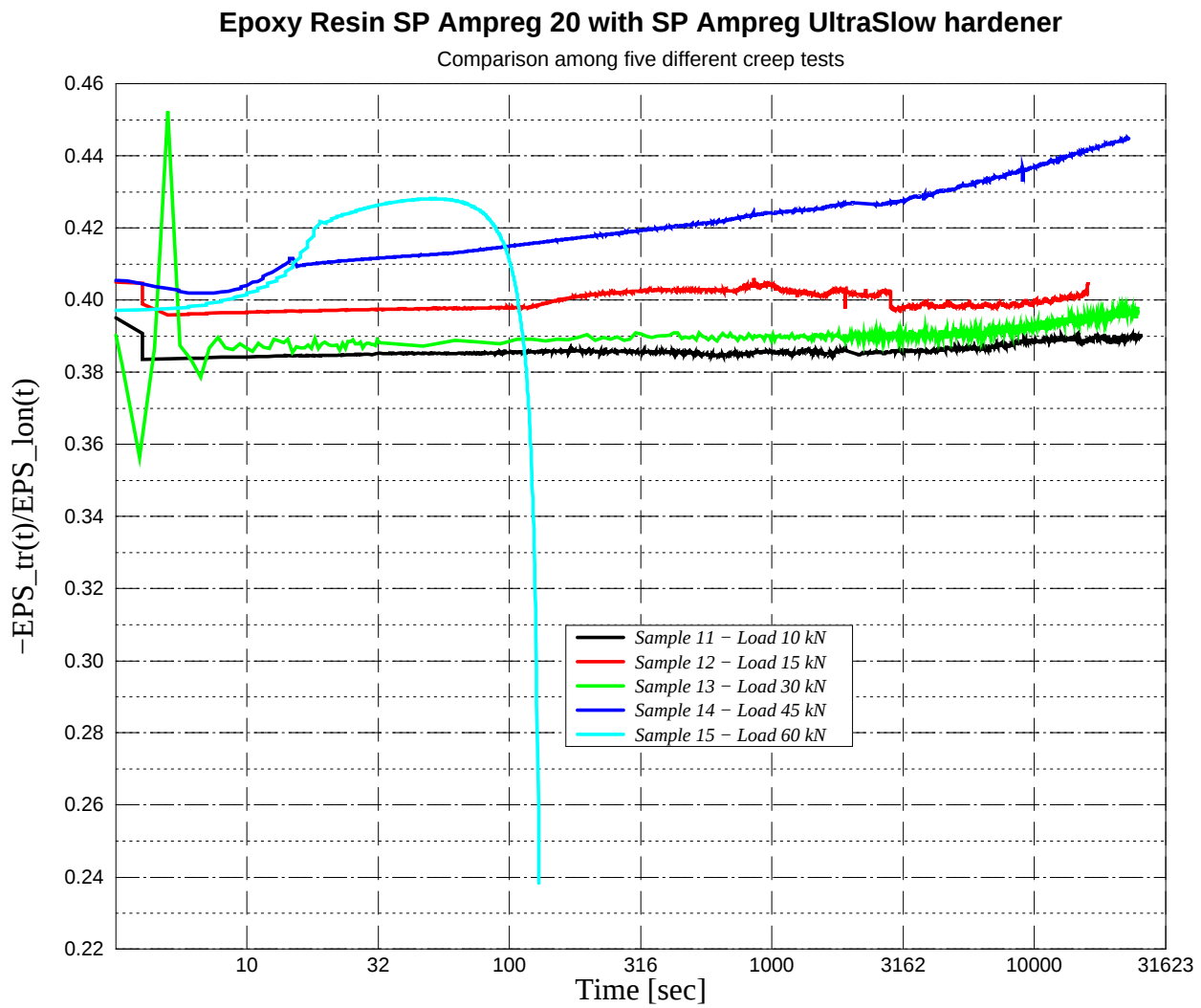


Figure 3.26: Creep tests: strain ratio–time curves at different instantaneous stress level

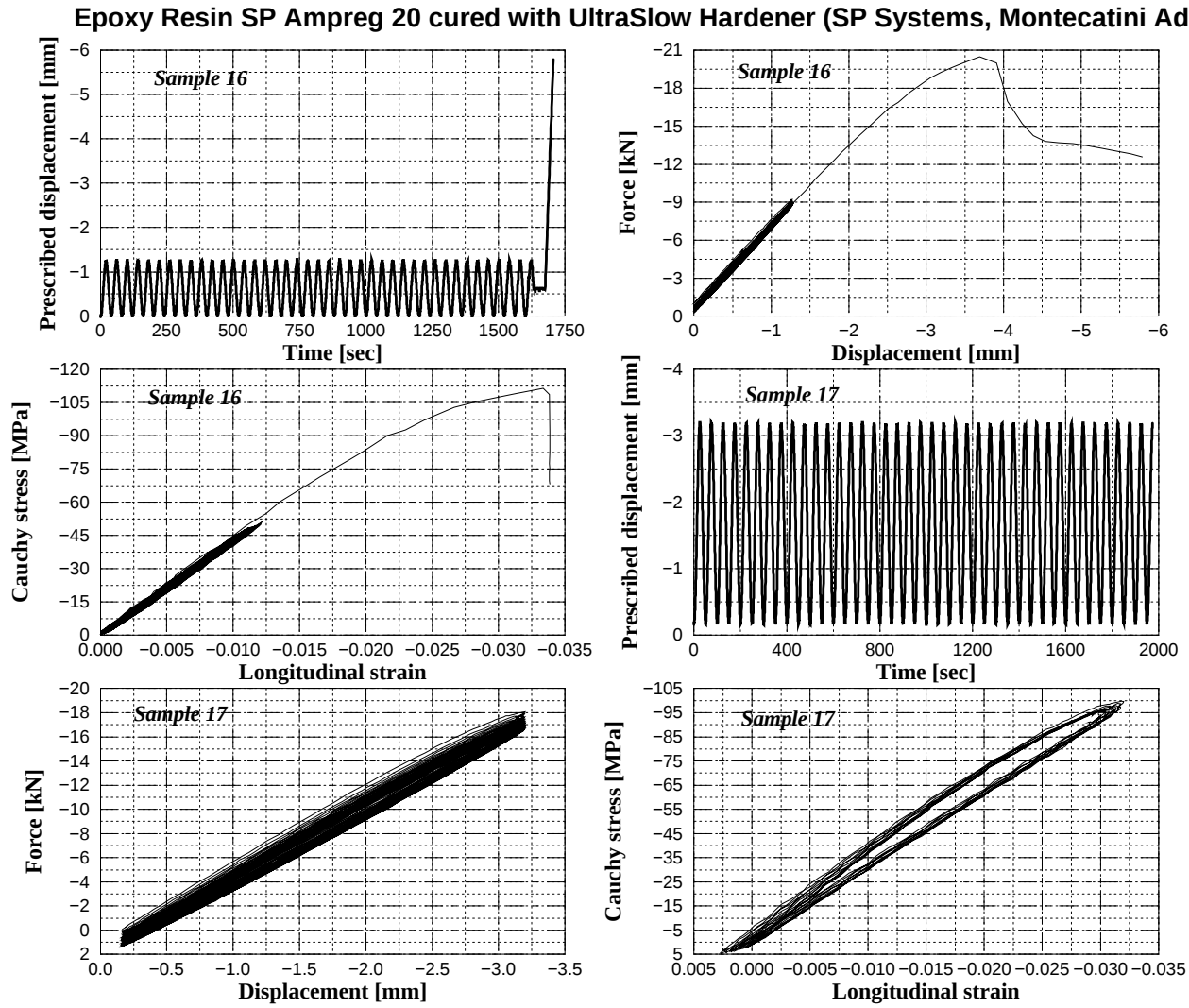


Figure 3.27: Cyclic tests: displacement–time, load–displacement, and stress–strain curves

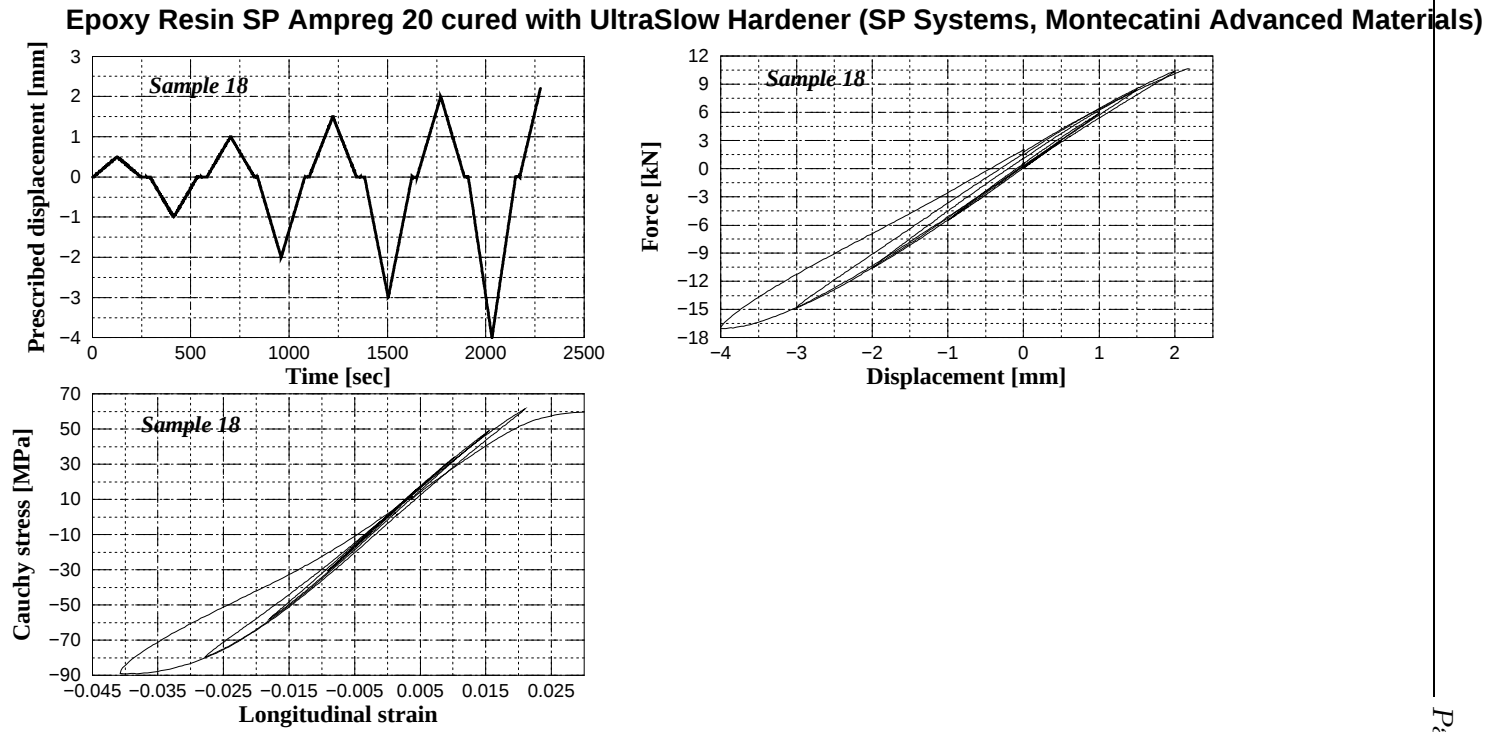


Figure 3.28: Cyclic tests: displacement–time, load–displacement, and stress–strain curves

Chapter 4

Syntactic foams: experimental results

The results reported in this chapter refer to six types of syntactic foams, whose different matrixes were made by combining the pure resins and the hardeners described in chapter 2. Together with these data, obtained by the author, other results are presented on similar syntactic foams, tested at the Laboratory for Tests on Structures of the Department of Structural Engineering, Politecnico of Milano [86].

In each of the following six sections constituting this chapter we shall deal with a different syntactic foam, for which we shall summarize the composition and report the results of the laboratory tests.

Part of these results has already been published in [9] and [16].

4.1 Syntactic foam type 1

The syntactic foam type 1 is constituted by:

- epoxy resin DGEBA DER 332, produced by Dow Chemicals, cured with the hardener DDM Fluka 32950;
- filler made by hollow glass microspheres produced under the name “ScotchliteTM Glass Bubbles” by 3M Italia [1]; in this case use is made of the spheres indicated with the name “K37”, with weight ratio of 0.25, corresponding to a volume fraction $f = 0.5153$.

It is important to note that the production modalities of this foam (resin and filler mixed by the “traditional” technique, see chapter 2 for more details) allowed us to obtain a foam with no “unwanted” voids; this is confirmed by the density measurements, always in agreement with the theoretical densities calculated from the component weight data.

This first type of syntactic foam has been tested at one volume fraction only, $f = 0.5153$. At this volume fraction, the composite density is $\rho^{(s)} = 0.7626 \text{ g/cm}^3$.

This material has been examined by means of the scanning electron microscopy (SEM), both before and after testing it, with the aim both of better understanding its internal structure and of investigating its fracture modalities. The first aspect deserves some

comments, which justify the application, at least to the syntactic foams produced by us, of the theory that will be developed in chapter 7.

The microstructure of this syntactic foam, that will be taken into account in chapter 11 also to construct numerical models, is shown in figures 4.1–4.5, obtained by means of the SEM. Figures 4.1 and 4.2 show polished sections of an untested specimen; in figure 4.1 it is important to observe that the inclusions are distributed more or less randomly, without local “lumps”. This gives ground to the essential hypothesis of *statistical homogeneity* of the composite, which will be properly defined in chapter 6 and will be always assumed in the theoretical developments. Figure 4.2 shows the geometric details of the interface between a microsphere and the resin.

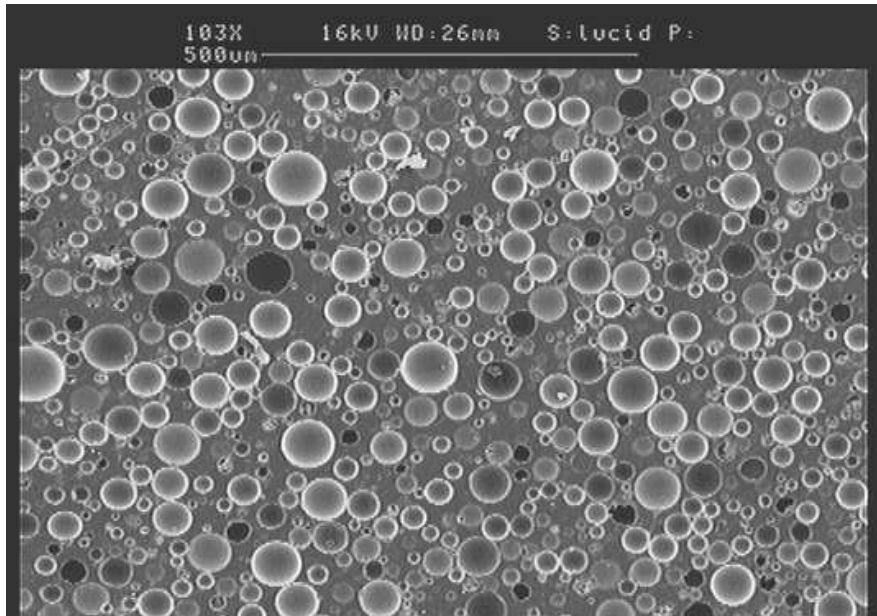


Figure 4.1: *Microstructure of syntactic foam type 1: polished section of an untested specimen*

Figures 4.3–4.5 show the fracture surface of a specimen; here one can observe how, at rupture, the hollow microspheres on the fracture surface are broken, or, if a microsphere is very stiff as the little one in figure 4.5, the matrix surrounding the filler is fractured without detach itself from the filler surface (the fact that the little microspheres are stiffer than the big ones will be shown in chapter 10, where the results of the K37 filler sieving and the related density measures will be reported). This observation supports the assumption underlying all the theory developed in the sequel of this work, i.e., that perfect adhesion exists between matrix and filler, at least in the linear elastic range.

On the other hand, this same observation contradicts a corresponding finding in a work by Hervé and Pellegrini [60], who report that, in their syntactic foam, at rupture most of the microspheres are intact, suggesting that detachment at the matrix-filler interface might be both a primary source of failure and an indication of damage occurring in the early stages of mechanical tests. We can only attribute this difference to different mechanical

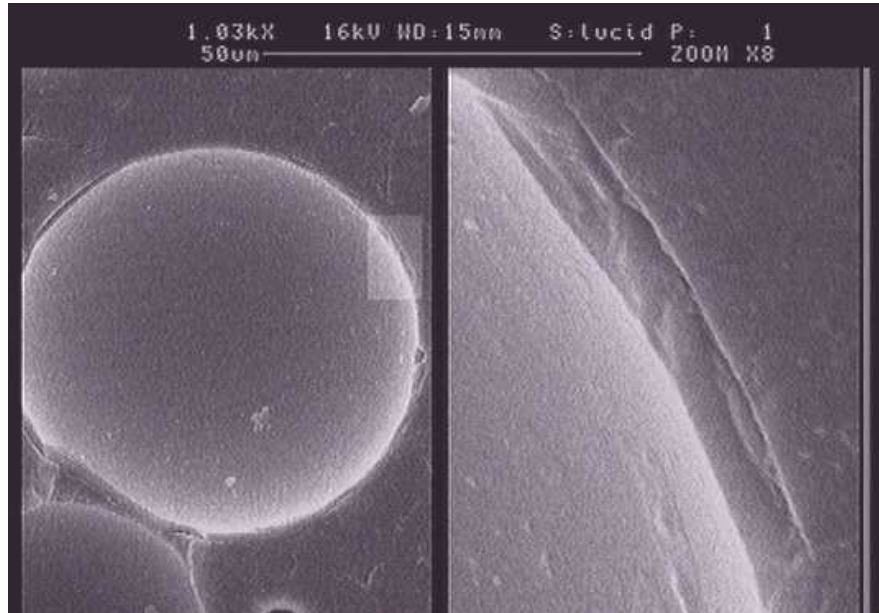


Figure 4.2: Microstructure of syntactic foam type 1: interface between filler and matrix of an untested specimen

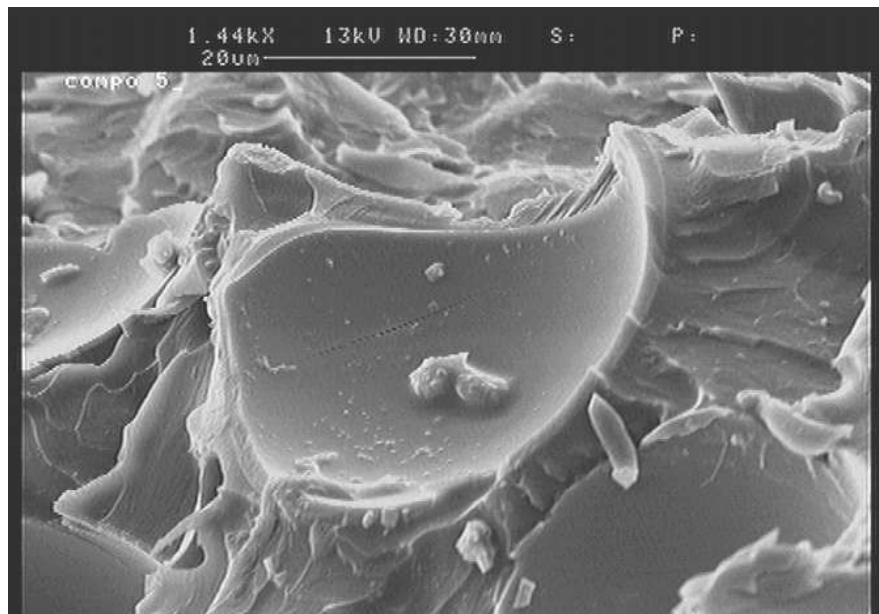


Figure 4.3: Microstructure of syntactic foam type 1: surface of fracture of a specimen

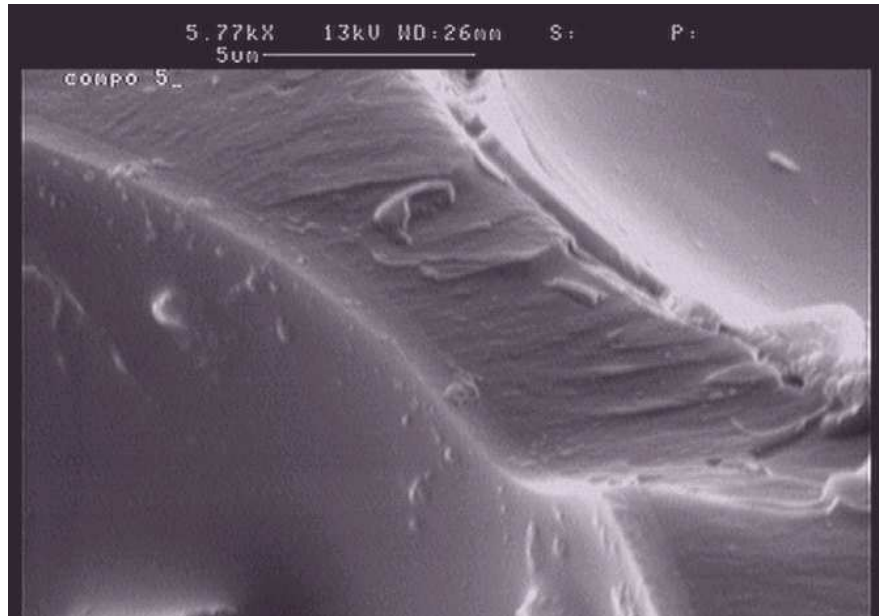


Figure 4.4: Microstructure of syntactic foam type 1: interface between filler and matrix on a fractured surface

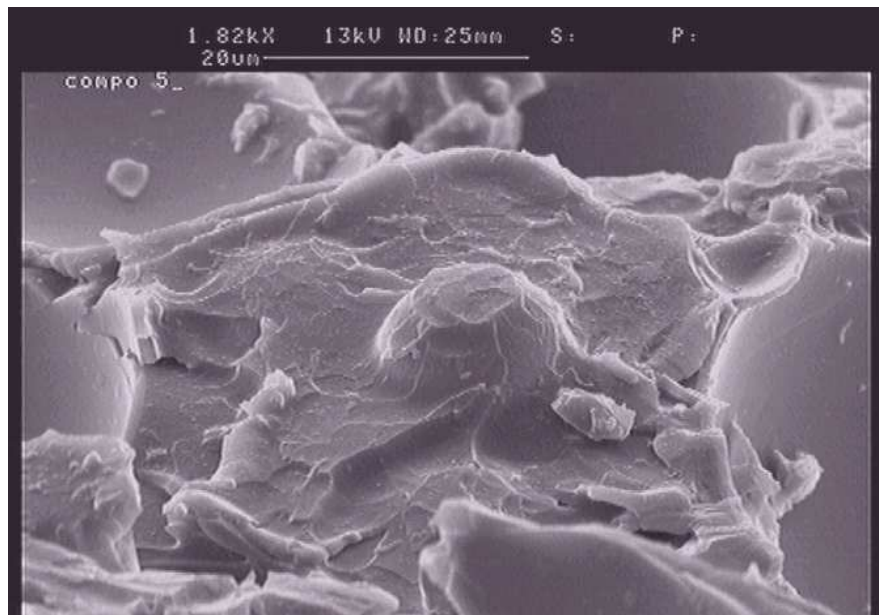


Figure 4.5: Microstructure of syntactic foam type 1: interface between filler and matrix on a fractured surface

and/or geometrical characteristics of the used materials (indeed, the inclusions used by Hervé and Pellegrini are much thicker than those used by us). Anyway, the fact that Hervé and Pellegrini found all their microspheres intact at rupture does not necessarily mean that there is not perfect adhesion between matrix and filler in the linear elastic range. Furthermore, as pointed out by Palumbo and Tempesti [93], a so-called “interphase” layer can appear around the outer surface of the inclusions, owing to an imperfect reticulation of the matrix due to the filler acting as heat sink in the syntactic foam during the curing, and, therefore, an imperfect adhesion between epoxy resin and microspheres can occur; anyway, Palumbo and Tempesti show that this problem can be fixed by curing the syntactic foam in a microwave field instead of curing it in a thermal field.



Figure 4.6: *Compressive failure of a specimen made by syntactic foam type 1*

Fifteen tests have been carried out on the syntactic foam type 1. The graphics plotted in figures 4.7–4.12 report all the data obtained from the first eleven tests, whose specimens were instrumented with strain gauges (see section 2.2). The results are practically deterministic. Indeed, comparing different tests of the same kind, one can not see appreciable differences, except for the strength in tension, observed equal to $\sigma_0^t = 28 \text{ MPa}$, $\sigma_0^t = 21 \text{ MPa}$, and $\sigma_0^t = 29 \text{ MPa}$ for the third, the fourth, and the eleventh tests respectively (samples 3, 4, and 11); anyway, for this brittle material, the strength in tension is the hardest datum to determine correctly, since it is strongly dependent upon the presence of microscopic flaws, mostly due to the turning. This is furthermore proved by the fact that two dog bone specimens were broken where their cross section is tapered along a surface approximately normal to their axis of cylindrical symmetry, i.e., in correspondence

of the most difficult part of the specimen to turn.

All the compressive tests were carried out up to the failure of the specimen, with the exception of the first one (sample 1) which was stopped to unload the specimen in order to investigate its cyclic behavior. The linear elastic range in compression lasts until the Cauchy stress reaches the value of $\sigma_{l.e.}^c \approx -40 \text{ MPa}$, which corresponds to a longitudinal strain $\varepsilon_{l.e.}^c \approx -0.011$; the strength in compression is equal to $\sigma_0^c \approx -83 \text{ MPa}$, to which a longitudinal strain of $\varepsilon_0^c \approx -0.029$ corresponds; after the maximum stress is reached, a very short softening range follows; all the specimens tested in compression until rupture fractured in a plane including their axis of cylindrical symmetry (see figure 4.6). De Runtz and Hoffman [39] observed this failure mode for syntactic foams made by glass microspheres defined as “very thick”. They found that kind of syntactic foams too brittle and heavy to be employed and, indeed, implicitly stated that the brittleness of glass-filled syntactic foams is somehow proportional to the filler heaviness.

Unfortunately, in the tests on sample 7 and sample 8 it was not possible to record strains higher than ≈ 0.023 . In torsion (sample 11) the ultimate shear stress is equal to $\tau_0 \approx 34 \text{ MPa}$, corresponding to a shear strain of about 3%. Note that even if sample 9 was 2 years aged and samples 10 and 11 were 3 years aged, they showed more or less the same mechanical properties as the young specimens; this confirms the results found for the epoxy resin DGEBA DER 332, for which the aging effect seems to be trifling.

The linear elastic range in tension lasts until the specimen fails, i.e., in tension and for the dimensions of the dog bone specimens reported in figure 2.4 the syntactic foam type 1 behaves in a perfectly brittle fashion. Finally, the cyclic tests (samples 1, 5, and 6) show the absence of plastic deformations; for these cyclic tests, since the transversal deformation was not measured, the Poisson ratio computed from the other tests on the same material was employed to obtain the Cauchy stress.

All the computed values of the elastic constants are collected in Table 4.1, where uniaxial compression is distinguished from uniaxial tension and the rate of prescribed displacement, the aging time, and the cycle number are reported. The first column refers to the shape of the employed specimens (see section 2.2). The results indicate that the elastic behavior of this material is practically symmetric in tension and compression, if one neglects a tendency to be slightly stiffer in tension. The average values of the elastic moduli are $E \approx 3500 \text{ MPa}$ and $\nu \approx 0.335$. It is further worth pointing out the quite good internal consistency among the different elastic moduli experimentally determined: the shear modulus computed from the above reported average values of the Young modulus and the Poisson ratio turns out to be $G \approx 1310 \text{ MPa}$, very close to the measured value of 1329 MPa .

Table 4.2 collects the Young modulus values computed for all cycles in the test on sample 5. The symbol (*) indicates those cycles for which the Young modulus was computed by a regression over a set of data whose corresponding maximum absolute value of the longitudinal strain was lower than 0.4%. The little damage found in doing cyclic tests as that on sample 5 could be explained by at least one of the following three different phenomena: (i) the damage occurring in the epoxy resin, (ii) the failure of an amount of microspheres which increases in every cycle, and, less likely for this particular syntactic foam, (iii) the damage occurring at the interface between the matrix and the filler. The eighth cycle was actually not completed (the specimen failed) and, furthermore, it furnished a too high Young modulus, which likely means that the strain gauges were coming

Sample	f	E [MPa]	ν	G [MPa]	Rate	Aging [years]	Stress State	Cycle #
1 CYL1	0.5153	3440	0.337		0.5 mm/min	0	comp	1
2 CYL1	0.5153	3460	0.336		0.5 mm/min	0	comp	1
3 DB1	0.5153	3530	0.333		0.2 mm/min	0	tens	1
4 DB1	0.5153	3530	0.333		0.2 mm/min	0	tens	1
5 DB1	0.5153	3480			0.25 mm/min	0	comp	1
5 DB1	0.5153	3480			0.1 mm/min	0	tens	2
6 DB1	0.5153	3480			0.25 mm/min	0	comp	1
6 DB1	0.5153	3530			0.1 mm/min	0	tens	2
7 CYL1	0.5153	3470	0.331		1.0 mm/min	0	comp	1
8 CYL1	0.5153	3450	0.345		1.0 mm/min	0	comp	1
9 DB1	0.5153	3524	0.336		0.25 mm/min	2	comp	1
9 DB1	0.5153	3571	0.333		0.1 mm/min	2	tens	2
10 DB3	0.5153	3505	0.5 mm/min		3	tens	1	
11 DB3	0.5153			1329	3 deg/min	3	tors	1

Table 4.1: *Experimental results for syntactic foam type 1 (DGEBA+DDM+K37): elastic constants*

off.

Cycle #	E_{comp} [MPa]	Rate [mm/min]	u_{max} [mm]	σ_{max} [MPa]	Stress State
1	3484	0.25	-0.5	-16	comp
2 (*)	3484	0.1	0.1	7.8	tens
3	3473	0.5	-1.0	-32	comp
4	3454	0.2	0.4	15	tens
5	3434	1.0	-2.0	-59	comp
6	3386	0.3	0.6	23	tens
7	3340	1.5	-3.0	-79	comp
8	3650	0.4	failure	17	tens

Table 4.2: *Young modulus values of a specimen (sample 5) of syntactic foam type 1 subjected to cyclic uniaxial loading*

Finally, four more tests (samples 12–15) were performed to get multiaxial failure points. To this purpose, specimens of the type DB3 were simultaneously twisted and longitudinally loaded. These specimens were not instrumented. They were three years aged, but, as already said, the aging effect should not play an important role. Actually, we were able to accomplish these tests only by applying an axial force first and then by twisting the specimens until failure while the axial force was kept constant. Both the axial force application rate and the crosshead angle rate were always kept constant and equal to 3 kN/min and 3 deg/min respectively. The first test was accomplished to check the failure torque obtained from the test on sample 11 and therefore we did not stretch the

specimen at all.

It is worth to mention that while the specimens were twisted, after having been subjected to the axial load, they significantly crept in the longitudinal direction owing to the constant axial force. This effect could affect the failure behavior, because, most likely, the creep makes the resin decreasing its self-equilibrated stress state to the prejudice of the filler; to investigate this phenomenon there would be the need of carrying out many more tests at different rates. It is anyway supposed that if the syntactic foam failure is due to the resin collapse, the creep should make the ultimate load increasing, contrary to the case in which the composite rupture is due to the glass failure. The simulation of the failure modalities for this composite is an open area of research, but some preliminary results have been obtained, which will be discussed in section 19.2.

Table 4.3 collects the final stress states at failure obtained from these four tests and their corresponding values in the principal stress plane. Figure 4.13 shows the angle versus torque plots and the axial creep on sample 14, which is the most affected by the resin viscosity because of the axial stress level to which it is subjected, whereas figure 4.14 reports the failure surface in both the $\sigma - \tau$ plane and principal stress components. Note that the shear stress corresponding to zero direct stress is the average between the results obtained from the tests on samples 11 and 12 and that the strength in compression is evicted from tests on specimens of the type CYL1 ($\sigma_{0,nom} = 85 \text{ MPa}$). The shear stress values are referred to the external specimen surface and have been computed by exploiting the linear elastic relation for circular cross sections, which should overestimate the shear stress in the nonlinear range. Moreover, both Table 4.3 and figure 4.13 report nominal stress values.

Sample	f	$\sigma_{0,nom}$ [MPa]	$\tau_{0,nom}$ [MPa]	Rate of torsion	Aging [years]	Stress State	σ_I [MPa]	σ_{II} [MPa]
12 DB3	0.5153	0.0	35.9	3 deg/min	3	tors	-35.9	35.9
13 DB3	0.5153	-40.0	47.2	3 deg/min	3	comp/tors	-71.3	31.3
14 DB3	0.5153	-58.0	39.4	3 deg/min	3	comp/tors	-77.9	19.9
15 DB3	0.5153	11.5	32.0	3 deg/min	3	tens/tors	-26.8	38.3

Table 4.3: *Experimental results for syntactic foam type 1 (DGEBA+DDM+K37): stress state at failure*

4.2 Syntactic foam type 2

The syntactic foam type 2 consists of:

- the same prepolymer DGEBA DER 332 as for syntactic foam type 1, but cured with a different hardener (type Laromin C252, produced by BASF);
- the same filler made by microspheres type K37 as for syntactic foam type 1.

This foam differs from the first one essentially because of the production modalities. Here, the “injection” technique was used (see section 2.1), in such a way as to obtain the highest possible volume fraction of filler. In this way, however, it is almost inevitable to introduce

also “unwanted” voids in the composite. In this case, both the volume fraction f of the filler and the volume fraction of these “unwanted” voids have been carefully measured by weighing the specimens, putting them into a muffle oven, and then taking weight of the dry glass; when the “injection” technique is adopted, unlike the case with the “traditional” technique, the exact weight fractions of microspheres and resin are a priori unknown: this is the reason why, to know them, one needs to burn the resin into a muffle oven.

Two cyclic tests were carried out on dog bone specimens type DB1 whose geometry details are reported in section 2.2; the results illustrated in figure 4.15 show an elastic-brittle behavior quite similar to that found for the syntactic foams type 1. It is interesting to note that the first specimen (sample 1) was produced employing silanized microspheres (see section 2.1): as one can see in Table 4.4, this specimen has an “unwanted” voids content v less than that found in the specimen produced with regular filler (sample 2); it is then likely that the silanization helps also in reducing the content of “unwanted” voids, allowing the production of a stiffer specimen, beside improving the ultimate behavior. Indeed, it is our opinion that most of the “unwanted” voids are entrapped at the interface between matrix and filler, i.e., where the resin, because of its viscosity, can not fill all the spaces left between adjacent microspheres, interstices that are too narrow when the maximum volume fraction of filler is the goal, as in the “injection” technique. Concerning the ultimate behavior, actually, sample 1, i.e. the silanized one, collapsed at a rupture displacement lower than that of sample 2; this is not contradictory since both the collapses occurred in tension, stress state for which the surface flaws due to the turn on the specimens, as above explained, are definitely more important in driving the failure than the defects in the interface between filler and matrix.

Table 4.4 shows the experimental elastic constants obtained for this syntactic foam; for these cyclic tests, the transversal deformation was also measured. Unlike the syntactic foam type 1, this composite does not exhibit an appreciable difference between the elastic moduli in compression and tension. The symbols f , m , and v refer to the filler, matrix, and “unwanted” void volume fractions respectively.

Sample	f	m	v	E [MPa]	ν	Rate [mm/min]	Stress State	Cycle #	Silanization
1 DB1	0.6058	0.3846	0.0096	3485	0.324	1	comp	1	yes
1 DB1	0.6058	0.3846	0.0096	3484	0.324	0.1	tens	2	yes
2 DB1	0.5835	0.3778	0.0387	3215	0.325	1	comp	1	no
2 DB1	0.5835	0.3778	0.0387	3289	0.324	0.1	tens	2	no

Table 4.4: *Experimental results for syntactic foam type 2 (DGEBA+Laromin+K37)*

4.3 Syntactic foam type 3

The syntactic foam type 3 is made up of:

- the epoxy resin SP Ampreg 20TM, produced by SP Systems, Montecatini Advanced Materials, with hardener “UltraSlow Hardener”, produced by SP Systems, Montecatini Advanced Materials;

- the same microspheres as those described for the syntactic foams type 1 and 2, again of the type K37, with various volume fractions and in some cases sifted in order to obtain a controlled granulometry. Fillers characterized by three different diameter sizes were employed: $32 \leq \Phi \leq 45 \mu m$, $45 \leq \Phi \leq 63 \mu m$, and $63 \leq \Phi \leq 90 \mu m$, where Φ indicates the diameter of one inclusion. Since the wall thickness of the K37 microspheres is *not* proportional to their outer radius, microspheres with different sizes show different stiffness; for more details about the K37 filler gradation see chapter 10 (in particular, Table 10.1).

This syntactic foam has been prepared in Brescia, and tested both in Brescia and in Milano. Its production modalities have been similar to those used for producing the syntactic foam type 2, i.e., injection with no control both on the volume fraction of the filler and on the presence of “unwanted” voids.

All the tests performed on this syntactic foam, as for the following syntactic foams type 4 and 5, were monotonic in uniaxial compression and, for the tests carried out in Brescia, the imposed displacement rate was kept equal to 0.5 mm/min .

Figures 4.16–4.17 show the four tests (samples 1–4) performed in Brescia on the syntactic foam made with the filler “as it is”, i.e. with K37 microspheres as furnished by the producer. This material, at least in compression, behaves like the syntactic foam type 1, also in terms of failure modality; its linear elastic range is practically deterministic and lasts until the Cauchy stress reaches the value of $\sigma_{l.e.}^c \approx -34 \text{ MPa}$, to which a longitudinal strain of $\varepsilon_{l.e.}^c \approx 0.01$ corresponds; the values of the strength σ_0^c are more dispersed than those observed for the syntactic foam type 1 and range from -58 MPa to -71 MPa , corresponding to strains varying from -0.020 to -0.024 .

One reason for this relatively high scatter can be found in the technique used to produce this material: with the “injection” technique, indeed, more microstructural imperfections, such as “unwanted” voids entrapped in the matrix, are introduced in the composite, making the material susceptible of untimely brittle failure. A second source of uncertainty in determining the strength characterizing the syntactic foam type 3 can be related to the size of the specimens: as said in chapter 2, the specimens obtained by employing the “injection” technique are smaller than those produced by means of the “traditional” technique; since the size of the microstructural flaws can be expected to be independent upon the employed method for the material production, but dependent upon the average dimensions of the filler particles, it is likely that the ultimate behavior of the syntactic foam type 3 would be more affected by the imperfections inside the composite than that of the syntactic foam type 1, both of them being filled with K37 microspheres.

Attention should be paid to the fact that the flaws which drive the failure are of a different kind depending on the stress state: for instance, in uniaxial tension, at least for the specimen size adopted by us (see previous syntactic foams type 1 and 2), the rupture is driven by the macroscopic superficial flaws due to the turning, whereas in uniaxial compression the microstructural flaws in the resin, in the glass, and in the interface between matrix and filler are those which trigger the failure. Finally, a third reason for the different dispersion in the strength results between the syntactic foams type 1 and 3 can be found in the behavior of their matrices: as pointed out in chapter 3, the resin SP Ampreg 20TM cured with the UltraSlow hardener is brittler than the epoxy resin obtained mixing DGEBA 332 and DDM 32950 hardener.

Figure 4.18 shows the results of the tests (samples 5 and 6) performed in Brescia on the syntactic foam constituted by the filler having diameter $32 \leq \Phi \leq 45 \mu m$. Unfortunately, in the test performed on sample 5 the longitudinal strain could not be measured for values greater than 0.0036.

Finally, figures 4.19 and 4.20 show the results of the three tests (samples 7–9) performed in Brescia on the syntactic foam made by the sifted filler with outer diameter $63 \leq \Phi \leq 90 \mu m$. It is apparent that this syntactic foam is less stiff and has a lower strength than that tested by means of samples 5 and 6; indeed, the microspheres used to fill samples 7–9 are lighter than those filling samples 5 and 6 (see Table 10.1).

For this syntactic foam, unfortunately, the “unwanted” voids content was not measured. Therefore, the composite density measurements allowed us to just evaluate the filler volume fractions by assuming the absence of “unwanted” voids; of course, these volume fractions are overestimates of the actual filler volume fractions.

All the relevant results regarding these syntactic foams are collected in Table 4.5. The

Sample	f^*	Filler	E_{comp} [MPa]	ν_{comp}	Rate [mm/min]
1 CYL2	0.665	“as it is”	3452	0.311	0.5
2 CYL2	0.647	“as it is”	3465	0.320	0.5
3 CYL2	0.659	“as it is”	3535	0.322	0.5
4 CYL2	0.659	“as it is”	3455	0.319	0.5
(Milano)	0.678	“as it is”	3150		
5 CYL2	0.601	$32 \leq \Phi \leq 45$	3847	0.305	0.5
6 CYL2	0.585	$32 \leq \Phi \leq 45$	3826	0.309	0.5
(Milano)	0.623	$32 \leq \Phi \leq 45$	3700		
(Milano)	0.704	$45 \leq \Phi \leq 63$	2900		
7 CYL2	0.626	$63 \leq \Phi \leq 90$	3075	0.294	0.5
8 CYL2	0.665	$63 \leq \Phi \leq 90$	2942	0.269	0.5
9 CYL2	0.633	$63 \leq \Phi \leq 90$	3153	0.314	0.5

Table 4.5: *Experimental results for syntactic foams type 3 (SP Ampreg 20TM + UltraSlow)*

results are divided into four rows, depending on the employed fillers. Here, the symbol f^* indicates that, as said, the volume fractions are derived from the wrong assumption of absence of “unwanted” voids.

The specimens tested in Milano [86] are significantly less stiff than those tested by us in Brescia, even at comparable fictitious volume fractions f^* . This indicates that the specimens tested in Milano contain more “unwanted” voids than those tested in Brescia.

4.4 Syntactic foam type 4

The syntactic foam type 4 has been obtained by mixing:

- the same epoxy resin SP Ampreg 20TM with UltraSlow Hardener that used to make syntactic foam type 3;

- again microspheres type K37.

This foam is similar to the preceding foam type 3, but in this case the composite was made by means of the “traditional” technique. Unlike for the syntactic foam type 1, it was not possible to produce a composite without “unwanted” voids entrapped in the matrix, probably because the viscosity of the slurry made by the epoxy resin SP Ampreg 20TM is higher than that of the composite whose matrix is the resin DGEBA DER 332, since the temperature of the curing process involving the first type of resin is lower than that of the hardening process of the resin DGEBA DER 332. Anyway, the volume fraction of the “unwanted” voids could be easily computed since the weight ratios were a priori known.

Unfortunately, for most of the tests, 14 overall, on this syntactic foam the longitudinal strain was recorded in the linear elastic range only. For this reason, in figures 4.21 and 4.22, only the tests are shown in which all the data were completely recorded (samples 7, 11 and 13).

The relevant results are summarized in Table 4.6.

Sample	f	m	v	E_{comp} [MPa]	ν_{comp}	Rate [mm/min]
1 CYL2	0.493	0.472	0.035	3324	0.344	0.5
2 CYL2	0.493	0.471	0.036	3339	0.336	0.5
3 CYL2	0.492	0.470	0.038	3340	0.339	0.5
4 CYL2	0.496	0.474	0.030	3399	0.333	0.5
5 CYL2	0.445	0.520	0.035	3411	0.344	0.5
6 CYL2	0.447	0.522	0.031	3392	0.343	0.5
7 CYL2	0.442	0.517	0.041	3358	0.344	0.5
8 CYL2	0.447	0.522	0.031	3389		0.5
9 CYL2	0.289	0.646	0.065	3309	0.363	0.5
10 CYL2	0.291	0.649	0.060	3341	0.362	0.5
11 CYL2	0.393	0.564	0.043	3407	0.349	0.5
12 CYL2	0.395	0.567	0.038	3477	0.349	0.5
13 CYL2	0.400	0.573	0.027	3426	0.345	0.5
14 CYL2	0.398	0.571	0.031	3424	0.350	0.5

Table 4.6: *Experimental results for syntactic foam type 4 (SP Ampreg 20TM+UltraSlow+K37)*

4.5 Syntactic foam type 5

The syntactic foam type 5 is constituted by:

- the same resin and hardener as for materials type 3 and 4;
- again “ScotchliteTM Glass Bubbles” produced by 3M Italia, but here of the type K1, with two different volume fractions. The spheres type K1 are thinner and lighter than the spheres type K37 used in all the previous foams.

This type of syntactic foam, tested at the Politecnico of Milano only, using machines (MTS 329.10 S) and measurement techniques similar to those used by the author to test the previous ones, contains “unwanted” voids in known volume fraction.

Samples of group 1 (to which the first row in Table 4.7 is referred) were produced by a former house of Intermarine SpA under the trademark Tencara 2000TM, whereas samples of group 2 were manufactured at the University of Brescia [114].

The relevant experimental results are summarized in Table 4.7 and are the average values of several tests done at the Politecnico of Milano [86]. As for the syntactic foams

Sample group	f	m	v	E_{comp} [MPa]	ν_{comp}
1	0.509	0.410	0.081	1610	0.347
2	0.523	0.421	0.056	1835	0.322

Table 4.7: *Experimental results for syntactic foams type 5 (SP Ampreg 20TM+UltraSlow+K1)*

filled with K37 microspheres, the syntactic foam type 5 clearly shows a brittle behavior, but its failure is accompanied by shear bands inclined of 45 degrees with respect the axis of cylindrical symmetry of the specimen [86].

4.6 Syntactic foam type 6

The syntactic foam type 6 is made up of:

- the same resin and hardener as for syntactic foam type 1;
- again “ScotchliteTM Glass Bubbles” produced by 3M Italia [1], but of the type H50, with volume fraction $f = 0.5153$, in such a way to compare this composite with the syntactic foam type 1. The spheres type H50 are thicker and heavier than the spheres type K37 and the filler weight ratio of this syntactic foam turns out to be equal to 0.3106. Furthermore, these microspheres come silanized by the manufacturer.

This syntactic foam was produced by means of the “traditional” technique; we have checked that it does not contain “unwanted” voids. Because of this, its density is $\rho^{(s)} = 0.8296 \text{ g/cm}^3$. None of the tested specimens was aged.

All the tests, 17 overall, were carried out on specimens of the type DB3 and only samples 1–8 were instrumented.

Table 4.8 collects all the elastic constant values obtained from the tests on this syntactic foam. Figures 4.23–4.25 show the results of the tests on samples 1–8.

Note that we could not measure the transversal strain ε_t on specimen of the type DB3; therefore, to compute the Cauchy stress (see equation (2.2.1)), we assumed

$$\varepsilon_t = -\nu_0 \varepsilon_l \quad (4.6.1)$$

ν_0 and ε_l being the effective (i.e., macroscopic) Poisson ratio and the longitudinal strain respectively. The effective Poisson ratio has been estimated $\nu_0 = 0.365$ by means of

Sample	f	E [MPa]	G [MPa]	Rate	Stress State	Cycle #
1 DB3	0.5153	4057	1542 1560	0.5 mm/min	comp	1
2 DB3	0.5153	4052		0.5 mm/min	comp	1
3 DB3	0.5153	4031		0.5 mm/min	tens	1
4 DB3	0.5153	4037		0.5 mm/min	tens	1
5 DB3	0.5153			3 deg/min	tors	1
6 DB3	0.5153			3 deg/min	tors	1
7 DB3	0.5153	4058		0.5 mm/min	comp	1
7 DB3	0.5153	3925		0.5 mm/min	comp	2
7 DB3	0.5153	3897		0.5 mm/min	comp	3
8 DB3	0.5153	4102		0.5 mm/min	comp	1

Table 4.8: *Experimental results for syntactic foams type 6 (DGEBA+DDM+H50)*

the analytical homogenization method that will be presented in chapter 7. Note that this approximation is not going to produce any significant error in the elastic moduli computation, since we would anyway get a maximum error of about $(1 + 0.4 \times 0.004)^2 - 1 = 0.32\%$ if we completely neglected the Poisson effect; anyway, from this approximation, a more conspicuous error arises in the Cauchy stress computation for high strain, by the way, owing to the groundlessness of equation (4.6.1) in the nonlinear range.

For this syntactic foam, the Young and shear moduli averages are $E = 4056 \text{ MPa}$ $G = 1551 \text{ MPa}$, respectively, to which an average Poisson ratio $\nu_0 = 0.308$ corresponds.

Unfortunately, these specimens, of the type DB3, in compression became unstable near failure. This is because the grip fixtures of the testing machine we used in this case (the MTS 858 Mini Bionix at the Laboratory of Biological Structure Mechanics of the Politecnico of Milano) could not grasp our specimens all along their grips, thus leaving a free span greater than what designed.

One cyclic test has been performed on this composite (sample 7). Only three compressive cycles could be completed before failure, because of the high maximum strain level imposed, which has been chosen in such a way as to investigate the composite hysteretic behavior; this behavior has been found to have the same characteristics as that of the matrix (see section 3.2). A little damage can be observed, as shown in Table 4.8. Note that this test is affected by a progressive grip fixture sliding which happened in the first loading ramp (see figure 4.25).

The fact that the linear elastic behavior is almost perfectly symmetric in tension and compression, for this syntactic foam in which the filler is quite heavy, gives ground to the conjecture that the non-symmetric linear elastic behavior of syntactic foams made up of lighter microspheres is due to the local instability of an amount of them, which causes the compressive stiffness to be lower than the tensile one.

The nine remaining tests (samples 9-17) have been performed to find failure envelope points, as done for the syntactic foams type 1. These specimens were not instrumented and, contrary to what done for syntactic foam type 1, they were simultaneously stretched and twisted. The crosshead angle rate was kept equal to 3 deg/min for all the tests, whereas the crosshead displacement rate was chosen differently for each test, depending

Sample	f	$\sigma_{0,nom}$ [MPa]	$\tau_{0,nom}$ [MPa]	Rate of torsion	Rate of stretch	Stress State	$\sigma_{I,nom}$ [MPa]	$\sigma_{II,nom}$ [MPa]
1-2 DB3	0.5153	-99.5	0.0	0 deg/min	0.5 mm/min	comp	-99.5	0.0
9 DB3	0.5153	-84.9	10.4	3 deg/min	1.4 mm/min	comp/tors	-86.2	1.3
10 DB3	0.5153	-90.7	25.4	3 deg/min	0.55 mm/min	comp/tors	-97.3	6.6
11 DB3	0.5153	-84.0	33.8	3 deg/min	0.36 mm/min	comp/tors	-95.9	11.9
12 DB3	0.5153	-79.6	48.2	3 deg/min	0.24 mm/min	comp/tors	-102.3	22.7
13 DB3	0.5153	-60.0	53.1	3 deg/min	0.16 mm/min	comp/tors	-91.0	31.0
14 DB3	0.5153	-36.7	56.2	3 deg/min	0.09 mm/min	comp/tors	-77.5	40.8
5-6 DB3	0.5153	0.0	41.5	3 deg/min	0.0 mm/min	tors	-41.5	41.5
15 DB3	0.5153	9.9	40.4	3 deg/min	0.04 mm/min	tens/tors	-35.7	45.7
16 DB3	0.5153	19.4	35.0	3 deg/min	0.09 mm/min	tens/tors	-27.0	46.4
17 DB3	0.5153	23.6	24.7	3 deg/min	0.16 mm/min	tens/tors	-15.6	39.2
3-4 DB3	0.5153	33.5	0.0	0 deg/min	0.5 mm/min	tens	0.0	33.5

Table 4.9: *Experimental results for syntactic foam type 6 (DGEBA+DDM+H50): stress state at failure*

on the failure envelope point we were looking for. The measured force, torque, axial displacement, and angle of these nine tests are reported in figures 4.26–4.34, in which we have synchronized the two abscissa axes related to the axial displacement and the rotation angle. Moreover, figure 4.35 shows all the nominal axial stress against shear stress curves. The relevant nominal stress values at failure are collected in Table 4.9. Again, the nominal shear stress, referred to the external specimen surface, has been approximately computed by means of the well known relation for circular-cross sectioned beams twisted in the linear elastic range. Note that the nominal compressive strength has been computed by means of the results of the tests on samples 1 and 2 only, because sample 8, which was tested in monotonic compression also, prematurely failed. Figure 4.36 shows the failure envelope both in the σ - τ plane and in the principal stress plane.

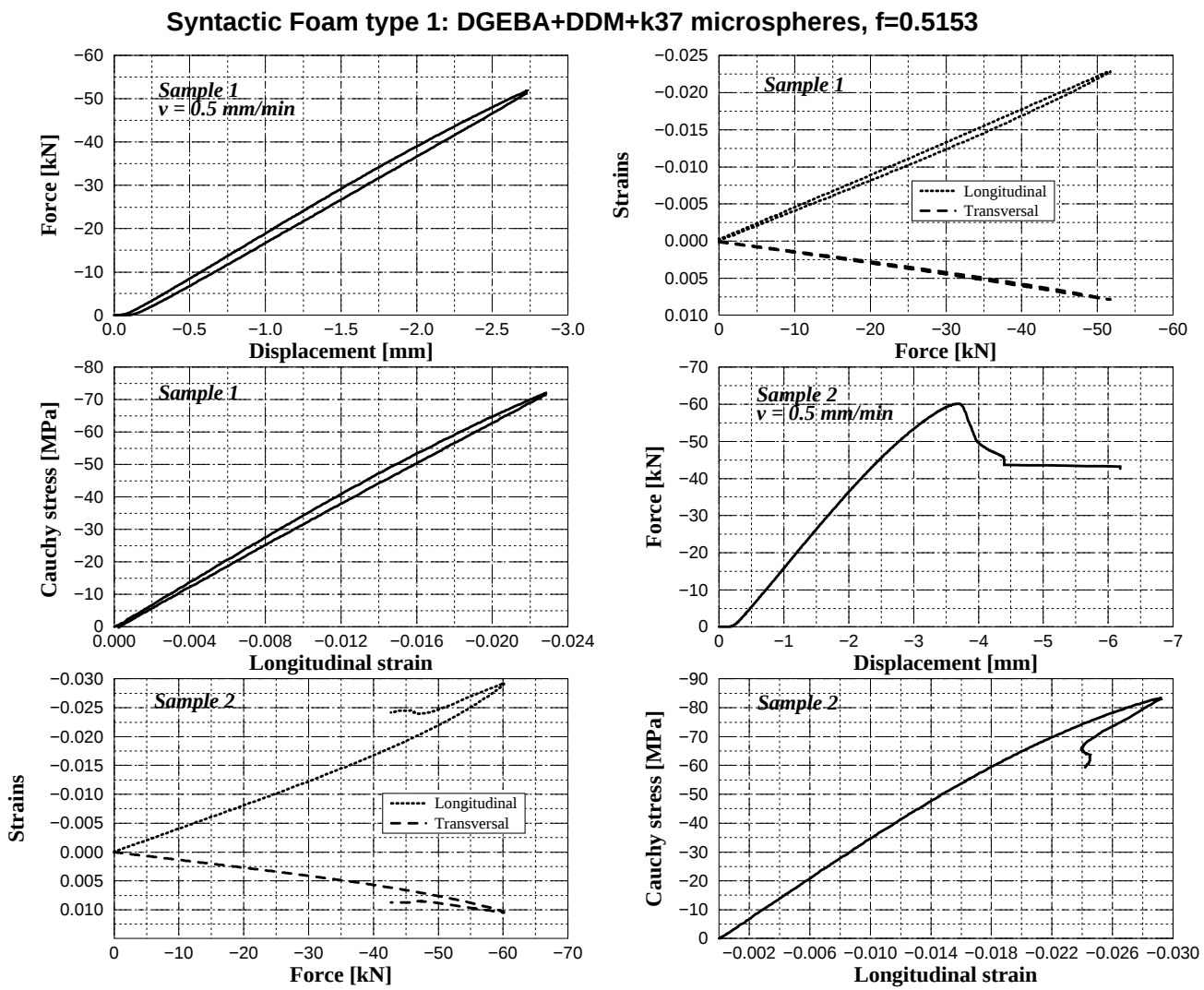


Figure 4.7: Compressive tests on syntactic foam type 1: load–displacement, strain–load, and stress–strain curves

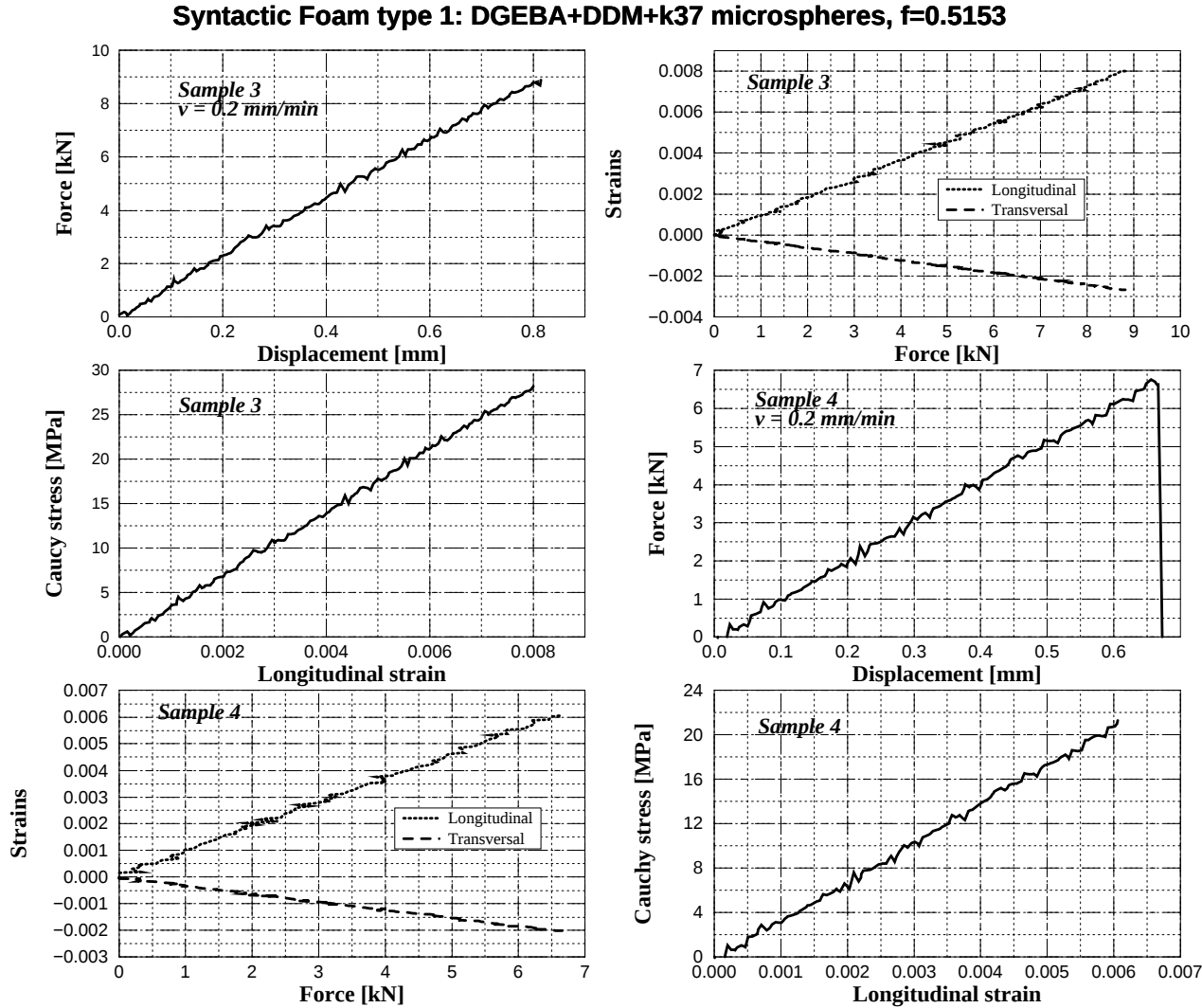


Figure 4.8: Tensile tests on syntactic foam type 1: load–displacement, strain–load, and stress–strain curves

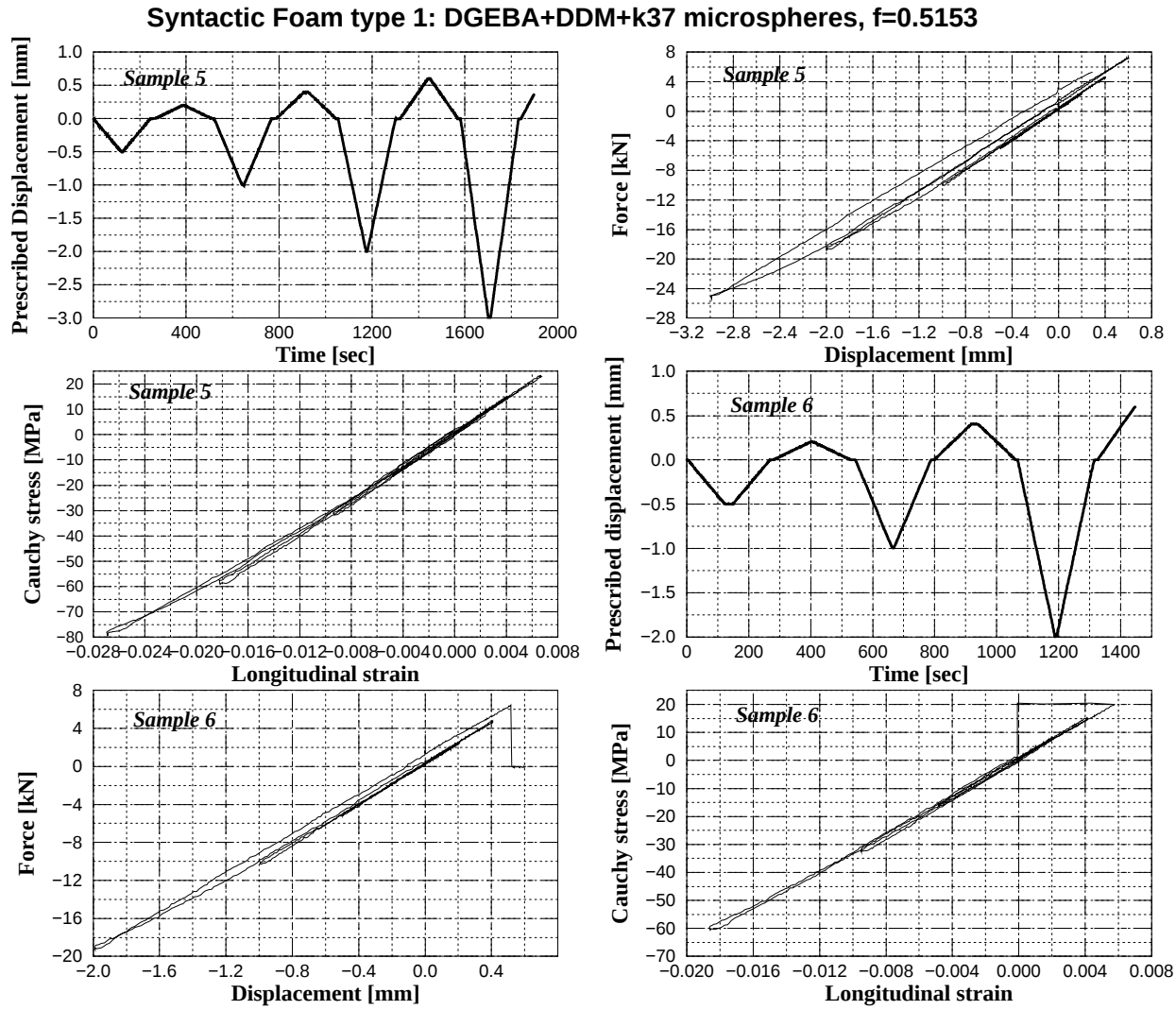


Figure 4.9: Cyclic tests on syntactic foam type 1: displacement–time, load–displacement, and stress–strain curves

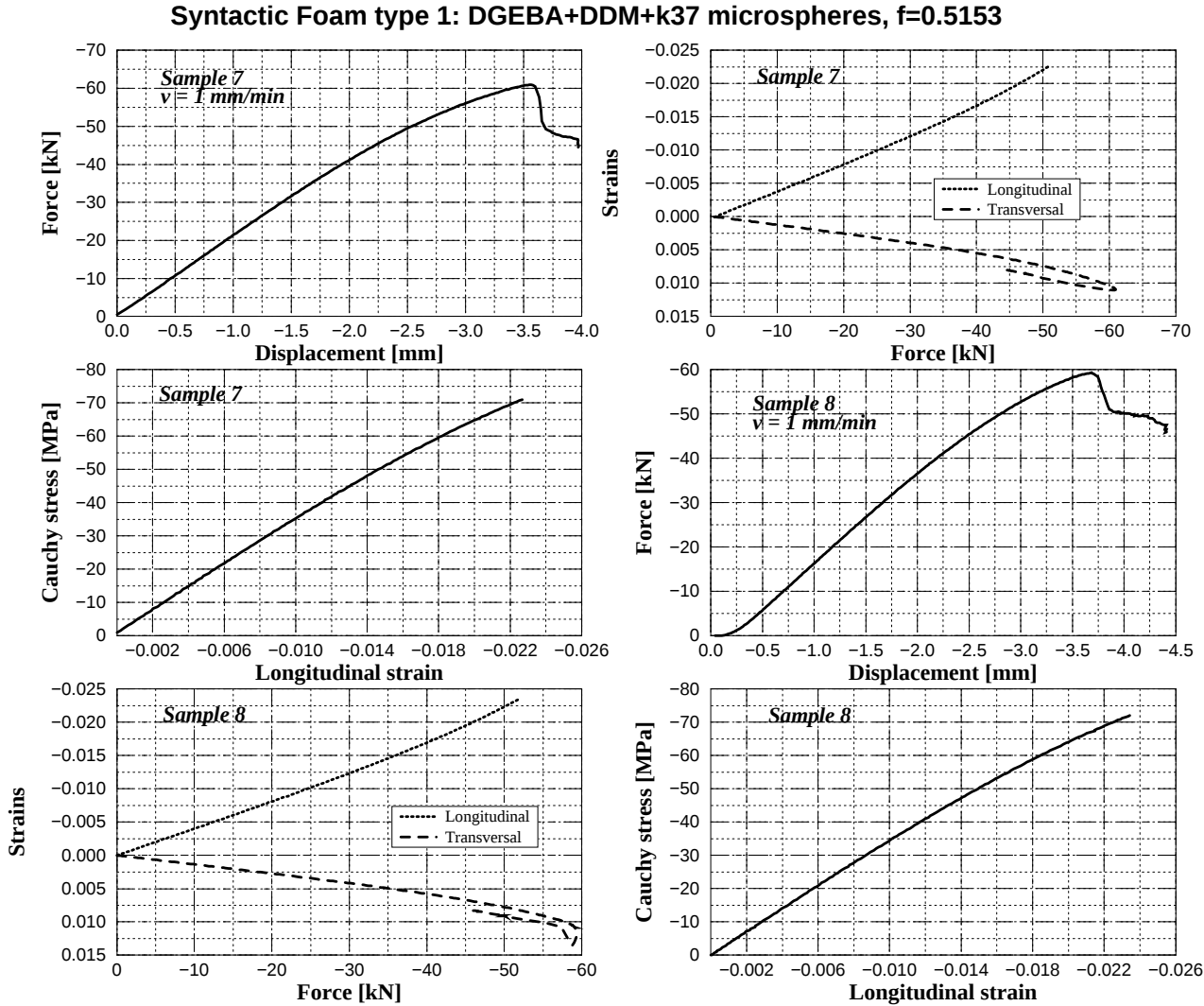


Figure 4.10: Compressive tests on syntactic foam type 1: load–displacement, strain–load, and stress–strain curves

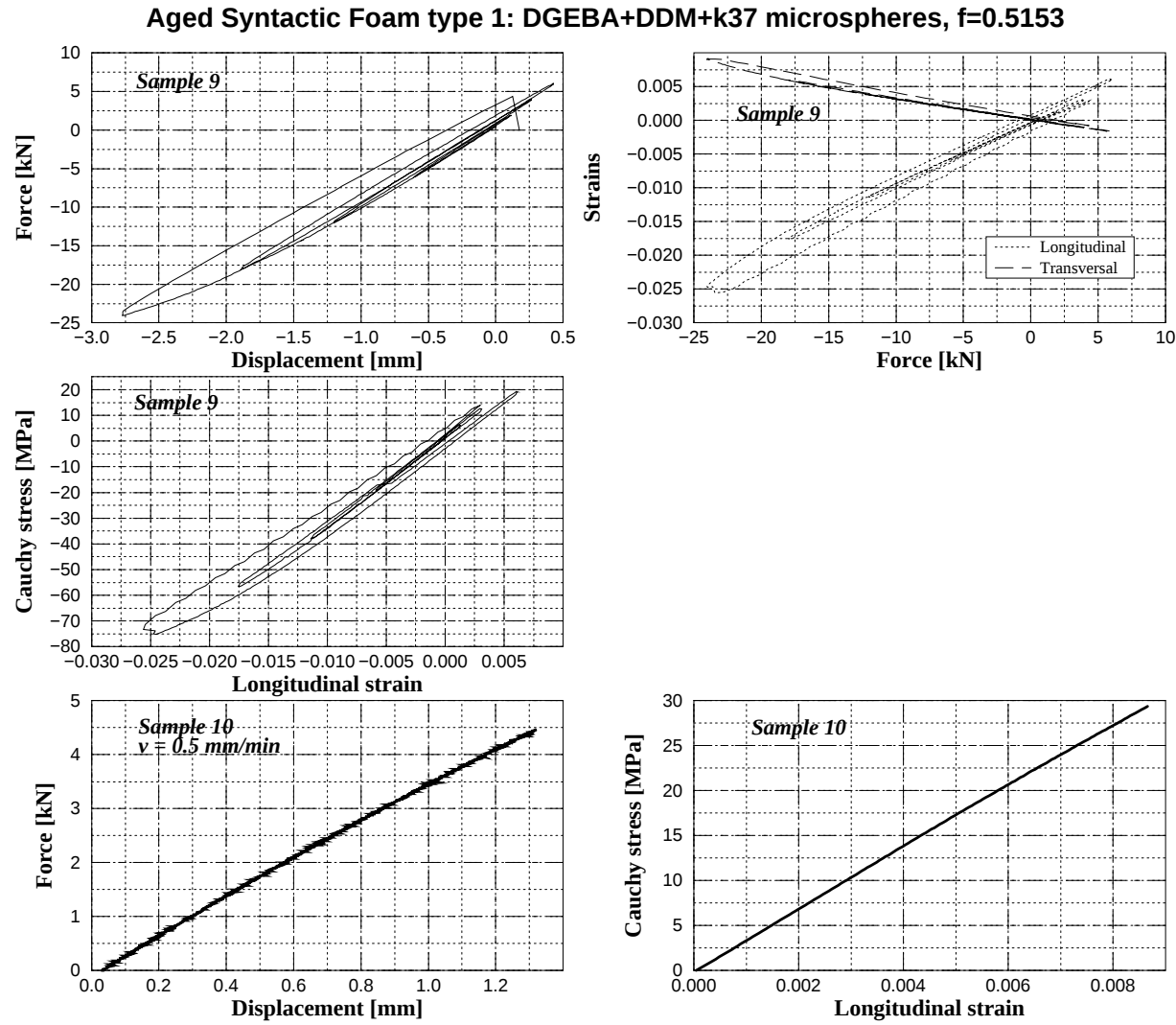


Figure 4.11: Cyclic and tensile tests on aged syntactic foam type 1: load–displacement, strain–load, and stress–strain curves

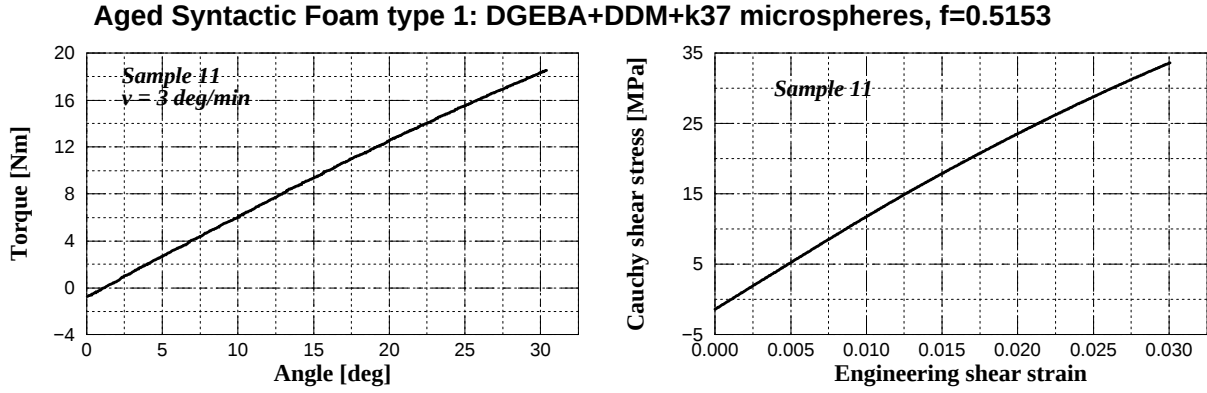


Figure 4.12: Torsion test on aged syntactic foam type 1: torque-angle and shear stress-engineering shear strain curves

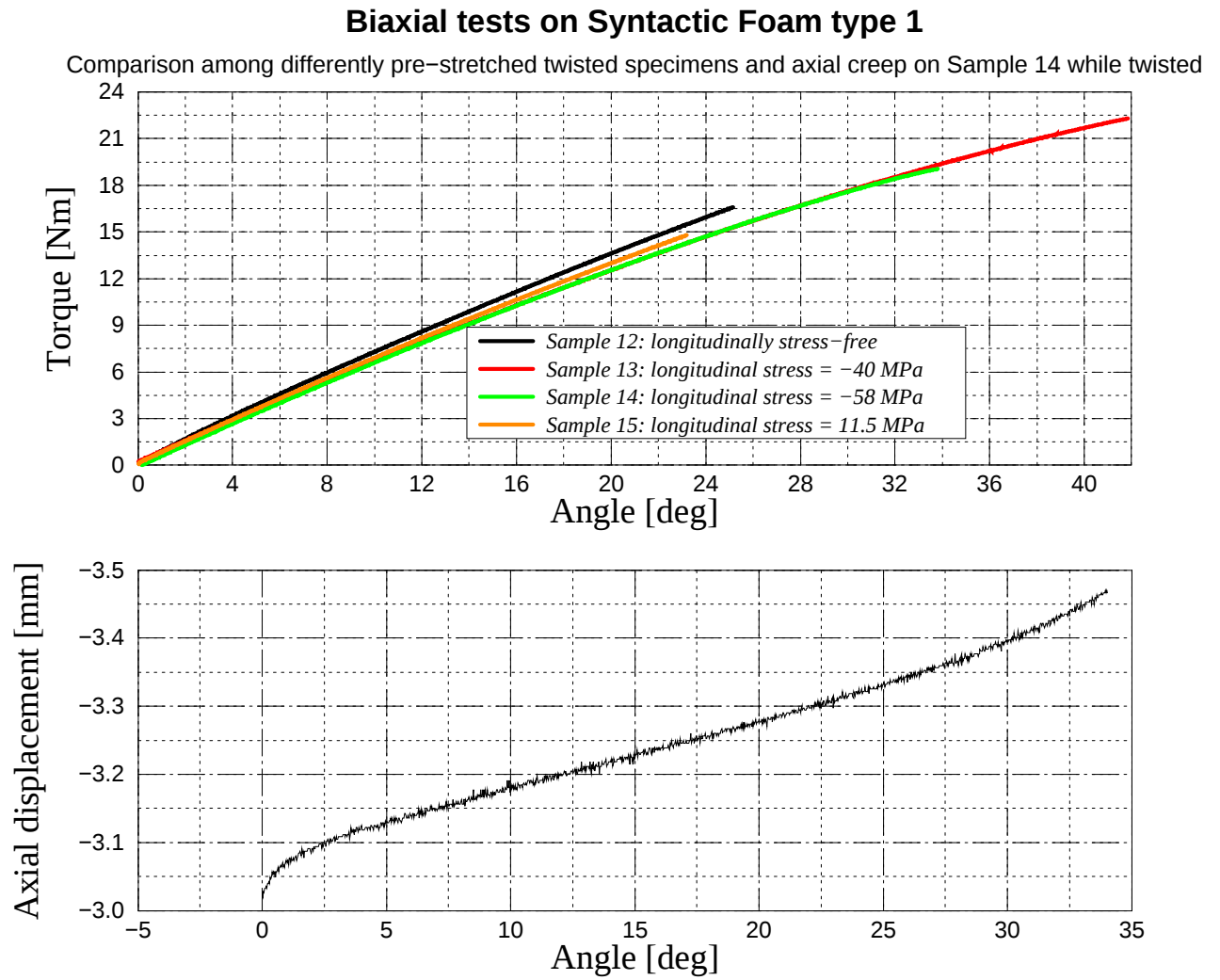


Figure 4.13: Biaxial tests on syntactic foam type 1: torque–angle curves and displacement–angle creep curve on sample 14

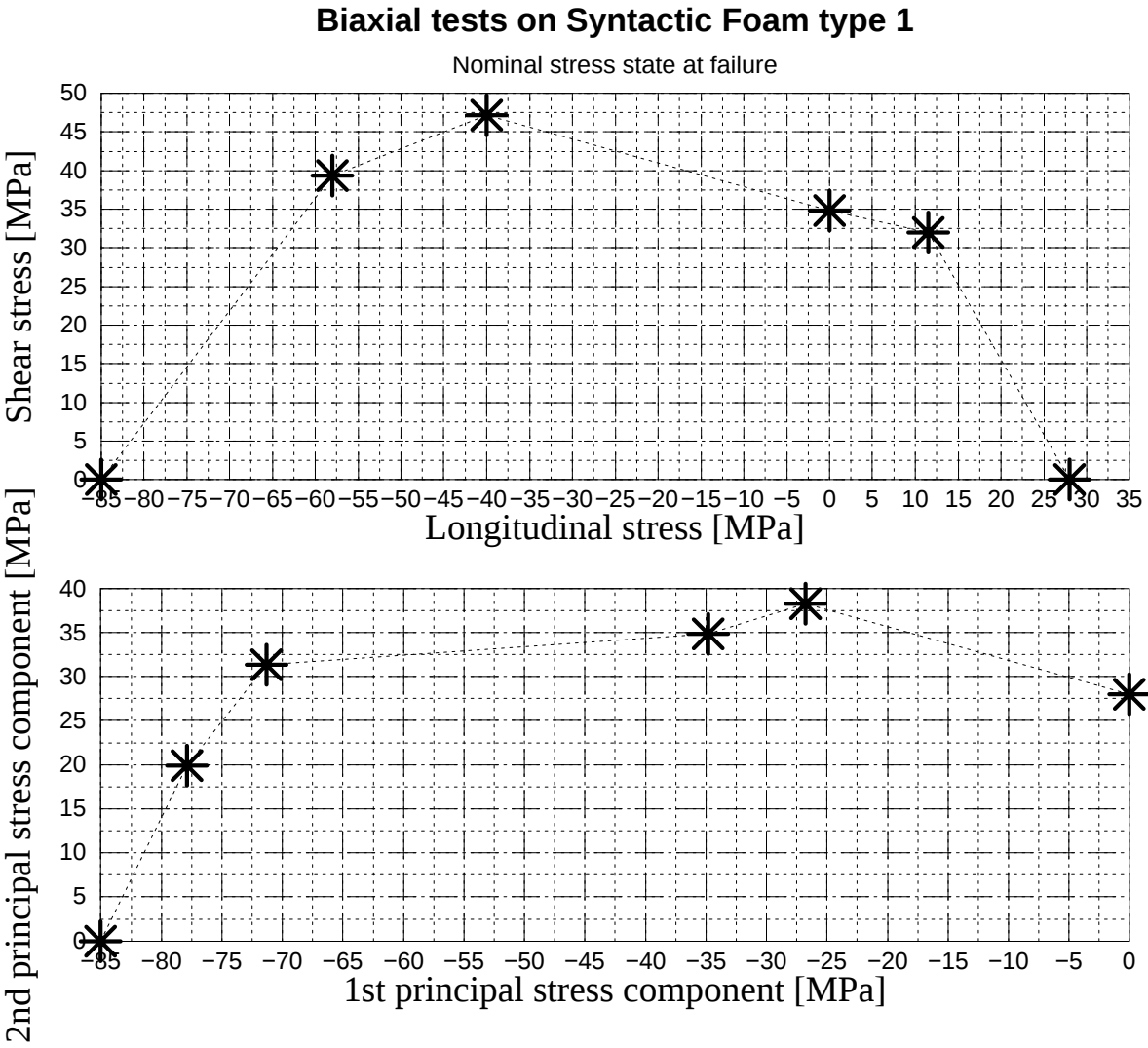


Figure 4.14: *Biaxial tests on syntactic foam type 1: failure envelope*

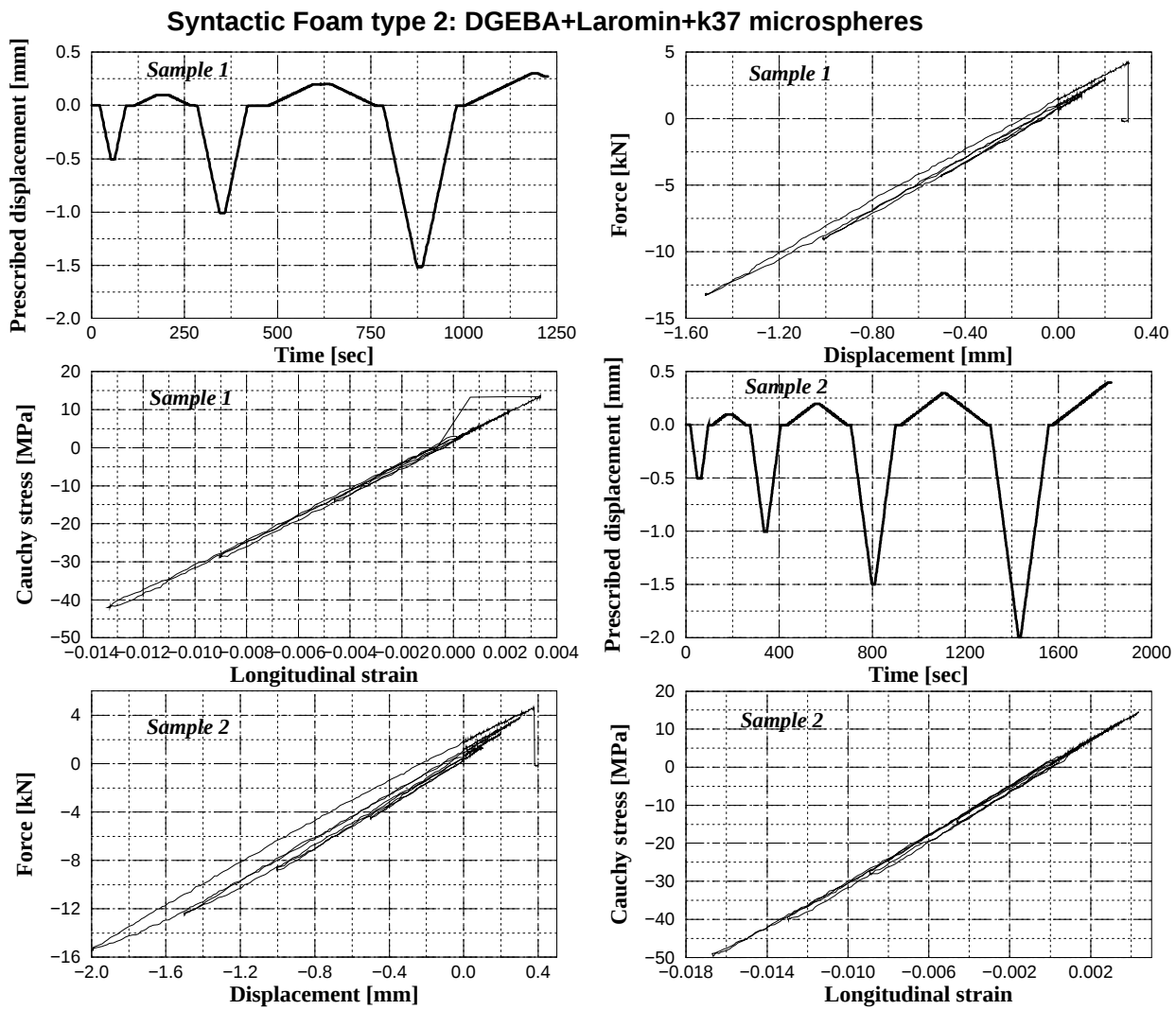


Figure 4.15: Cyclic tests on syntactic foam type 2: displacement–time, load–displacement, and stress–strain curves

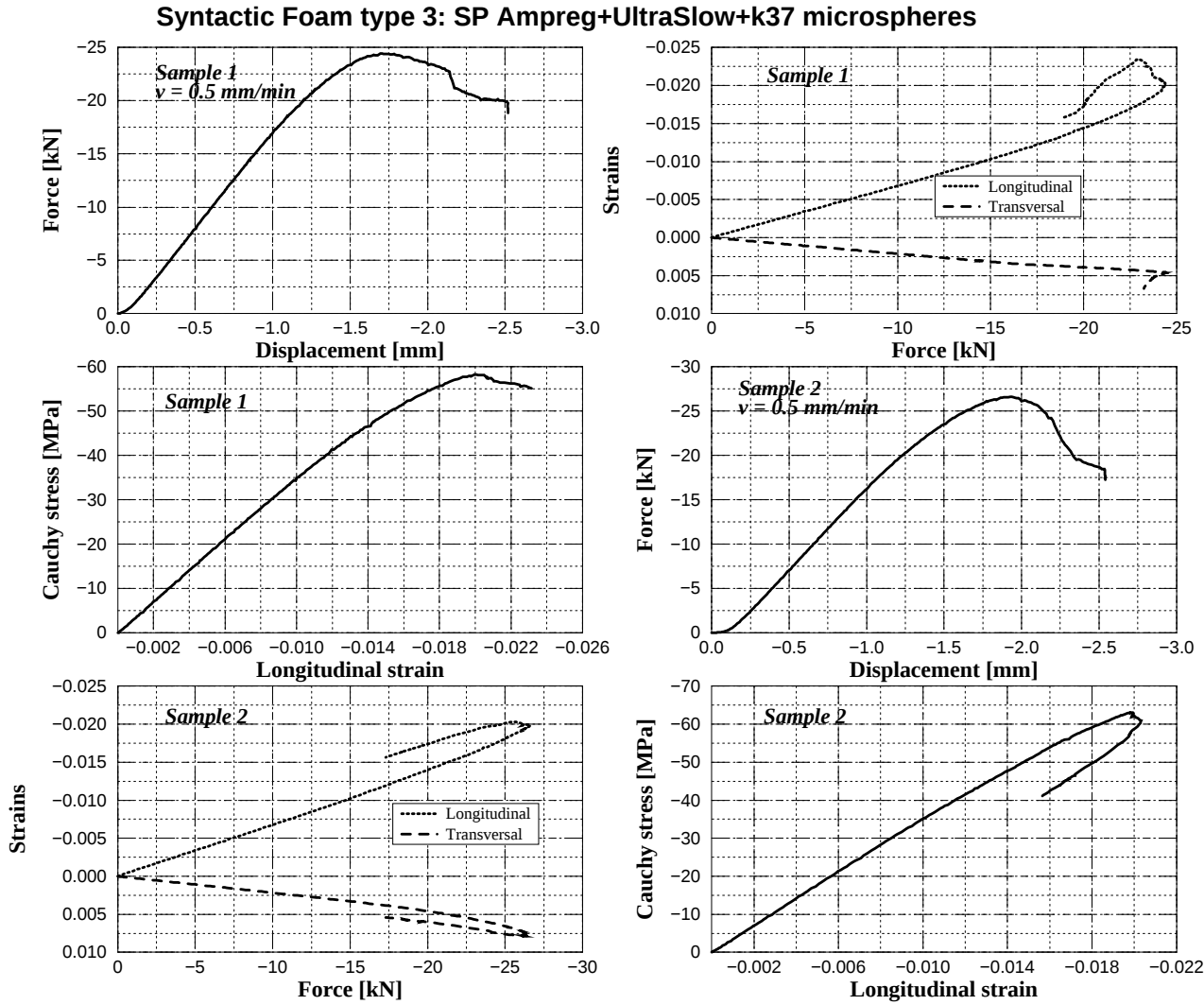


Figure 4.16: Monotonic compressive tests on syntactic foam type 3: load–displacement, strain–load, and stress–strain curves

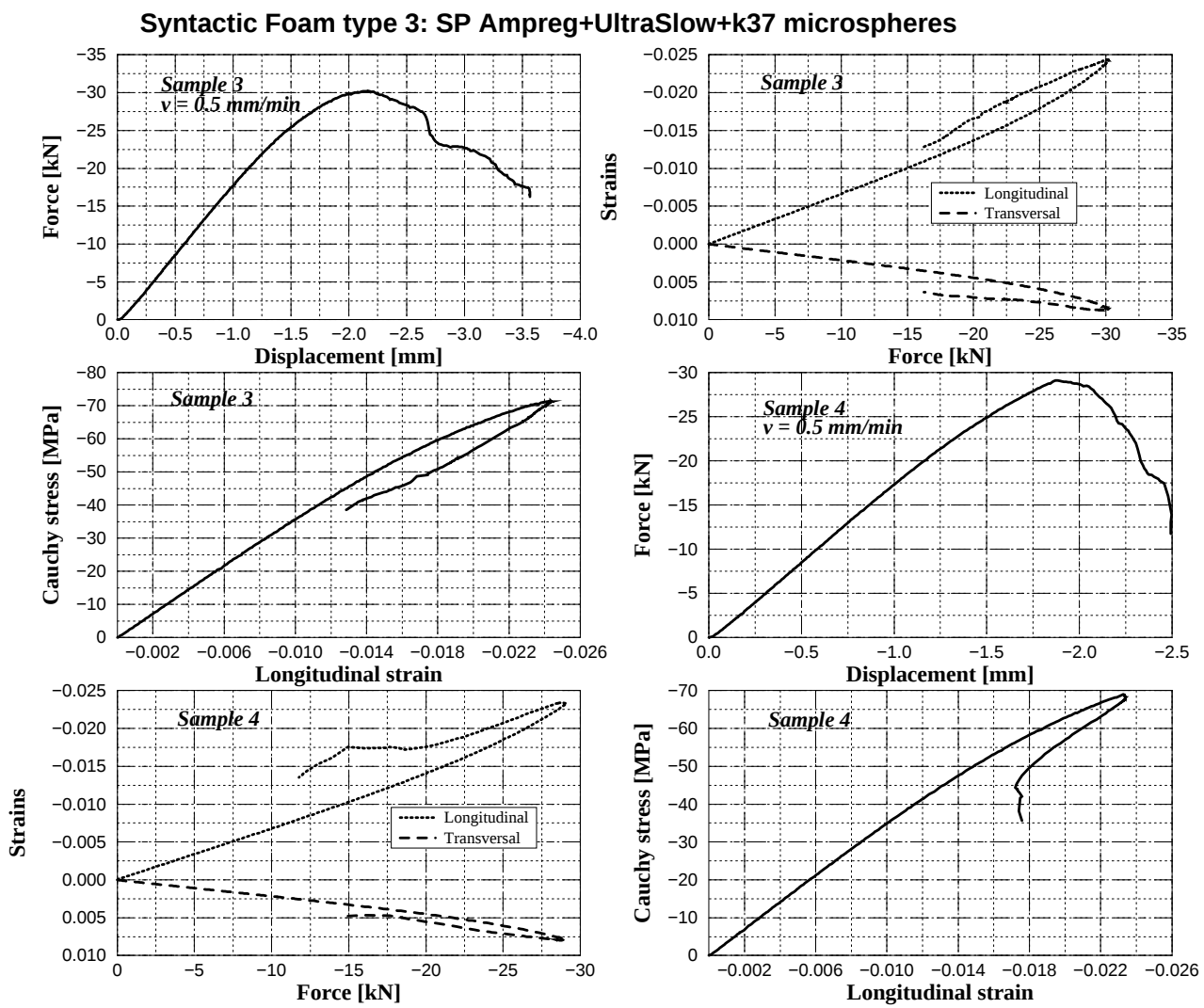


Figure 4.17: Monotonic compressive tests on syntactic foam type 3: load–displacement, strain–load, and stress–strain curves

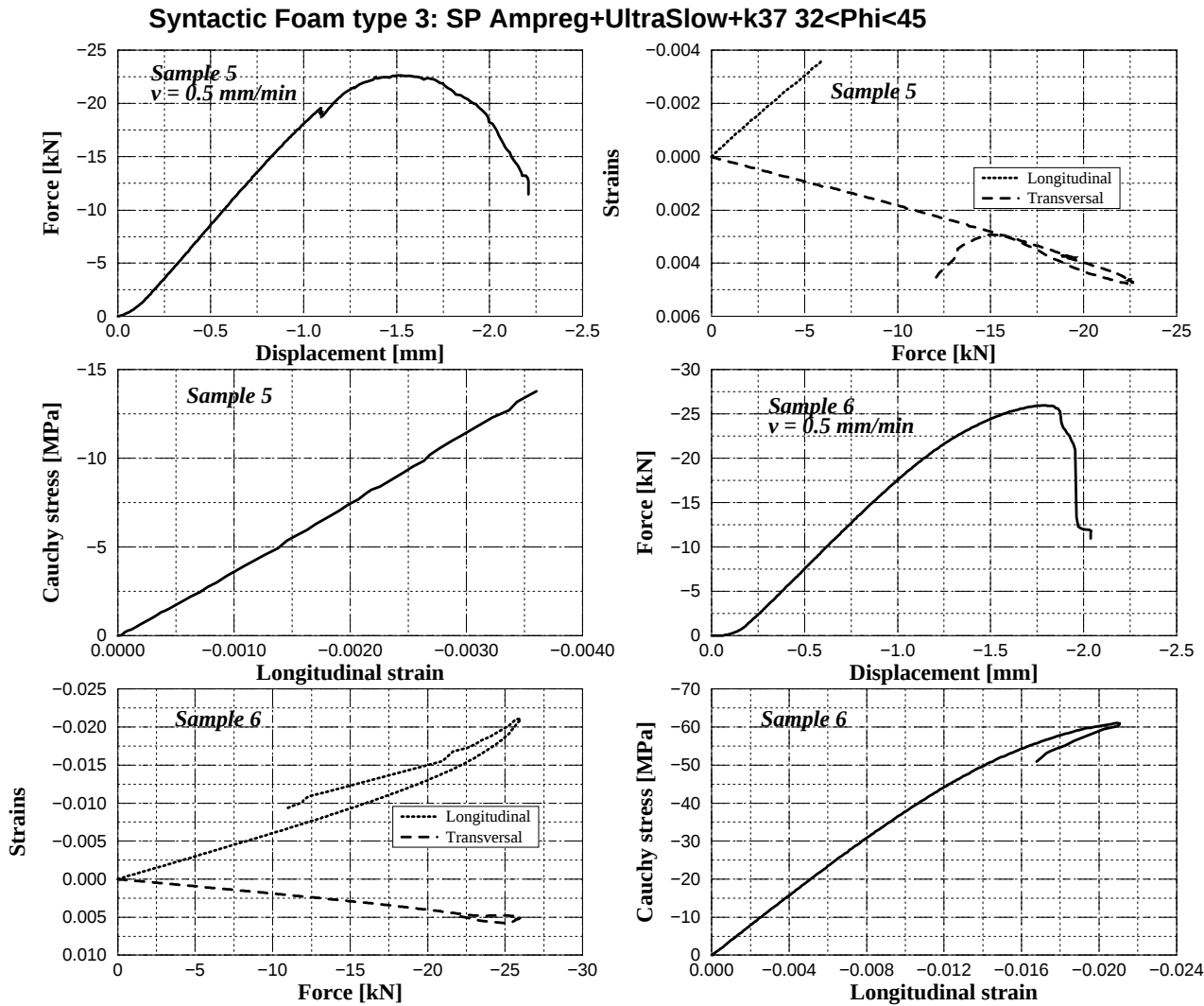


Figure 4.18: Monotonic compressive tests on syntactic foam type 3: load–displacement, strain–load, and stress–strain curves

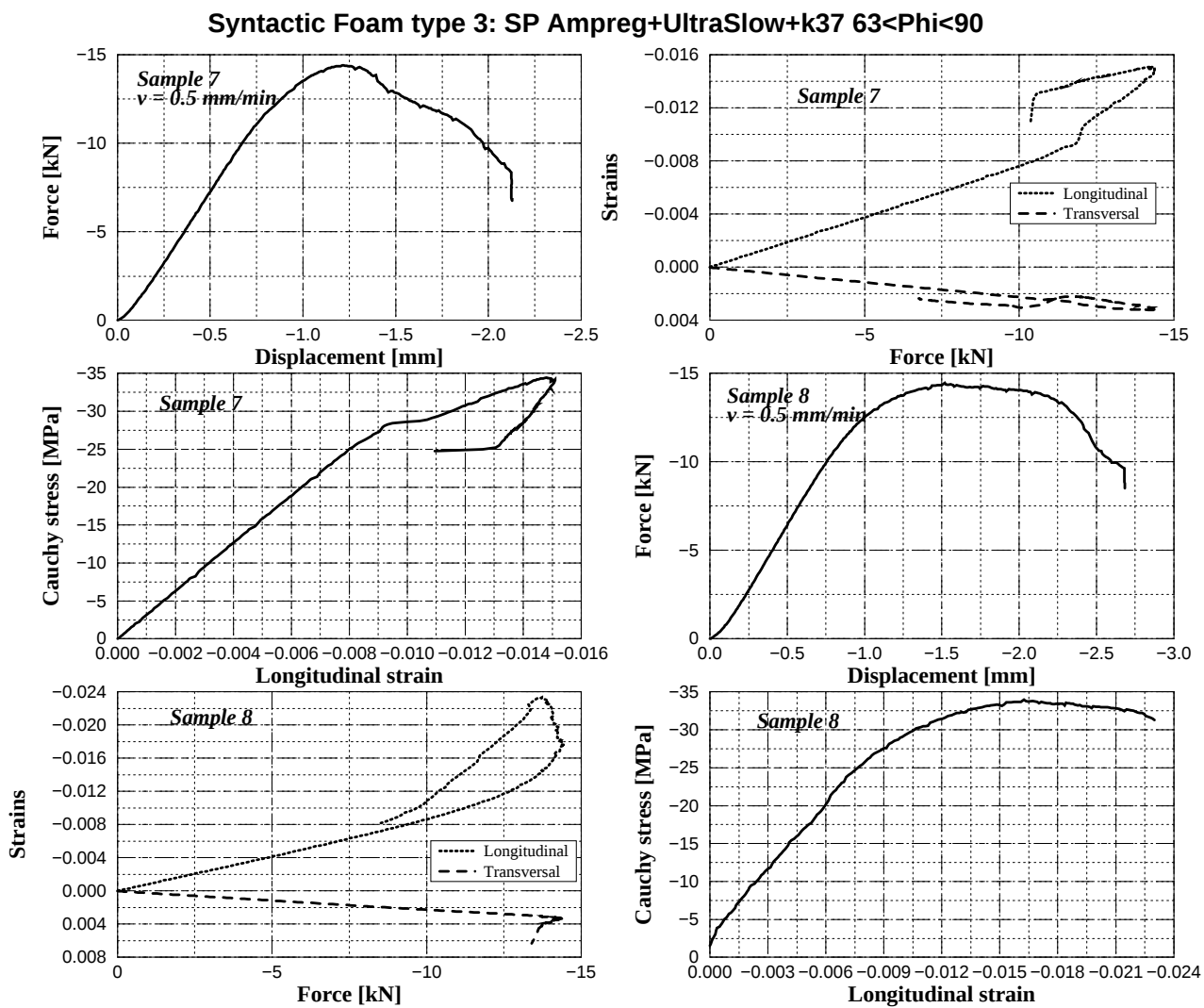


Figure 4.19: Monotonic compressive tests on syntactic foam type 3: load–displacement, strain–load, and stress–strain curves

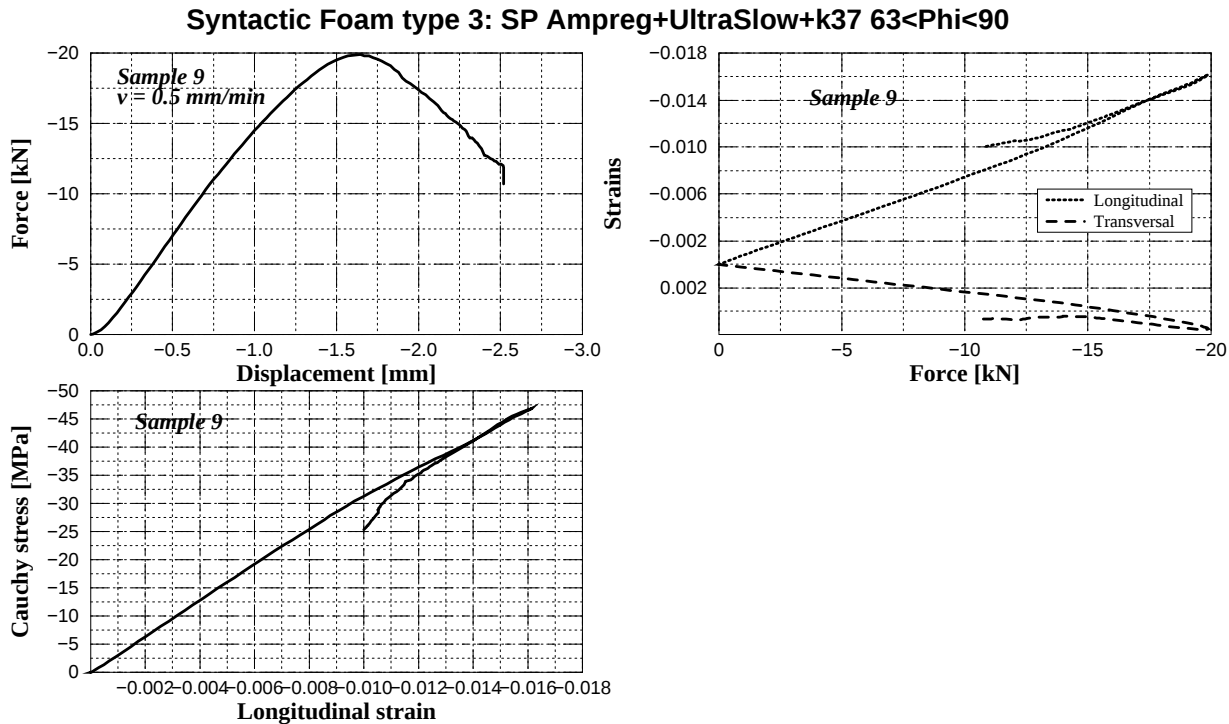


Figure 4.20: Monotonic compressive tests on syntactic foam type 3: load-displacement, strain-load, and stress-strain curves

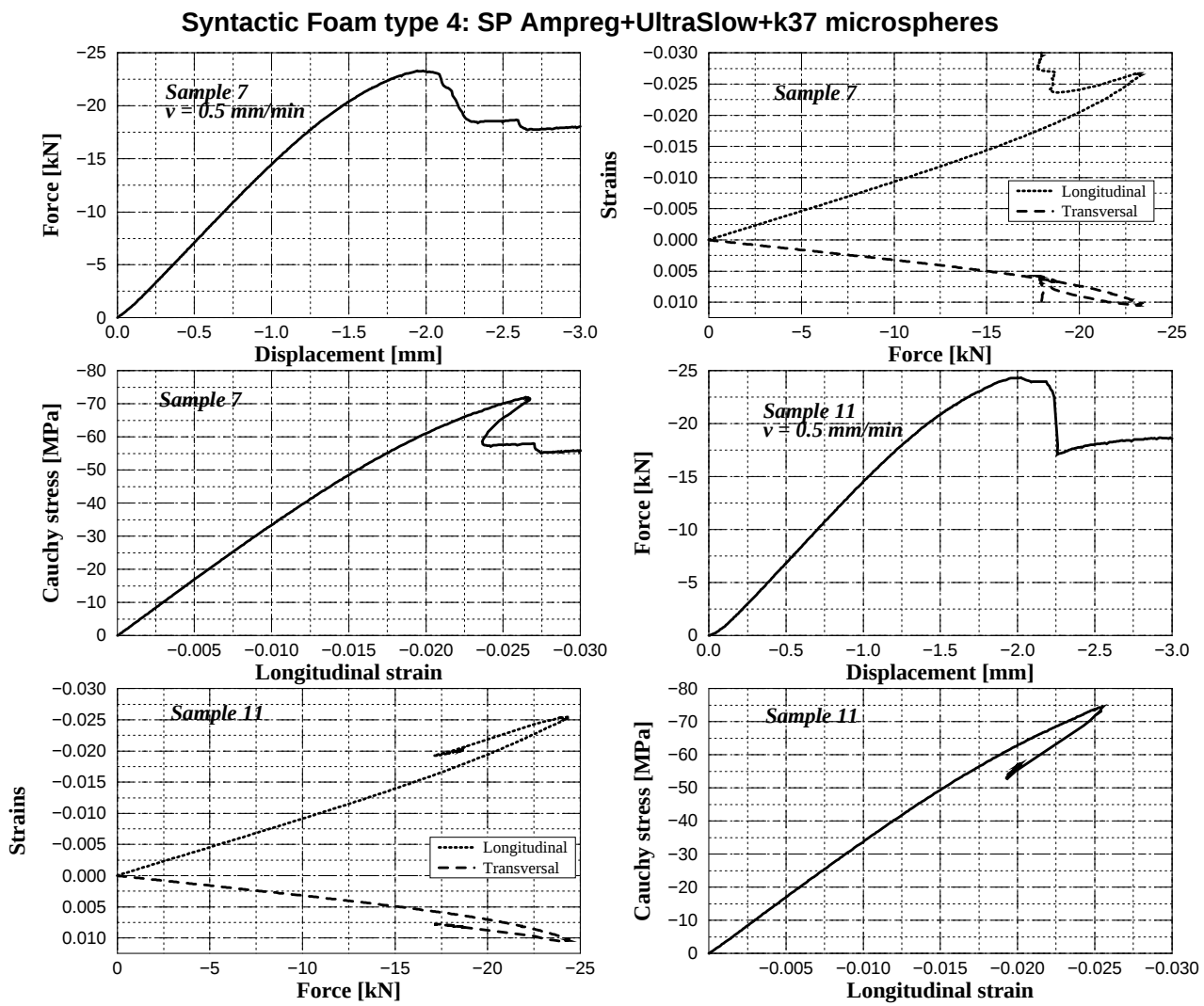


Figure 4.21: Monotonic compressive tests on syntactic foam type 4: load–displacement, strain–load, and stress–strain curves

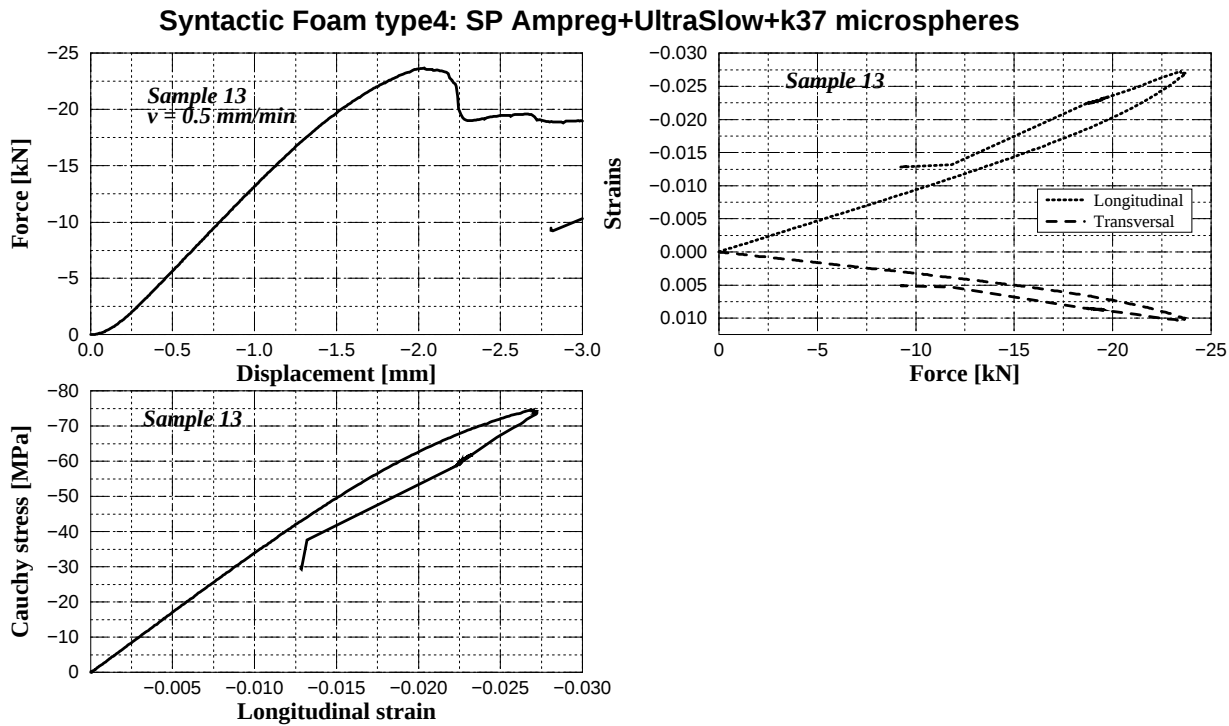


Figure 4.22: Monotonic compressive tests on syntactic foam type 4: load-displacement, strain-load, and stress-strain curves

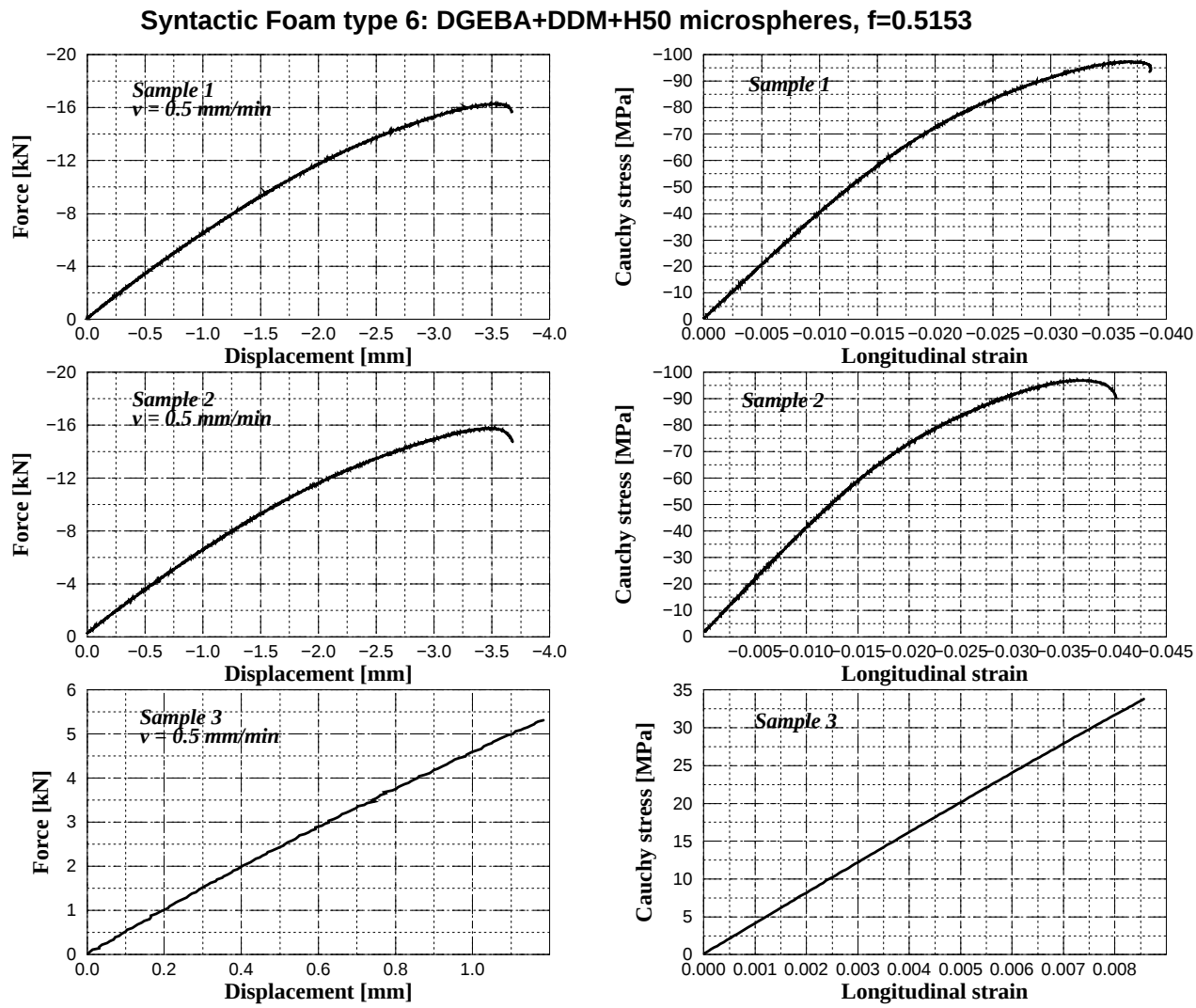


Figure 4.23: Monotonic compressive tests on syntactic foam type 6: load–displacement and stress–strain curves

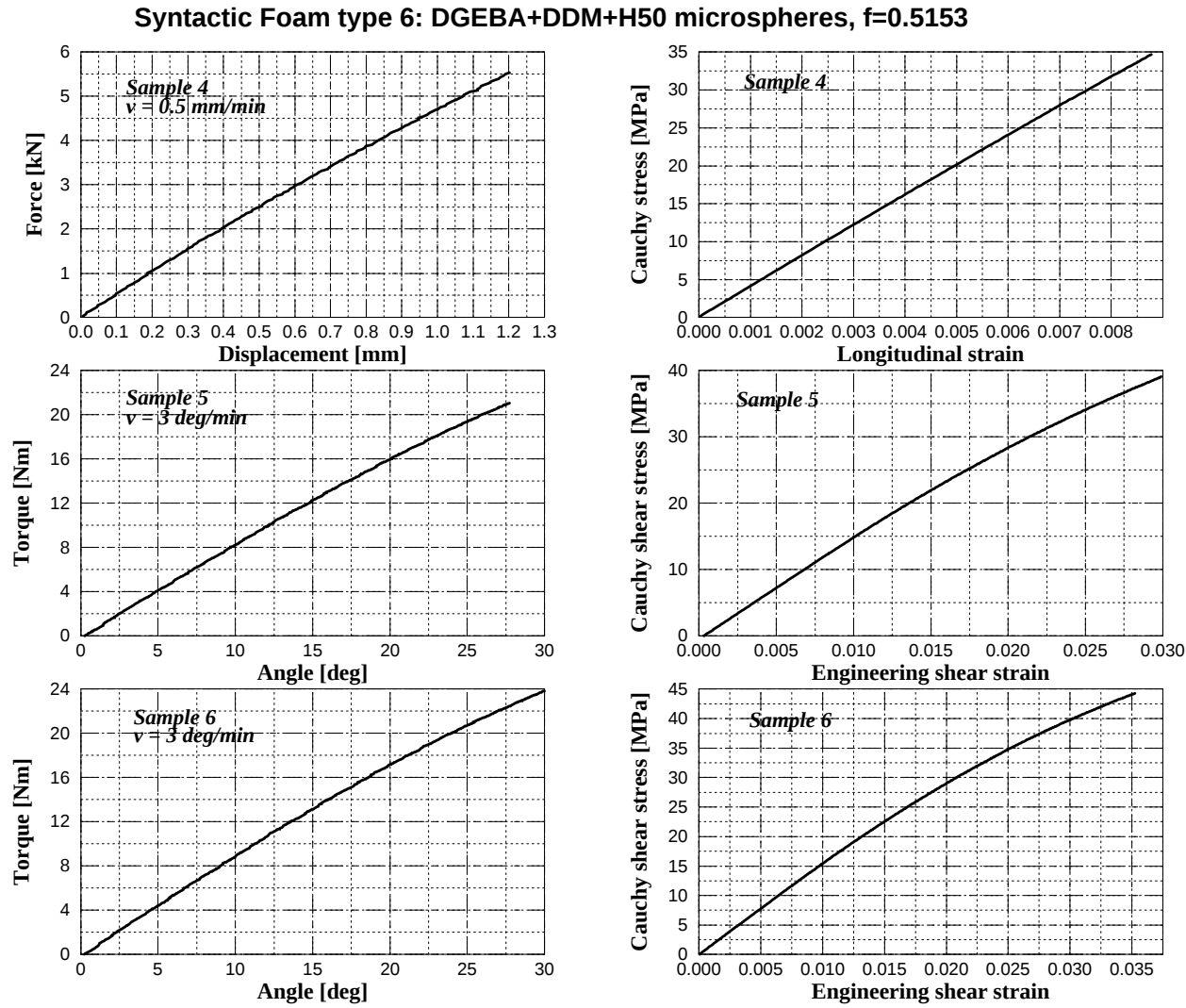


Figure 4.24: Monotonic compressive tests on syntactic foam type 6: load–displacement and stress–strain curves

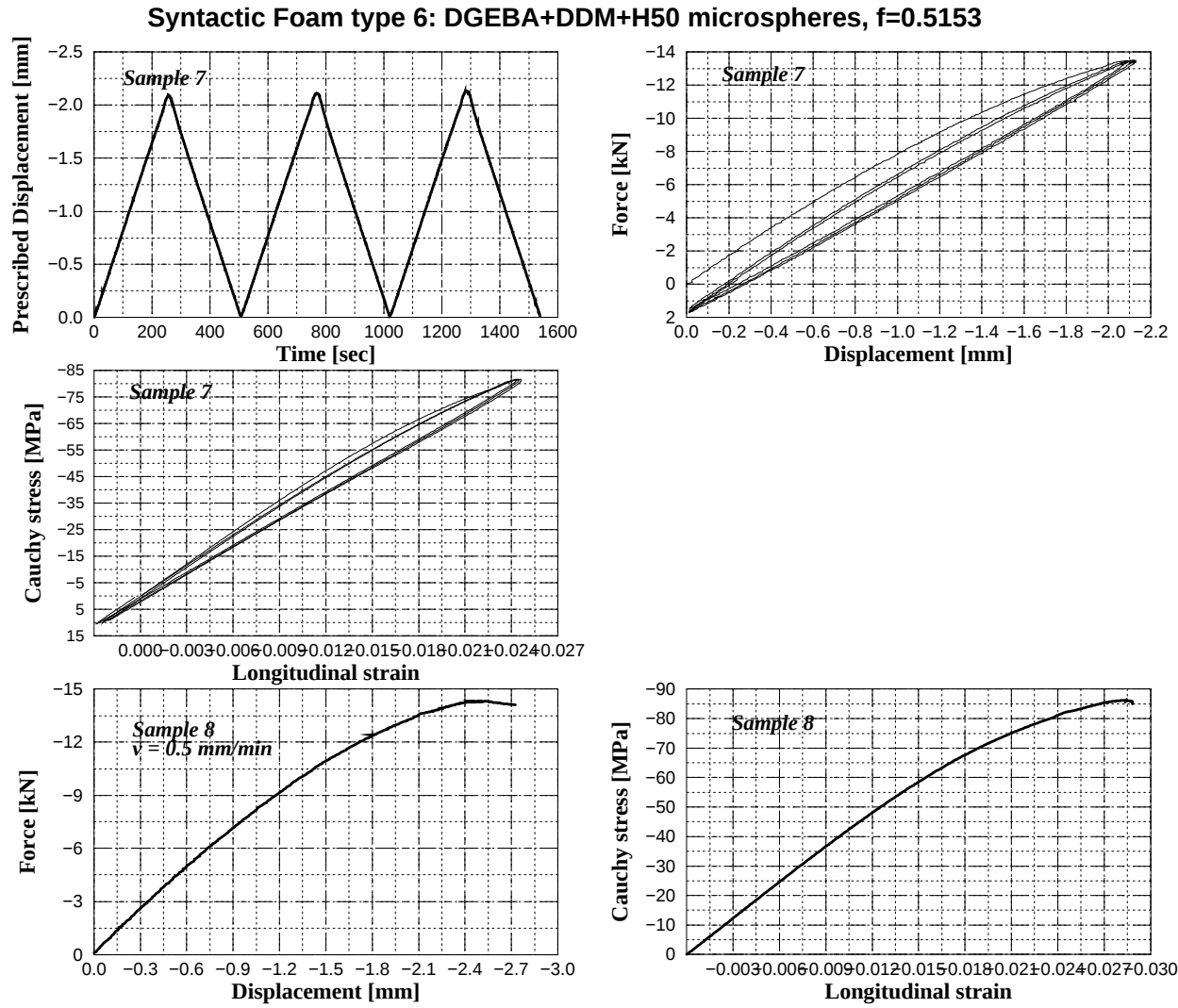


Figure 4.25: Cyclic and monotonic compressive tests on syntactic foam type 6: displacement–time, load–displacement, and stress–strain curves

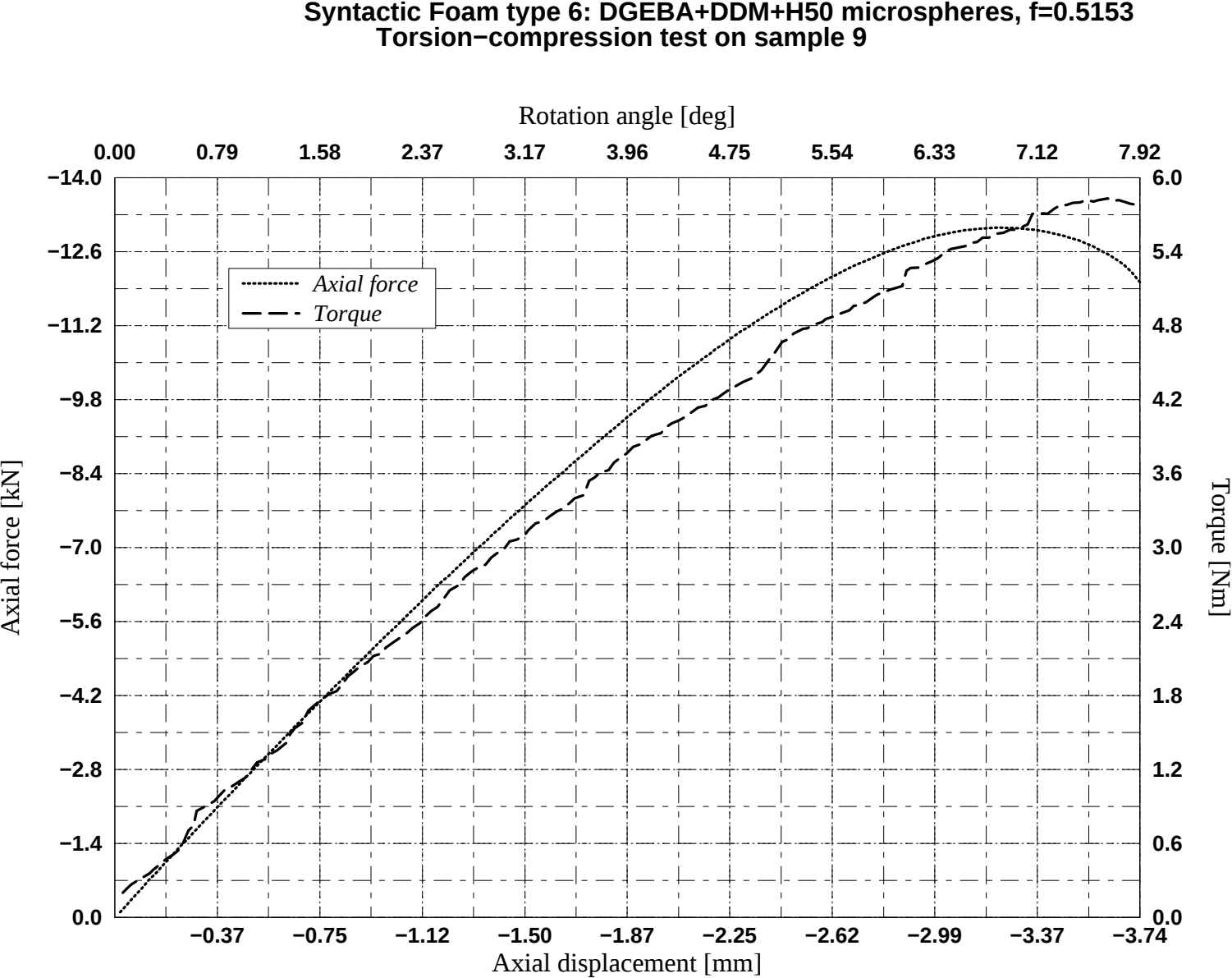


Figure 4.26: Biaxial test on syntactic foam type 6, sample 9: axial force and torque against axial displacement and angle

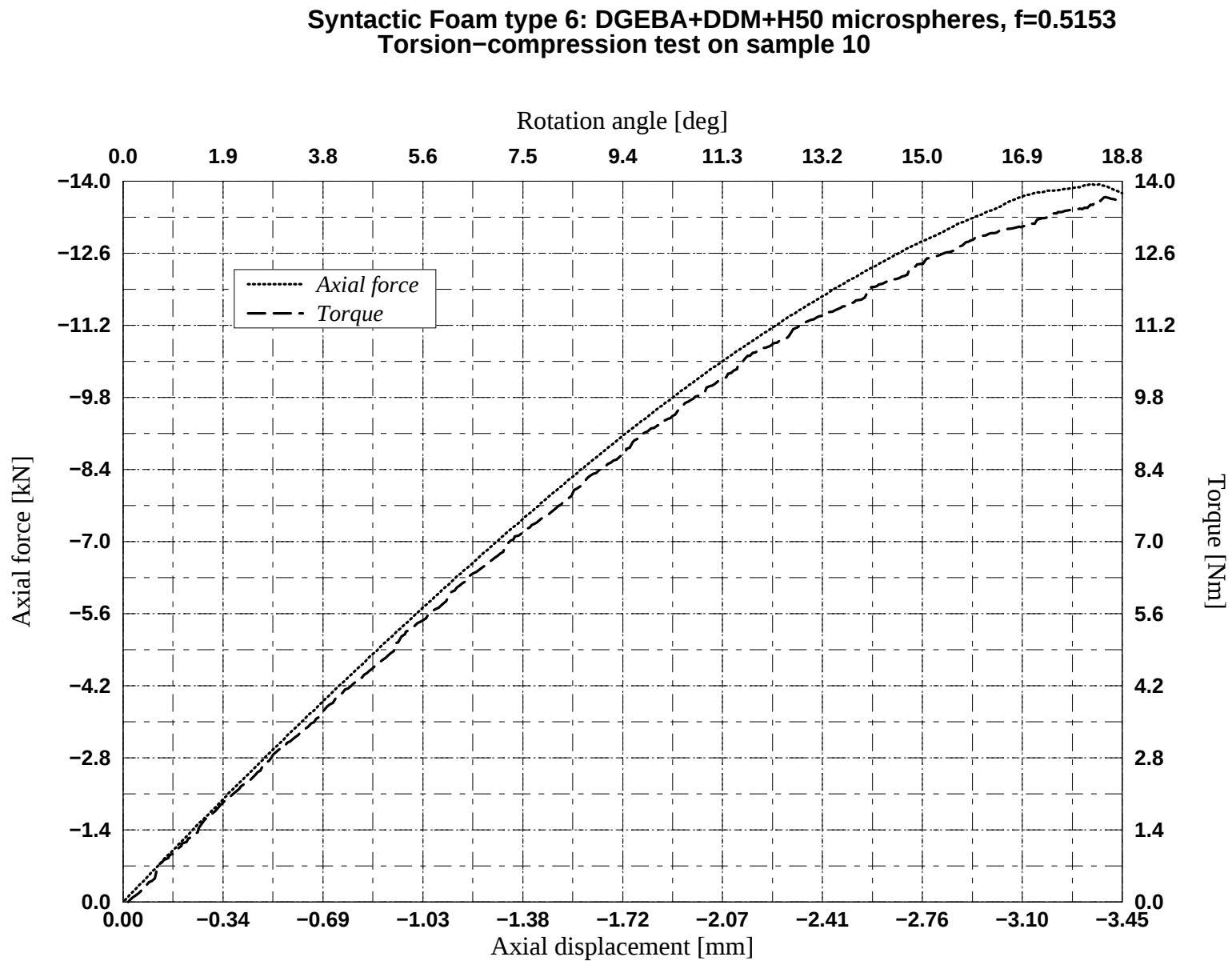


Figure 4.27: Biaxial test on syntactic foam type 6, sample 10: axial force and torque against axial displacement and angle

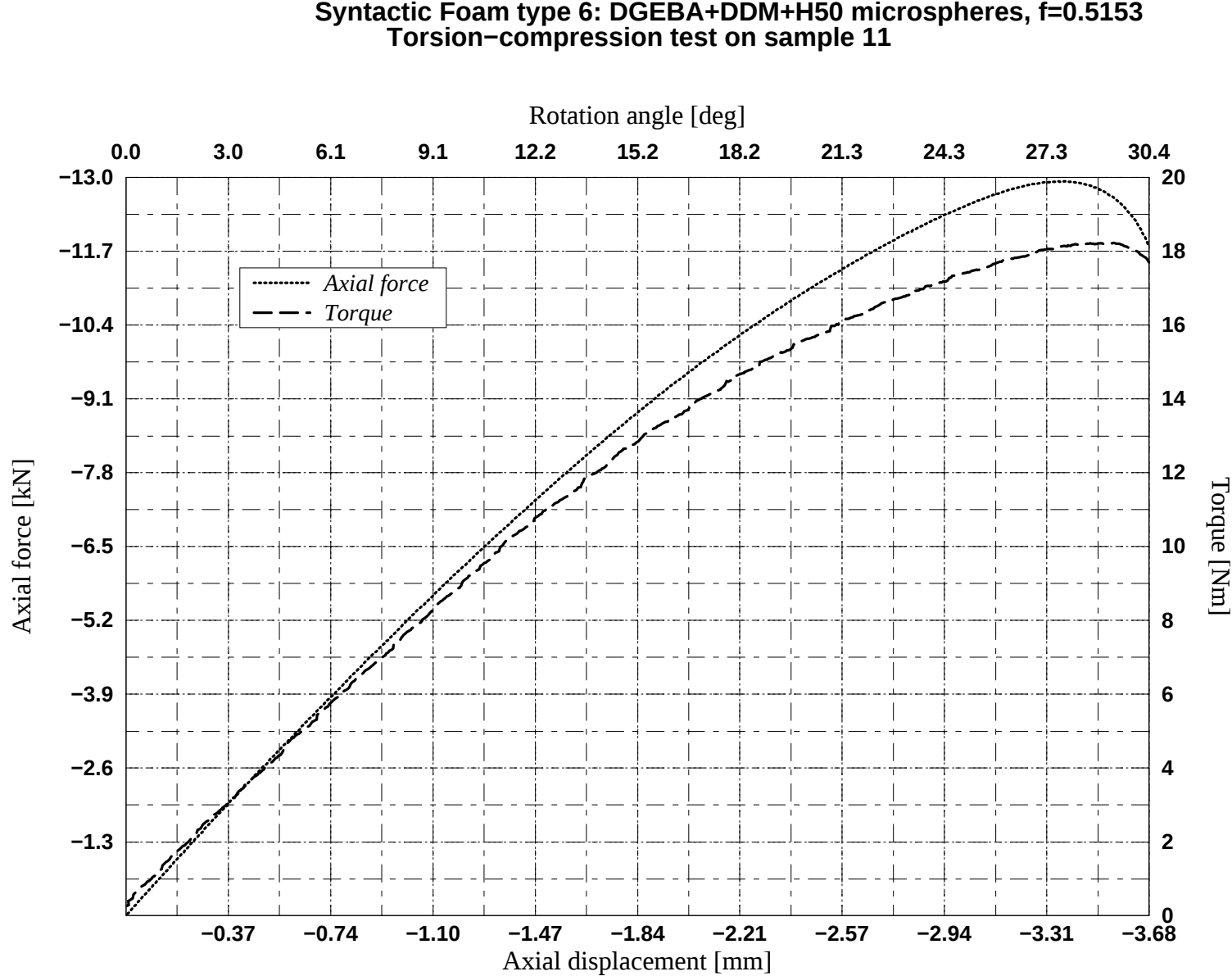


Figure 4.28: Biaxial test on syntactic foam type 6, sample 11: axial force and torque against axial displacement and angle

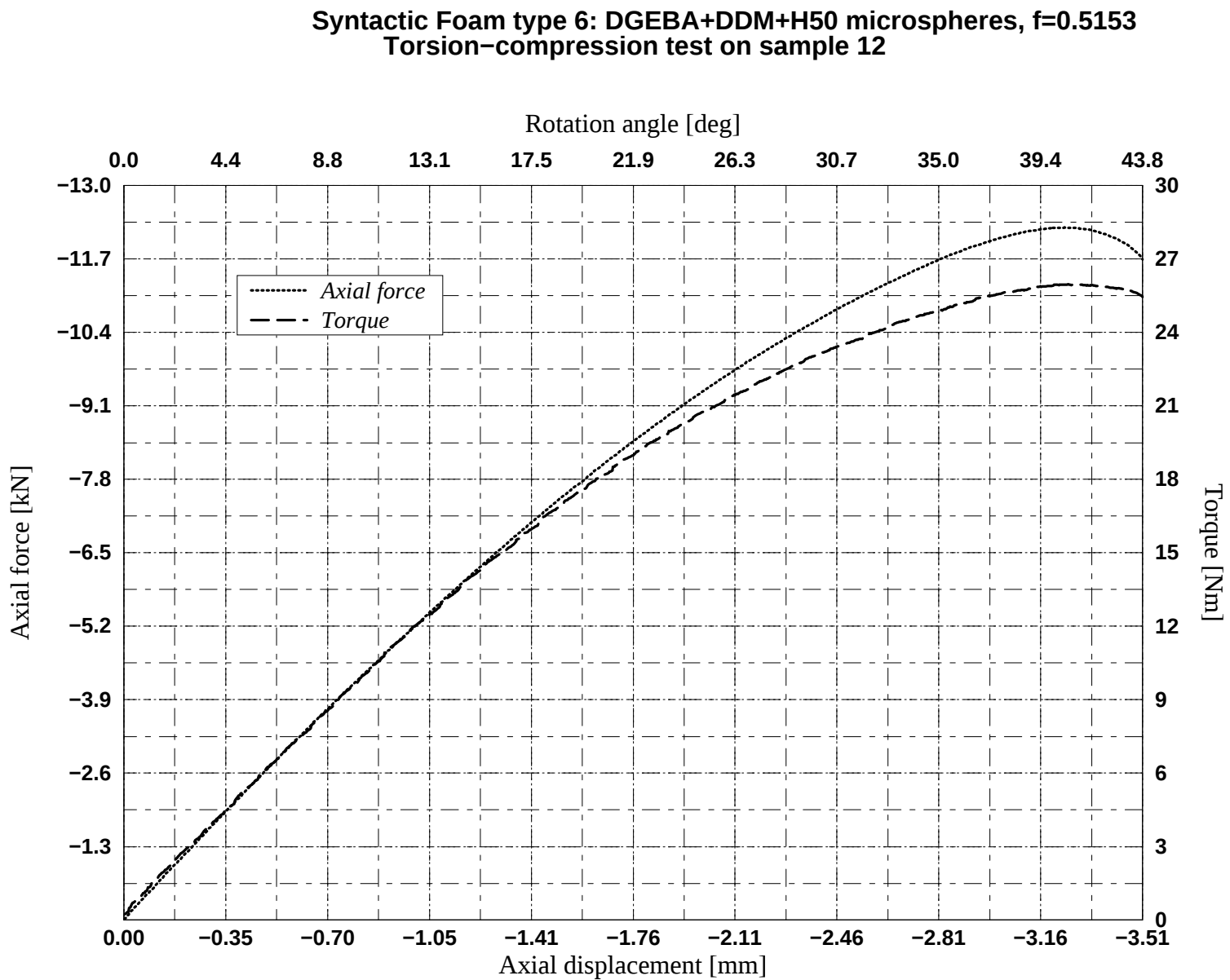


Figure 4.29: Biaxial test on syntactic foam type 6, sample 12: axial force and torque against axial displacement and angle

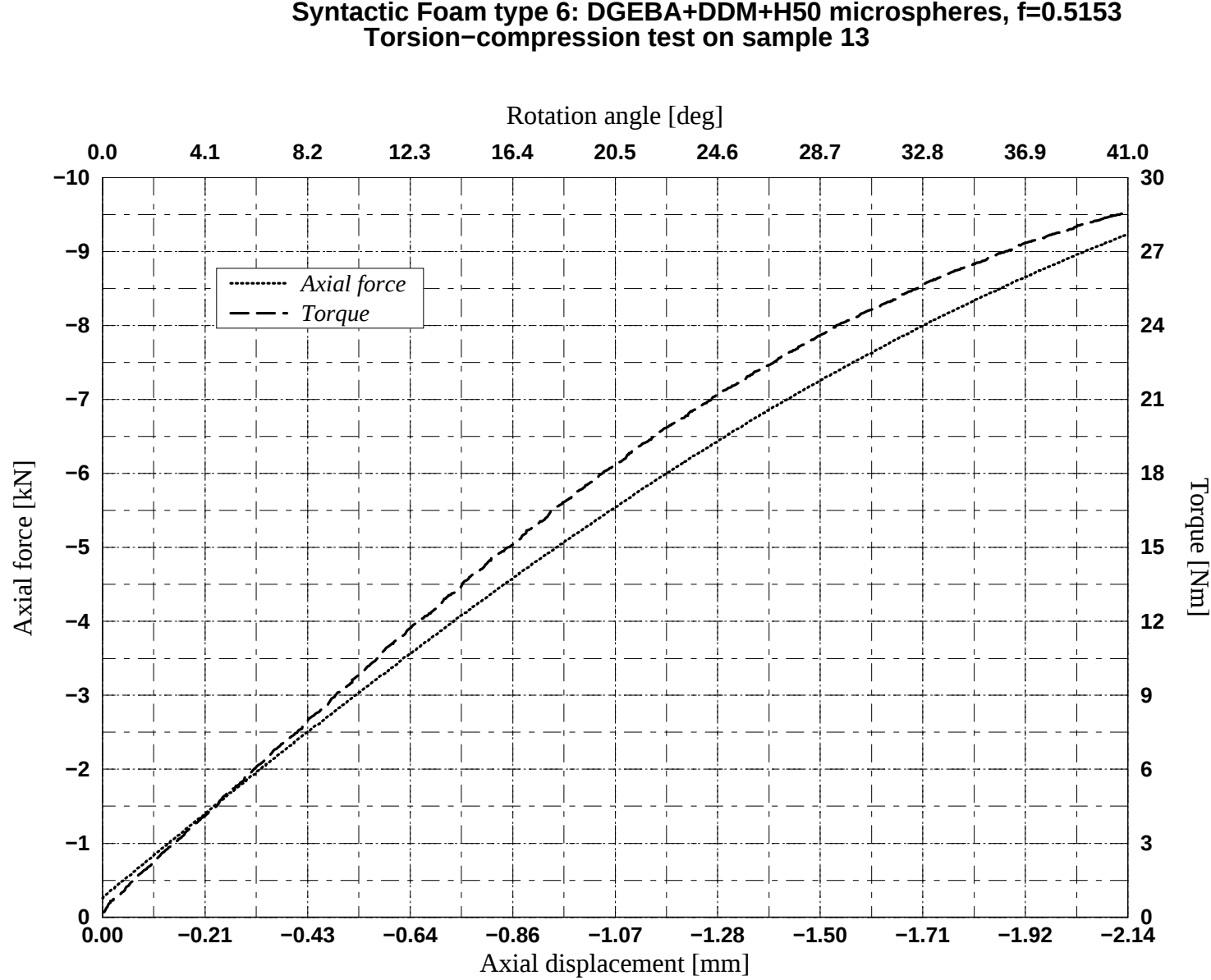


Figure 4.30: Biaxial test on syntactic foam type 6, sample 13: axial force and torque against axial displacement and angle

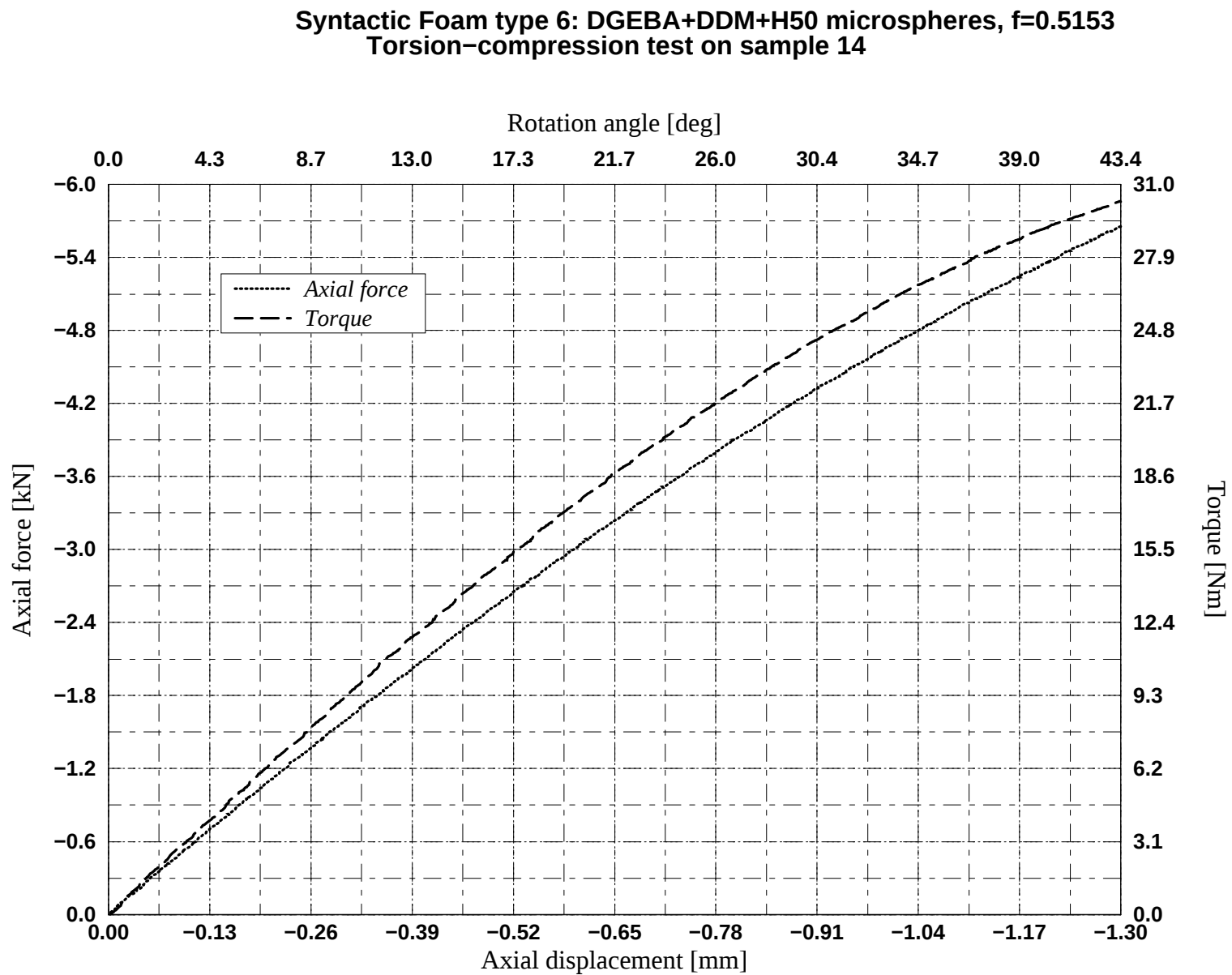


Figure 4.31: Biaxial test on syntactic foam type 6, sample 14: axial force and torque against axial displacement and angle

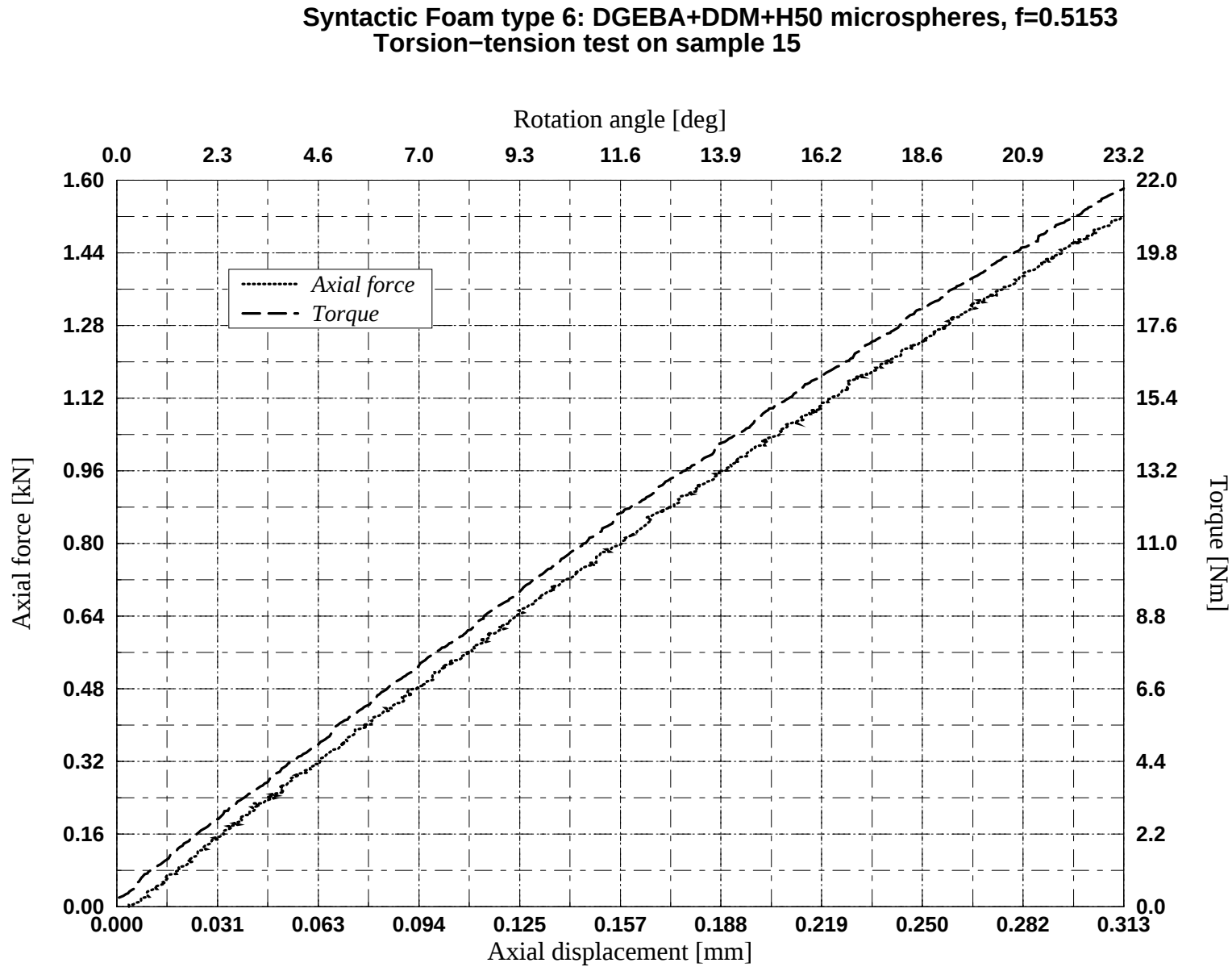


Figure 4.32: Biaxial test on syntactic foam type 6, sample 15: axial force and torque against axial displacement and angle

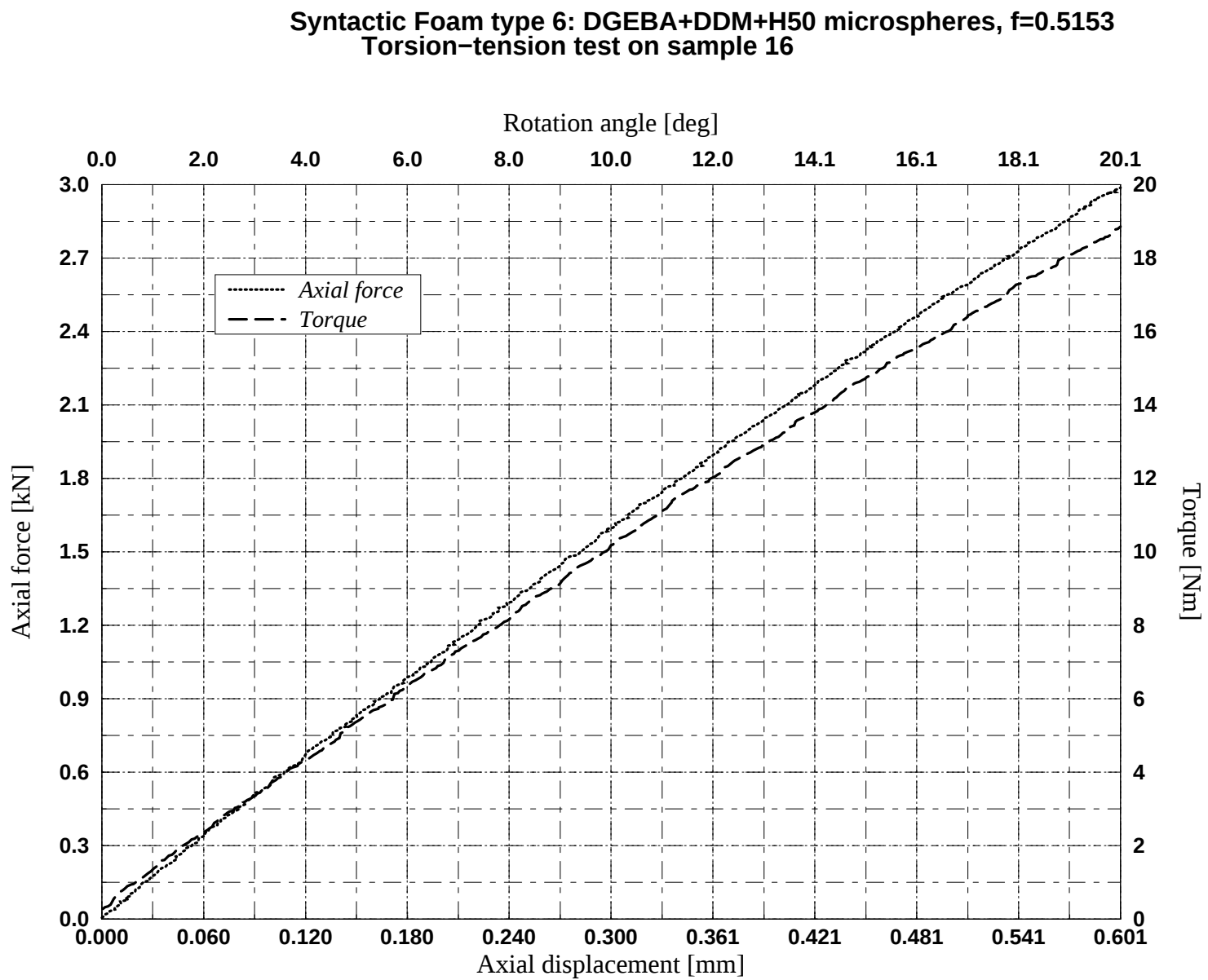


Figure 4.33: Biaxial test on syntactic foam type 6, sample 16: axial force and torque against axial displacement and angle

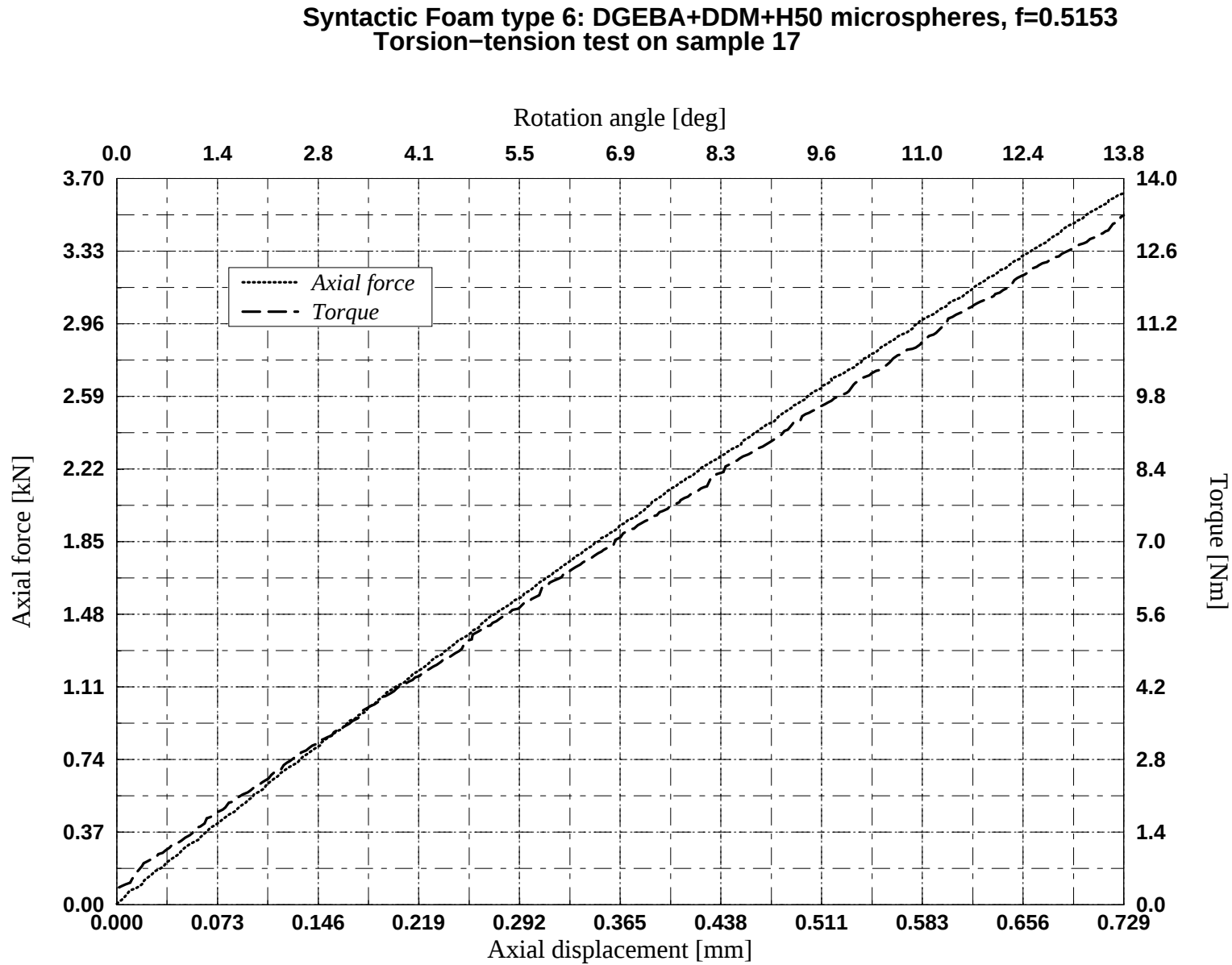


Figure 4.34: Biaxial test on syntactic foam type 6, sample 17: axial force and torque against axial displacement and angle

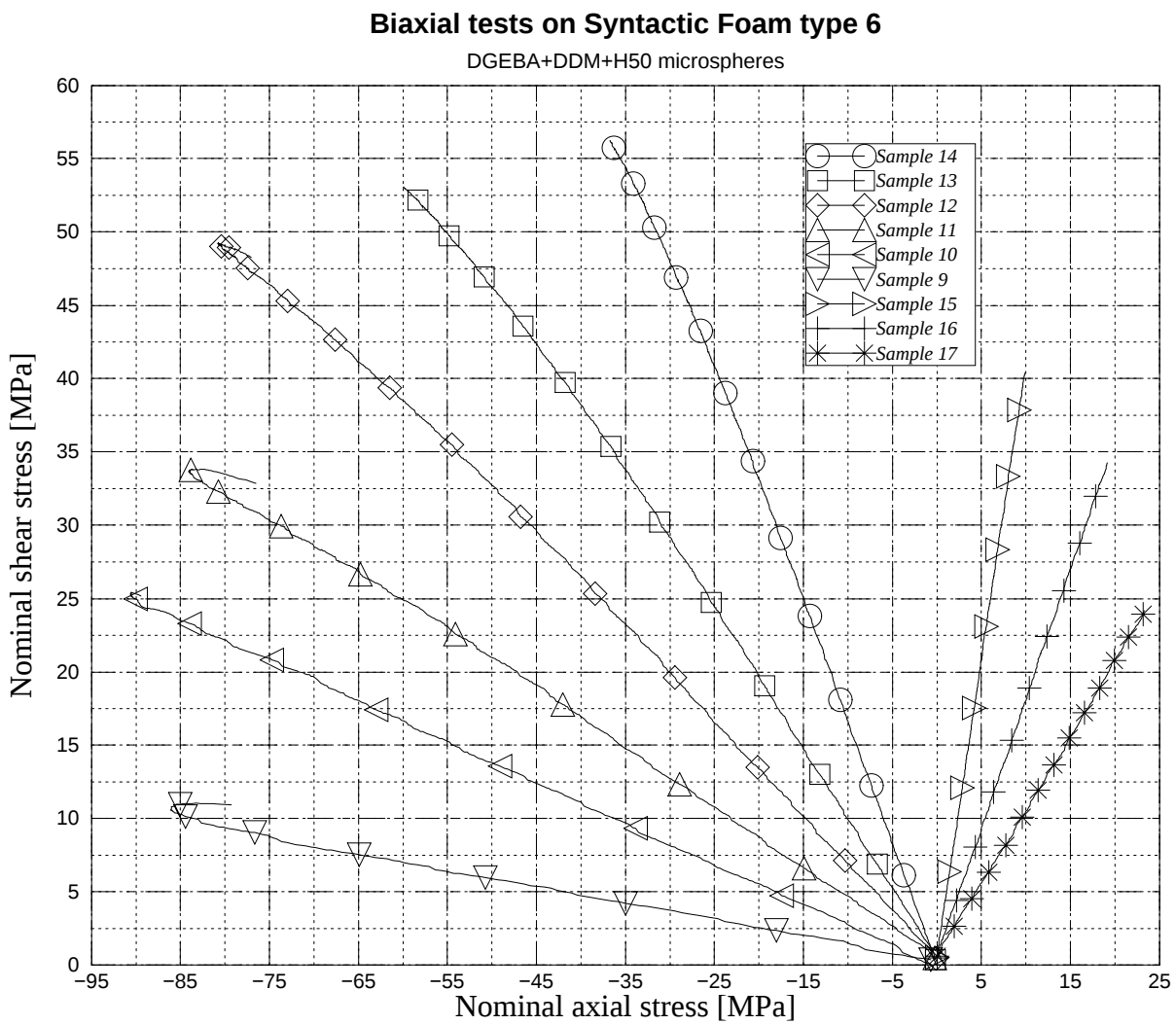


Figure 4.35: Biaxial test on syntactic foam type 6: nominal shear stress–nominal axial stress curves

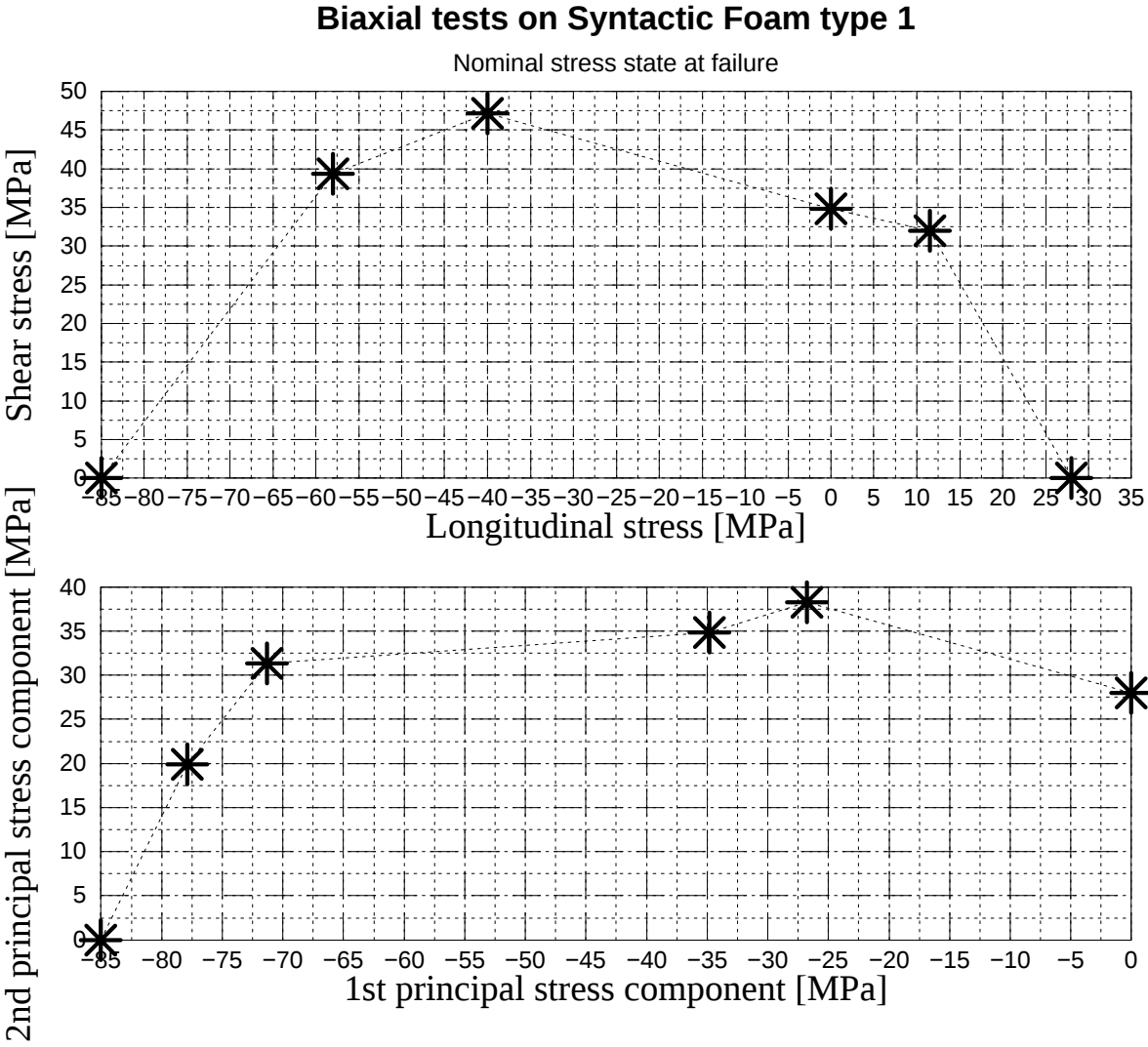


Figure 4.36: *Biaxial tests on syntactic foam type 6: failure envelope*

Part II

Linear elastic behavior

Chapter 5

Introduction

5.1 Overview

One fundamental step in both the design and the analysis of syntactic foams concerns the evaluation of their linear elastic behavior. The computation of the so-called *effective* (i.e., macroscopic) elastic moduli of syntactic foams can be tackled by means of *homogenization techniques* (see section 6.1 for formal definitions). However, the use of standard homogenization methods is somewhat made difficult for syntactic foams by the presence of a void phase, which may cause some classical bounding techniques to furnish zero lower bounds and that causes, more generally, a poor behavior of methods which can not properly account for the connectedness of the matrix, a crucial feature if a void phase is present.

We have been able to find four methods, put forward in the literature to deal with the computation of the effective elastic moduli of syntactic foams. The simplest one is due to Nielsen [91], who suggested to first homogenize the inclusion alone, using, for the shear modulus, a very simple formula, and then to choose from any of the standard methods available to homogenize particulate composites. We shall briefly show, in appendix 7.A, that the very simple sequential homogenization method proposed in [91] in several cases produces results which can not be accepted even from an engineering viewpoint.

More refined approaches are due to Lee and Westmann [79] and to Huang and Gibson [68]. The first one made use of Hashin’s Composite Sphere Assemblage (CSA) technique [56], modified to account for hollow inclusions, thereby obtaining a single result for the effective bulk modulus, and bounds for the shear modulus. The second one used a similar approach, which requires the knowledge of elastic solutions for the problem of a cube of finite size, containing a hollow sphere centered on its centroid. Both techniques, however, produce rather inaccurate results, specially for high volume fractions of filler.

The fourth method is given by Hervé and Pellegrini [60]. Starting from a work by Christensen and Lo [37], who considered a material containing filled homogeneous spherical inclusions, and who computed only a “Self-Consistent Scheme” estimate of the effective elastic moduli, Hervé and Pellegrini studied the problem of a composite material made by n -layered isotropic spherical inclusions, and, exploiting the theory of the Morphologically Representative Patterns (MRP, Bornert, Stolz, and Zaoui [26]), were able to compute a complete set of estimates of the effective elastic moduli. In this case the used MRP is similar to the “composite sphere” of Hashin [56], here defined by an $(n-1)$ -layered sphere,

included within a spherical shell of matrix, whose thickness is such that the volume fraction of the composite sphere (an n -layered inclusion) is the same as that of the syntactic foam.

Hervé and Pellegrini were able to find the complete elastic solution of the problem of such an MRP embedded within an infinite medium made by an arbitrary elastic isotropic material. Starting from this solution, they computed estimates of the elastic moduli of both standard foams (in which the MRP is a 2-layered inclusion — the void and the matrix) and of syntactic foams, in which the MRP is a 3-layered inclusion.

When trying to apply the results of Hervé and Pellegrini [60] to real syntactic foams, however, one may encounter some difficulties. A first source of uncertainty is given by the presence of “unwanted” voids in the composite, a consequence of the production modalities. This fact is quite important, and it is admittedly one of the sources of scatter in the experimental results reported by Huang and Gibson [68], as well as a possible source of discrepancy between theoretical estimates and experimental results. A second one derives from the fact that quite often the filler particles exhibit a significant scatter in their density, not taken into account by the solution of Hervé and Pellegrini. Even when the filler particles are nominally identical to each other, such as, for instance, in the material studied by Huang and Gibson [68], such scatter, due to the production modalities of the particles, is not negligible. A final (and minor) difficulty is given by the rather involved aspect of the formulae in the paper of Hervé and Pellegrini, which are particularized and explicitly written only in the case of standard foams.

5.2 Summary

In the following chapters, we both give some explicit formulae for the estimates of the elastic moduli of syntactic foams, and illustrate how to extend the result of Hervé and Pellegrini [60], for the 3-layered inclusion case, to account for the presence both of “unwanted” voids and of a graded filler. This extension allows us to estimate also the elastic moduli of a syntactic foam constituted by a resin filled with different fillers, each of them made by different materials. The proposed method is again based on the MRP theory and consists of the superposition of multiple MRPs into the same Representative Volume Element; the elastic solution required to compute all the relevant averages is that found by Hervé and Pellegrini [60], in which both matrix and inclusions are taken to be isotropic linear elastic, and the interfaces between the phases are considered perfectly bonded.

The micromechanical model used consists of a composite sphere surrounded by an infinite homogeneous and isotropic medium, whose stiffness may be chosen arbitrarily. Homogeneous boundary conditions are applied at infinity; in this way, coinciding solutions in terms of the effective elastic moduli are found both for stress and displacement boundary conditions, for any choice of the elastic properties of the surrounding medium.

According to the theory of the Morphologically Representative Pattern-based bounding in elasticity [26], the approach followed in this work, as in Hervé and Pellegrini [60], gives MRP-based estimates which contain, as particular cases, the extension of several classical methods: the Self-Consistent Scheme (Hill [66] and Budiansky [30]), the Voigt and Reuss bounds (Voigt [123], Reuss [100]), the Hashin-Shtrikman bounds (Hashin and Shtrikman [57] and [58]), and the Mori-Tanaka estimate (Mori and Tanaka [88]).

In chapter 6 some linear homogenization procedures will be briefly reviewed and par-

ticularized to the case of syntactic foams, whereas in chapter 7 the above mentioned ad hoc homogenization formulae for syntactic foams will be derived. Next (chapters 8 and 9), we shall compare the analytical results both with the few experimental results we have been able to find in the literature and with the results of the tests reported in the first part of this thesis. The two different production modalities of syntactic foams described in chapter 2, the “traditional” technique and the “injection” technique, which lead to different microstructures, can justify the need to take into account in the analytical calculations the presence of air cavities entrapped in the matrix.

Moreover, in chapter 10, we shall analyze the effect of the filler gradation on the effective elastic moduli computation for the syntactic foams produced and tested by us.

The analytical predictions will also be compared with the results of numerical simulations, performed on unit cell models (chapter 11).

Chapter 12 illustrates an interesting application of these materials being concerned with an example of the use of syntactic foams in structural applications, as the core of non conventional sandwich panels.

Finally, in chapter 13, we shall compute the effective linear thermal expansion coefficient of syntactic foams, basing our calculations on the formulae derived in chapter 7 for homogenizing the linear elastic moduli.

Some of the main results presented in this second part of the thesis have already been published in a more compact form in [12], [9], [15], [14], and [16].

Chapter 6

Review of some linear homogenization methods

6.1 General definitions

A composite is a heterogeneous material whose properties vary from point to point on a length scale l , called *microscale*, which is much smaller than both the scale of variation of the loading conditions and the overall body dimensions which are characterized by the length L defining the *macroscale*. At the macroscale level the composite can be regarded as a continuum medium characterized by uniform properties; such properties will be in the following equivalently referred to as *effective*, or *homogenized*, or *overall*, or *macroscopic*.

Any region occupied by material over which the composite properties are constant at the microscale level will be called *phase*; therefore, a composite material is a continuum in which a number of discrete homogeneous continua are bonded together. Any region of the heterogeneous body characterized by a length scale L' such that $l/L' \ll 1$, which is then macroscopically seen as homogeneous, is called *Representative Volume Element* (hereafter shortened in RVE; for more details about the RVE definition see for instance Hill [64]); if any possible RVE has the same effective properties, the composite is then defined *statistically homogeneous*. The micromechanical properties can vary over the RVE in a complicated fashion dependent upon the composite microstructure, but statistical homogeneity¹ will be always assumed in the sequel of this work.

The determination of the composite effective properties requires the solution of a boundary value problem, or an equivalent variational problem, defined on the RVE by the equilibrium and compatibility equations, the constitutive law, and the boundary conditions. This kind of problem can in general be solved only numerically (for instance by means of either the Finite Element Method or the Boundary Element Method) provided that all the morphological features of the RVE microstructure are exactly known. Unfortunately, when the RVE consists of an entangled three-dimensional mixture of phases, both the Finite Element Method and the Boundary Element Method are too expensive

¹Statistical homogeneity is strictly defined, from the statistics viewpoint, by requiring that the so-called n -point correlation functions (which describe the composite morphology by representing the probability of finding simultaneously n points in n prescribed phases) are insensitive to translations. This, together with a proper ergodic assumption, allows us to simplify the computation of the n -point correlation functions; see, e.g., Willis [131].

and difficulties may even arise in meshing the problem. Furthermore, since for most composites the microstructure is random, the problem is not deterministic and only estimates or bounds of the effective properties can be obtained in terms of statistical n -point correlation functions characterizing few fundamental microstructure features (for further insight see [131]).

In this chapter a unified approach is followed (see, for instance, [136]) which allows us to include as particular cases some of the most important homogenization techniques for linear elastic composites whose different phases are perfectly bonded one each other. This approach is based on Eshelby's solution [45] and it is the starting point for deriving the MRP-based theory, that will be exploited to compute the effective elastic moduli of syntactic foams in the next chapter.

Consider an RVE free from body forces occupying a region Ω of the space and made up of N phases, each occupying a region Ω_r , $r = 1, \dots, N$:

$$\Omega = \bigcup_{r=1}^N \Omega_r \quad (6.1.1)$$

As already pointed out, the computation of the macroscopic properties of a composite is meaningful if the RVE is chosen in such a way that the size of its homogeneous inclusions is small compared to the RVE size $|\Omega|$, in which the symbol $|\cdot|$ means the volume of $\cdot$.

Let $\langle \cdot \rangle$ and $\varpi^{(r)}$ denote spatial averages over Ω and Ω_r respectively, i.e.:

$$\langle \cdot \rangle = \frac{1}{|\Omega|} \int_{\Omega} \cdot \, d\Omega \quad (6.1.2)$$

$$\varpi^{(r)} = \frac{1}{|\Omega_r|} \int_{\Omega_r} \cdot \, d\Omega_r \quad (6.1.3)$$

The volume fraction c_r of the phase r is:

$$\frac{|\Omega_r|}{|\Omega|} = c_r \quad \sum_{r=1}^N c_r = 1 \quad (6.1.4)$$

As it will be shown below, a formal step in the computation of the effective moduli of a composite consists of estimating the stress $\bar{\sigma}_{ij}^{(r)}$ or strain $\bar{\varepsilon}_{ij}^{(r)}$ average over each phase r for a given *homogeneous*² (or *uniform*) macroscopic stress Σ_{ij} or strain E_{ij} chosen alternatively as boundary condition for the RVE; being x_i , $i = 1, \dots, 3$, the cartesian coordinates of a suitable reference frame and n_i the components of the outward normals to the RVE external surface Γ ,

$$u_i(\Gamma) = E_{ij}x_j \quad (6.1.5)$$

is the displacement field to be imposed on the RVE surface Γ when the displacement approach is adopted, and

$$t_j(\Gamma) = \Sigma_{ij}n_i \quad (6.1.6)$$

²The term *homogeneous* is used because in order to compute the effective elastic moduli of heterogeneous materials it is expedient to apply boundary conditions which would produce homogeneous fields in homogeneous materials. More insight about the convenience of this choice will be given later (see the comment after equations (6.1.7)).

are the imposed tractions for the dual force approach. The boundary conditions (6.1.5) are called kinematic, or Dirichlet, or essential boundary conditions, whereas the boundary conditions (6.1.6) are called static or von Neumann boundary conditions. A well-defined RVE must furnish overall properties independent upon the boundary conditions.

The so-called mixed boundary conditions have been also proposed to be applied to the RVE instead of the mentioned uniform ones (Hazanov and Huet [59]). Mixed boundary conditions are useful because they can represent experimental set-ups; for instance, in a uniaxial test, uniform displacements are usually applied to the crosshead section only, whereas the remaining specimen surface is stress-free; in section 18.3, we shall exploit this kind of mixed boundary conditions to simulate the nonlinear uniaxial behavior of syntactic foams. Moreover, when looking for the effective elastic moduli of a composite by means of Finite Element analyses on a model smaller than the actual RVE, such as the so-called unit cell (introduced and discussed below), Hazanov and Huet [59] proved that the use of mixed boundary conditions furnishes better estimates than those obtainable by applying uniform boundary conditions to the model.

The relations between the local field averages over each phase and their macroscopic counterparts are defined as:

$$\Sigma_{ij} \stackrel{\text{def}}{=} \langle \sigma_{ij} \rangle = \sum_{r=1}^N c_r \bar{\sigma}_{ij}^{(r)} \quad E_{ij} \stackrel{\text{def}}{=} \langle \varepsilon_{ij} \rangle = \sum_{r=1}^N c_r \bar{\varepsilon}_{ij}^{(r)} \quad (6.1.7)$$

Note that, since Σ_{ij} and E_{ij} are constant tensors, relations (6.1.7) agree with the boundary conditions (6.1.5) or (6.1.6) because of the divergence theorem.

One of the most useful results for the theoretical developments is Hill's lemma [64] which states that if either of the boundary conditions (6.1.5) or (6.1.6) is assumed, then

$$\Sigma_{ij} E_{ij} = \langle \sigma_{ij}^* \varepsilon_{ij}^* \rangle \quad (6.1.8)$$

in which σ_{ij}^* and ε_{ij}^* do not have to be the real solution in the RVE, but it is sufficient that $\sigma_{ij,i}^* = 0 \forall j$ and that ε_{ij}^* be a compatible strain field. In other words, it is not needed that σ_{ij}^* and ε_{ij}^* be related by the constitutive law.

If the composite has a periodic microstructure, the effective properties can be exactly determined by studying, instead of the whole RVE, a *unit cell* which consists of the smallest heterogeneous entity that can build the whole composite if periodically repeated. For a unit cell far from the boundary of the whole body

- the vector $\sigma_{ij} n_i(\mathbf{x})$ evaluated on the external surface is antiperiodic, and
- the local tensor $\varepsilon_{ij}(\mathbf{u}(\mathbf{x}))$ can be splitted into its average, E_{ij} , and a fluctuating term associated with the periodic local displacement field $u_i^*(\mathbf{x})$:

$$\varepsilon_{ij}(\mathbf{u}(\mathbf{x})) = E_{ij} + \varepsilon_{ij}(\mathbf{u}^*(\mathbf{x})) \quad (6.1.9)$$

Therefore, the proper boundary conditions to be applied to the unit cell read:

$$u_i(\Gamma) = E_{ij} x_j + u_i^*(\Gamma) \quad , \quad u_i^*(\Gamma) \bowtie \quad , \quad \sigma_{ij}(\Gamma) n_i - \bowtie \quad (6.1.10)$$

in which $\bowtie$ and $-\bowtie$ indicate respectively periodic and antiperiodic fields with respect to the geometry of the unit cell.

The unit cell model is often exploited in Finite Element analyses since such a model is enormously cheaper than those in which a whole RVE is meshed. Terada et al. [115] have shown that the unit cell model can provide reasonable estimates even for the overall properties of heterogeneous materials whose microstructure is random. Therefore, in spite of the lack of periodicity in the microstructure of syntactic foams, in chapter 11 Finite Element analyses on unit cells will be performed for these composites also.

For a thorough examination of the boundary condition subject, see for instance [106]. In the following, unless differently specified, the displacement approach will be adopted, i.e., the boundary value problem on the RVE will be analyzed by assuming the boundary conditions (6.1.5).

The overall linear elastic constitutive law reads

$$\Sigma_{ij} = L_{ijkl}^{(0)} E_{kl} \quad (6.1.11)$$

in which $L_{ijkl}^{(0)}$ is the linear elastic stiffness tensor that has to be determined; for isotropic materials $L_{ijkl}^{(0)}$ can be for instance expressed by means of the effective bulk modulus K_0 and the effective shear modulus G_0 , via the following “spectral” decomposition [126]:

$$L_{ijkl}^{(0)} = 2G_0 K_{ijkl} + 3K_0 J_{ijkl} \quad (6.1.12)$$

in which K_{ijkl} and J_{ijkl} are isotropic and idempotent (i.e., each one is equal to its second-order product with itself) fourth-order tensors reading:

$$J_{ijkl} = \frac{1}{3} \delta_{ij} \delta_{kl} \quad (6.1.13)$$

$$K_{ijkl} = I_{ijkl} - J_{ijkl} \quad (6.1.14)$$

where δ_{ij} is the Kronecker delta (i.e., the second-order unit tensor) and

$$I_{ijkl} = \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \quad (6.1.15)$$

is the fourth-order unit tensor which links symmetric second-order tensors. Moreover it is useful to note that any component of the tensor $K_{ijmn} J_{mnkl}$ is equal to 0.

The microscopic constitutive law depends on the spatial position x_i and reads

$$\sigma_{ij}(\mathbf{x}) = L_{ijkl}(\mathbf{x}) \varepsilon_{kl}(\mathbf{x}) \quad (6.1.16)$$

Since the elastic moduli are constant over each phase, the function $L_{ijkl}(\mathbf{x})$ is piecewise constant:

$$L_{ijkl}(\mathbf{x}) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) L_{ijkl}^{(r)} \quad (6.1.17)$$

where $\chi^{(r)}(\mathbf{x})$ is the characteristic function of the phase r , that is equal to 1 if $\mathbf{x} \in \Omega_r$ and 0 otherwise, and

$$L_{ijkl}^{(r)} = 2G^{(r)} K_{ijkl} + 3K^{(r)} J_{ijkl} \quad (6.1.18)$$

$G^{(r)}$ and $K^{(r)}$ being the shear and bulk moduli of the phase r respectively.

Defining the *strain localization tensors* $A_{ijkl}^{(r)}(\mathbf{x})$ (see [64] for more details) by

$$\varepsilon_{ij}^{(r)}(\mathbf{x}) = A_{ijkl}^{(r)}(\mathbf{x}) E_{kl} \quad (6.1.19)$$

equation (6.1.16) can be rewritten as

$$\sigma_{ij}(\mathbf{x}) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) L_{ijmn}^{(r)} A_{mnkl}^{(r)}(\mathbf{x}) E_{kl} \quad (6.1.20)$$

Since the composite is assumed to be statistically homogeneous, averaging equation (6.1.20) the unknown effective stress Σ_{ij} can be simply expressed as the following function of the volume fractions c_r and the averaged localization tensors over each phase:

$$\Sigma_{ij} = \sum_{r=1}^N c_r L_{ijmn}^{(r)} \overline{A}_{mnkl}^{(r)} E_{kl} \quad (6.1.21)$$

in which, note that

$$\overline{A}_{ijkl}^{(r)} E_{kl} = \overline{\varepsilon}_{ij}^{(r)} \quad (6.1.22)$$

Finally, comparing equations (6.1.11) and (6.1.21), which for any chosen E_{ij} have to furnish the same Σ_{ij} , the expression of the searched effective elastic moduli is obtained:

$$L_{ijkl}^{(0)} = \sum_{r=1}^N c_r L_{ijmn}^{(r)} \overline{A}_{mnkl}^{(r)} \quad (6.1.23)$$

Let us further define the *stress concentration tensors* $B_{ijkl}^{(r)}(\mathbf{x})$, since we shall need them in chapter 17 where some of the nonlinear homogenization procedures available in the literature will be reviewed. The stress field average over each phase r can be related to the overall one on the RVE:

$$\overline{\sigma}_{ij}^{(r)} = \overline{B}_{ijkl}^{(r)} \Sigma_{kl} \quad (6.1.24)$$

Therefore, dually to the displacement approach, we can find an expression for the effective compliance $M_{ijkl}^{(0)}$:

$$M_{ijkl}^{(0)} = \sum_{r=1}^N c_r M_{ijmn}^{(r)} \overline{B}_{mnkl}^{(r)} \quad (6.1.25)$$

where

$$M_{ijkl}^{(r)} = \frac{1}{2G^{(r)}} K_{ijkl} + \frac{1}{3K^{(r)}} J_{ijkl} \quad (6.1.26)$$

is the compliance of the phase r .

In the derivation of linear elastic homogenization procedures, equations (6.1.24) and (6.1.25) are usually exploited when the boundary conditions (6.1.6) are applied to the RVE.

6.2 The Eshelby solution

Focusing our attention on the displacement approach, to estimate $L_{ijkl}^{(0)}$ one has to evaluate the averaged localization tensors $\bar{A}_{ijkl}^{(r)}$. Since the elastic solution is not known of a RVE characterized by a *general* microstructural morphology and subjected to the boundary conditions (6.1.5), the problem of computing $\bar{A}_{ijkl}^{(r)}$ has to be treated by introducing assumptions which allow us to estimate the overall properties of composites by describing their particular morphology only approximately; it is also possible to obtain bounds to the effective properties: they do not furnish direct estimates, but they are useful since they can be used to validate estimates. The derivations of both direct estimates and bounds can be unified, at least when the phases of the composite are isotropic, by exploiting the Eshelby solution [45] of the problem of an ellipsoidal homogeneous inclusion H (also called inhomogeneity in the following), whose stiffness is $L_{ijkl}^{(H)}$, surrounded by an unbounded reference homogeneous medium, of stiffness $L_{ijkl}^{(R)}$, subjected to the homogeneous strain $E_{ij}^{(R)}$ at infinity. Eshelby's solution gives the homogeneous (i.e., uniform) strain field inside the inclusion:

$$\varepsilon_{ij}^{(H)} = \left(I_{ijkl} + P_{ijmn}^{(R)} (L_{mnkl}^{(H)} - L_{mnkl}^{(R)}) \right)^{-1} E_{kl}^{(R)} \quad (6.2.1)$$

in which $P_{ijkl}^{(R)} = S_{ijmn}^{(E)} M_{mnkl}^{(R)}$, where $S_{ijkl}^{(E)}$ is the Eshelby tensor, that is dimensionless and depends upon the ratio between the principal inclusion axes and the Poisson ratio of the reference medium, and $M_{ijkl}^{(R)} = \frac{1}{2G^{(R)}} K_{ijkl} + \frac{1}{3K^{(R)}} J_{ijkl}$ is the reference medium compliance. For a spherical isotropic inclusion, $S_{ijkl}^{(E)}$ reads

$$S_{ijkl}^{(E)} = \alpha_R J_{ijkl} + \beta_R K_{ijkl} \quad (6.2.2)$$

in which

$$\alpha_R = \frac{3K^{(R)}}{3K^{(R)} + 4G^{(R)}} \quad \beta_R = \frac{6(K^{(R)} + 2G^{(R)})}{5(3K^{(R)} + 4G^{(R)})} \quad (6.2.3)$$

The physical meaning of the Eshelby tensor is as follows: an inhomogeneity H subjected to the stress-free strain $\varepsilon_{ij}^{(sf)}$ would deform by $\varepsilon_{ij}^{(sf)}$ if free, but, because of the constraint due to the presence of the surrounding medium R , the actual strain field along the inhomogeneity is equal to $S_{ijkl}^{(E)} \varepsilon_{kl}^{(sf)}$. It is important to note that the result which states that the inhomogeneity turns out to be subjected to a uniform strain field in the Eshelby problem is strictly related to the chosen ellipsoidal shape. See Mura [90] and Asaro and Barnett [8] for more insight about existing solutions of Eshelby's problem.

One possible way to estimate $\bar{A}_{ijkl}^{(r)}$ is to assume that the strain field average $\bar{\varepsilon}_{ij}^{(r)}$ over each phase r in the RVE subjected to the boundary conditions (6.1.5) is the same as that of an ellipsoidal inclusion H_r , characterized by the same stiffness $L_{ijkl}^{(r)}$, embedded into a reference unbounded homogeneous medium subjected to a suitably defined homogeneous strain $E_{ij}^{(R)}$ at infinity. How to choose $L_{ijkl}^{(r)}$ will be made clear in the following; the shape and orientation of H_r have to be specified from what is known about each phase r . This assumption therefore corresponds to writing

$$\bar{\varepsilon}_{ij}^{(r)} = T_{ijkl}^{(R,r)} E_{kl}^{(R)} \quad (6.2.4)$$

in which

$$T_{ijkl}^{(R,r)} = \left(I_{ijkl} + P_{ijmn}^{(R)} (L_{mnkl}^{(r)} - L_{mnkl}^{(R)}) \right)^{-1} \quad (6.2.5)$$

Then

$$E_{ij} = \sum_{r=1}^N c_r \bar{\varepsilon}_{ij}^{(r)} = \sum_{r=1}^N c_r T_{ijkl}^{(R,r)} E_{kl}^{(R)} \quad (6.2.6)$$

i.e.,

$$E_{ij}^{(R)} = \left(\sum_{r=1}^N c_r T_{ijkl}^{(R,r)} \right)^{-1} E_{kl} \quad (6.2.7)$$

Finally, substituting equations (6.2.4) and (6.2.6) into (6.1.22) and observing that the expression so obtained holds for any $E_{ij}^{(R)}$ one obtains:

$$\bar{A}_{ijkl}^{(r)} = T_{ijmn}^{(R,r)} \left(\sum_{r=1}^N c_r T_{mnkl}^{(R,r)} \right)^{-1} \quad (6.2.8)$$

Replacing equation (6.2.8) into equation (6.1.23) it is then possible to evaluate the overall elastic moduli $L_{ijkl}^{(0)}$ as a function of the surrounding medium choice.

Since the Eshelby solution does not account for particle interaction, attempts of taking it into account can be made by choosing a suitable surrounding homogeneous medium.

For the sake of completeness, we remark that the averaged strain localization tensors can be expressed also as

$$\bar{A}_{ijkl}^{(r)} = \left(L_{ijmn}^* + L_{ijmn}^{(r)} \right)^{-1} \left(L_{mnkl}^* + L_{mnkl}^{(0)} \right) \quad (6.2.9)$$

in which

$$L_{ijkl}^* = \left(P_{ijkl}^{(R)} \right)^{-1} - L_{ijkl}^{(R)} \quad (6.2.10)$$

is the *constraint tensor* (Hill, [66]) which can be defined as the “stiffness of the cavity” left in the Eshelby problem when the inhomogeneity is removed and its effect is accounted for by imposing in the so-obtained hole a homogeneous stress-free strain $\bar{\varepsilon}_{ij}^*$ (this definition is sensible as long as the strain field in the inhomogeneity in the Eshelby problem is uniform), which has the same effect as the traction distribution over the interface:

$$t_i^* = -L_{jikl}^* \bar{\varepsilon}_{kl}^* n_j \quad (6.2.11)$$

In the following sections 6.3–6.7, we shall present some classical homogenization techniques based on the approximation (6.2.8). To discriminate these techniques from those based on the Eshelby problem of a heterogeneous inclusion (which is the foundation of the MRP theory; see section 6.8 and chapter 7 for more details), the former ones will be indicated with the term “classical” all over the sequel of this thesis, with the exception of this chapter where the term “classical” will be often omitted since we shall describe only “classical” homogenization methods.

6.3 The dilute approximation

One of the simplest ways to estimate the overall properties of composite materials is to take the so-called *dilute approximation*, which applies to both particulate and fiber composites (i.e., *matrix-based composites*) and consists of completely neglecting the particle interaction by assuming $\bar{A}_{ijkl}^{(r)} = T_{ijkl}^{(m,r)}$ (i.e., the reference medium has the matrix properties and the far-field applied to it in the Eshelby problem is coincident with the homogeneous field applied to RVE); obviously, this approximation furnishes acceptable estimates for very low volume fractions of filler only; this is not the case of syntactic foams, which may even contain hollow spheres for an amount of about 60% of the whole volume. Moreover, note that this estimate does not precisely fit into the general homogenization approach reviewed in this chapter since, after having chosen the elastic constants of the reference medium, the averaged localization tensors should in general be computed from equation (6.2.8).

6.4 The Voigt and Reuss bounds

It can be easily shown that when the reference medium is chosen as infinitely stiff, the *Voigt estimate* [123], also called *rule of mixtures*, is obtained, which is a *rigorous* upper bound to $L_{ijkl}^{(0)}$ and corresponds to the choice $A_{ijkl}^{(r)} = I_{ijkl}$ for each phase r :

$$L_{ijkl}^{(0,Voigt)} = \sum_{r=1}^N c_r L_{ijkl}^{(r)} \quad (6.4.1)$$

Dually, when $L_{ijkl}^{(R)}$ vanishes, the *Reuss estimate* [100] is found, which provides to a *rigorous* lower bound to $L_{ijkl}^{(0)}$:

$$L_{ijkl}^{(0,Reuss)} = \left(\sum_{r=1}^N c_r M_{ijkl}^{(r)} \right)^{-1} \quad (6.4.2)$$

Both $L_{ijkl}^{(0,Voigt)}$ and $L_{ijkl}^{(0,Reuss)}$ are *rigorous* bounds in the sense that they hold for any morphology. If seen as direct estimates, they represent a composite in which there is no interaction among the phases which are all considered on an equal footing (e.g., the fact that the matrix is a continuous phase in matrix-based composites can not be taken into account); by the way, this is because these estimates do not depend on the tensor $P_{ijkl}^{(R)}$ that, with both the Voigt and Reuss assumption, trivially disappears. For instance, the Voigt and Reuss estimates of composites constituted by isotropic phases always predict an isotropic overall behavior, in spite of the actual microstructure which may give strongly anisotropic real behavior, as for fiber-reinforced composites.

6.5 The Hashin–Shtrikman bounds

This approach based on the Eshelby problem can also include the *Hashin–Shtrikman bounds* ([57] and [58]) which are closer to each other than (or, in a few cases, coincident to) the Voigt and Reuss estimates. The Hashin–Shtrikman bounds can be easily obtained

as suggested by Walpole [124]: if $L_{ijkl}^{(R)}$ is such that $L_{ijkl}^{(R)} - L_{ijkl}^{(r)}$ is positive (negative) semidefinite for all r , then so is $L_{ijkl}^{(HS)} - L_{ijkl}^{(0)}$, in which $L_{ijkl}^{(HS)}$ is the predicted stiffness; for instance, for isotropic and *well-ordered* phases (i.e., $K^{(1)} \leq K^{(2)} \leq \dots \leq K^{(N)}$ implies $G^{(1)} \leq G^{(2)} \leq \dots \leq G^{(N)}$ where $K^{(r)}$ and $G^{(r)}$ with $r = 1, \dots, N$ are the bulk and shear moduli of the phase r), that is usually the case of syntactic foams, if $L_{ijkl}^{(R)}$ is chosen as the stiffest or the most compliant phase of the composite, one obtains the Hashin–Shtrikman upper or lower bound respectively. The Hashin–Shtrikman bounds improve the Voigt–Reuss ones because they implicitly account for the n -point correlation functions, up to order two, describing some fundamental feature of the particle interaction, through the microstructural tensor $P_{ijkl}^{(R)}$. In particular, the Hashin–Shtrikman bounds, in their earliest version ([57] and [58]), were derived for well-ordered macroscopically isotropic composites: in this case, their derivation can be shown to be dependent upon the choice of n -point correlation functions which describe an isotropic distribution of the phases; for this kind of morphology, the Hashin–Shtrikman bounds are *rigorous* (i.e., they hold for any macroscopically isotropic composite). Among the extensions of the Hashin–Shtrikman bounds for linear elastic composites, it is important to recall the work of Walpole, who, by the way, re-derived and generalized them for the cases of *badly-ordered* composites [124] and for macroscopically transversely isotropic composites [125]. Willis ([130] and [131]) showed both the variational nature of equation (6.2.8) and the possibility of taking into account phase distributions more general than the simple isotropic one by means of the tensor $P_{ijkl}^{(R)}$. Bornert, Stolz, and Zaoui [26] extended the Hashin–Shtrikman bounds, as well as any other “classical” estimates, to the theory of the so-called Morphologically Representative Patterns (MRP), which substantially extends the theory reported in this chapter by accounting for heterogeneous inclusions in the Eshelby problem; for more insight, see next chapter 7. Luciano and Willis [84] addressed the problem of accounting for configuration-dependent body forces in the Hashin–Shtrikman procedure.

Bounds are also available which account for microstructural information described by n -point correlation functions of order higher than 2; in the case in which they can be derived *for a particular morphology* these bounds result to be sharper than the Hashin–Shtrikman ones, that, from the statistical viewpoint, are seen as first-order bounds (see, for instance, [117]).

6.5.1 The Hashin–Shtrikman bounds for syntactic foams

Since in the next chapter the Hashin–Shtrikman bounds will be employed as reference bounds to validate direct estimates of effective elastic moduli of syntactic foams, here we have derived their expressions for these composites. We assume that both the elastic moduli of the inclusion wall are greater than those analogous of the matrix, i.e., $K^{(i)} > K^{(m)}$ and $G^{(i)} > G^{(m)}$.

Because of the presence of the void phase, the lower bound is null, whereas there is the need of choosing the shape of the phases to derive the upper bound. According to the fact that the inclusion wall is the stiffest phase, and then it is used as unbounded medium in the Eshelby problem, we can take any simply connected shape for this phase, but not that of a hollow sphere. Another approximation has to be introduced in the choice of the matrix shape, which is here assumed to be spherical, thus at least preserving the overall

isotropy and the diagonal-symmetric overall stiffness (Benveniste, Dvorak, and Chen [19]). No problems arise in choosing the void shape, which is taken spherical as it is.

K_0 and G_0 being the effective bulk and shear moduli respectively, the “classical” Hashin–Shtrikman bounds read:

$$K_0^{CHSL} \leq K_0 \leq K_0^{CHSU} \quad G_0^{CHSL} \leq G_0 \leq G_0^{CHSU} \quad (6.5.1)$$

where

$$K_0^{CHSL} = G_0^{CHSL} = 0 \quad (6.5.2)$$

$$K_0^{CHSU} = \frac{f\left(1 - \frac{a^3}{b^3}\right)K^{(i)} + (1-f)\frac{3K^{(i)}K^{(m)}}{(3K^{(m)} + 4G^{(i)})\alpha_i}}{f\frac{a^3}{b^3}\frac{3K^{(i)}}{4G^{(i)}} + (1-f)\frac{3(K^{(i)} - K^{(m)})}{(3K^{(m)} + 4G^{(i)})} + 1} \quad (6.5.3)$$

$$G_0^{CHSU} = \frac{f\left(1 - \frac{a^3}{b^3}\right)G^{(i)} + (1-f)\frac{G^{(i)}}{\left(1 + \frac{G^{(i)}(9K^{(i)} + 8G^{(i)})}{6G^{(m)}(K^{(i)} + 2G^{(i)})}\right)\beta_i}}{f\frac{a^3}{b^3}\frac{6(K^{(i)} + 2G^{(i)})}{9K^{(i)} + 8G^{(i)}} + (1-f)\frac{G^{(i)} - G^{(m)}}{G^{(m)} + \frac{G^{(i)}(9K^{(i)} + 8G^{(i)})}{6(K^{(i)} + 2G^{(i)})}} + 1} \quad (6.5.4)$$

in which α_i and β_i are as defined in equation (6.2.3), a and b are the average inner and outer radii respectively of the hollow spheres characterizing the filler (see chapters 7 and 10 for more details), f is the filler volume fraction, and $K^{(m)}$, $G^{(m)}$, $K^{(i)}$, and $G^{(i)}$ are the bulk and shear moduli of the matrix and the inclusion wall respectively.

6.6 The Mori–Tanaka Method

A suitable method to estimate the effective properties of matrix-based composites is the *Mori–Tanaka Method* [88], which can be obtained by choosing the stiffness of the reference surrounding medium equal to that of the matrix. In this way the continuity of the matrix is taken into account, but its effect is obviously overestimated. Note that this procedure makes the far-field $E_{ij}^{(R)}$ remotely loading the unbounded medium in the Eshelby problem equal to the strain average over the matrix in the RVE (Benveniste [18]).

Often, well-ordered particulate composites are made up of isotropic spherical solid inclusions stiffer than the matrix, in which they are isotropically distributed; this morphology gives an example in which the Mori–Tanaka estimate coincides with the Hashin–Shtrikman lower bound; on the contrary, standard foams consist of a matrix lightened with air cavities: in this case, the Mori–Tanaka estimate coincides with the Hashin–Shtrikman upper bound; no-one of the above mentioned cases is that of syntactic foams, in which the most compliant phase, i.e. the voids, is not continuous and, usually, the matrix is not the stiffest phase either, being more compliant than the inclusion wall.

6.6.1 The Mori–Tanaka estimate for syntactic foams

The Mori–Tanaka estimate for syntactic foams can be obtained by exploiting equations (6.1.23) and (6.2.8), in which an assumption has to be made on the shape of the phases making up the composite. The spherical shape of the inclusions constituting the void phase makes equations (6.2.2) and (6.2.3) suitable. The shape of the matrix phase, actually very entangled, is not needed, because its Eshelby problem is trivially homogeneous in the Mori–Tanaka procedure. Contrariwise, an approximation has to be made to solve the Eshelby problem related to the solid part of the filler (i.e., its wall), which is constituted by spherical shells, that are not simply connected and, then, the Eshelby problem for this phase can not be defined in the strict “classical” sense, which requires the inclusion to be homogeneous; to define a “classical” Eshelby problem for this third phase also, the inclusion wall is assumed to be constituted by spherical solid inclusions. This approximation makes sense at least owing to the local isotropy of the real inclusions and makes us to be sure to obtain a diagonal-symmetric overall stiffness [19]. In this case, after some algebra, equation (6.1.23) can be easily expressed in terms of the phase data, obtaining the Mori–Tanaka estimates of the effective bulk modulus, K_0^{CMT} , and of the effective shear modulus, G_0^{CMT} :

$$K_0^{CMT} = \frac{(1-f)K^{(m)} + f\left(1 - \frac{a^3}{b^3}\right) \frac{3K^{(i)}K^{(m)}}{(3K^{(i)} + 4G^{(m)})\alpha_m}}{f\frac{a^3}{b^3} \frac{3K^{(m)}}{4G^{(m)}} - f\left(1 - \frac{a^3}{b^3}\right) \frac{3(K^{(i)} - K^{(m)})}{(3K^{(i)} + 4G^{(m)})} + 1} \quad (6.6.1)$$

$$G_0^{CMT} = \frac{(1-f)G^{(m)} + f\left(1 - \frac{a^3}{b^3}\right) \frac{G^{(m)}}{\left(1 + \frac{G^{(m)}(9K^{(m)} + 8G^{(m)})}{6G^{(i)}(K^{(m)} + 2G^{(m)})}\right)\beta_m}}{f\frac{a^3}{b^3} \frac{6(K^{(m)} + 2G^{(m)})}{9K^{(m)} + 8G^{(m)}} - f\left(1 - \frac{a^3}{b^3}\right) \frac{G^{(i)} - G^{(m)}}{G^{(i)} + \frac{G^{(m)}(9K^{(m)} + 8G^{(m)})}{6(K^{(m)} + 2G^{(m)})}} + 1} \quad (6.6.2)$$

in which α_m and β_m are as defined in equation (6.2.3).

Among the various possible ways for particularizing the above results (a similar speculation could be done for the Hashin–Shtrikman bounds (6.5.3) and (6.5.4) as well), let us mention that if one sets either $K^{(i)} = K^{(m)}$ and $G^{(i)} = G^{(m)}$ or $a = b$, equations (6.6.1) and (6.6.2) reduce to the Hashin–Shtrikman bounds for standard foams with spherical cavities.

6.7 The Self–Consistent Scheme

The *Self–Consistent Scheme* ([66] and [30]) approximates the interaction among the phases by assuming that each phase is, in turn, embedded in an unbounded region characterized by the effective unknown stiffness. In this case, the far-field $E_{ij}^{(R)}$ turns out to be equal to that applied to the RVE; therefore, the above derived general equations simplify according to:

$$\sum_{r=1}^N c_r T_{ijkl}^{(0,r)} = I_{ijkl} \quad (6.7.1)$$

This estimate is suitable for granular composites, such as polycrystals, in which a continuous matrix does not exist (therefore all the phases may be reasonably treated on equal footing) and any phase consists of grains with identical lattice orientation. Furthermore, it is well known ([66], for instance) that the Self-Consistent Scheme can furnish accurate results only if the composite *contrast* (i.e., the ratio between two analogous moduli, typically the Young moduli, of the stiffest and the most compliant phases) is not too high; otherwise, the Self-Consistent estimate tends to coincide, for a wide range of volume fractions, with the bound which furnishes the worst estimate between the two Hashin–Shtrikman bounds in the particular case considered. For instance, for standard foams the Self-Consistent Scheme estimates zero overall moduli, which is the trivial result furnished by the Hashin–Shtrikman lower bound for any volume fraction, for volume fraction of voids greater than 0.5, whereas for rigid inclusions in an incompressible matrix it predicts infinite value of the overall shear modulus, i.e., the Hashin–Shtrikman upper bound, for volume fraction of the inclusions greater than 0.4.

Since the presence of a void phase in syntactic foams makes their contrast infinite too, the Self-Consistent estimate is not convenient for these composites.

Unfortunately, both the Mori–Tanaka and Self-Consistent methods can not in general give assurance of furnishing an effective stiffness tensor which satisfies the fundamental diagonal symmetry condition. This drawback does not appear at least for composites in which the phases are treated as aligned inclusions of similar shape, or for two-phase materials; see Benveniste, Dvorak, and Chen [19] for more insight into both the Mori–Tanaka and Self-Consistent methods.

6.7.1 The Self-Consistent estimate for syntactic foams

Even if the Self-Consistent Scheme is not suitable for syntactic foams, for the sake of completeness, let us write down the nonlinear system to be solved in order to obtain the Self-Consistent estimates K_0^{CSC} and G_0^{CSC} . With the same notation for syntactic foams used in the preceding subsections 6.5.1 and 6.6.1 and assuming a spherical shape for any phase, we get, directly from equation (6.7.1):

$$\frac{f \frac{a^3}{b^3}}{1 - \alpha_0^{CSC}} + \frac{f \left(1 - \frac{a^3}{b^3}\right)}{1 + \alpha_0^{CSC} \left(\frac{K^{(i)}}{K_0^{CSC}} - 1\right)} + \frac{1 - f}{1 + \alpha_0^{CSC} \left(\frac{K^{(m)}}{K_0^{CSC}} - 1\right)} = 1 \quad (6.7.2)$$

$$\frac{f \frac{a^3}{b^3}}{1 - \beta_0^{CSC}} + \frac{f \left(1 - \frac{a^3}{b^3}\right)}{1 + \beta_0^{CSC} \left(\frac{G^{(i)}}{G_0^{CSC}} - 1\right)} + \frac{1 - f}{1 + \beta_0^{CSC} \left(\frac{G^{(m)}}{G_0^{CSC}} - 1\right)} = 1 \quad (6.7.3)$$

in which α_0^{CSC} and β_0^{CSC} are functions of K_0^{CSC} and G_0^{CSC} according to equations (6.2.3). The roots of K_0^{CSC} and G_0^{CSC} to be chosen among those obtainable from the system (6.7.2)–(6.7.3) are those whose values are positive and lower than the greater between the analogous moduli of matrix and inclusion wall.

6.8 Other methods and further extensions

Let us first mention the work of Dvorak and Srinivas [44] who found new first-order estimates of the effective elastic properties of composites by choosing the stiffness $L_{ijkl}^{(R)}$ of the unbounded medium in the Eshelby problem as a function of the stiffnesses and the volume fractions of the phases; $L_{ijkl}^{(R)}$ can be determined in such a way as to obtain estimates which lie between the Hashin–Shtrikman bounds. Moreover, a particular choice of $L_{ijkl}^{(R)}$ has been shown to predict effective elastic moduli very close to those estimated by means of the Self-Consistent method, without having implicit equations to be solved.

Then, it is here important to mention two other approximate ways, different from the Mori–Tanaka one, for taking into account the connectedness of the matrix in matrix-based composites. The first one is the *Differential Self-Consistent Scheme* (Zimmermann [137], McLaughlin [85]), that will be briefly recalled in appendix 7.D, and the second one consists in the *Hashin Composite Sphere Assemblage* (CSA, Hashin [56]), that will be fundamental in the next chapter, where it will be extensively described in deriving estimates of the elastic moduli of syntactic foams. Both these methods can fit into the theoretical frame reported in this chapter. In the Differential Self-Consistent Scheme the RVE is filled up step-by-step by adding at each step an infinitesimal amount of filler into a composite, already homogenized by means of the “classical” Self-Consistent Scheme, which consists of the matrix and the part of filler already put into the RVE. The CSA can instead be framed into the above reported theory by extending the Eshelby problem to the case of a multi-phase inclusion embedded into a reference medium (see the next chapter for more details). Furthermore, the CSA, together with the research of Christensen and Lo [37], can be seen as the starting point of the already mentioned MRP theory [26], which, in the next chapter, will be exploited to derive an ad hoc linear elastic homogenization procedure for syntactic foams. In that context, it will be shown that the Self-Consistent estimate is the best one for particulate composites like syntactic foams in which it is possible to extend the Eshelby solution to the case of a more complicated heterogeneous inclusion (the so-called Morphologically Representative Pattern, MRP) that is able to account for the connectedness of the matrix by itself. In this case the “classical” Self-Consistent Scheme becomes the so-called *Generalized Self-Consistent Scheme* [37], or, equivalently, the *Self-Consistent MRP-based estimate*, if seen from the viewpoint of the MRP theory. When it is possible to choose a MRP which can appropriately describe the composite morphology, all the “classical” Self-Consistent Scheme drawbacks briefly reported above disappear and the only reason for applying a homogenization technique different from the Self-Consistent one, thus obtaining other MRP-based estimates, is that, as said, the Self-Consistent Scheme furnishes an implicit algorithm, which is really more expensive than anyone else, most of all if there is the need of describing a complicated microstructure.

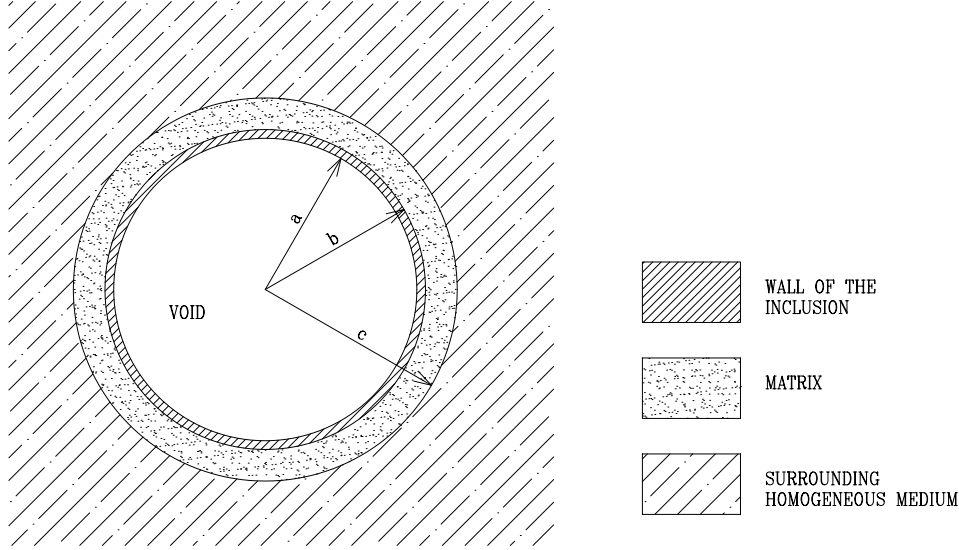
Chapter 7

Analytical derivation of the effective moduli of syntactic foams with graded filler and “unwanted” voids

7.1 Introduction to the chosen homogenization approach

To the purpose of analyzing the micromechanics of syntactic foams, a particular Eshelby problem is defined, in the following called *four-phase model*, which consists of a composite sphere [56] surrounded by an unbounded homogeneous medium of arbitrary elastic constants (figure 7.1). The composite sphere is defined by an inner hollow spherical shell, made by the filler material, surrounded by a shell of matrix material. The thickness of the external shell is such that the cubic power of the ratio between the outer radius of the inclusion, b , and the outer radius of the composite sphere, c , is equal to the volume fraction f of the filler of the composite. Obviously, being c_i the volume fraction of the solid part of the filler, i.e. the inclusion wall, and c_v the void volume fraction, $f = c_i + c_v$ holds.

The presence, in the four-phase model, of the surrounding medium allows us to extend the “classical” estimates reviewed in the previous chapter to their “composite sphere”-based version, i.e., a special choice of an MRP-based version. The various estimates of the effective moduli of the composite can in fact be obtained by varying the stiffness of the surrounding medium, which governs the displacements and tractions around the composite sphere (at a distance from the center of the composite sphere $r = c$) associated to prescribed boundary conditions at infinity, and therefore influences the homogenization. When the stiffness of the surrounding medium vanishes or becomes infinite, the Reuss or Voigt “composite sphere”-based estimates are obtained respectively; these estimates coincide with the Lee and Westmann bounds [79]. When the elastic moduli of the surrounding medium are chosen equal to the unknown effective ones of the syntactic foam, we have the Self-Consistent Scheme “composite sphere”-based estimate (i.e., the Christensen and Lo estimate modified for hollow spherical inclusions). If the stiffness of the surrounding medium is taken as that of the matrix, we have the Mori-Tanaka “com-

Figure 7.1: *The four phase model*

posite sphere”-based estimate, while if it is taken equal to either the most compliant or the stiffest phase of the composite, we obtain the Hashin–Shtrikman “composite sphere”-based bounds. Since the most compliant phase of a syntactic foam is the void, the lower bounds “composite-sphere”-based of Reuss and Hashin–Shtrikman coincide, while the Hashin–Shtrikman “composite sphere”-based upper bound improves the Voigt one, since the stiffest phase of a syntactic foam is not infinitely stiff.

Since syntactic foams are treated as macroscopically homogeneous and isotropic media, we need to estimate two elastic constants, the effective bulk modulus K_0 and the effective shear modulus G_0 .

To compute estimates of the effective elastic constants there is the need of starting by solving the elastic problem defined on the four-phase model of figure 7.1, subjected to homogeneous boundary condition at infinity.

Indicating with $t_j^{(R)}$ the tractions applied at infinity on the four-phase model, the corresponding boundary condition, in general, is as follows:

$$t_j^{(R)} = \Sigma_{ij}^{(R)} n_i \quad (7.1.1)$$

where $\Sigma_{ij}^{(R)}$ represents the *homogeneous* stress field applied to the boundary of the four-phase model, and n_i indicates the components of the outward normals to the external surface of the body. Dually, indicating with $u_i^{(R)}$ the displacements prescribed at infinity on the four-phase model, the corresponding boundary condition, in general, reads as follows:

$$u_i^{(R)} = E_{ij}^{(R)} x_j \quad (7.1.2)$$

where x_j , $j = 1, \dots, 3$, are the cartesian coordinates referred to a reference frame with the

origin in the center of the composite sphere in the four-phase model, and $E_{ij}^{(R)}$ represents the *homogeneous* strain field applied to the boundary of the four-phase model.

When computing the effective moduli of a macroscopically homogeneous and isotropic medium, it is convenient to apply to the micromechanical model two different kinds of homogeneous boundary conditions in two distinct steps: purely volumetric boundary conditions to estimate K_0 and purely deviatoric boundary conditions to estimate G_0 . As purely deviatoric boundary conditions, it is usual to apply *simple shear* boundary conditions, which derive from a second-order tensor in which all the direct components are equal to zero (“simple shear tensor”); this is sensible because any deviatoric second-order tensor can be transformed, by subjecting it to an appropriate rotation of the reference system, into a “simple shear tensor”. Taking into account the macroscopic isotropy of the analyzed material, one can see that the choice of simple shear boundary conditions is a completely general choice.

Furthermore, under a suitable hypothesis on the convexity of the Total Potential Energy of the heterogeneous medium (hypothesis that, of course, holds in the linear elastic case), it is well known that the effective behavior of the composite is independent upon the applied loading conditions (see, for instance, [64]).

For both the elastic solutions reported in the two following sections, concerning respectively the shear modulus and the bulk modulus homogenizations, it will be shown that the homogenization results coincide if tractions or displacements are imposed at infinity as boundary conditions. Both those elastic solutions are mostly classical (see, for instance, [60]), but we need to re-derive them in order to extend the model to account for the filler gradation and, if it is the case, for the “unwanted” voids entrapped in the matrix.

7.2 The shear modulus derivation for the case in which the RVE is made by one composite sphere type only

As done by Hervé and Pellegrini [60], to compute estimates of the effective shear modulus we must apply a simple shear boundary condition at the four-phase model. Using Love’s results (Love [83]) for the case of simple shear, the problem can be solved in terms of spherical solid harmonics of integral degree 2 and -3 (Hashin [56]).

Following Hashin’s procedure, we can either choose to apply a simple shear stress condition such as:

$$\Sigma_{12}^{(R)} = \Sigma_{21}^{(R)} = \tau \neq 0; \quad \text{all other components } \Sigma_{ij}^{(R)} = 0 \quad (7.2.1)$$

or a simple shear strain condition, i.e.:

$$E_{12}^{(R)} = E_{21}^{(R)} = \frac{\gamma}{2} \neq 0; \quad \text{all other components } E_{ij}^{(R)} = 0 \quad (7.2.2)$$

which correspond, respectively, to the following choices of simple shear, in tractions and displacements:

$$t_1^{(R)} = \tau \frac{x_2}{r}, \quad t_2^{(R)} = \tau \frac{x_1}{r}, \quad t_3^{(R)} = 0 \quad (7.2.3)$$

$$u_1^{(R)} = \frac{\gamma}{2} x_2, \quad u_2^{(R)} = \frac{\gamma}{2} x_1, \quad u_3^{(R)} = 0 \quad (7.2.4)$$

where $r = \sqrt{x_1^2 + x_2^2 + x_3^2}$ is the distance from the center of the composite sphere. In both cases we can write the displacements in the whole volume in the following form

$$u_1 = U_A^{(\zeta)}(r)x_2 + U_B^{(\zeta)}(r)x_1^2x_2 \quad (7.2.5)$$

$$u_2 = U_A^{(\zeta)}(r)x_1 + U_B^{(\zeta)}(r)x_1x_2^2 \quad (7.2.6)$$

$$u_3 = U_B^{(\zeta)}(r)x_1x_2x_3 \quad (7.2.7)$$

where the index ζ becomes i in the wall of the inclusion, m in the matrix shell, and s in the surrounding medium and $U_A^{(\zeta)}(r)$ and $U_B^{(\zeta)}(r)$ are defined as follows for the different regions of the four-phase model:

- in the surrounding medium ($r \geq c$)

$$U_A^{(s)}(r) = S_1 + \frac{a^5}{r^5}S_2 + \frac{a^3}{r^3}S_4 \quad (7.2.8)$$

$$U_B^{(s)}(r) = -5\frac{a^5}{r^7}S_2 + (\alpha_{-3}^{(s)} - 5)\frac{a^3}{r^5}S_4 \quad (7.2.9)$$

- in the matrix shell ($b \leq r \leq c$)

$$U_A^{(m)}(r) = M_1 + \frac{a^5}{r^5}M_2 + \frac{r^2}{a^2}M_3 + \frac{a^3}{r^3}M_4 \quad (7.2.10)$$

$$U_B^{(m)}(r) = -5\frac{a^5}{r^7}M_2 + \alpha_2^{(m)}\frac{1}{a^2}M_3 + (\alpha_{-3}^{(m)} - 5)\frac{a^3}{r^5}M_4 \quad (7.2.11)$$

- in the wall of the hollow inclusion ($a \leq r \leq b$)

$$U_A^{(i)}(r) = I_1 + \frac{a^5}{r^5}I_2 + \frac{r^2}{a^2}I_3 + \frac{a^3}{r^3}I_4 \quad (7.2.12)$$

$$U_B^{(i)}(r) = -5\frac{a^5}{r^7}I_2 + \alpha_2^{(i)}\frac{1}{a^2}I_3 + (\alpha_{-3}^{(i)} - 5)\frac{a^3}{r^5}I_4 \quad (7.2.13)$$

The constants $\alpha_2^{(\zeta)}$ and $\alpha_{-3}^{(\zeta)}$ (the subscripts 2 and -3 indicate the degree of the spherical harmonics from which these constants derive) depend upon the Poisson ratio $\nu^{(\zeta)}$ of each different region of the four-phase model ($\zeta = i, m, s$) in the following manner:

$$\alpha_2^{(\zeta)} = -2\frac{7 - 10\nu^{(\zeta)}}{7 - 4\nu^{(\zeta)}} \quad (7.2.14)$$

$$\alpha_{-3}^{(\zeta)} = 2\frac{4 - 5\nu^{(\zeta)}}{1 - 2\nu^{(\zeta)}} \quad (7.2.15)$$

The dimensionless constants S_1 , S_2 , S_4 , M_1 , M_2 , M_3 , M_4 , I_1 , I_2 , I_3 , and I_4 must be determined from the appropriate conditions on displacements and tractions at the three interfaces (the inner surface of the inclusion is considered an interface, between void and inclusion, as well) and by prescribing the boundary conditions at infinity.

First, let us provide the expression of the relevant local strain in the matrix, which is a meaningful step of the calculations needed to write down the mentioned interface and boundary conditions, if the Love solutions are not directly exploited, and which will be of use in section 18.2.1, where the strain field over the matrix will be needed:

$$\begin{aligned}\varepsilon_{12}^{(m)} &= \frac{1}{2} \left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1} \right) = M_1 + \frac{a^5}{r^5} M_2 + \frac{r^2}{a^2} M_3 + \frac{a^3}{r^3} M_4 + \\ &+ \left(-10 \frac{a^5}{r^7} M_2 + (\alpha_2^{(m)} + 2) \frac{1}{a^2} M_3 + (\alpha_{-3}^{(m)} - 8) \frac{a^3}{r^5} M_4 \right) \frac{x_1^2 + x_2^2}{2} + \\ &+ \left(35 \frac{a^5}{r^9} M_2 + 5(5 - \alpha_{-3}^{(m)}) \frac{a^3}{r^7} M_4 \right) x_1^2 x_2^2\end{aligned}\quad (7.2.16)$$

The interface conditions give the following equations:

- vanishing of tractions at $r = a$:

$$2I_1 - 8I_2 + C_1^{(i)} I_3 + C_3^{(i)} I_4 = 0 \quad (7.2.17)$$

$$40I_2 + C_2^{(i)} I_3 + C_4^{(i)} I_4 = 0 \quad (7.2.18)$$

- continuity of displacements at $r = b$:

$$I_1 + \frac{a^5}{b^5} I_2 + \frac{b^2}{a^2} I_3 + \frac{a^3}{b^3} I_4 = M_1 + \frac{a^5}{b^5} M_2 + \frac{b^2}{a^2} M_3 + \frac{a^3}{b^3} M_4 \quad (7.2.19)$$

$$-5 \frac{a^7}{b^7} I_2 + \alpha_2^{(i)} I_3 + (\alpha_{-3}^{(i)} - 5) \frac{a^5}{b^5} I_4 = -5 \frac{a^7}{b^7} M_2 + \alpha_2^{(m)} M_3 + (\alpha_{-3}^{(m)} - 5) \frac{a^5}{b^5} M_4 \quad (7.2.20)$$

- continuity of tractions at $r = b$:

$$\begin{aligned}G^{(i)} \left(2I_1 - 8 \frac{a^5}{b^5} I_2 + C_1^{(i)} \frac{b^2}{a^2} I_3 + C_3^{(i)} \frac{a^3}{b^3} I_4 \right) &= \\ &= G^{(m)} \left(2M_1 - 8 \frac{a^5}{b^5} M_2 + C_1^{(m)} \frac{b^2}{a^2} M_3 + C_3^{(m)} \frac{a^3}{b^3} M_4 \right)\end{aligned}\quad (7.2.21)$$

$$G^{(i)} \left(40 \frac{a^7}{b^7} I_2 + C_2^{(i)} I_3 + C_4^{(i)} \frac{a^5}{b^5} I_4 \right) = G^{(m)} \left(40 \frac{a^7}{b^7} M_2 + C_2^{(m)} M_3 + C_4^{(m)} \frac{a^5}{b^5} M_4 \right) \quad (7.2.22)$$

- continuity of displacements at $r = c$:

$$M_1 + \frac{a^5}{c^5} M_2 + \frac{c^2}{a^2} M_3 + \frac{a^3}{c^3} M_4 = S_1 + \frac{a^5}{c^5} S_2 + \frac{a^3}{c^3} S_4 \quad (7.2.23)$$

$$-5 \frac{a^7}{c^7} M_2 + \alpha_2^{(m)} M_3 + (\alpha_{-3}^{(m)} - 5) \frac{a^5}{c^5} M_4 = -5 \frac{a^7}{c^7} S_2 + (\alpha_{-3}^{(s)} - 5) \frac{a^5}{c^5} S_4 \quad (7.2.24)$$

- continuity of tractions at $r = c$:

$$\begin{aligned}G^{(m)} \left(2M_1 - 8 \frac{a^5}{c^5} M_2 + C_1^{(m)} \frac{c^2}{a^2} M_3 + C_3^{(m)} \frac{a^3}{c^3} M_4 \right) &= \\ &= G^{(s)} \left(2S_1 - 8 \frac{a^5}{c^5} S_2 + C_3^{(s)} \frac{a^3}{c^3} S_4 \right)\end{aligned}\quad (7.2.25)$$

$$G^{(m)} \left(40 \frac{a^7}{c^7} M_2 + C_2^{(m)} M_3 + C_4^{(m)} \frac{a^5}{c^5} M_4 \right) = G^{(s)} \left(40 \frac{a^7}{c^7} S_2 + C_4^{(s)} \frac{a^5}{c^5} S_4 \right) \quad (7.2.26)$$

In all the preceding equations $G^{(m)}$, $G^{(i)}$, and $G^{(s)}$ indicate the shear moduli of the matrix, of the inclusion, and of the surrounding medium respectively, whereas coefficients $C_1^{(\zeta)}$, $C_2^{(\zeta)}$, $C_3^{(\zeta)}$, and $C_4^{(\zeta)}$ are defined as follows:

$$\begin{aligned} C_1^{(\zeta)} &= \frac{14 + 4\nu^{(\zeta)}}{7 - 4\nu^{(\zeta)}} & C_2^{(\zeta)} &= 4 \frac{7 - 4\nu^{(\zeta)} - (7 - 10\nu^{(\zeta)})(2 + \nu^{(\zeta)})}{(7 - 4\nu^{(\zeta)})(1 - 2\nu^{(\zeta)})} \\ C_3^{(\zeta)} &= 2 \frac{1 + \nu^{(\zeta)}}{1 - 2\nu^{(\zeta)}} & C_4^{(\zeta)} &= \frac{-24}{1 - 2\nu^{(\zeta)}} \end{aligned} \quad (7.2.27)$$

where index ζ becomes i , m , and s in the various regions of the four-phase model.

The elastic problem is completed by another equation, to be added to the system (7.2.17)–(7.2.27), which follows from the prescribed boundary condition of uniform simple shear at infinity. Both boundary conditions of simple shear stress and simple shear strain give directly the value of constant S_1 : condition (7.2.3) furnishes $S_1 = \tau/(2G^{(s)})$, while condition (7.2.4) gives $S_1 = \gamma/2$. Since the results of any linear elastic homogenization procedure are independent upon the amplitudes τ and γ , S_1 can, for instance, be arbitrarily set equal to $S_1 = 1$. This indicates that the displacement approach is equivalent to the dual force approach, which, by the way, means that for every choice of the surrounding medium we obtain a single value of the estimates of the effective moduli of the composite (not just bounds for those particular estimates).

Among different possible approaches — which would all yield the same result — to the computation of the estimate of the effective shear modulus, G_0^{est} , the simplest appears to go through the computation of the localization tensors (Hill, [64]). To this purpose, we use, as our reference RVE, Hashin's Composite Sphere Assemblage (CSA), which implies that the composite material (and consequently its representative volume) is seen as an assemblage of infinite composite spheres of arbitrarily different outer diameters, chosen in such a way that they can fill the whole space.

Since the surrounding medium in the four-phase model is unbounded, the strain average over a composite sphere does not depend upon the composite sphere outer radius c , but it depends only on the ratios a/b and b/c , and, of course, on the phase moduli. Then, it is straightforward to recognize that, when neither the filler gradation nor the “unwanted” voids entrapped in the matrix are taken into account (i.e., when the RVE is considered as made by one composite sphere type only), *the averages over a single composite sphere of both the strain, $\bar{\varepsilon}_{ij}^{(c.s.)}$, and the stress, $\bar{\sigma}_{ij}^{(c.s.)}$, are equal to the homogeneous strain, E_{ij} , and the homogeneous stress, Σ_{ij} , respectively, applied to the RVE (made by a CSA), when there is a prescribed uniform strain, $E_{ij}^{(R)}$, or stress, $\Sigma_{ij}^{(R)}$, at infinity on the four-phase model (given, in this case, by equations (7.2.4) and (7.2.3) respectively).* Then, using for instance the displacement approach, for which boundary conditions (7.2.4) apply, the coefficients of the localization tensor of interest here are $\bar{\varepsilon}_{12}^{(m)}/\bar{\varepsilon}_{12}^{(c.s.)}$ and $\bar{\varepsilon}_{12}^{(i)}/\bar{\varepsilon}_{12}^{(c.s.)}$, where $\bar{\varepsilon}_{12}^{(m)}$ and $\bar{\varepsilon}_{12}^{(i)}$ are the averages of the shear strains in the matrix and in the wall of the inclusion respectively (there is not the need to compute the strain average over the void inside the inclusion $\bar{\varepsilon}_{12}^{(v)}$ because it disappears in the homogenization procedure, the shear modulus of the void being equal to zero). Using Love's solution, and Green's theorem to compute the appropriate averages, we can write the following relations:

$$\bar{\varepsilon}_{12}^{(m)} = M_1 + \left(1 + \frac{1}{5}\alpha_2^{(m)}\right) \frac{c^5 - b^5}{a^2(c^3 - b^3)} M_3 \quad (7.2.28)$$

$$\bar{\varepsilon}_{12}^{(i)} = I_1 + \left(1 + \frac{1}{5}\alpha_2^{(i)}\right) \frac{b^5 - a^5}{a^2(b^3 - a^3)} I_3 \quad (7.2.29)$$

$$\bar{\varepsilon}_{12}^{(c.s.)} = M_1 + \left(1 + \frac{1}{5}\alpha_2^{(m)}\right) \frac{c^2}{a^2} M_3 + \frac{1}{5}\alpha_{-3}^{(m)} \frac{a^3}{c^3} M_4 \quad (7.2.30)$$

and finally, as a consequence of the average operations and taking into account that $E_{12} = \varepsilon_{12}^{(c.s.)}$, the constitutive relation $2G_0^{est} \langle \varepsilon_{12} \rangle = \langle \sigma_{12} \rangle$ leads to

$$G_0^{est} = G^{(m)}(1 - f) \frac{\bar{\varepsilon}_{12}^{(m)}}{\bar{\varepsilon}_{12}^{(c.s.)}} + G^{(i)} f \left(1 - \frac{a^3}{b^3}\right) \frac{\bar{\varepsilon}_{12}^{(i)}}{\bar{\varepsilon}_{12}^{(c.s.)}} \quad (7.2.31)$$

Replacing results (7.2.28)–(7.2.30) into equation (7.2.31) we obtain G_0^{est} as a function of the geometry and the materials of the composite sphere and of the stiffness of the surrounding medium in the four-phase model:

$$\begin{aligned} G_0^{est} = & \frac{G^{(m)} \left(\frac{c^3 - b^3}{c^3} M_1 + \left(1 + \frac{1}{5}\alpha_2^{(m)}\right) \frac{c^5 - b^5}{a^2 c^3} M_3 \right) + G^{(i)} \left(\frac{b^3 - a^3}{c^3} I_1 + \left(1 + \frac{1}{5}\alpha_2^{(i)}\right) \frac{b^5 - a^5}{a^2 c^3} I_3 \right)}{M_1 + \left(1 + \frac{1}{5}\alpha_2^{(m)}\right) \frac{c^2}{a^2} M_3 + \frac{1}{5}\alpha_{-3}^{(m)} \frac{a^3}{c^3} M_4} \end{aligned} \quad (7.2.32)$$

In the case of the Self-Consistent “composite sphere”-based estimate ($G^{(s)} = G_0^{est}$), which corresponds to a material in which the composite spheres are distributed in a “perfectly disordered” way,¹ equation (7.2.32) becomes implicit in the unknown effective shear modulus $G_0^{est} = G_0^{SC}$ and, by the way, according to equation (6.7.1), we have $\bar{\varepsilon}_{12}^{(c.s.)} = \frac{\gamma}{2}$. In this case, the result is found by computing the significant root of the following quadratic equation (derived from equation (7.2.32) by means of some lengthy algebra):

$$\left(40H_1 \frac{a^5}{c^5}\right) \left(\frac{G_0^{SC}}{G^{(m)}}\right)^2 + \left(2F_4 - F_2 - 8(F_1 + 3F_3) \frac{a^5}{c^5}\right) \left(\frac{G_0^{SC}}{G^{(m)}}\right) + \frac{F_2 F_3 - F_1 F_4}{H_1} = 0 \quad (7.2.33)$$

whose coefficients F_1, F_2, F_3, F_4 and H_1 are given in appendix 7.B.

The significant root for G_0^{SC} is positive (i.e., greater than the value of the shear modulus of the void), and lower than the highest value between the shear modulus of the matrix, $G^{(m)}$, and the shear modulus of the inclusion, $G^{(i)}$.

It is worth noting that the here exploited homogenization method based on the MRP theory has the advantage of providing a Self-Consistent final equation (7.2.33) easier to solve than that provided by the “classical” Self-Consistent Scheme (see chapter 6), whose solution in general requires the computation of the roots of high order polynomial functions

¹In [75], Kröner defined from the statistical viewpoint “perfectly disordered” composites as those heterogeneous materials in which the properties of each phase are not correlated with those of adjacent phases, making the two-point correlation functions collapsing into Dirac’s delta functions; this definition holds for the “punctual case” only, i.e. for the “classical” case described in chapter 6 in which estimates of material properties are not dependent upon a MRP choice, making the volume fractions of the phases and the choice of the surrounding homogeneous medium the only parameters used to describe the morphology of the composite. As pointed out by Bornert et al. [25], the mathematical definition of “perfectly disordered distribution of MRPs” is not clear yet.

(for syntactic foams, see equations (6.7.2)–(6.7.3)). This difference arises from the fact that, when only one composite sphere can account for both all the composite phases and their morphology as assumed in this section, the MRP theory requires the solution of just one Eshelby problem. Instead, with the “classical” approach there is the need of averaging as many Eshelby solutions as the number of the phases. In the next section 7.3, it will be shown that the Self-Consistent solution for the effective bulk modulus based on the four-phase model is even explicit.

The solution of equation (7.2.33) can not be particularized to that of Christensen and Lo (valid for solid inclusions), because if we set $a = 0$ the solution becomes singular. To obtain the Christensen and Lo result we must replace equations (7.2.17) and (7.2.18) with $I_2 = 0$ and $I_4 = 0$, and, since in equations (7.2.8)–(7.2.13) a was employed to make the unknown coefficients dimensionless, we must set it equal to any arbitrary non-zero value each time it appears with that meaning. Note that in equations (7.2.29), (7.2.31), and (7.2.32) a has the meaning of inclusion inner radius also; therefore, equation (7.2.29) must be replaced with $\bar{\varepsilon}_{12}^{(i)} = I_1 + \left(1 + \frac{1}{5}\alpha_2^{(i)}\right)\frac{b^2}{a^2}I_3$, a has to be set equal to zero in equation (7.2.31), and equation (7.2.32) has to be re-derived according to these changes.

If we prescribe $a = b$, the results (7.2.32) and (7.2.33) can be used to estimate the effective shear modulus of standard foams.

It is now possible to compare some estimates given by (7.2.32)–(7.2.33) with other theoretical predictions. These estimates are plotted in figure 7.2, for three different sets of component data, as a function of the volume fraction of the filler, and are compared with both the “classical” Voigt estimate and the rigorous “classical” Hashin–Shtrikman upper bound (the lower bound, which coincides with the “classical” Reuss estimate, is null because of the presence of a void phase), the latter computed using equation (6.5.4). Furthermore, both the “classical” and the “composite sphere”-based versions are computed of the Mori–Tanaka estimate, which is claimed to be suitable for particulate composites, as syntactic foams are. Equation (7.2.32) furnishes both the Lee–Westmann bounds and the Mori–Tanaka “composite sphere”-based estimate, whereas equation (6.6.2) gives the “classical” Mori–Tanaka estimate.

First of all, care must be taken to distinguish between two different “bounding” approaches. A first one is based on the choice of a MRP; therefore, it has bounding meaning only for the particular morphology (such as that of the composite sphere) used to compute the relevant elastic solutions. On the contrary, the “classical” Hashin–Shtrikman bounds ([57] and [58]), furnish rigorous bounds at least for any macroscopically isotropic composite material (not only for a CSA or for another particular morphology), but do not allow us to account for any morphological feature of the composite itself (i.e., such as the connectedness of the matrix) beyond the volume fraction of the phases.

Let us anticipate that it is possible to apply the Mori–Tanaka procedure in another “non-classical” sense, by modeling syntactic foams as two-phase particulate composites, in which one phase, the whole filler, is a heterogeneous phase. In this case, there is the need of computing the Eshelby tensor for the hollow sphere by means of elastic solutions similar to those reported in this section and in the next one. Contrary to the “classical” Mori–Tanaka method, in this way we do not introduce any approximation about the shape of the phases (matrix, inclusion’s wall, and inclusion’s void) when solving the Eshelby problems; in other words, this method is expected to show a good accuracy in predicting the elastic

moduli of syntactic foams because it is able to take into account that any void inside a filler particle is always surrounded by an inclusion wall. Moreover, this method accounts, even if approximately, for the connectedness of the matrix. This approach lies in principle halfway between the “classical” Mori–Tanaka method and the MRP–based theory (even if it can be seen as a particular case of the MRP–based theory); actually, in appendix 7.C we shall prove that *this approach exactly leads to the Mori–Tanaka “composite sphere”–based estimate*, obtainable by setting the stiffness of the reference medium equal to that of the matrix in equation (7.2.32).

The curves of figure 7.2 refer to a syntactic foam constituted by a matrix of elastic constants $E^{(m)} = 5000 \text{ MPa}$, $\nu^{(m)} = 0.4$ and a filler made up of glassy hollow spheres characterized by $E^{(i)} = 70110 \text{ MPa}$ and $\nu^{(i)} = 0.23$. Three plots are drawn, each referring to a different ratio between the outer and the inner radius of the hollow inclusions: $a/b = 0.50$, $a/b = 0.93$ and $a/b = 0.97$ (i.e., a range from very thick to very thin inclusions).

The “classical” Hashin–Shtrikman bounds are not close enough to each other to give a good estimate of the effective shear modulus of syntactic foams; this is trivial because the lower bound is always null when one phase is the void. Thus, this rigorous bounding approach here can not be used alone, but it is however a useful tool to validate any other estimate. The bounds proposed by Lee and Westmann (recall that they are the Voigt and Reuss bounds based on the composite sphere), on the other hand, are close to each other only for low volume fractions of filler, but this situation seldom happens in the actual field of applications of syntactic foams. The “classical” Mori–Tanaka estimate gives an effective shear modulus even lower than that predicted by the Lee–Westmann lower bound. This is because the “classical” Mori–Tanaka estimate can not take into account that, in a syntactic foam, the voids are included inside the inclusion wall and that the solid part of the inclusion (usually made of glass) is structurally shaped as spherical shell, instead of smaller solid spheres, as assumed in deriving equation (6.6.2); thus, the void effect is overestimated on the effective compliance, or, that is the same, the stiffness of the whole filler is underestimated on the overall moduli. Finally, the Mori–Tanaka “composite sphere”–based estimate predicts an effective shear modulus very close to that predicted by the Self–Consistent “composite sphere”–based estimate, here taken as reference estimate. The results shown in figure 7.2 can be further commented as follows:

- the “classical” Voigt estimate is much higher than the “classical” Hashin–Shtrikman upper bound;
- the Self–Consistent estimate of the effective shear modulus given by equation (7.2.33) falls below both the upper bounds; in particular, it falls below the “classical” Hashin–Shtrikman bound, which indicates, as obvious, that the composite spheres distribution on the RVE deriving from the Self–Consistent approach may be adequate to describe syntactic foams as macroscopically isotropic three-phase composites;
- the Lee and Westmann upper bound tends to exceed the “classical” Hashin–Shtrikman upper bound for $f \rightarrow 1$;
- from the engineering viewpoint, and with this particular set of data, the “microstructural” apparent stiffness of the thinner inclusions is lower than that of the matrix, while that of the thicker ones is greater; this is indicated by the change of slope of

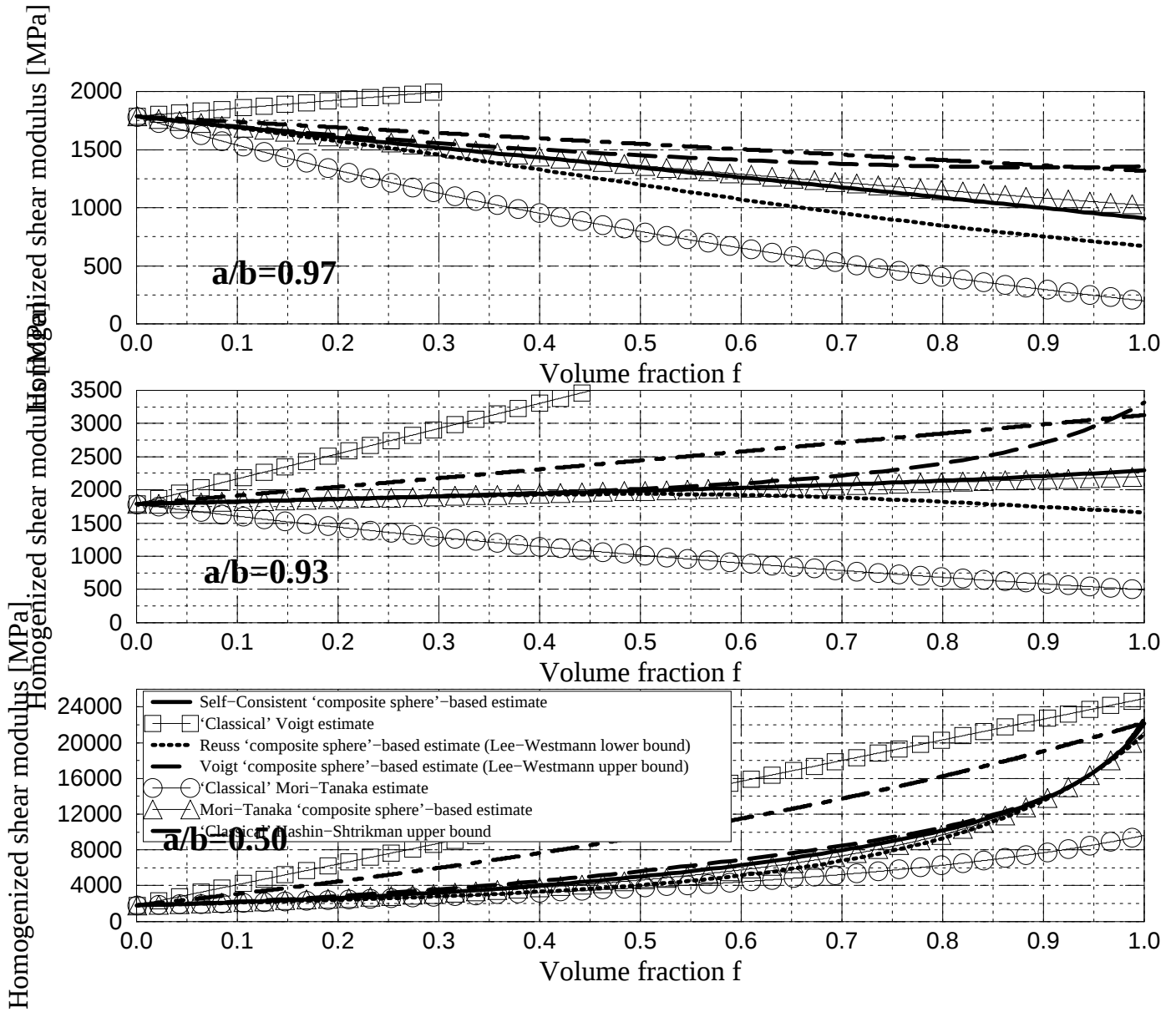


Figure 7.2: Different estimates for the effective shear modulus

the shear modulus, predicted by equation (7.2.33) when changing the thickness of the wall of the inclusions. The bounds are not always able to correctly catch this feature, which may prove essential for the “optimum” design of such a composite (see chapter 12 for an example of application);

- the difference between the predictions given by the bounds of Lee and Westmann and those given by equation (7.2.33) is more or less constant over the considered range of ratios a/b , of the order of $\pm 10\%$ for $f = 0.6$. This difference increases for $f \rightarrow 1$, for all ratios a/b ;
- from the above considerations and assuming that the Hashin–Shtrikman “composite sphere”–based upper bound should furnish too stiff estimates and that the Mori–Tanaka “composite sphere”–based estimate should overvalue the role of the matrix in the composite, it may be concluded that the Self–Consistent “composite sphere”–based estimate, arising from equation (7.2.33), is the most accurate homogenization technique among those here proposed to estimate the elastic moduli of syntactic foams; for this reason, as already said, it will be used, in the sequel of this work, as reference estimate.

7.3 The bulk modulus derivation for the case in which the RVE is made by one composite sphere type only

In the case of a syntactic foam made by one composite sphere type only (i.e., when both the filler gradation and the “unwanted” voids are not considered) the Voigt and Reuss “composite sphere”–based estimates of the effective bulk modulus (its extremum lower and upper bounds) are coincident. Therefore, for this special case, the effective bulk modulus K_0^{est} of a syntactic foam modeled with the CSA morphological approximation can be unambiguously estimated. As shown by Lee and Westmann [79], one could use a simpler model than the four–phase model to compute this homogenization, but it is necessary to use the more general approach involving the four–phase model, as used for instance by Hervé and Pellegrini [60], to extend, in the next section, this homogenization technique to consider the filler gradation and the presence of “unwanted” voids entrapped in the matrix.

To compute the effective bulk modulus one has to apply homogeneous volumetric boundary conditions to the four–phase model (figure 7.1). As said, since the boundary conditions are applied to the four–phase model at infinity, it is possible to choose displacement boundary conditions as well as force boundary conditions without making the result of the homogenization dependent upon this choice. Then, choosing displacement boundary conditions, one has:

$$E_{11}^{(R)} = E_{22}^{(R)} = E_{33}^{(R)} = \theta \neq 0; \quad \text{all other components } E_{ij}^{(R)} = 0 \quad (7.3.1)$$

where θ is an arbitrary constant known term, whose magnitude, as obvious, does not affect the effective bulk modulus.

This linear elastic problem is characterized by the following radial displacement fields (Timoshenko and Goodier [116]):

- in the surrounding medium ($r \geq c$)

$$u_r(r) = T_1 r + T_2 \frac{a^3}{r^2} \quad (7.3.2)$$

- in the matrix shell ($b \leq r \leq c$)

$$u_r(r) = P_1 r + P_2 \frac{a^3}{r^2} \quad (7.3.3)$$

- in the wall of the hollow inclusion ($a \leq r \leq b$)

$$u_r(r) = J_1 r + J_2 \frac{a^3}{r^2} \quad (7.3.4)$$

The boundary and interface conditions allow us to write the following system in the unknown dimensionless coefficients $J_1, J_2, P_1, P_2, T_1, T_2$:

- vanishing of tractions at $r = a$:

$$3K^{(i)} J_1 - 4G^{(i)} J_2 = 0 \quad (7.3.5)$$

- continuity of tractions at $r = b$:

$$3K^{(i)} J_1 - 4G^{(i)} J_2 \frac{a^3}{b^3} = 3K^{(m)} P_1 - 4G^{(m)} P_2 \frac{a^3}{b^3} \quad (7.3.6)$$

- continuity of displacements at $r = b$:

$$J_1 + J_2 \frac{a^3}{b^3} = P_1 + P_2 \frac{a^3}{b^3} \quad (7.3.7)$$

- continuity of tractions at $r = c$:

$$3K^{(m)} P_1 - 4G^{(m)} P_2 \frac{a^3}{c^3} = 3K^{(s)} T_1 - 4G^{(s)} T_2 \frac{a^3}{c^3} \quad (7.3.8)$$

- continuity of displacements at $r = c$:

$$P_1 + P_2 \frac{a^3}{c^3} = T_1 + T_2 \frac{a^3}{c^3} \quad (7.3.9)$$

- boundary conditions (7.3.1) at $r \rightarrow \infty$:

$$T_1 = \theta \quad (7.3.10)$$

It is now possible to compute the relevant averages of the strain field:

$$\bar{\varepsilon}_{kk}^{(m)} = 3P_1 \quad (7.3.11)$$

$$\bar{\varepsilon}_{kk}^{(i)} = 3J_1 \quad (7.3.12)$$

$$\bar{\varepsilon}_{kk}^{(c.s.)} = 3\left(P_1 + P_2 \frac{a^3}{c^3}\right) \quad (7.3.13)$$

where ε_{kk} indicates the first strain invariant. Then, following the same path of reasoning leading to the shear modulus estimates (7.2.32), one can find the solution for the effective bulk modulus of a syntactic foam made by one composite sphere type only and modeled by the CSA morphology, that is unique, i.e. independent upon the surrounding medium stiffness (Lee and Westmann [79]):

$$K_0^{est} = K^{(m)} \frac{\delta\left(1 + \frac{b^3}{c^3}\gamma\right) + \kappa\left(1 - \frac{b^3}{c^3}\right)\gamma}{\delta\left(1 - \frac{b^3}{c^3}\right) + \kappa\left(\gamma + \frac{b^3}{c^3}\right)} \quad (7.3.14)$$

where

$$\gamma = \frac{4G^{(m)}}{3K^{(m)}} \quad \delta = \frac{4G^{(i)}}{3K^{(m)}}\left(1 - \frac{a^3}{b^3}\right) \quad \kappa = \frac{4G^{(i)}}{3K^{(i)}} + \frac{a^3}{b^3} \quad (7.3.15)$$

7.4 Extension to consider both the filler gradation and the presence of “unwanted” voids

Here, the linear elastic homogenization procedure derived in sections 7.2 and 7.3 is extended to take into account the filler gradation and the presence of “unwanted” voids entrapped in the matrix. In appendix 7.D an approximate but simple method will be proposed to deal with the presence of a small amount of “unwanted” voids.

For a syntactic foam filled by spheres exhibiting different ratios between the inner and outer radii, and including air cavities in the matrix, we consider, as our RVE, a Composite Sphere Assemblage made by N types of composite spheres, each characterized by a known ratio a_λ/b_λ , $\lambda = 1, \dots, N$. *The presence of “unwanted” voids is taken into account by simply considering a type of inclusion with wall thickness $b_\lambda - a_\lambda = 0$, i.e., $a_\lambda/b_\lambda = 1$.* The RVE is therefore made up of N types of composite spheres that have variable size and that fill the whole space, as sketched in figure 7.3; we assume that *every* composite sphere is such that the cubic power of the ratio between the outer radius of the inclusion and the outer radius of the composite sphere itself is equal to the volume fraction, f , of the filler in the syntactic foam. There are other ways to prescribe that the volume fraction of the filler in such a model is equal to the volume fraction f of the studied composite; here, the analysis of this aspect has not been pursued in detail.

Let us describe the procedure to homogenize the shear modulus first. For each composite sphere λ we consider the four-phase model of figure 7.1, with the boundary conditions (7.2.2) at infinity, and compute the relevant elastic solution $\varepsilon_{ij}^{(\zeta),\lambda}$.

Following the path of reasoning already reported in chapter 6 for the “classical” case (see equations (6.2.1)–(6.2.4)), we now prescribe that the applied strain field E_{12} at the boundary of the RVE coincides with the volume average of the corresponding local fields in such an ensemble of composite spheres, i.e.:

$$E_{12} \stackrel{\text{def}}{=} \langle \varepsilon_{12} \rangle = \frac{1}{|\Omega|} \int_{\Omega} \varepsilon_{12}(\mathbf{x}) \, d\Omega \quad (7.4.1)$$

i.e., by taking into account the presence of N different composite spheres,

$$E_{12} = \sum_{\lambda=1}^N f_{\lambda} \bar{\varepsilon}_{12}^{(c.s.),\lambda} \quad (7.4.2)$$

where the symbol f_{λ} indicates the fraction of the filler type λ to the whole filler, and $\bar{\varepsilon}_{12}^{(c.s.),\lambda}$ indicates the volume average computed on the single composite sphere λ .

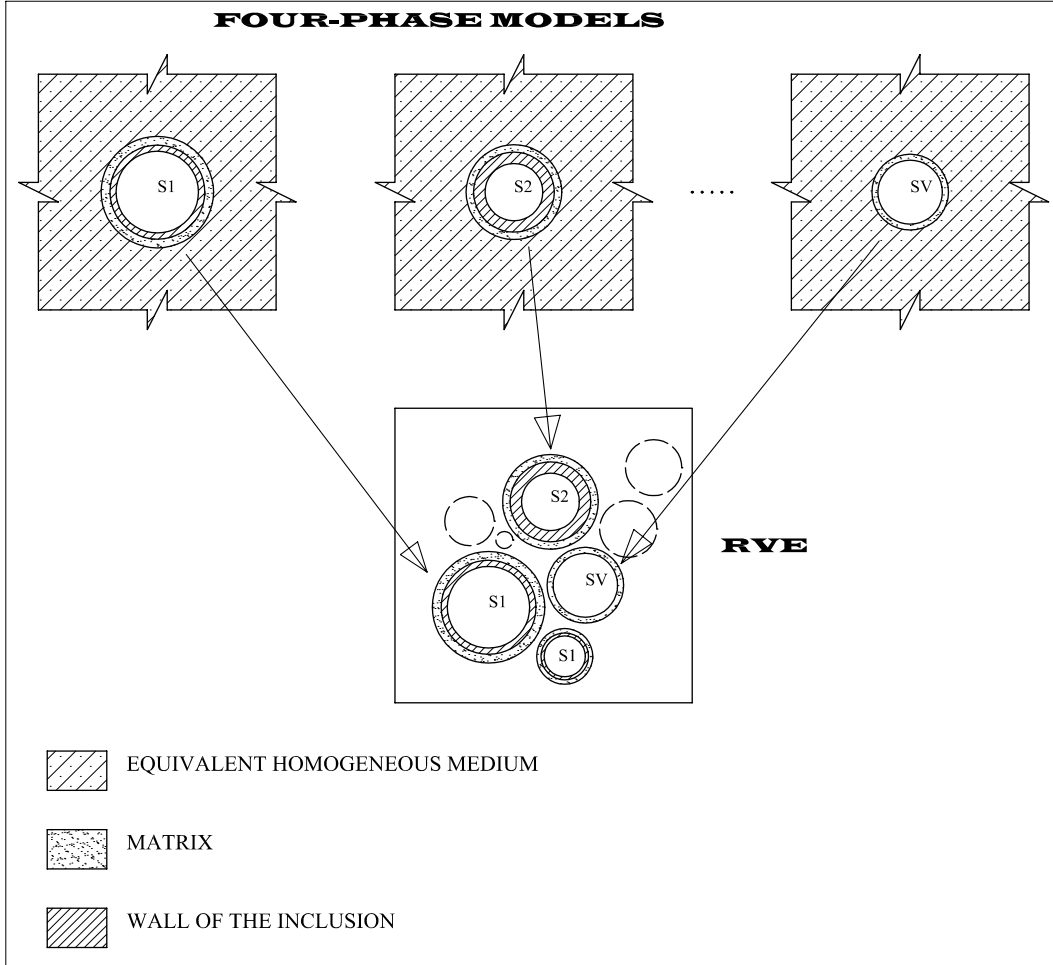


Figure 7.3: *The micromechanical model used to take into account both the “unwanted” voids and the filler gradation*

By writing the average stress–strain relationship for the RVE

$$2G_0^{est} \langle \varepsilon_{12} \rangle = \langle \sigma_{12} \rangle \quad (7.4.3)$$

one can obtain the desired estimate for the homogenized shear modulus. In fact, the volume average of the stress σ_{12} can be written, on the basis of the local strain fields, as

$$\langle \sigma_{12} \rangle = \frac{2}{|\Omega|} \int_{\Omega} G(\mathbf{x}) \varepsilon_{12}(\mathbf{x}) \, d\Omega =$$

$$\begin{aligned}
&= \frac{2}{|\Omega|} \left(\sum_{\lambda=1}^N \left(\int_{\Omega_\lambda^{(i)}} G_\lambda^{(i)} \varepsilon_{12}(\mathbf{x}) \, d\Omega + \int_{\Omega_\lambda^{(m)}} G_\lambda^{(m)} \varepsilon_{12}(\mathbf{x}) \, d\Omega \right) \right) = \\
&= 2 \sum_{\lambda=1}^N \left(G_\lambda^{(i)} f_\lambda^{(i)} \bar{\varepsilon}_{12}^{(i),\lambda} + G_\lambda^{(m)} f_\lambda^{(m)} \bar{\varepsilon}_{12}^{(m),\lambda} \right)
\end{aligned} \tag{7.4.4}$$

where $G_\lambda^{(i)}$ indicates the shear modulus of the inclusion material in composite sphere λ , $f_\lambda^{(m)}$ and $f_\lambda^{(i)}$ indicate the volume fraction of matrix and inclusion materials of the composite sphere λ respectively and $\bar{\varepsilon}_{12}^{(\zeta),\lambda}$ indicates the volume average of the shear strain over layer ζ of composite sphere λ , i.e.,

$$\bar{\varepsilon}_{12}^{(\zeta),\lambda} = \frac{1}{|\Omega_\lambda^{(\zeta)}|} \int_{\Omega_\lambda^{(\zeta)}} \varepsilon_{12}(\mathbf{x}) \, d\Omega \tag{7.4.5}$$

Here, we have used the symbol $G_\lambda^{(m)}$ to indicate a different shear modulus of the matrix associated to each different composite sphere λ . Although such distinction is unnecessary in a linear analysis, where the shear modulus of the matrix is constant over the whole RVE, it may become of some importance in a nonlinear analysis, as it will be discussed in chapters 17 and 18.

Replacing results (7.4.4) and (7.4.2) into equation (7.4.3) it is then possible to estimate the homogenized shear modulus G_0^{est} :

$$G_0^{est} = \frac{\sum_{\lambda=1}^N \left(G_\lambda^{(i)} f_\lambda^{(i)} \bar{\varepsilon}_{12}^{(i),\lambda} + G_\lambda^{(m)} f_\lambda^{(m)} \bar{\varepsilon}_{12}^{(m),\lambda} \right)}{\sum_{\lambda=1}^N f_\lambda \bar{\varepsilon}_{12}^{(c.s.),\lambda}} \tag{7.4.6}$$

Finally, recalling that, owing to the definitions,

$$f_\lambda^{(i)} = \frac{|\Omega_\lambda^{(i)}|}{|\Omega|} = f_\lambda f \left[1 - \left(\frac{a_\lambda}{b_\lambda} \right)^3 \right] \tag{7.4.7}$$

$$f_\lambda^{(m)} = \frac{|\Omega_\lambda^{(m)}|}{|\Omega|} = f_\lambda (1 - f) \tag{7.4.8}$$

equation (7.4.6) can be rewritten as follows:

$$G_0^{est} = \frac{\sum_{\lambda=1}^N f_\lambda \left\{ G_\lambda^{(i)} f \left[1 - \left(\frac{a_\lambda}{b_\lambda} \right)^3 \right] \bar{\varepsilon}_{12}^{(i),\lambda} + G_\lambda^{(m)} (1 - f) \bar{\varepsilon}_{12}^{(m),\lambda} \right\}}{\sum_{\lambda=1}^N f_\lambda \bar{\varepsilon}_{12}^{(c.s.),\lambda}} \tag{7.4.9}$$

The volume averages over the RVE and over the single layers all contain the shear modulus $G^{(s)}$ of the arbitrary surrounding medium in the four-phase model of figure 7.1; therefore, one can obtain several estimates of the homogenized shear modulus by choosing different values for $G^{(s)}$. The best choice is the Self-Consistent one, in which $G^{(s)} = G_0^{est}$ and,

by the way, $\sum_{\lambda=1}^N f_{\lambda} \bar{\varepsilon}_{12}^{(c.s.),\lambda} = \frac{\gamma}{2}$; in this case, equation (7.4.9) is implicit in the unknown G_0^{est} .

In section 7.2 all the equations needed to compute the relevant averages of the strain fields involved on equation (7.4.9) are given. Note that it is necessary to solve the system (7.2.17)–(7.2.27) (setting S_1 , as described in section 7.2, as dependent from the boundary conditions (7.2.2)) and to compute the averages (7.2.28)–(7.2.30) for each type of composite sphere λ , for $\lambda = 1, \dots, N$. In the case in which “unwanted” voids have to be accounted for (i.e., $a_{\lambda} = b_{\lambda}$), to avoid numerical problems, equation (7.2.29) must be replaced with

$$\bar{\varepsilon}_{12}^{(i),\lambda} = I_{1,\lambda} + \left(1 + \frac{1}{5}\alpha_2^{(i)}\right) \frac{a_{\lambda}^4 + a_{\lambda}^3 b_{\lambda} + a_{\lambda}^2 b_{\lambda}^2 + a_{\lambda} b_{\lambda}^3 + b_{\lambda}^4}{a_{\lambda}^2(a_{\lambda}^2 + a_{\lambda} b_{\lambda} + b_{\lambda}^2)} I_{3,\lambda} = I_{1,\lambda} + \frac{5 + \alpha_2^{(i)}}{3} I_{3,\lambda} \quad (7.4.10)$$

The computation of the homogenized bulk modulus K_0^{est} follows exactly the same path, starting, however, from volumetric boundary conditions (7.3.1) at infinity on the four-phase model.

By proceeding in the same way as for the shear modulus one thus arrives at the following expression of K_0^{est} :

$$K_0^{est} = \frac{\sum_{\lambda=1}^N f_{\lambda} \left\{ K_{\lambda}^{(i)} f \left[1 - \left(\frac{a_{\lambda}}{b_{\lambda}} \right)^3 \right] \bar{\varepsilon}_{kk}^{(i),\lambda} + K_{\lambda}^{(m)} (1 - f) \bar{\varepsilon}_{kk}^{(m),\lambda} \right\}}{\sum_{\lambda=1}^N f_{\lambda} \bar{\varepsilon}_{kk}^{(c.s.),\lambda}} \quad (7.4.11)$$

where ε_{kk} is the volumetric strain. Again, in section 7.3 all the equations necessary to apply equation (7.4.11) are furnished: there is the need to solve the system (7.3.5)–(7.3.10) and to compute the averages (7.3.11)–(7.3.13) for each type of composite sphere λ , i.e. N times.

Note that in both equations (7.4.9) and (7.4.11) both the shear and the bulk moduli of the infinite surrounding medium appear in the averages of the local fields, that depend in any case upon both moduli. Therefore, in the Self-Consistent case the computation of the homogenized moduli is coupled, except for the trivial case of a single inclusion type ($N = 1$). Of course, the Self-Consistent case has the little advantage of simplifying equation (7.4.11) since its denominator becomes equal to 3θ .

Appendixes to Chapter 7

7.A Discussion of the sequential homogenization technique proposed by Nielsen [91]

Nielsen [91] suggested a sequential homogenization method, to calculate the effective elastic properties of syntactic foams, that consists of the a priori “homogenization” of the hollow sphere alone, followed by the homogenization of the syntactic foam seen as a matrix filled by solid spheres. Since in this manner the voids are eliminated, any “classical” homogenization method would be effective; for instance, the Hashin–Shtrikman approach would furnish rigorous bounds that frequently would be close enough to give a good estimate for a composite filled with solid inclusions. But the real composite is not filled with solid inclusions, and this is reflected into a poor performance of the rigorous Hashin–Shtrikman bounds which, even if close to each other, are rather distant from the actual values of the homogenized moduli of the real syntactic foam.

The single hollow sphere is not macroscopically homogeneous and, therefore, the determination of its “effective” elastic properties is meaningless. Nevertheless, it is practically possible to “homogenize” it by means of the same direct approach one can use for a RVE; if the volumetric and then the simple shear boundary conditions are applied at the outer surface of the hollow sphere, it is possible to calculate the stored strain energy by means of Love’s results (the same used in chapter 7). Then, these strain energies can be imposed equal to those stored by a solid sphere, with the same outer radius and subjected to the same boundary conditions, and thus it is possible to determine the “homogenized” properties of the filler. In this appendix this “false” homogenization is indicated by writing it between double commas.

Both the volumetric boundary conditions on forces and on displacements give the same expression for the “homogenized” bulk modulus, $K^{(f)}$, which is then unambiguously defined. For the effective bulk modulus of the syntactic foam, K_0 , this sequential homogenization is indeed correct if applied to the CSA model and if the RVE is characterized by one composite sphere only. In fact, in the four-phase model, to isotropic boundary conditions at infinity correspond isotropic fields of forces and displacements at both the interface between the composite sphere and the surrounding medium (at $r = c$) and at the interface between the inclusion and the matrix (at $r = b$).

Thus, the unique solution for the “homogenized” bulk modulus for the filler (superscript f) is

$$K^{(f)} = \frac{K^{(i)} \left(1 - \frac{a^3}{b^3}\right)}{1 + \frac{1 + \nu^{(i)}}{2(1 - 2\nu^{(i)})} \frac{a^3}{b^3}} \quad (7.A.1)$$

This expression can also be obtained from the specialization of equation (7.3.14) to $b = c$.

The “homogenization” of the shear modulus of the filler, on the contrary, is ambiguously defined. Indeed, the force-type and the displacement-type “homogenizations”, in simple shear, give different results. Furthermore, it is not known how a simple shear condition at the boundary of a RVE is transferred to the outer surface of an inclusion. In the CSA model, the force and displacement fields at the outer surface of an inclusion, due to a simple shear boundary condition at infinity, are still of simple shear, but mixed in forces and displacements, and depend in a complex way both upon the microstructure of the composite and the elastic moduli of the phases.

However, in consequence of the theorem of minimum Complementary Energy, the value of the “homogenized” shear modulus for the simple shear stress boundary condition, $G_{low}^{(f)}$, is the lower bound for the “homogenized” shear modulus of the filler, $G^{(f)}$. The expression for $G_{low}^{(f)}$ can be found by setting $b = c$ in the equations that furnish the Reuss “composite sphere”-based estimate from equation (7.2.32).

Dually, owing to the theorem of minimum Total Potential Energy, the “homogenized” shear modulus for simple shear strain boundary condition, $G_{up}^{(f)}$ is the upper bound for $G^{(f)}$. $G_{up}^{(f)}$ can be found by specialization of the results given in chapter 7, in terms of the Voigt “composite sphere”-based estimate for $b = c$.

Nielsen [91] proposes a really simple formula to evaluate the “homogenized” shear modulus of a hollow sphere:

$$G_N^{(f)} = G^{(i)} \frac{1 - \frac{a^3}{b^3}}{1 + \frac{a^3}{b^3}} \quad (7.A.2)$$

This expression lies between the upper and lower bounds, i.e., $G_{low}^{(f)} \leq G_N^{(f)} \leq G_{up}^{(f)}$, as shown in figure 7.4.

In figure 7.4 a fourth curve, obtained from the specialization of equation (7.2.33) to $b = c$, for the “homogenization” of a hollow sphere is plotted. This “homogenization” would have meaning in terms of a CSA morphology if referred to a fictitious material constituted only by hollow spheres, packed according to the CSA structure. This model would well represent a “foam” made by glass with voids; but the attempt to extrapolate its results to a single hollow sphere is obviously meaningless. We have discussed also this result only to show that there are many possible choices to estimate the “homogenized” shear modulus of a hollow sphere, and to make it clear that none of them is based on a morphology, because the single hollow sphere is not macroscopically homogeneous.

The results of the sequential homogenization approach of Nielsen for the syntactic foam are compared in figure 7.5 with the results given by the method proposed in this dissertation, for three different choices of matrix. The filler is in all cases made by the

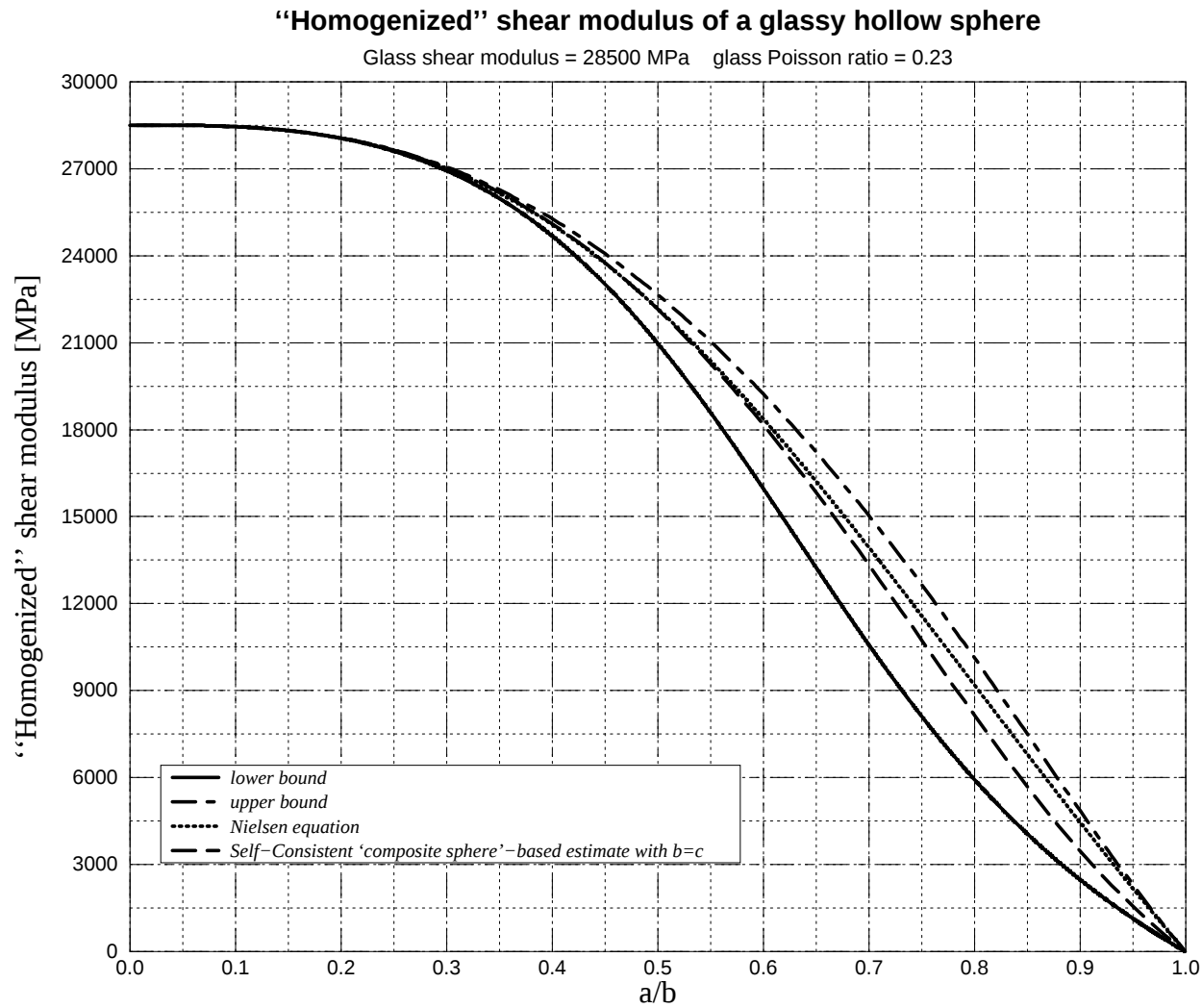


Figure 7.4: “Homogenized” shear modulus of a glassy hollow sphere

glassy hollow spheres type K37, which have an average ratio between the internal and external radius, $a/b = 0.9501$ (see chapters 9 and 10). This inclusion has a “microstructural” stiffness “equivalent” to a continuum with Young modulus of the order of 4000 *MPa*. We have plotted curves corresponding to matrices having (i) a much larger Young modulus (20000 *MPa*) than the “homogenized” filler, (ii) a Young modulus (5000 *MPa*) comparable to that of the “homogenized” filler and (iii) a Young modulus (50 *MPa*) much smaller than that of the “homogenized” filler. For each choice of the matrix three curves are drawn: two are obtained using Nielsen’s formula (7.A.2) to homogenize the inclusions, followed by the two rigorous Hashin–Shtrikman bounds; the third is obtained by means of the four-phase model discussed in this work.

It is important to recall that the sequential application of Nielsen’s formula (7.A.2) and of the rigorous Hashin–Shtrikman bounds destroys the rigorous bounding nature of Hashin–Shtrikman results for the composite. This can be appreciated in all the three cases shown in figure 7.5, where the solutions given by equations (7.2.33) and (7.3.14) always tend to fall out of the bounds themselves; in one case the Self-Consistent “composite sphere”-based estimate is even totally below both bounds.

Only for the case of a very stiff matrix all the results tend to get close to each other, and the sequential approach seems to give acceptable results, at least for volume fractions not too large. The error becomes much larger, and actually not acceptable even from an engineering viewpoint, for the more likely situation, shown in the second graph, where the Young modulus of the filler is of the same order of magnitude as that of the “homogenized” inclusion. This would be the case, for instance, if the matrix were made by a standard epoxy resin.

7.B The coefficients of equation (7.2.33)

The coefficients F_1, F_2, F_3, F_4 and H_4 of equation (7.2.33) are defined as follows. If a , b and c are the radii of the composite sphere, as illustrated in figure 7.1, define:

$$C_1 = \frac{21}{5} \frac{b}{a} - 6\nu^{(i)} \frac{b^3}{a^3} + \frac{3}{20} (7 + 5\nu^{(i)}) \frac{a^4}{b^4} \quad (7.B.1)$$

$$C_2 = \frac{2}{5} (7 - 5\nu^{(i)}) \frac{b}{a} + (5 - 4\nu^{(i)}) \frac{a^2}{b^2} - \frac{9}{5} \frac{a^4}{b^4} \quad (7.B.2)$$

$$C_3 = \frac{21}{5} \frac{b}{a} - (7 - 4\nu^{(i)}) \frac{b^3}{a^3} - \frac{1}{10} (7 + 5\nu^{(i)}) \frac{a^4}{b^4} \quad (7.B.3)$$

$$C_4 = \frac{2}{5} (7 - 5\nu^{(i)}) \frac{b}{a} + 2(1 - 2\nu^{(i)}) \frac{a^2}{b^2} + \frac{6}{5} \frac{a^4}{b^4} \quad (7.B.4)$$

$$C_5 = \frac{42}{5} + 6\nu^{(i)} \frac{b^2}{a^2} - \frac{6}{5} (7 + 5\nu^{(i)}) \frac{a^5}{b^5} \quad (7.B.5)$$

$$C_6 = \frac{4}{5} (7 - 5\nu^{(i)}) - 4(5 - \nu^{(i)}) \frac{a^3}{b^3} + \frac{72}{5} \frac{a^5}{b^5} \quad (7.B.6)$$

$$C_7 = \frac{21}{5} - (7 + 2\nu^{(i)}) \frac{b^2}{a^2} + \frac{2}{5} (7 + 5\nu^{(i)}) \frac{a^5}{b^5} \quad (7.B.7)$$

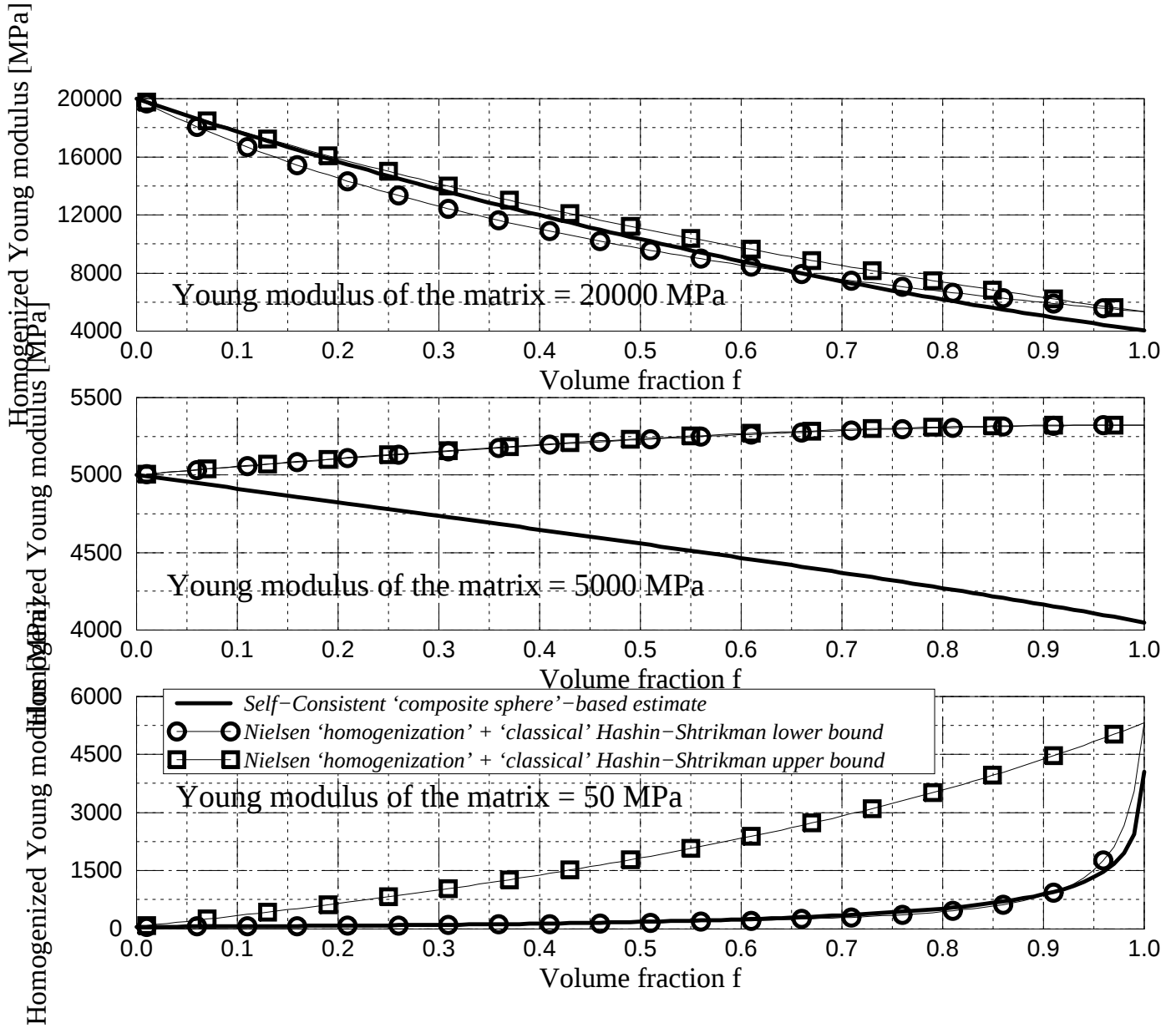


Figure 7.5: Effect of the Nielsen procedure on the effective Young modulus of syntactic foams

$$C_8 = \frac{2}{5}(7 - 5\nu^{(i)}) + 2(1 + \nu^{(i)})\frac{a^3}{b^3} - \frac{24}{5}\frac{a^5}{b^5} \quad (7.B.8)$$

then

$$D_1 = \left(C_5(C_4 - C_2) + C_6(C_1 - C_3) \right) \frac{b}{a} - 2 \frac{G^{(m)}}{G^{(i)}} (C_1 C_4 - C_2 C_3) \quad (7.B.9)$$

$$D_2 = \left((C_2 C_5 - C_1 C_6)(7 - 4\nu^{(m)}) + 6(C_3 C_6 - C_4 C_5)\nu^{(m)} \right) \frac{b^3}{a^3} + \\ - 6 \frac{G^{(m)}}{G^{(i)}} \nu^{(m)} (C_1 C_4 - C_2 C_3) \frac{b^2}{a^2} \quad (7.B.10)$$

$$D_3 = \left(C_5(2C_2 + 3C_4) - C_6(2C_1 + 3C_3) \right) \frac{a^4}{b^4} + 24 \frac{G^{(m)}}{G^{(i)}} (C_1 C_4 - C_2 C_3) \frac{a^5}{b^5} \quad (7.B.11)$$

$$D_4 = \left((C_4 C_5 - C_3 C_6)(5 - 4\nu^{(m)}) + 2(C_1 C_6 - C_2 C_5)(1 - 2\nu^{(m)}) \right) \frac{a^2}{b^2} + \\ + 4 \frac{G^{(m)}}{G^{(i)}} (5 - \nu^{(m)}) (C_1 C_4 - C_2 C_3) \frac{a^3}{b^3} \quad (7.B.12)$$

$$D_5 = \left(C_7(C_4 - C_2) + C_8(C_1 - C_3) \right) \frac{b}{a} - \frac{G^{(m)}}{G^{(i)}} (C_1 C_4 - C_2 C_3) \quad (7.B.13)$$

$$D_6 = \left((C_2 C_7 - C_1 C_8)(7 - 4\nu^{(m)}) + 6(C_3 C_8 - C_4 C_7)\nu^{(m)} \right) \frac{b^3}{a^3} + \\ + \frac{G^{(m)}}{G^{(i)}} (7 + 2\nu^{(m)}) (C_1 C_4 - C_2 C_3) \frac{b^2}{a^2} \quad (7.B.14)$$

$$D_7 = \left(C_7(2C_2 + 3C_4) - C_8(2C_1 + 3C_3) \right) \frac{a^4}{b^4} - 8 \frac{G^{(m)}}{G^{(i)}} (C_1 C_4 - C_2 C_3) \frac{a^5}{b^5} \quad (7.B.15)$$

$$D_8 = \left((C_4 C_7 - C_3 C_8)(5 - 4\nu^{(m)}) + 2(C_1 C_8 - C_2 C_7)(1 - 2\nu^{(m)}) \right) \frac{a^2}{b^2} + \\ - 2 \frac{G^{(m)}}{G^{(i)}} (1 + \nu^{(m)}) (C_1 C_4 - C_2 C_3) \frac{a^3}{b^3} \quad (7.B.16)$$

then again

$$H_1 = \frac{D_3 D_6 - D_2 D_7}{D_1 D_7 - D_3 D_5} \frac{c}{a} - 6\nu^{(m)} \frac{c^3}{a^3} + 3 \frac{D_2 D_5 - D_1 D_6}{D_1 D_7 - D_3 D_5} \frac{a^4}{c^4} \quad (7.B.17)$$

$$H_2 = \frac{D_3 D_8 - D_4 D_7}{D_1 D_7 - D_3 D_5} \frac{c}{a} + (5 - 4\nu^{(m)}) \frac{a^2}{c^2} + 3 \frac{D_4 D_5 - D_1 D_8}{D_1 D_7 - D_3 D_5} \frac{a^4}{c^4} \quad (7.B.18)$$

$$H_3 = \frac{D_3 D_6 - D_2 D_7}{D_1 D_7 - D_3 D_5} \frac{c}{a} - (7 - 4\nu^{(m)}) \frac{c^3}{a^3} - 2 \frac{D_2 D_5 - D_1 D_6}{D_1 D_7 - D_3 D_5} \frac{a^4}{c^4} \quad (7.B.19)$$

$$H_4 = \frac{D_3 D_8 - D_4 D_7}{D_1 D_7 - D_3 D_5} \frac{c}{a} + 2(1 - 2\nu^{(m)}) \frac{a^2}{c^2} - 2 \frac{D_4 D_5 - D_1 D_8}{D_1 D_7 - D_3 D_5} \frac{a^4}{c^4} \quad (7.B.20)$$

$$H_5 = 2 \frac{D_3 D_6 - D_2 D_7}{D_1 D_7 - D_3 D_5} + 6\nu^{(m)} \frac{c^2}{a^2} - 24 \frac{D_2 D_5 - D_1 D_6}{D_1 D_7 - D_3 D_5} \frac{a^5}{c^5} \quad (7.B.21)$$

$$H_6 = 2 \frac{D_3 D_8 - D_4 D_7}{D_1 D_7 - D_3 D_5} - 4(5 - \nu^{(m)}) \frac{a^3}{c^3} - 24 \frac{D_4 D_5 - D_1 D_8}{D_1 D_7 - D_3 D_5} \frac{a^5}{c^5} \quad (7.B.22)$$

$$H_7 = \frac{D_3 D_6 - D_2 D_7}{D_1 D_7 - D_3 D_5} - (7 + 2\nu^{(m)}) \frac{c^2}{a^2} + 8 \frac{D_2 D_5 - D_1 D_6}{D_1 D_7 - D_3 D_5} \frac{a^5}{c^5} \quad (7.B.23)$$

$$H_8 = \frac{D_3 D_8 - D_4 D_7}{D_1 D_7 - D_3 D_5} + 2(1 + \nu^{(m)}) \frac{a^3}{c^3} + 8 \frac{D_4 D_5 - D_1 D_8}{D_1 D_7 - D_3 D_5} \frac{a^5}{c^5} \quad (7.B.24)$$

and, finally,

$$F_1 = \left((H_1 - H_3) \frac{H_6 H_1 - H_5 H_2}{H_1 H_4 - H_3 H_2} + H_5 \right) \frac{c}{a} \quad (7.B.25)$$

$$F_2 = \left((2H_1 + 3H_3) \frac{H_6 H_1 - H_5 H_2}{H_1 H_4 - H_3 H_2} - 3H_5 \right) \frac{a^4}{c^4} \quad (7.B.26)$$

$$F_3 = \left((H_1 - H_3) \frac{H_8 H_1 - H_7 H_2}{H_1 H_4 - H_3 H_2} + H_7 \right) \frac{c}{a} \quad (7.B.27)$$

$$F_4 = \left((2H_1 + 3H_3) \frac{H_8 H_1 - H_7 H_2}{H_1 H_4 - H_3 H_2} - 3H_7 \right) \frac{a^4}{c^4} \quad (7.B.28)$$

7.C An alternative approach for the derivation of the Mori–Tanaka “composite sphere”–based estimate

This appendix is concerned with the derivation of the formulae needed to homogenize syntactic foams modeled as two phase particulate composites, in which the filler is a single heterogeneous “phase” that consists of the inclusion voids and the inclusion walls. In other words, here we compute the effective elastic moduli of syntactic foams by solving two different Eshelby problems: the first consists of a hollow spherical inclusion embedded in an unbounded matrix, whereas in the second, trivially homogeneous, a matrix inclusion is surrounded by the matrix itself. This approach is in principle different from the other two already exploited to derive Mori–Tanaka estimates of the overall elastic constants of syntactic foams: to derive the “classical” Mori–Tanaka estimate we considered three Eshelby problems, each concerned with a homogeneous inclusion (see subsection 6.6.1), whereas the Mori–Tanaka “composite sphere”–based estimate (see sections 7.2–7.3) has been obtained by solving only one Eshelby problem, described by means of the four–phase model of figure 7.1. Note that the reason for choosing the matrix as reference medium in the approach here proposed is that, unlike in the “composite sphere”–based approach of sections 7.2–7.3, it is the only way to account for the matrix connectedness.

As already said in section 7.2, in this appendix it will be proved that the homogenization method here put forward leads to the same results as the Mori–Tanaka “composite sphere”–based estimate.

Although it is known that the Mori–Tanaka procedure should overestimate the matrix role in the composite, in section 7.2 the good accuracy of its “composite sphere”–based version has already been shown, at least for the chosen set of data. In sections 8.1 and 18.3, this procedure will be further compared with the Self–Consistent one proposed in sections 7.2–7.4.

The Mori–Tanaka procedure, unlike the Self–Consistent one, makes the homogenization of the elastic moduli an explicit problem. Therefore, the Mori–Tanaka procedure may be convenient, when it turns out to be reasonably accurate, if one wants to implement an economical code to homogenize composites. Actually, since in sections 7.2 and 7.3 we

have derived a second-order algebraic equation, whose relatively inexpensive solution gives the Self-Consistent estimate in the case in which neither the filler gradation nor the “unwanted” voids are accounted for, the above statement is practically true when one of these two last morphological features must be considered (and then the Self-Consistent Scheme becomes fully implicit and coupled in the effective elastic moduli). Moreover, if modeling the syntactic foam nonlinear behavior is the goal, the adopted linear elastic homogenization procedure has in general to be applied many times (as it will be explained in chapter 17), thus making the Self-Consistent Scheme approach sometimes too expensive. Owing to the above mentioned forthcoming proof, this appendix might be useful to give more insight about how to choose between the Self-Consistent and Mori-Tanaka “composite sphere”-based estimates (see chapters 17 and 18 also) and will further simplify the second one.

As said, to accomplish the Mori-Tanaka homogenization as proposed in this appendix, there is the need of solving the Eshelby problem of a hollow sphere embedded into an unbounded matrix. It is possible to solve this linear elastic problem by splitting its general boundary conditions into their deviatoric and volumetric parts, as done in sections 7.2 and 7.3 respectively. Since the technicalities are definitely similar to those reported in sections 7.2 and 7.3, we will give the final equations only.

Let us start by writing the equations needed to compute the effective shear modulus for the case in which the filler gradation is not accounted for. Applying the far-field (7.2.2) to the unbounded matrix, the Mori-Tanaka procedure furnishes $\bar{\varepsilon}_{12}^{(m)} = \gamma/2$; therefore it is possible to derive the following estimate for the effective shear modulus of the syntactic foam, completely similar to equation (7.2.31):

$$G_0^{MT} = \frac{G^{(m)} + G^{(i)} \frac{f}{1-f} \left(1 - \frac{a^3}{b^3}\right) \frac{2\bar{\varepsilon}_{12}^{(i)}}{\gamma}}{1 + \frac{f}{1-f} \frac{2\bar{\varepsilon}_{12}^{(h)}}{\gamma}} \quad (7.C.1)$$

in which $\bar{\varepsilon}_{12}^{(i)}$ is given in equation (7.2.29) and $\bar{\varepsilon}_{12}^{(h)}$ is the average of $\varepsilon_{12}(\mathbf{x})$ over the whole hollow sphere:

$$\bar{\varepsilon}_{12}^{(h)} = I_1 + \left(1 + \frac{1}{5}\alpha_2^{(i)}\right) \frac{b^2}{a^2} I_3 + \frac{1}{5}\alpha_{-3}^{(i)} \frac{a^3}{b^3} I_4 \quad (7.C.2)$$

where the dimensionless coefficients I_1 , I_3 , and I_4 have to be computed by solving the following linear elastic system in the unknown I_1 , I_2 , I_3 , I_4 , M_1 , M_2 , and M_4 :

$$2I_1 - 8I_2 + C_1^{(i)} I_3 + C_3^{(i)} I_4 = 0 \quad (7.C.3)$$

$$40I_2 + C_2^{(i)} I_3 + C_4^{(i)} I_4 = 0 \quad (7.C.4)$$

$$I_1 + \frac{a^5}{b^5} I_2 + \frac{b^2}{a^2} I_3 + \frac{a^3}{b^3} I_4 = M_1 + \frac{a^5}{b^5} M_2 + \frac{a^3}{b^3} M_4 \quad (7.C.5)$$

$$-5\frac{a^7}{b^7} I_2 + \alpha_2^{(i)} I_3 + (\alpha_{-3}^{(i)} - 5)\frac{a^5}{b^5} I_4 = -5\frac{a^7}{b^7} M_2 + (\alpha_{-3}^{(m)} - 5)\frac{a^5}{b^5} M_4 \quad (7.C.6)$$

$$G^{(i)} \left(2I_1 - 8\frac{a^5}{b^5} I_2 + C_1^{(i)} \frac{b^2}{a^2} I_3 + C_3^{(i)} \frac{a^3}{b^3} I_4\right) = G^{(m)} \left(2M_1 - 8\frac{a^5}{b^5} M_2 + C_3^{(m)} \frac{a^3}{b^3} M_4\right) \quad (7.C.7)$$

$$G^{(i)} \left(40 \frac{a^7}{b^7} I_2 + C_2^{(i)} I_3 + C_4^{(i)} \frac{a^5}{b^5} I_4 \right) = G^{(m)} \left(40 \frac{a^7}{b^7} M_2 + C_4^{(m)} \frac{a^5}{b^5} M_4 \right) \quad (7.C.8)$$

$$M_1 = \frac{\gamma}{2} \quad (7.C.9)$$

Likewise, the bulk modulus homogenization requires the following calculation:

$$K_0^{MT} = \frac{K^{(m)} + K^{(i)} \frac{f}{1-f} \left(1 - \frac{a^3}{b^3} \right) \frac{\bar{\varepsilon}_{kk}^{(i)}}{3\theta}}{1 + \frac{f}{1-f} \frac{\bar{\varepsilon}_{kk}^{(h)}}{3\theta}} \quad (7.C.10)$$

in which $\bar{\varepsilon}_{kk}^{(i)}$ is as in equation (7.3.12) and $\bar{\varepsilon}_{kk}^{(h)}$ is the first strain invariant averaged over the whole hollow sphere:

$$\bar{\varepsilon}_{kk}^{(h)} = 3 \left(J_1 + J_2 \frac{a^3}{b^3} \right) \quad (7.C.11)$$

The dimensionless coefficients J_1 and J_2 can be computed by solving the following linear system of unknown J_1 , J_2 , P_1 , and P_2 :

$$3K^{(i)} J_1 - 4G^{(i)} J_2 = 0 \quad (7.C.12)$$

$$3K^{(i)} J_1 - 4G^{(i)} J_2 \frac{a^3}{b^3} = 3K^{(m)} P_1 - 4G^{(m)} P_2 \frac{a^3}{b^3} \quad (7.C.13)$$

$$J_1 + J_2 \frac{a^3}{b^3} = P_1 + P_2 \frac{a^3}{b^3} \quad (7.C.14)$$

$$P_1 = \theta \quad (7.C.15)$$

It is important to note that *the solution of equations (7.C.10)–(7.C.15) furnishes exactly the Lee–Westmann expression (7.3.14) if the volume fraction f in (7.C.10) is written as function of a fictitious radius c : $c = b/\sqrt[3]{f}$ (contrary to the MRP approach of sections 7.2–7.4, where c is the outer radius of the composite sphere, in the Mori–Tanaka procedure here proposed c has no physical meaning).*

To account for the filler gradation it is necessary to solve the systems (7.C.3)–(7.C.9) and (7.C.12)–(7.C.15) for any different hollow sphere λ characterizing the f_λ volume fraction of filler. With obvious extension of the equations (7.C.1) and (7.C.10) to this case, as done in section 7.4 for the “composite sphere”-based approach, we obtain:

$$G_0^{MT} = \frac{G^{(m)} + G^{(i)} \frac{f}{1-f} \sum_{\lambda=1}^N f_\lambda \left(1 - \frac{a_\lambda^3}{b_\lambda^3} \right) \frac{2\bar{\varepsilon}_{12}^{(i),\lambda}}{\gamma}}{1 + \frac{f}{1-f} \sum_{\lambda=1}^N f_\lambda \frac{2\bar{\varepsilon}_{12}^{(h),\lambda}}{\gamma}} \quad (7.C.16)$$

$$K_0^{MT} = \frac{K^{(m)} + K^{(i)} \frac{f}{1-f} \sum_{\lambda=1}^N f_\lambda \left(1 - \frac{a_\lambda^3}{b_\lambda^3} \right) \frac{\bar{\varepsilon}_{kk}^{(i),\lambda}}{3\theta}}{1 + \frac{f}{1-f} \sum_{\lambda=1}^N f_\lambda \frac{\bar{\varepsilon}_{kk}^{(h),\lambda}}{3\theta}} \quad (7.C.17)$$

Obviously, this method can account for the presence of “unwanted” voids too: it is sufficient to set $a = b$ for the hollow sphere λ representing the air cavities, paying attention to the fact that $\bar{\varepsilon}_{12}^{(i)}$ becomes singular and then it has to be set equal to an arbitrary finite value to avoid numerical problems.

Finally, the main point of this appendix is to show that equations (7.C.16) and (7.C.17) are completely equivalent to equations (7.4.9) and (7.4.11) in their Mori–Tanaka version. To prove it, it is sufficient to show that the localization coefficients for all the phases are the same for the two methods. This is equivalent to show that the far-field strain applied to the unbounded medium localizes over the matrix and the filler wall exactly in the same way for the two methods. This is trivial for the filler strain localization, since the four-phase model used in chapter 7, in the Mori–Tanaka case, exactly collapses into the three-phase model exploited for deriving equations (7.C.16) and (7.C.17). The same proof for the matrix can be obtained quite easily too: the Mori–Tanaka procedure reported in this appendix trivially furnishes $\bar{\varepsilon}_{12}^{(m)} = \gamma/2$ and $\bar{\varepsilon}_{kk}^{(m)} = 3\theta$, whereas by applying the Mori–Tanaka assumption to equations (7.2.28) and (7.3.11) we get:

$$\bar{\varepsilon}_{12}^{(m)} = M_1 + \left(1 + \frac{1}{5}\alpha_2^{(m)}\right) \frac{c^5 - b^5}{a^2(c^3 - b^3)} M_3 = S_1 + \left(1 + \frac{1}{5}\alpha_2^{(m)}\right) \frac{c^5 - b^5}{a^2(c^3 - b^3)} S_3 = \frac{\gamma}{2} \quad (7.C.18)$$

being $M_1 = S_1 = \gamma/2$ and $M_3 = S_3 = 0$, and

$$\bar{\varepsilon}_{kk}^{(m)} = 3P_1 = 3T_1 = 3\theta \quad (7.C.19)$$

being $P_1 = T_1 = \theta$.

The fact that equations (7.C.16) and (7.C.17) are equivalent to equations (7.4.9) and (7.4.11) in their Mori–Tanaka version is theoretically interesting; this is the same as stating that if in the Christensen and Lo three-phase model [37] the unbounded medium were replaced with the matrix, the “classical” Mori–Tanaka estimate would be found, which is then coincident with the Mori–Tanaka “composite sphere”-based estimate if the filler is homogeneous (at least for most of the common filler shapes, like the solid spheres concerned with in [37]). Furthermore, equations (7.C.16) and (7.C.17) are algebraically simpler than equations (7.4.9) and (7.4.11).

The above proof highlights a drawback of the Mori–Tanaka “composite sphere”-based estimate: even if the filler gradation is accounted for, the localization over any matrix shell furnishes the same value, equal to the average over the whole matrix, independently upon the considered composite sphere λ . This is not the case with the Self-Consistent “composite sphere”-based estimate, which is then in principle the only capable to try to describe how the strain localizes over the matrix depending on the microstructure. This may be useful for homogenizing the syntactic foam behavior beyond the linear elastic range (see chapters 17 and 18).

Of course, the present proof is about the Mori–Tanaka “composite sphere”-based estimate of the elastic moduli. For what concerns its extension to the nonlinear behavior (see chapter 18), in general things are not the same. Indeed, the strain over the matrix can in this case be localized using different average orders, in order to better catch the overall behavior. Therefore, it turns out that the two micromechanical models compared in this appendix (one based on the four-phase model and the other, here introduced, in

which the syntactic foam is seen as a two phase particulate composite in which the filler is a “heterogeneous phase”) may show different results.

Finally, let us observe that the RVE that we can build by means of the approach here put forward does not need any geometrical approximation, such as the CSA. Indeed, since in this approach the Eshelby problem involving the matrix as inclusion is trivially homogeneous, we can choose any suitable number of inhomogeneities with different shapes in such a way to fill up all the space left by the hollow spheres in the RVE.

7.D Dimensionless abaci to homogenize voids into a matrix: application to syntactic foams

In this appendix an approximate but simple approach is proposed to deal with syntactic foams in which it is necessary to take the presence of “unwanted” voids entrapped in the matrix into account. This approach allows one to avoid the implementation of equations (7.4.9) and (7.4.11) and, as it will be shown in section 8.1, it may give sufficiently accurate results.

It is well known that, from a theoretical viewpoint, a sequential homogenization is in general incorrect if different homogenization steps do not correspond to different scales. However, here we propose to apply equations (7.2.33) and (7.3.14) after the “unwanted” voids have been homogenized with the matrix. The results obtained from this method are supposed to be accurate enough for syntactic foams containing a small amount of “unwanted” voids, that anyway is usually the case. Alternatively, such a homogenization procedure can be reasonably considered to be correct when the geometric scales of voids and inclusions differ by at least one order of magnitude. In syntactic foams, unfortunately, this is not always the case, by the way it being very difficult to know shape and dimensions of the “unwanted” voids.

We first calculate the elastic moduli of a fictitious matrix, $K^{(fm)}$ and $G^{(fm)}$, filled with the “unwanted” voids and thus less stiff than the real matrix; then, apply equations (7.2.33) and (7.3.14) to include the presence of the filler into such a matrix. Of course, we have to neglect the filler gradation if we want to avoid the implementation of equations (7.4.9) and (7.4.11), which is the main purpose of the method here put forward.

To carry out the first homogenization we use the Differential Self-Consistent Scheme (DSCS, [137] or [85]), that, by the way, is in itself the emblem of the sequential homogenization. The strength of the DSCS lies in the fact that the “classical” Self-Consistent Scheme is applied sequentially, in a differential way, to a composite which has, instantaneously, an extremely dilute suspension of inclusions, which in principle guarantees for the good behavior of any homogenization technique. Of course, the DSCS, beside being difficult to apply, has the drawback of being a “continuously sequential” homogenization technique, reason for which it is able to “exactly” represent only unreal RVEs in which the filler is “infinitely graded”, in the sense that at each infinitesimal step the added filler should be made up of inclusions much bigger than those already homogenized (for more details, see [36]). Anyway, this drawback should not cause too large errors in the effective moduli estimation if the volume fraction of voids is small enough, as it is usual for syntactic foams.

Assuming, for the sake of simplicity, that the “unwanted” voids have a spherical shape, the DSCS equations read:

$$\frac{dK^{(fm)}}{ds} = \left(\frac{1}{1-s} \right) \left(\frac{K^{(fm)}}{\alpha^{(fm)} - 1} \right) \quad (7.D.1)$$

$$\frac{dG^{(fm)}}{ds} = \left(\frac{1}{1-s} \right) \left(\frac{G^{(fm)}}{\beta^{(fm)} - 1} \right) \quad (7.D.2)$$

where, as defined in equation (6.2.3),

$$\alpha^{(fm)} = \frac{3K^{(fm)}}{3K^{(fm)} + 4G^{(fm)}} \quad \beta^{(fm)} = \frac{6(K^{(fm)} + 2G^{(fm)})}{5(3K^{(fm)} + 4G^{(fm)})} \quad (7.D.3)$$

and s is the ratio between the volume of “unwanted” voids and that of the foam made by the matrix plus the “unwanted” voids.

Equations (7.D.1) and (7.D.2), nonlinear coupled differential equations, allow us to calculate $K^{(fm)}(s)$ and $G^{(fm)}(s)$ numerically, with the initial conditions $K^{(fm)}(s=0) = K^{(m)}$ and $G^{(fm)}(s=0) = G^{(m)}$.

One of the reasons for preferring, in our case, the DSCS method for the foam homogenization can be understood from the curves shown in figures 7.6 and 7.7. Here, we have plotted $K^{(fm)}$ and $G^{(fm)}$, as functions of s , given by different homogenization techniques. The considered matrix has a bulk modulus $K^{(m)} = 8150 \text{ MPa}$ and a shear modulus $G^{(m)} = 1750 \text{ MPa}$; this elastic constants correspond to the polyester resin used by Huang and Gibson [68] as matrix for their syntactic foam, containing “unwanted” voids too, and will be of use in next section 8.1.

Huang and Gibson [68] used a homogenization technique to include the presence of “unwanted” voids in the matrix which gives too high elastic moduli, even greater than those predicted by the rigorous “classical” Hashin–Shtrikman upper bound. The “classical” Self–Consistent Scheme, in the case of foams, gives, as it is well known, elastic moduli which vanish for a volume fraction $s \geq 0.5$ and, therefore, overestimates the foam compliance. The particularization of equations (7.2.33) and (7.3.14) to this case furnishes results whose excessive stiffness is indicated by the coincidence of equation (7.3.14), for $a = b$, with the “classical” Hashin–Shtrikman upper bound. Since equation (7.2.33) gives a shear modulus stiffer than that given by the DSCS method, we may conjecture that the DSCS might be on the whole accurate enough, for this material. Of course, there would be the need of comparing its predictions with experimental results, but, as said, we do not even know shape and dimensions of the “unwanted” voids we want to homogenize. Furthermore, the use of the DSCS seems to be somehow consistent with the serial homogenization of the filler, if accomplished by means of the Self–Consistent “composite sphere”–based method.

In spite of the complexity of equations (7.D.1)–(7.D.3), the proposed method becomes very simple to apply if the dimensionless abaci plotted in figures 7.8 and 7.9 are used to compute $K^{(fm)}$ and $G^{(fm)}$. It is worth noting that the shear modulus of a material containing voids is almost independent upon the Poisson ratio of the continuous phase.

In section 8.1, we shall test this technique by simulating the elastic behavior of the syntactic foam studied by Huang and Gibson [68].

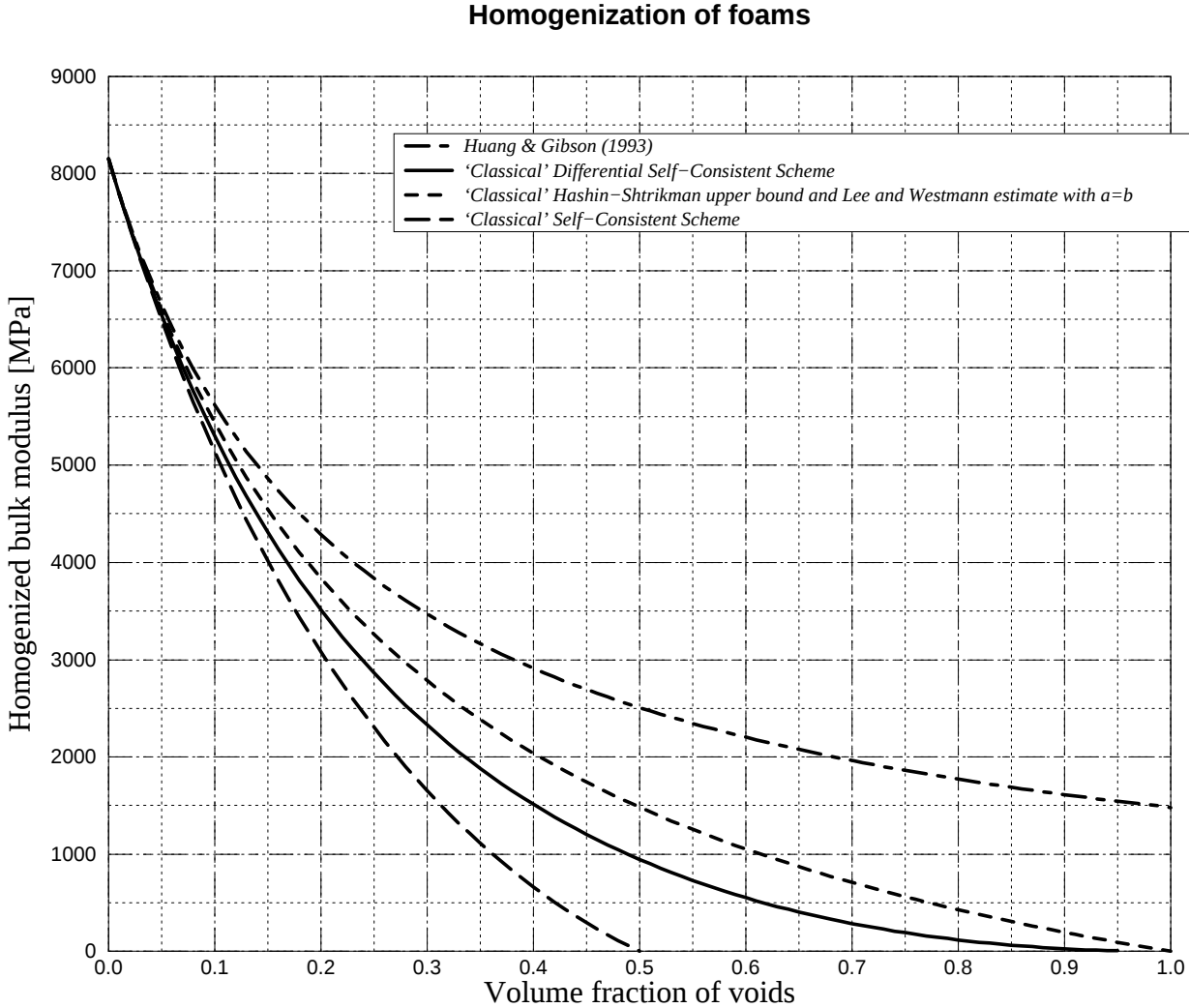


Figure 7.6: Effective bulk modulus of a standard foam

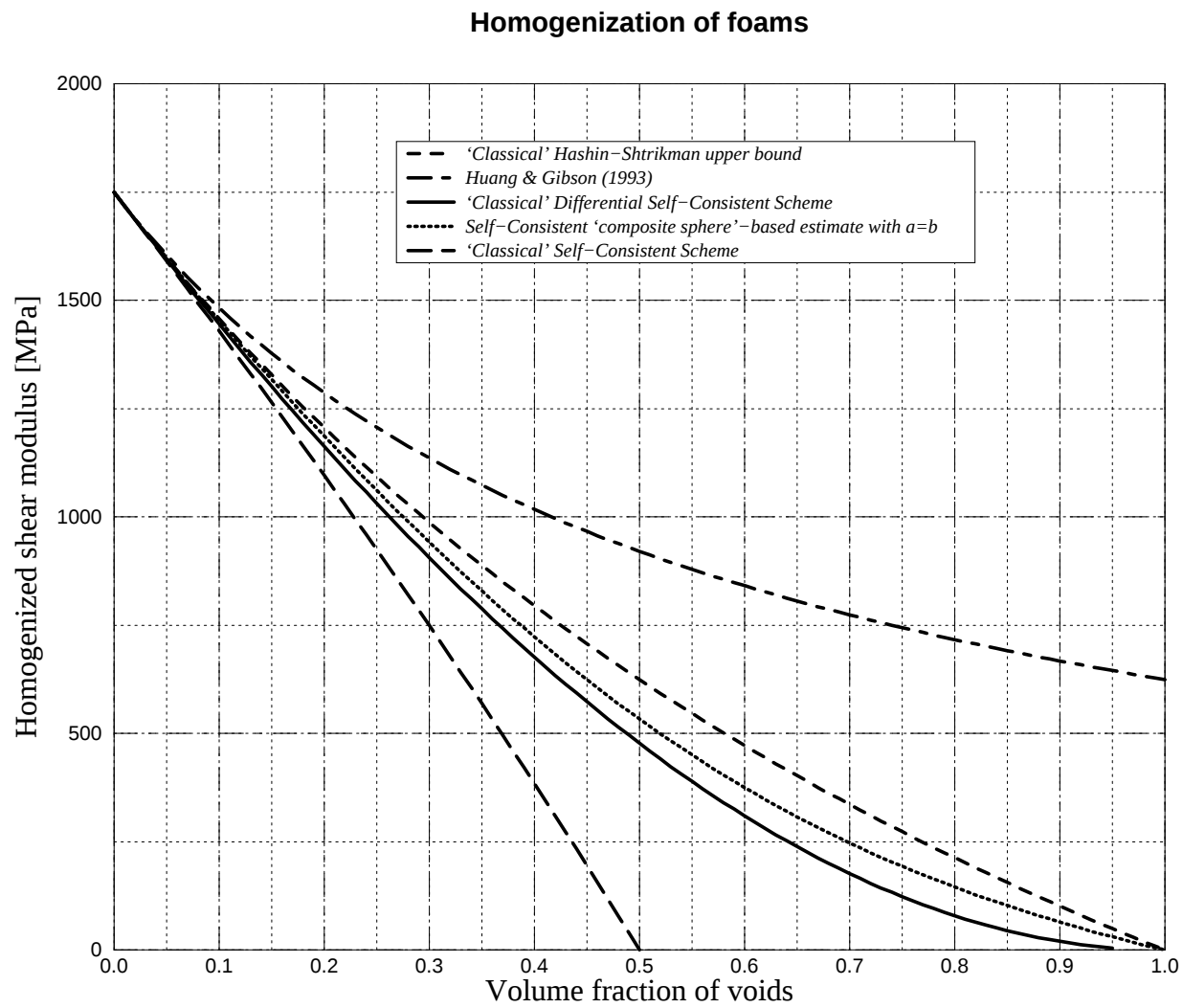


Figure 7.7: Effective shear modulus of a standard foam

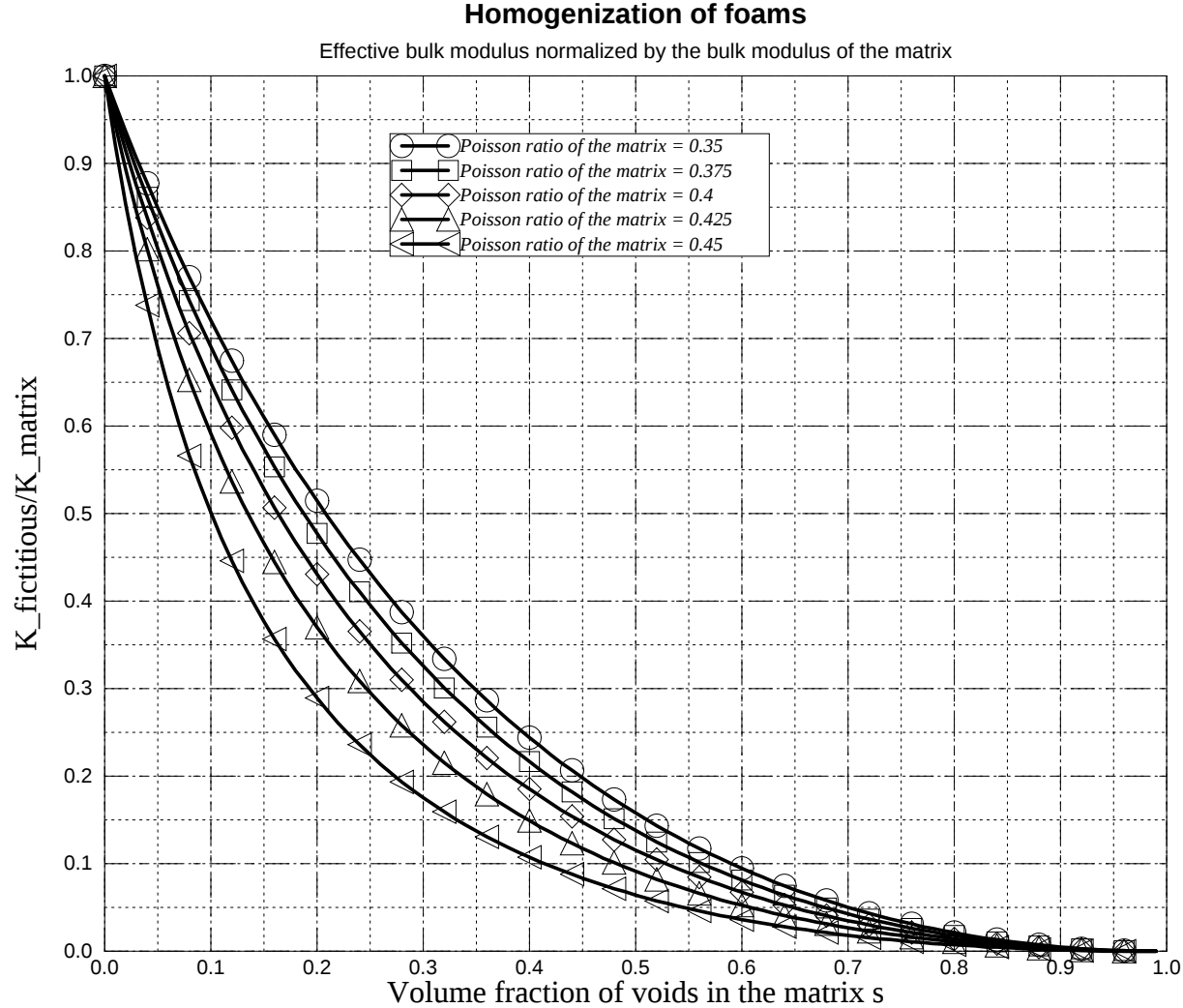


Figure 7.8: Normalized effective bulk modulus of a standard foam as a function of both the matrix Poisson ratio and the volume fraction of voids

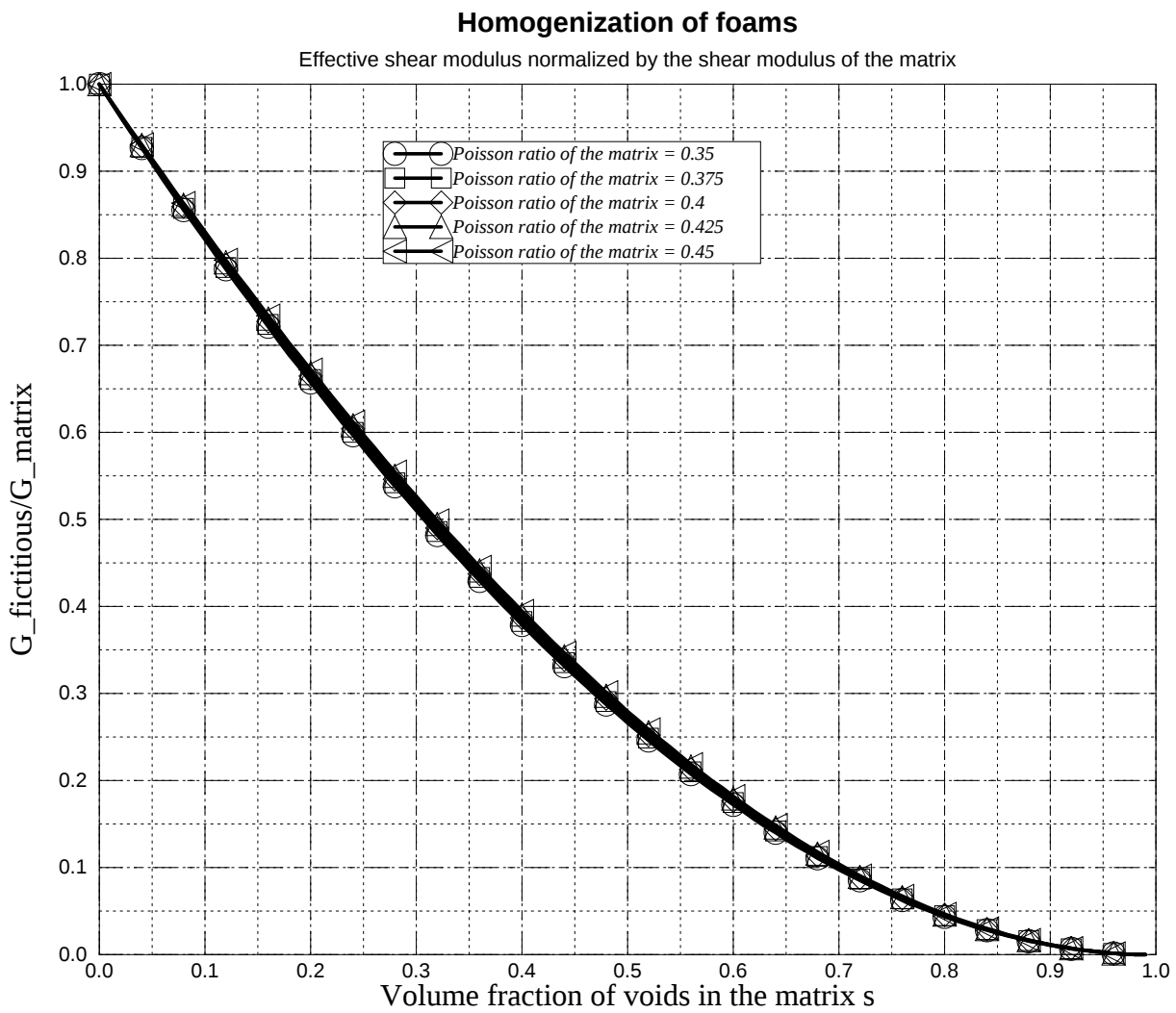


Figure 7.9: Normalized effective shear modulus of a standard foam as a function of both the matrix Poisson ratio and the volume fraction of voids

Chapter 8

Comparison between reference experimental results and analytical estimates

We could find only two works ([68] and [73]), in the literature, giving experimental results in a way complete enough to allow the computation of the elastic moduli estimates by the technique developed in chapter 7.

Experimental results on syntactic foam elastic moduli are reported also in [60], [31], and [39].

Hervé and Pellegrini [60], however, provide inconsistent information about the filler geometry, in that their indications about the particle density do not agree with their wall thickness data, which makes it impossible to reconstruct both their experimental results and their analytical estimates.

The results of [31], concerning a syntactic foam made by phenolic microspheres, would have been a very useful test for checking the accuracy of the method illustrated in chapter 7, since the elastic properties of the basic ingredients of that foam are very different from all the other composites tested in this work. Unfortunately, we could not find, in [31], sufficient data for applying the homogenization techniques.

In [39] neither the elastic constants nor the densities of both the matrix and the filler are given.

8.1 The Huang and Gibson results

The experimental results of Huang and Gibson [68] are particularly interesting with respect to the problem of the “unwanted” voids entrapped in the matrix of the syntactic foam produced by them. In their paper, Huang and Gibson do actually furnish values of the volume fractions of such voids, thus enabling us to homogenize their syntactic foam using both the techniques described in section 7.4 and appendix 7.D. We have no information at all about the granulometry of their filler, that will therefore be characterized by the average values of wall thickness only.

All the necessary data are taken from the microstructural characterization of dog-bone specimens given in [68], shown in Table 8.1, where f is the volume fraction of the filler,

v is the volume fraction of the “unwanted” voids and m is the volume fraction of the matrix. Huang and Gibson observed, by analyzing the filler by Scanning Electron Microscopy (SEM), that the microspheres they employed have a ratio between the inner and the outer radii roughly constant at $a/b = 0.983$. Since they used Scotchlite glass bubbles produced by 3M Industrial Specialties Division as filler, it is likely that they employed K1 microspheres, for which the average ratio a/b is equal to 0.9836, as given in the 3M Italia datasheet (3M Italia [1]). Huang and Gibson characterized the polyester resin they employed by measuring the Young modulus by means of a tensile test, obtaining the value $E^{(m)} = 4890 \text{ MPa}$, and by assuming the Poisson ratio of the resin $\nu^{(m)} = 0.4$, as they found in Hull [70]. For the glass they took a shear modulus of $G^{(i)} = 28500 \text{ MPa}$ and a Poisson ratio of $\nu^{(i)} = 0.23$. Table 8.1 reports the experimental values of the Young modulus obtained by uniaxial tension tests, together with the analytical estimates computed using equations (7.4.9) and (7.4.11). In figure 8.1 we have plotted the results of both the

Specimen	f [%]	m [%]	v [%]	E [MPa] (experimental, [68])	E_0^{SC} [MPa] (7.4.9)-(7.4.11)	E_0^{MT} [MPa] (7.C.16)-(7.C.17)
D1	0.00	100.00	0.00	4890	4890	4890
D2	2.41	97.21	0.38	4770	4732	4732
D3	5.17	92.79	2.04	4340	4446	4447
D4	8.31	89.48	2.21	4370	4284	4288
D5	9.41	88.53	2.06	3300	4247	4251
D6	17.54	77.66	4.80	3330	3665	3689
D7	17.19	74.07	8.74	3120	3375	3417
D8	18.45	71.19	10.36	2860	3204	3260
D9	24.51	65.62	9.87	2680	3007	3079
D10	27.17	59.61	13.22	2320	2677	2783
D11	30.20	56.20	13.60	2290	2544	2665
D12	35.33	46.97	17.70	2170	2113	2288

Table 8.1: *Microstructural characterization of dog-bone specimens (from Huang and Gibson, [68]) compared with the analytical Young modulus estimates*

homogenization methods proposed in chapter 7: the agreement with the experimental data is extremely good from the qualitative viewpoint, and, except for case D5, quite acceptable also from the quantitative viewpoint. For the Self-Consistent “composite sphere”-based estimate, the maximum error between the predicted and experimental Young modulus values is of about 14% (case D5 excluded). When the volume fraction of filler becomes significant, the Mori-Tanaka “composite sphere”-based estimate predicts elastic moduli stiffer than those computed with the Self-Consistent “composite sphere”-based estimate.

Furthermore, figure 8.1 shows the continuous curve obtained by neglecting the presence of air cavities entrapped in the matrix (i.e., considering the plain matrix instead of the system matrix plus voids). The comparison with the results of the “correct” homogenization (equations (7.4.9)–(7.4.11)) indicates that the presence of “unwanted” voids in the matrix has a significant effect on the overall elastic properties of the composite.

The application of the same homogenization technique to the same composite is performed also by Hervé and Pellegrini [60] *without taking into account the presence of “un-*

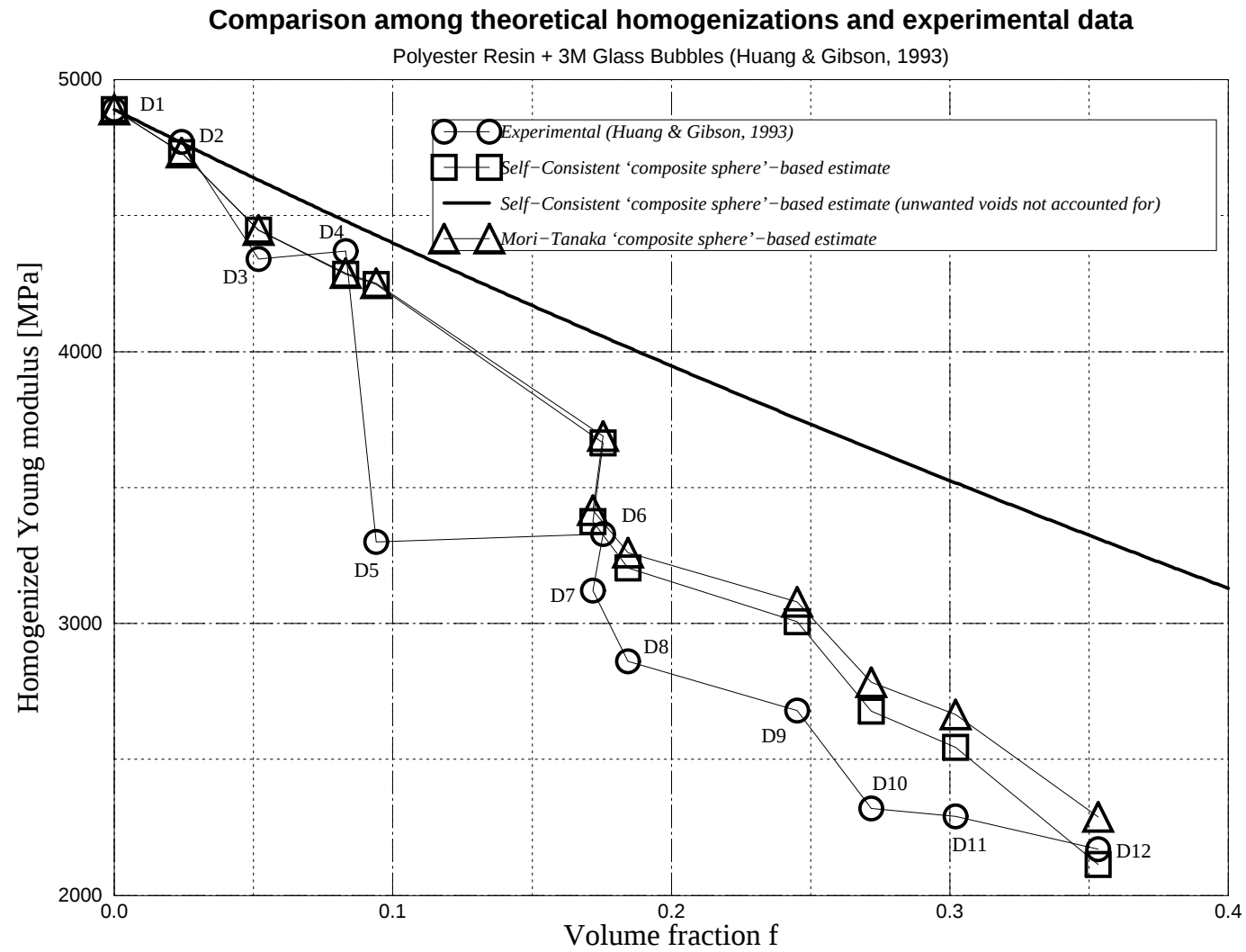
wanted” voids. Huang and Gibson too compute the homogenized elastic moduli of their material, by means of their own homogenization method but again without properly taking the void phase into account; indeed, to account for the “unwanted” voids Huang and Gibson propose to compute the stiffness of a fictitious matrix, weaker than the real one. Unfortunately, as explained in appendixes 7.A and 7.D, the use of a sequential homogenization can not give assurance of obtaining accurate estimates of the effective moduli; indeed, the results of Huang and Gibson, as well as those of Hervé and Pellegrini, become rather poor for volume fractions of filler higher than $f = 0.08$, when, as apparent from the data of Table 8.1, the “unwanted” void content becomes significant. Hervé and Pellegrini attribute the discrepancy between their estimates and the experimental results to the testing modalities (uniaxial tension tests), that, in their opinion, induce debonding between matrix and filler and therefore weaken the composite. Although this effect might certainly arise (and is avoided by the experimental technique used by Hervé and Pellegrini), we feel that, at reasonably low values of loading, it should be much less significant than the effect of the presence of voids in the matrix. Our computations seem indeed to confirm this hypothesis.

Let us now test the method proposed in appendix 7.D by applying it to the syntactic foams of Huang and Gibson.

Specimen	s [%]	$K^{(fm)}$ [MPa] (7.D.1)-(7.D.3)	$G^{(fm)}$ [MPa] (7.D.1)-(7.D.3)	$E_{0,seq}$ [MPa] DSCS+(7.2.33)-(7.3.14)	E_0^{SC} [MPa] (7.4.9)-(7.4.11)
D1	0.00	8150	1750	4890	4890
D2	0.39	8011	1734	4734	4732
D3	2.15	7408	1679	4447	4446
D4	2.41	7325	1671	4287	4284
D5	2.35	7369	1675	4250	4247
D6	5.82	6320	1567	3667	3665
D7	10.55	5180	1426	3361	3375
D8	12.70	4738	1364	3187	3204
D9	13.07	4666	1353	2999	3007
D10	18.15	3790	1211	2663	2677
D11	19.48	3590	1175	2535	2544
D12	27.37	2598	969	2101	2113

Table 8.2: *Estimates of the Young modulus of the syntactic foam experimentally characterized by Huang and Gibson [68]*

Table 8.2 shows the volume fraction of “unwanted” voids referred to the matrix, $s = v/(v + m)$, the fictitious bulk and shear moduli of the matrix, $K^{(fm)}$ and $G^{(fm)}$, obtained from equations (7.D.1)–(7.D.3), and the Young modulus estimates, $E_{0,seq}$, computed using the proposed sequential homogenization technique. The comparison of these results with the effective moduli E_0^{SC} , previously obtained using equations (7.4.9)–(7.4.11), shows that from the engineering viewpoint the sequential technique put forward in appendix 7.D is a good method at least to homogenize syntactic foams similar to that produced by Huang and Gibson.



8.2 The Kinra and Ker results

Here, we shall make use of both the Self-Consistent and the Mori–Tanaka estimates based on one composite sphere only, because the data available in [73] do not allow the use of the more accurate homogenization method of section 7.4; furthermore, nothing in [73] is said about the presence of “unwanted” voids, even if Kinra and Ker found actual values of the filler volume fraction slightly different from the nominal ones. Actually, the real composition of the composite produced by Kinra and Ker would be particularly difficult to investigate because of its production modalities, which can not give assurance of leaving all the microspheres unbroken. This syntactic foams is indeed made up of hollow glass microspheres (Microballoons Eccospheres FTD 202 produced by Emerson and Cuming, Inc.) into a plexiglas matrix (polymethylmethacrylate — in the following shortened in PMMA — produced by Buehler Transoptic Powder, Ltd.); since the PMMA is initially in a powder state, to make the composite the PMMA is cold mixed with the filler and then the whole mixture is warmed up and pressed: Kinra and Ker themselves pointed out that this procedure can destroy some microspheres, even if they took pains to avoid this problem.

The experiments of Kinra and Ker are based on ultrasonic wave propagation. In this case, the phase velocities of the longitudinal and shear waves in a material, C_1 and C_2 respectively, can be related to the Lamé constants G and λ through the material density ρ :

$$\lambda + 2G = \rho C_1^2 \quad (8.2.1)$$

$$G = \rho C_2^2 \quad (8.2.2)$$

where, as it is well known, λ and G can be related to the Young modulus and the Poisson ratio:

$$\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)} \quad G = \frac{E}{2(1+\nu)} \quad (8.2.3)$$

By means of this method, Kinra and Ker indirectly provided the elastic moduli of the PMMA, the glass, and the produced syntactic foams.

The PMMA density, Young modulus, and Poisson ratio are $\rho^{(m)} = 1.16 \text{ g/cm}^3$, $E^{(m)} = 5383 \text{ MPa}$, and $\nu^{(m)} = 0.3317$ respectively.

About the glass properties, Kinra and Ker gave a density $\rho^{(i)} = 2.5 \text{ g/cm}^3$, to which $E^{(i)} = 62881 \text{ MPa}$ and $\nu^{(i)} = 0.1980$ correspond. Moreover, Buehler Transoptic Powder, Ltd. gives the the particle density, the mean external radius, and the mean wall thickness of the filler Microballoons Eccospheres FTD 202 as equal to $\rho^{(fil)} = 0.238 \text{ g/cm}^3$, $b = 45 \text{ }\mu\text{m}$, and $t = 1.2 \text{ }\mu\text{m}$ respectively. The mean value of the ratio a/b between the inner and the outer radii of the inclusions can be computed in two different ways. The first consists of exploiting the following relation

$$\frac{a}{b} = \sqrt[3]{1 - \frac{\rho^{(fil)}}{\rho^{(i)}}} \quad (8.2.4)$$

which furnishes $a/b = 0.9672$, whereas the second is to make use of the given data for b and t , from which we get $a/b = 0.9733$. The difference between these two a/b values is quite relevant, if judged from the viewpoint of the sensibility of the homogenization procedures to the parameter a/b . Luckily, this incoherence is not a problem in this case. If we take the value $a/b = 0.9733$, we must recompute the glass elastic moduli according to

equations (8.2.1)–(8.2.4): inverting equation (8.2.4), the value $\rho^{(fil)} = 0.238 \text{ g/cm}^3$ implies $\rho^{(i)} = 3.05 \text{ g/cm}^3$ and, then, equations (8.2.1) and (8.2.2) give $E^{(i)} = 76767 \text{ MPa}$ (and $\nu^{(i)} = 0.1980$). Having checked that the set of data $a/b = 0.9672$ and $E^{(i)} = 62881 \text{ MPa}$ for the glass furnishes practically the same effective moduli as the set $a/b = 0.9733$ and $E^{(i)} = 76767 \text{ MPa}$, we do not have to worry about this choice to estimate the elastic moduli of the syntactic foams tested by Kinra and Ker.

We shall come back to the important discussion of the determination of the glass properties in chapter 9.

Figure 8.2 shows the good agreement between the experimental data of Kinra and Ker and the two analytical estimates, both furnishing practically coincident results; the maximum error between experimental data and analytical estimates is about 9% and it corresponds to the highest filler volume fractions ($f = 0.3716$ and $f = 0.4345$) and to the estimation of $\lambda_0 + 2G_0$. However, the above mentioned sources of uncertainty about the real composite microstructure can explain the fact that the analytical results overestimate the experimental ones; indeed, both the presence of “unwanted” voids and the failure of a significant amount of microspheres in producing the composite, if accounted for, would make the elastic moduli estimates lower than those here predicted.

It is curious to observe that Nielsen [91] had to change in an apparently arbitrary way the material and geometrical data of both matrix and filler to make his homogenization procedure (see appendix 7.A) work with this same set of experimental data.

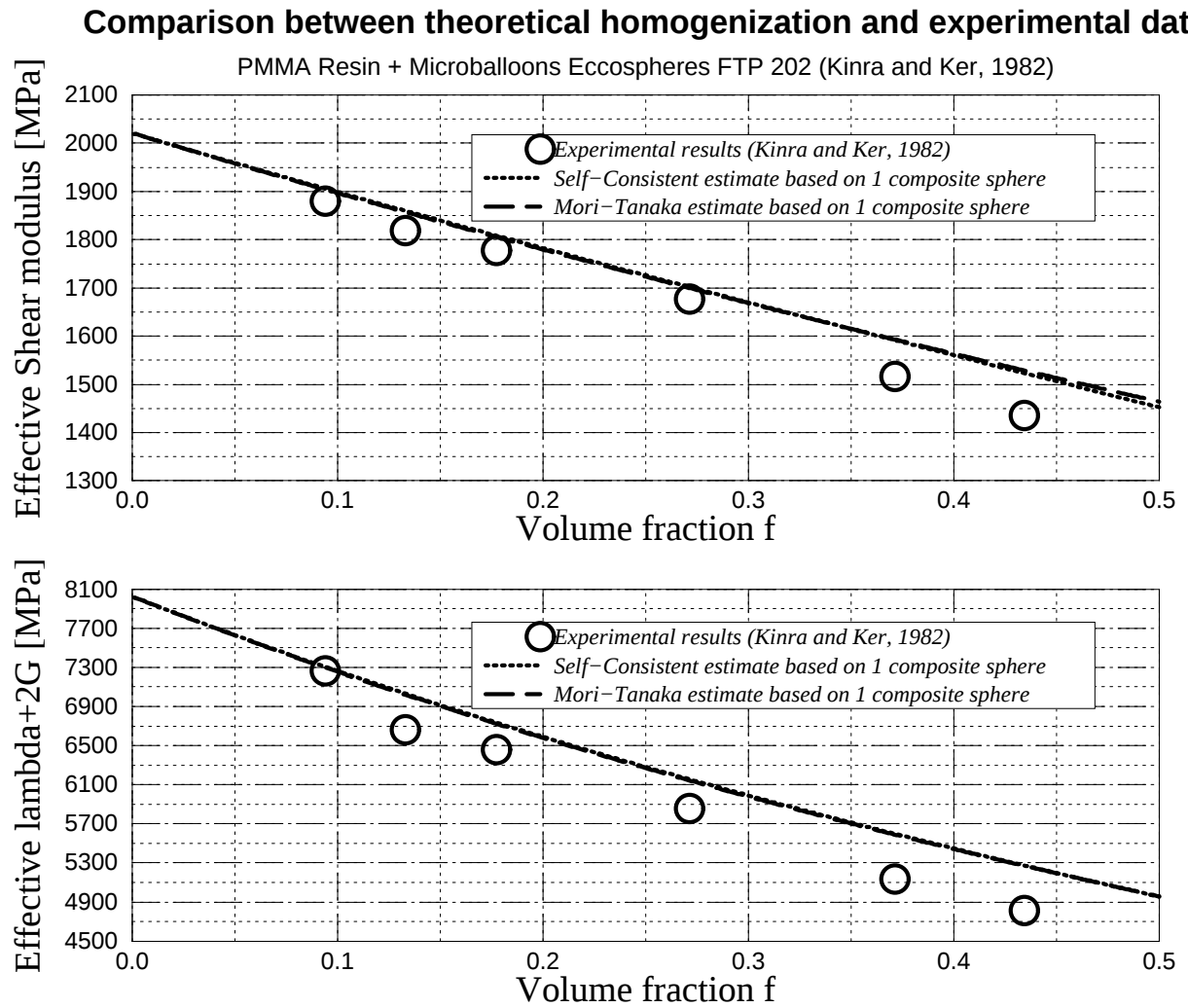


Figure 8.2: Comparison among theoretical homogenizations and experimental data

Chapter 9

Comparison between our experimental results and analytical estimates

9.1 Introduction

Throughout all this chapter we shall always deal with fillers characterized only by the average values of wall thickness and diameter, whereas we shall consider, in several cases, composites including voids. The analysis of a composite whose filler gradation is known will be done in chapter 10, where it will be shown that the use the average geometrical data of the filler only does not give any substantial difference with respect to the use of the more refined homogenization procedure which accounts for the filler gradation; note that this might not hold for fillers different from those employed to make the syntactic foams of chapter 4 (as it will be shown in chapter 10) and outside the linear elastic range.

The relevant mechanical properties of the filler are just the elastic constants of its glass, which have been taken, as a first attempt, equal to: Young modulus $E^{(i)} = 70110 \text{ MPa}$; Poisson coefficient $\nu^{(i)} = 0.23$. These values are not indicated in the data sheet available from the producer (3M Italia [1]), and have been found in [68], where apparently use is made of microspheres of the same brand. However, as it is going to be shown in the following, there is a rather strong source of uncertainty, with respect to the data values for this glass. Furthermore, together with the elastic moduli of the wall of the inclusions, to characterize the stiffness of the filler inside the syntactic foam, one has to know the ratio between the inner and the outer radii, a/b , of the hollow microspheres employed. There are two ways to compute it: the first one by employing the average geometrical data provided in 3M Italia [1], that, for instance, furnish the average value $a/b = 0.9501$ for the complete K37 batch (the average diameter of spheres type K37 is $50 \mu\text{m}$, and their average wall thickness is $1.28 \mu\text{m}$); the second one consists in obtaining the average value of a/b from the particle density, known and equal to $\rho_{K37} = 0.37 \text{ gr/cm}^3$, by exploiting equation (8.2.4). For instance, Huang and Gibson indicate a density of their glass $\rho^{(i)} = 2.5 \text{ g/cm}^3$, but, in order to obtain internal consistency in the data provided in [1], we need to use $\rho^{(i)} = 2.6 \text{ g/cm}^3$. This may indicate that also the above quoted values of the elastic moduli might be incorrect; this will be commented upon later in this chapter.

The elastic moduli of the employed matrixes are those experimentally measured in chapter 3, even if, as explained in section 4.1, it is not sure that epoxy resins cured as matrixes for syntactic foams have exactly the same elastic moduli as those exhibited by the plain epoxy resins.

In the following six sections, we summarize the main characteristics of the basic “ingredients” of each of the six syntactic foams already described in chapter 4 and compare the results of the laboratory tests (see chapter 4) with the corresponding analytical predictions.

9.2 Syntactic foam type 1

- Epoxy resin DGEBA DER 332, produced by Dow Chemicals, with hardener DDM Fluka 32950. The basic properties of this resin, in the fully hardened state, are (see chapter 3): Young modulus $E^{(m)} = 2800 \text{ MPa}$, Poisson coefficient $\nu^{(m)} = 0.41$; density $\rho^{(m)} = 1.18 \text{ g/cm}^3$.
- filler “K37” microspheres, produced under the name “ScotchliteTM Glass Bubbles” by 3M Italia [1], with a volume fraction $f = 0.5153$;
- composite made by means of the “traditional” technique.

Since this syntactic foams has not “unwanted” voids, it is possible to predict its elastic moduli by means of equations (7.2.33) and (7.3.14), thus obtaining: $E_0 = 3300 \text{ MPa}$, $\nu_0 = 0.36$. By comparing these values with those reported in Table 4.1 of chapter 4, one can find that the Young modulus is underestimated by a 6%, while the Poisson coefficient is overestimated by the same amount. This performance can be considered acceptable, specially in the presence of several sources of uncertainty on the basic data. For instance, as said before, the exact value of the Young modulus of the glass used to produce the filler is not known, and the value suggested by Huang and Gibson, who seem to have used the same glass spheres, has been chosen. However, as said, their value of the glass density does not agree with the data found in 3M Italia [1], which suggests that our glass might be different from theirs. If we use, for the Young modulus of glass, the value $E^{(i)} = 77500 \text{ MPa}$, as suggested in Brandt [29] for a low alkali glass, we find, for the composite, $E_0 = 3450 \text{ MPa}$, practically the exact result.

9.3 Syntactic foam type 2

- Epoxy resin DGEBA as before, with a different hardener (type Laromin C252, produced by BASF). As already pointed out in section 3.1, it is possible to assume for this epoxy resin the same elastic moduli characterizing the resin constituted by DGEBA DER 332 and DDM 32950.
- filler made by hollow glass microspheres type K37 as before;
- composite made by means of the “injection” technique.

We refer our following comments to Table 4.4 of chapter 4. The theoretical predictions, obtained using equations (7.4.9)–(7.4.11) and taking $N = 2$ (i.e., 2 different composite spheres: $\lambda = 1$ corresponds to the actual filler type K37, and $\lambda = 2$ corresponds to the voids), give for sample 1 a Young modulus $E_0 = 3333 \text{ MPa}$ and a Poisson ratio $\nu_0 = 0.347$; instead, for sample 2, they furnish $E_0 = 3128 \text{ MPa}$ and $\nu_0 = 0.341$; note that these values have been obtained by using $E^{(i)} = 70110 \text{ MPa}$ for the glass. The analytical predictions of the Young modulus have a maximum error, with respect the experimental data, of about 4%, whereas the analytical estimates of Poisson ratio overestimate the experimental ones by roughly 6%. These are reasonably good results, considering the already mentioned sources of uncertainty on the starting data. Actually, if we consider $E^{(i)} = 77500 \text{ MPa}$, we get, for sample 1, $E_0 = 3513 \text{ MPa}$ and $\nu_0 = 0.348$ and, for sample 2, $E_0 = 3295 \text{ MPa}$ and $\nu_0 = 0.343$; these Young modulus values are in excellent agreement with the experimental results, whereas this is not the case with the Poisson ratio values, worse than those computed by adopting $E^{(i)} = 70110 \text{ MPa}$.

9.4 Syntactic foam type 3

- Epoxy resin SP Ampreg 20TM, produced by SP Systems, Montecatini Advanced Materials, with hardener “UltraSlow Hardener”, produced by SP Systems, Montecatini Advanced Materials. The material properties of this epoxy resin are (see chapter 3): $E^{(m)} = 3640 \text{ MPa}$, $\nu^{(m)} = 0.39$, and the density is $\rho^{(m)} = 1.15 \text{ g/cm}^3$;
- the same microspheres described for the syntactic foam types 1 and 2, again of the type K37, with various volume fractions and in some cases sifted, as explained in chapter 4. The filler having diameter range $32 \leq \Phi \leq 45$ is characterized by the ratio $a/b = 0.9372$, whereas if $45 \leq \Phi \leq 63$ we measured $a/b = 0.9661$, and when $63 \leq \Phi \leq 90$ we got $a/b = 0.9530$; these data, important to compute the following estimates, have been obtained as explained in chapter 10;
- composite made by means of the “injection” technique.

In Table 9.1 we report all the data already collected in Table 4.5 of chapter 4 plus the analytical estimates, obtained by using $E^{(i)} = 70110 \text{ MPa}$. Since the volume fraction f^* here available is affected by the presence of the “unwanted” voids, which is then not accounted for, we got systematic overestimates of the Young modulus in the analytical predictions which, as expected, are in excess up to 23% in the case of the material tested in Milano, and up to about 12% in the case of the tests done in Brescia.

This tendency of the theoretical predictions to overestimate the stiffness of the material is maintained throughout all the cases reported in Table 4.5. The last three rows of this Table refer to syntactic foams produced by inclusion of microspheres taken from the K37 batch but sifted. The theoretical results, for all these cases, are always better when the volume fractions are smaller; for instance, for the case with $f^* = 0.585$ and $32 \leq \Phi \leq 45 \text{ } \mu\text{m}$, the estimates have an error of +14%, whereas the tests done in Milano on the composite with the same granulometry, but with $f^* = 0.623$, find the analytical predictions to be in error of 19%. Again, this is a result of the uncertainty about the “unwanted” voids content, that should increase when f^* increases. All the analytical results, however, are reasonable approximations of the experimental ones.

Syntactic Foam SP+UltraSlow	f^*	E_c [MPa]	ν_c	E_0 [MPa] (7.2.33)-(7.3.14)	ν_0 (7.2.33)-(7.3.14)	Filler
Sample 1	0.665	3452	0.311	3861	0.327	“as it is”
Sample 2	0.647	3465	0.320	3854	0.329	“as it is”
Sample 3	0.659	3535	0.322	3859	0.328	“as it is”
Sample 4	0.659	3455	0.319	3859	0.328	“as it is”
(Milano)	0.678	3150		3866	0.326	“as it is”
Sample 5	0.601	3847	0.305	4379	0.337	$32 \leq \Phi \leq 45$
Sample 6	0.585	3826	0.309	4357	0.339	$32 \leq \Phi \leq 45$
(Milano)	0.623	3700		4410	0.335	$32 \leq \Phi \leq 45$
(Milano)	0.704	2900		2981	0.317	$45 \leq \Phi \leq 63$
Sample 7	0.626	3075	0.294	3712	0.330	$63 \leq \Phi \leq 90$
Sample 8	0.665	2942	0.269	3716	0.326	$63 \leq \Phi \leq 90$
Sample 9	0.633	3153	0.314	3712	0.330	$63 \leq \Phi \leq 90$

Table 9.1: *Experimental and analytical results for syntactic foams type 3*

9.5 Syntactic foam type 4

- Epoxy resin SP Ampreg 20TM with the same hardener as in foam type 3, with the same mechanical properties;
- same glassy hollow microspheres as in the preceding foams (type K37);
- composite made by means of the “traditional” technique.

In Table 9.2 we summarize the experimental results already reported in Table 4.6 of chapter 4 and compare them with the analytical predictions.

The analytical results, obtained from equations (7.4.9)–(7.4.11) in their Self-Consistent version used as hereabove explained for the estimate of the effective properties of the syntactic foam type 2, seem quite accurate for small volume fractions, and tend to lose some accuracy only for $f \geq 0.45$; the maximum errors are of about 7%, an acceptable result anyway. Note that for this foam, in spite of the fact that we again used $E^{(i)} = 70110$ MPa, the theoretical effective Young moduli always overestimate the experimental ones.

9.6 Syntactic foam type 5

- Same resin and hardener as for materials type 3 and 4;
- again “ScotchliteTM Glass Bubbles” produced by 3M Italia [1], but of the type K1. The spheres type K1 have an average diameter of $70 \mu m$ and an average wall thickness of $0.58 \mu m$ to which corresponds a ratio between the inner and the outer radii $a/b = 0.9836$;
- composite made by means of the “injection” technique.

Syntactic Foam SP+UltraSlow+K37	f	m	v	E_c [MPa]	ν_c	E_0 [MPa] (7.4.9)-(7.4.11)	ν_0 (7.4.9)-(7.4.11)
Sample 1	0.493	0.472	0.035	3324	0.344	3541	0.337
Sample 2	0.493	0.471	0.036	3339	0.336	3534	0.337
Sample 3	0.492	0.470	0.038	3340	0.339	3519	0.336
Sample 4	0.496	0.474	0.030	3399	0.333	3579	0.338
Sample 5	0.445	0.520	0.035	3411	0.344	3528	0.342
Sample 6	0.447	0.522	0.031	3392	0.343	3557	0.342
Sample 7	0.442	0.517	0.041	3358	0.344	3483	0.341
Sample 8	0.447	0.522	0.031	3389		3557	0.342
Sample 9	0.289	0.646	0.065	3309	0.363	3272	0.350
Sample 10	0.291	0.649	0.060	3341	0.362	3307	0.351
Sample 11	0.393	0.564	0.043	3407	0.349	3455	0.345
Sample 12	0.395	0.567	0.038	3477	0.349	3492	0.346
Sample 13	0.400	0.573	0.027	3426	0.345	3573	0.348
Sample 14	0.398	0.571	0.031	3424	0.350	3543	0.347

Table 9.2: *Experimental and analytical results for syntactic foam type 4*

The relevant average results, both experimental and analytical, are collected in Table 9.3.

The analytical results overestimate the experimental ones by a 15% in the first case, and by a 6% in the second. It is difficult to precisely catch the source of these errors, scattered among different reasons. One possible explanation, however, lies in the brittleness of the very thin K1 spheres, broken in significant percentage during the production process of the material. The real syntactic foam, in this case, is obviously rather softer than what appears to the analytical model. This observation helps to explain also part of the error, illustrated in figure 8.1, arising when applying the homogenization technique to the foam of Huang and Gibson. Their foam makes use of spheres type K1 too, and therefore also in their case one should expect the analytical predictions to overestimate experimental results.

Syntactic Foam SP+UltraSlow+K1	f	m	v	E_c [MPa]	ν_c	E_0 [MPa] (7.4.9)-(7.4.11)	ν_0 (7.4.9)-(7.4.11)
Average 1	0.509	0.410	0.081	1610	0.347	1856	0.318
Average 2	0.523	0.421	0.056	1835	0.322	1953	0.320

Table 9.3: *Experimental and analytical results for syntactic foams type 5*

As for the syntactic foams types 3 and 4, the analytical estimates for the syntactic foam type 5 exceed the experimental results, in spite of the use of $E^{(i)} = 70110 \text{ MPa}$. Even if the elastic moduli estimation for the syntactic foam type 3 could not be done properly because of the lack of information about the “unwanted” void content and despite the just mentioned source of the possible stiffness overestimation for the syntactic foam type 5, this fact seems to indicate that the matrix SP Ampreg 20TM is not well characterized

by the moduli $E^{(m)} = 3640 \text{ MPa}$ and $\nu^{(m)} = 0.39$ obtained in section 3.3. Perhaps, the curing of this epoxy resin is affected by the presence of the filler, thus providing a matrix softer than the plain epoxy resin.

9.7 Syntactic foam type 6

- Same resin and hardener as for the syntactic foam type 1;
- again “ScotchliteTM Glass Bubbles” produced by 3M Italia [1], but of the type H50. The spheres type H50 have an average diameter of $50 \mu\text{m}$ and an average wall thickness of $3.42 \mu\text{m}$ to which corresponds a ratio between the inner and the outer radii $a/b = 0.9313$ (see next Table 10.2 for more details);
- composite made by means of the “traditional” technique.

For this syntactic foam, the Self-Consistent estimate based on one composite sphere furnishes a Young modulus $E = 3850 \text{ MPa}$ and a shear modulus $G = 1411 \text{ MPa}$. The theoretical moduli underestimate the experimental results (see Table 4.8) by about the 5% for the Young modulus and by about the 9% for the shear modulus. Again, if the Young modulus of the glass is taken $E^{(i)} = 77500 \text{ MPa}$, in place of the value $E^{(i)} = 70110 \text{ MPa}$ used in the just mentioned estimate, the homogenization gives $E = 4020 \text{ MPa}$ and $G = 1473$, very close to the experimental data.

Chapter 10

Influence of the filler gradation

As already mentioned, and as visible also in figure 4.1, the ratio a/b , between the inner and the outer radius of the used microspheres, in reality, at least for this type of filler (glassy microspheres type K37 — see chapter 4) can hardly be considered as constant.

In order to evaluate the scatter of the ratios a/b for the filler used in the syntactic foams types 1–4, described in chapter 4, the K37 spheres were sifted using 5 sifts, thus obtaining 5 “monodispersed” sifted samples. Then the particle density, ρ_λ , and the volume fraction, f_λ , of all the sifted samples, were measured ($\lambda = 1, \dots, 5$). The obtained results are shown in Table 10.1, in which the value of the ratio between the inner and the outer radius of any sifted sample of filler, a_λ/b_λ , is computed assuming that the density of the glass is equal to 2.6 g/cm^3 and making use of equation (8.2.4) in which ρ_{K37} has to be substituted with ρ_λ . Let us recall that the average diameter of the K37 spheres is $\Phi = 50 \text{ }\mu\text{m}$, and that the

λ	Diameter [μm]	f_λ [—]	ρ_λ [g/cm^3]	a_λ/b_λ [—]
1	$\Phi \geq 90$	0.0906	0.2928	0.9610
2	$63 \leq \Phi \leq 90$	0.6481	0.3494	0.9530
3	$45 \leq \Phi \leq 63$	0.0551	0.2552	0.9661
4	$32 \leq \Phi \leq 45$	0.1737	0.4594	0.9372
5	$\Phi \leq 32$	0.0325	0.6920	0.9020

Table 10.1: *Wall thickness characterization for the filler K37*

average ratio a/b is equal to 0.9501 (data given in 3M Italia [1]). Note that “average ratio a/b ” means the ratio a/b of a fictitious hollow sphere that has the same particle density of the real filler, which then has to be computed as

$$\frac{a}{b} = \sqrt[3]{\sum_{\lambda=1}^N f_\lambda \left(\frac{a_\lambda}{b_\lambda} \right)^3} \quad (10.0.1)$$

It is then apparent, from the results shown in Table 10.1, that there is some deviation, from the average values, both for the wall thicknesses and specially for the diameters of the hollow spheres.

Figure 10.1 compares the Self-Consistent “composite sphere”-based estimate, obtained by considering only the average value (10.0.1) for the inclusions with those obtained by considering $N = 5$ as shown in Table 10.1, for the case of the syntactic foam type 1 described in sections 4.1 and 9.2, considering the full range of filler volume fractions, and assuming the absence of “unwanted” voids. The results are shown as relative errors, for both the shear and the bulk modulus, assuming the estimate which makes use of 5 composite spheres as the “correct” one.

It is apparent that the differences are in this case relatively small between the values obtained by using just the average value for the ratio a/b and those obtained from the more accurate data of Table 10.1. The maximum difference is in fact of about 2%. This suggests that, for the morphology of these syntactic foams, and considering the difficulty of obtaining accurate information about the real values of the microsphere geometry, for all practical purposes it is sufficient to characterize the filler by means of its average value of the ratio a/b .

This conclusion, however, may not always be valid, depending upon the actual filler gradation. To check this, we have considered a fictitious (and rather extreme) case, in which the filler has the following distribution of ratios between the inner and the outer radii:

$$a_\lambda/b_\lambda = 0.91, \ 0.92, \ 0.93, \ 0.94, \ 0.96, \ 0.97, \ 0.98, \ 0.99$$

each with equal volume fraction $f_\lambda = 0.125$; the average ratio corresponding to this distribution is equal to 0.9508, roughly equal to that of the K37 filler. Figure 10.2 shows the relative error between the predictions of the single inclusion model and those of the multiple inclusion model, for three types of matrix material: (i) an extremely stiff matrix ($E^{(m)} = 280000 \text{ MPa}$), (ii) the DGEBA resin of syntactic foams type 1, 2, and 6 of the preceding chapter ($E^{(m)} = 2800 \text{ MPa}$), and (iii) an extremely compliant matrix ($E^{(m)} = 28 \text{ MPa}$). The other relevant elastic constants are $\nu^{(m)} = 0.41$, $E^{(i)} = 70110 \text{ MPa}$, and $\nu^{(i)} = 0.23$.

Figure 10.2 illustrates both the shear modulus and the bulk modulus errors. In this way, we can appreciate the differences in the predictions of the two models for a range of ratios between the stiffness of the matrix and that of the inclusions.

It is apparent that now the two models, based on two very different RVEs, may yield significantly different results, with the “exact” elastic moduli always lower than those based on the average values of the wall thickness of the filler. Also, as obvious, the results of the two models tend to become coincident when the stiffness of the matrix becomes much larger than that of the inclusions. These results are obtained considering inclusions all made by the same material with a very large scatter in the particle density ρ_λ ; of course, the same technique might turn useful also to take into account the presence of inclusions made by different materials.

For the sake of completeness, we report in Table 10.2 the filler characterization for the filler H50. The difference between the estimate involving all the filler details and that accomplished by means of a composite sphere only is trifling for this filler too. The data of both Tables 10.1 and 10.2 will be of use in chapter 18, where the effect of the filler gradation will be investigated on the homogenization of the syntactic foam behavior beyond the linear elastic range.

Finally, it is worth to mention to a “spontaneous” but approximate way to take the filler

λ	Diameter [μm]	f_λ [—]	ρ_λ [g/cm^3]	a_λ/b_λ [—]
1	$\Phi \geq 125$	0.00087	-	-
2	$90 \leq \Phi \leq 125$	0.0041	-	-
3	$63 \leq \Phi \leq 90$	0.0881	0.4555	0.9378
4	$45 \leq \Phi \leq 63$	0.5848	0.4993	0.9314
5	$32 \leq \Phi \leq 45$	0.3043	0.5207	0.9282
6	$\Phi \leq 32$	0.01775	-	-

Table 10.2: Wall thickness characterization for the filler H50

gradation of syntactic foams into account. This method has been for instance exploited by Wei et al. [128] and consists of accounting for the filler gradation by exploiting a sequential homogenization, in which at each step the hollow spheres of equal particle density are homogenized into the matrix. This homogenization procedure is in principle similar to those discussed in appendix 7.D and section 8.1 to take the “unwanted” voids into account. As already pointed out, this kind of sequential homogenization is in general theoretically wrong and can not give assurance of obtaining accurate estimates of the elastic moduli, but exceptions do of course exist, for instance in the case in which the filler particle density is not too scattered and the filler volume fraction is small enough.

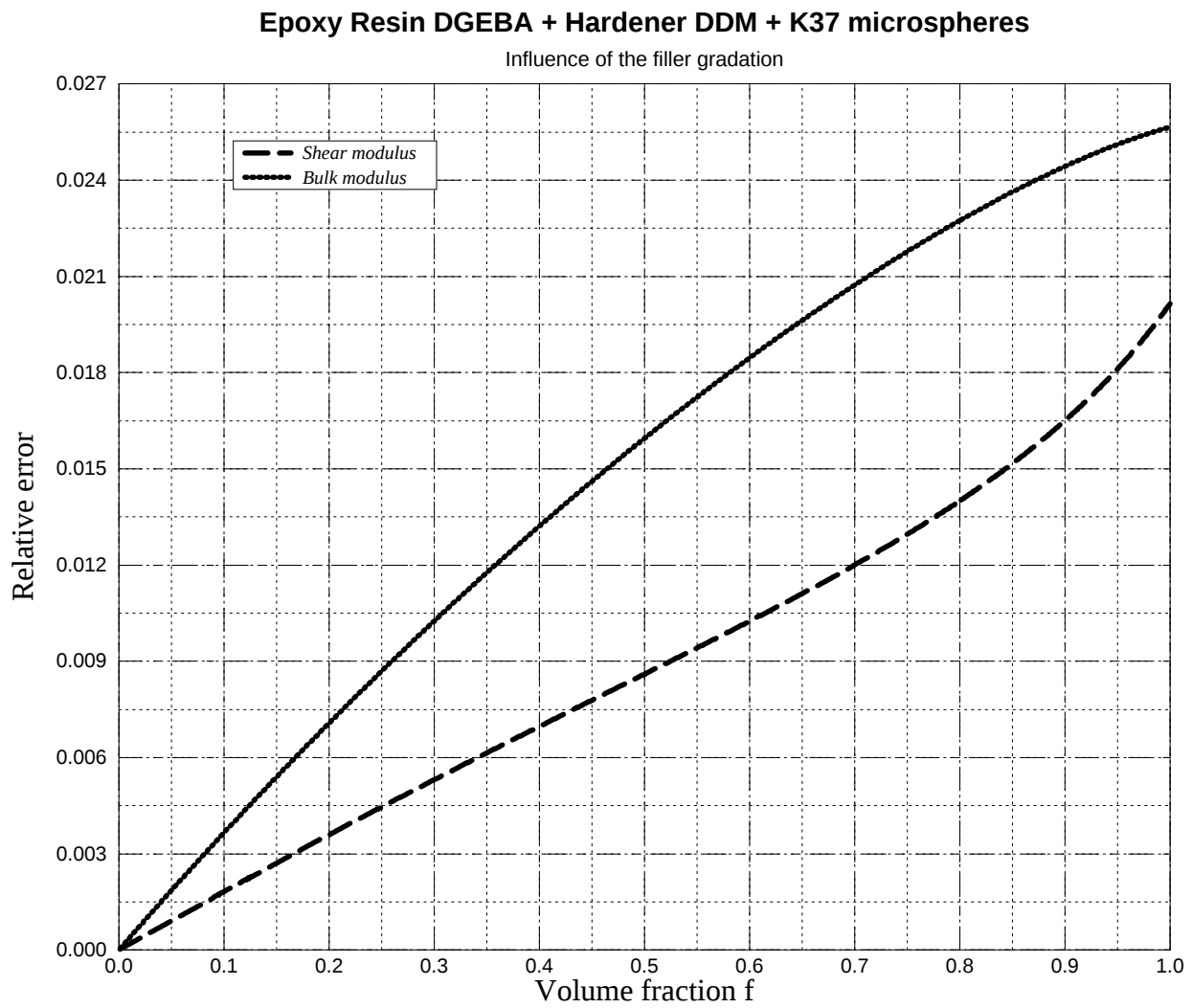


Figure 10.1: Influence of the K37 microsphere gradation

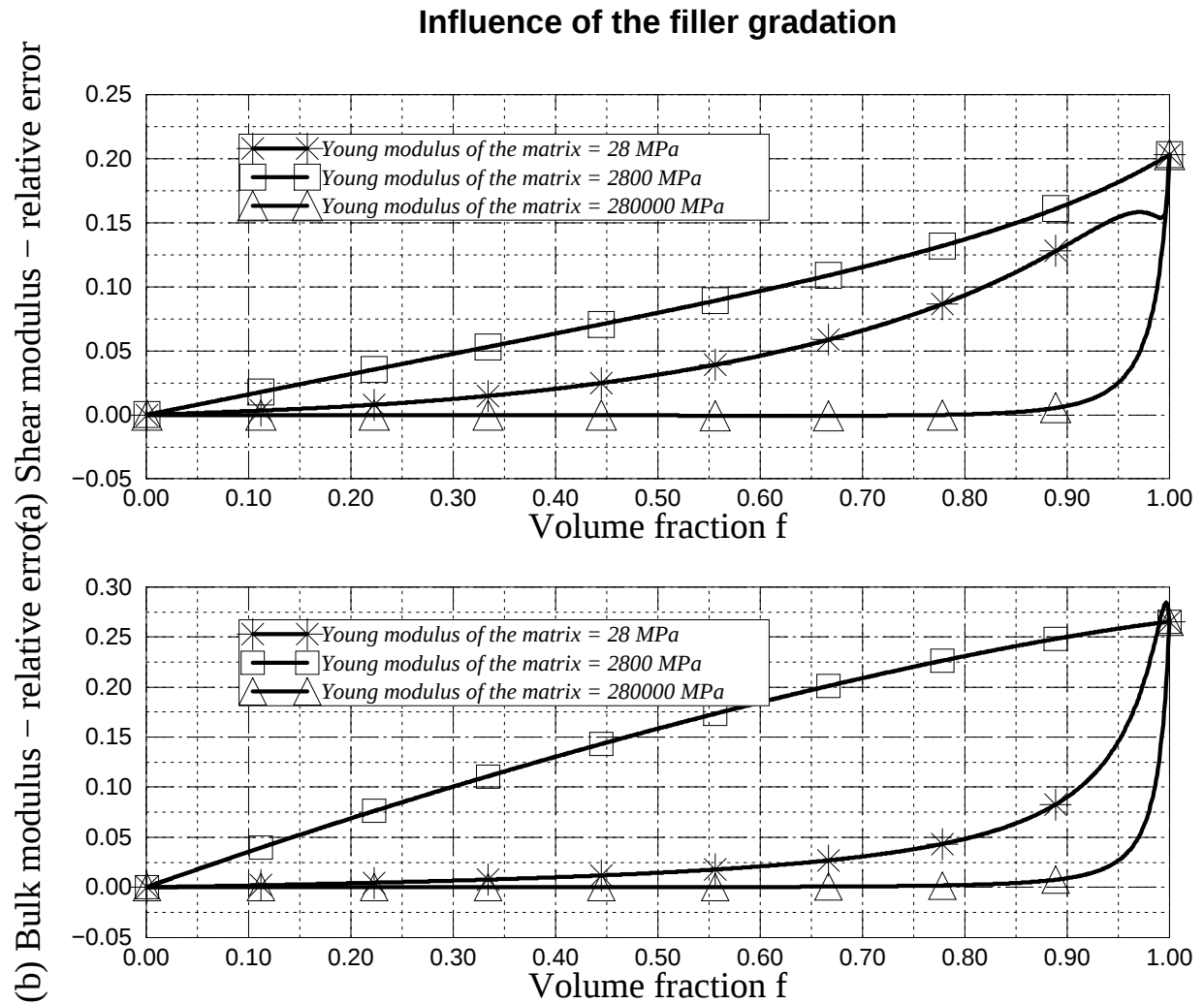


Figure 10.2: Influence of the filler gradation of a fictitious filler

Chapter 11

Comparison between predictions of numerical simulations and analytical estimates

The effectiveness of estimates (7.2.33) and (7.3.14) is here checked, for the sake of completeness, against the results given by Finite Element simulations.

The microstructure of the studied composite allows us to construct numerical models in terms of so-called “unit cells” (see section 6.1), which require a minimum computational effort and can therefore be used to test the validity of theoretical predictions over a wide range of base parameters.

Let us recall that, from the examination of the Scanning Electron Microscope images, shown and commented briefly in chapter 4, one can draw two important conclusions:

- the assumption of statistical homogeneity can be taken as valid for the study of this material; moreover, also the assumption of spatial periodicity of the microstructure may be invoked without introducing substantial errors;
- the assumption of perfect adhesion between the two phases seems to be valid up to the rupture of the material, and, therefore, more so in the linear elastic range. This might not hold for very high volume fractions, where the lack of matrix can lead to imperfect bonding. In this extreme situation one should expect experimental values of the elastic moduli systematically smaller than both the analytical and numerical predictions, if these are based — as they indeed usually are — on the perfect bonding assumption.

From the computational viewpoint the last part of the first observation allows us to simulate the results of uniaxial tests on cylindrical specimens by means of an axisymmetric unit cell, with the appropriate boundary conditions (6.1.10) enforcing the periodicity of the microstructure. Such model is shown in figure 11.1, where the mesh used to study one quarter of the unit cell, together with the deformed shape, is displayed.

The unit cell has been subjected to uniaxial periodic boundary conditions; this expedient allowed us to estimate, for each analysis, both the effective Poisson ratio and the effective Young modulus by computing respectively the transversal displacement and the dual variable conjugated to that applied on the top side of the unit cell (uniaxial forces or

displacements). This kind of “numerical simulation of a uniaxial test” is a useful method and it is cheaper than the “correct” homogenization procedure which consists of computing as many elastic solutions (same geometry, different and “independent” boundary conditions) as the number of independent effective elastic moduli to evaluate (just 2, in the case of overall isotropy).

For a discussion of unit cell calculations, as well as of the relevant boundary conditions, see, for instance, [119].

We have compared analytical with numerical results for a range of syntactic foams, similar to the foam type 1 described in sections 4.1 and 9.2. The basic materials are the same; we have here extended the analysis to cover four choices of microspheres, taken from the standard catalog given by the producer (3M Italia [1]). Table 11.1 shows the average details of the considered inclusions, as given in [1]. The results of our analyses

Sphere Type	Density [g/cm ³]	Median Diameter [μm]	Wall Thickness [μm]	a/b [—]
K1	0.125	70.00	0.58	0.9836
K15	0.15	70.00	0.70	0.9802
S22	0.22	40.00	0.59	0.9709
K37	0.37	50.00	1.28	0.9501

Table 11.1: *Average details of the considered microspheres [1]*

are shown in figures 11.2 and 11.3, in terms of Young modulus and Poisson coefficient of the composite respectively. Each figure includes four curves, computed analytically using equations (7.2.33) and (7.3.14), on the basis of the moduli of the two phases (in this case, $E^{(m)} = 2800 \text{ MPa}$, $\nu^{(m)} = 0.41$, $E^{(i)} = 70110 \text{ MPa}$, and $\nu^{(i)} = 0.23$) and of the given average ratios a/b for the four different sets of spheres considered; numerical results are superimposed as filled symbols, corresponding to volume fractions of filler equal to 0.2, 0.3, 0.4, 0.5153, and 0.6. All the numerical results have been obtained using the Finite Element code ABAQUS (Hibbitt, Karlsson & Sorensen [63]), employed in the linear elastic range and exploiting its “*MPC” and “*EQUATION” options, which allow the necessary periodicity boundary conditions to be prescribed on the external sides of the model.

The results of figure 11.2 confirm that the analytical estimates of the Young modulus predict with good accuracy all the essential features of the dependency from both the volume fraction and the inclusion geometry. The differences between the analytical and the numerical results are always lower than about 7%, the numerical results being stiffer than the analytical for the light spheres (K1) and more flexible for the heavy spheres (K37).

It may be useful to recall that the axisymmetric unit cell, even in the case of real periodicity of microstructure, is an approximation of the unit cell necessary to reconstruct the three-dimensional solid, because the unit cell model corresponds to a circular cylinder with a spherical inclusion, and no packing of circular cylinders fills the space. Therefore, the numerical results are in themselves affected by a slightly heavier approximation than that inherent into a Finite Element model. In consideration of this, the curves of figure 11.2 show an excellent agreement between analytical and numerical results.

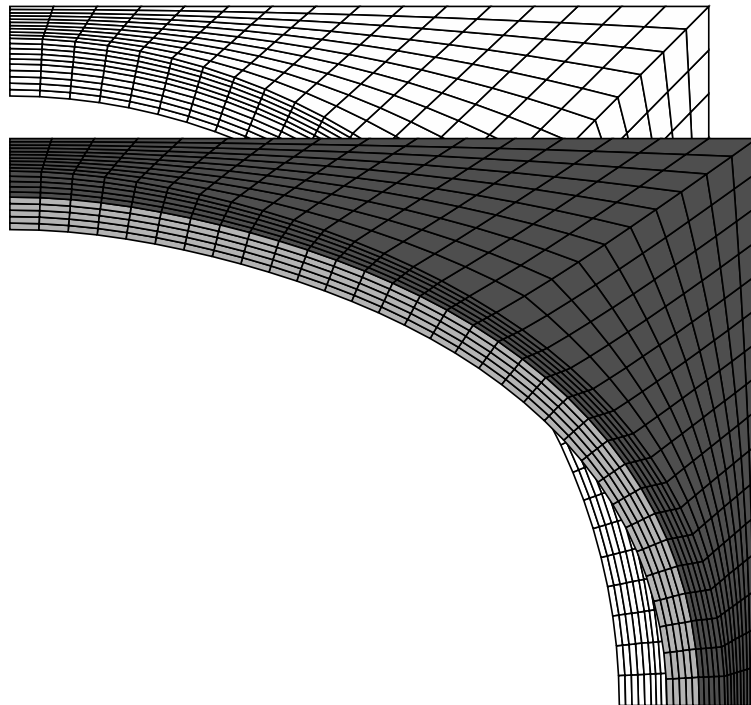


Figure 11.1: *The unit cell model*

Things are essentially the same also in terms of Poisson coefficient (figure 11.3), where, now, the numerical results underestimate the analytical ones for the light spheres and overestimate the analytical ones for the heavy spheres, with differences again up to $\pm 7\%$. The largest differences between the numerical and the analytical results appear for the K1 spheres, at high volume fractions. At these volume fractions ($f \geq 0.6$), however, the spherical inclusions are close to their limit packing, and the numerical model inevitably includes several badly shaped elements; in this situation a further loss of accuracy must therefore be expected in the numerical results. On the other hand, the analytical results also tend to become more and more inaccurate as the filler volume fraction becomes high. In any case, the results shown in figures 11.2 and 11.3 must be considered satisfactory; for a better understanding of the situation figure 11.4 shows the numerical and analytical predictions in terms of bulk and shear moduli for the K1 microspheres only. Even if this is the case where the differences are largest, the agreement is quite good.

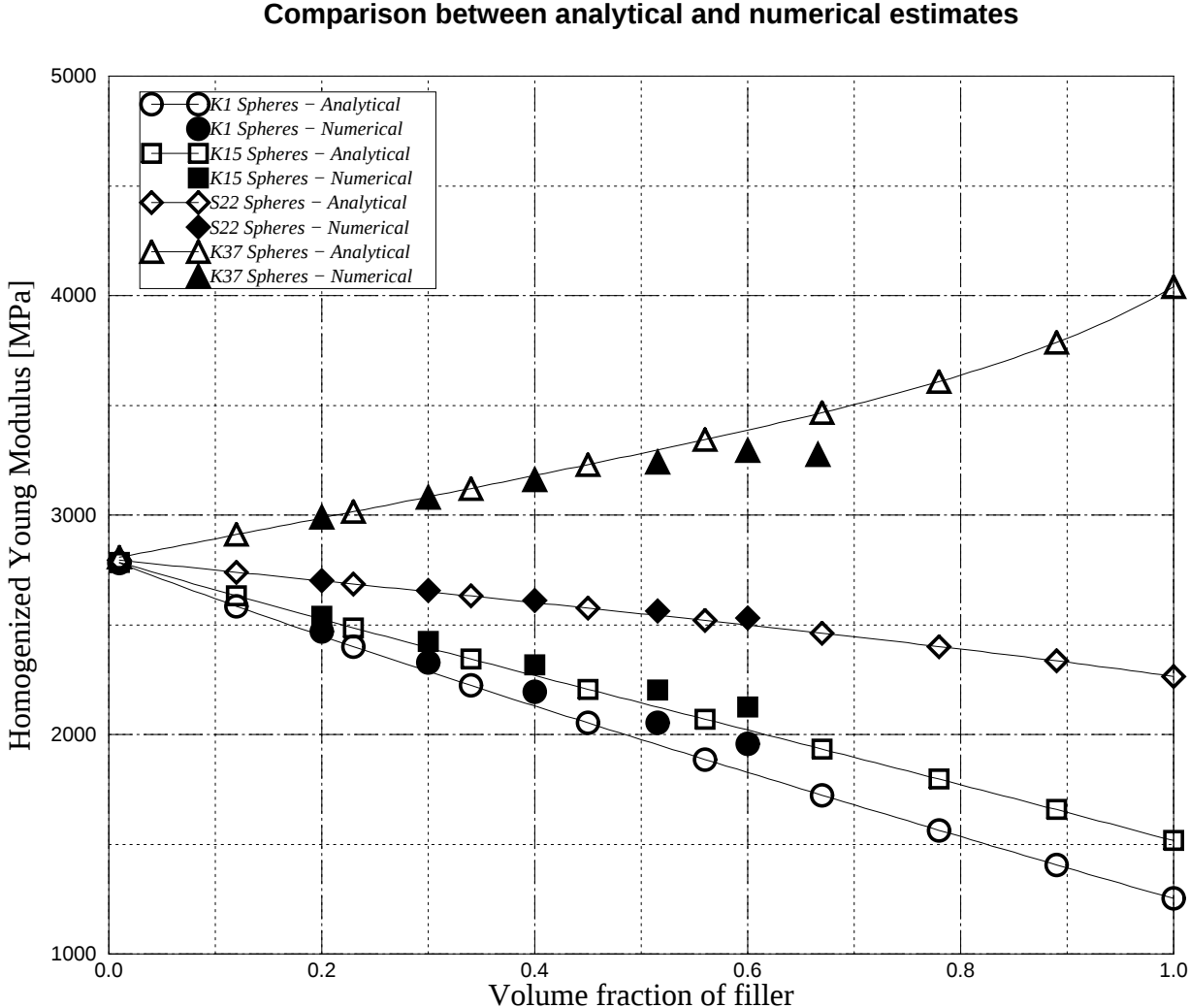


Figure 11.2: Comparison between analytical and numerical estimates of the effective Young modulus

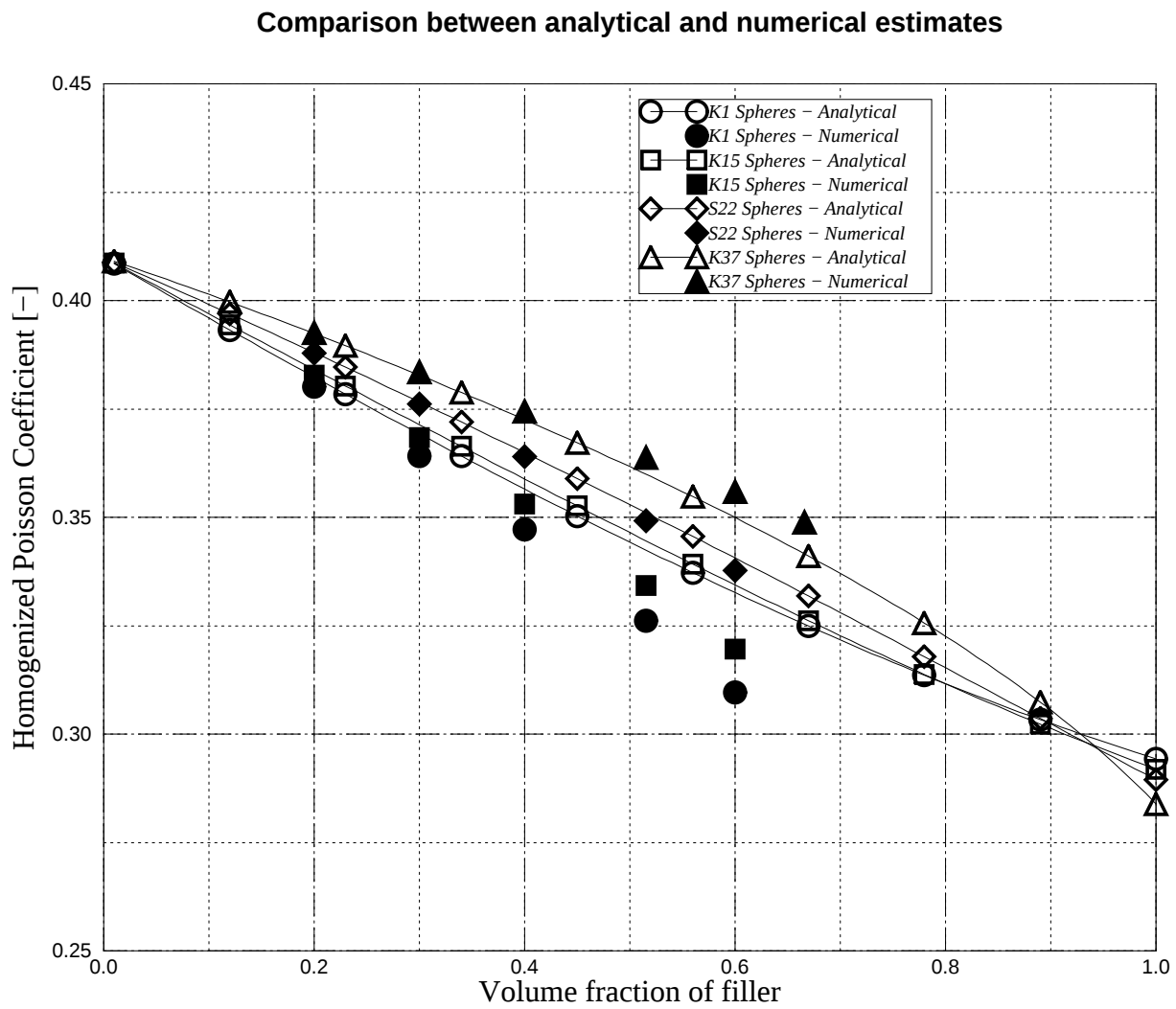


Figure 11.3: Comparison between analytical and numerical estimates of the effective Poisson ratio

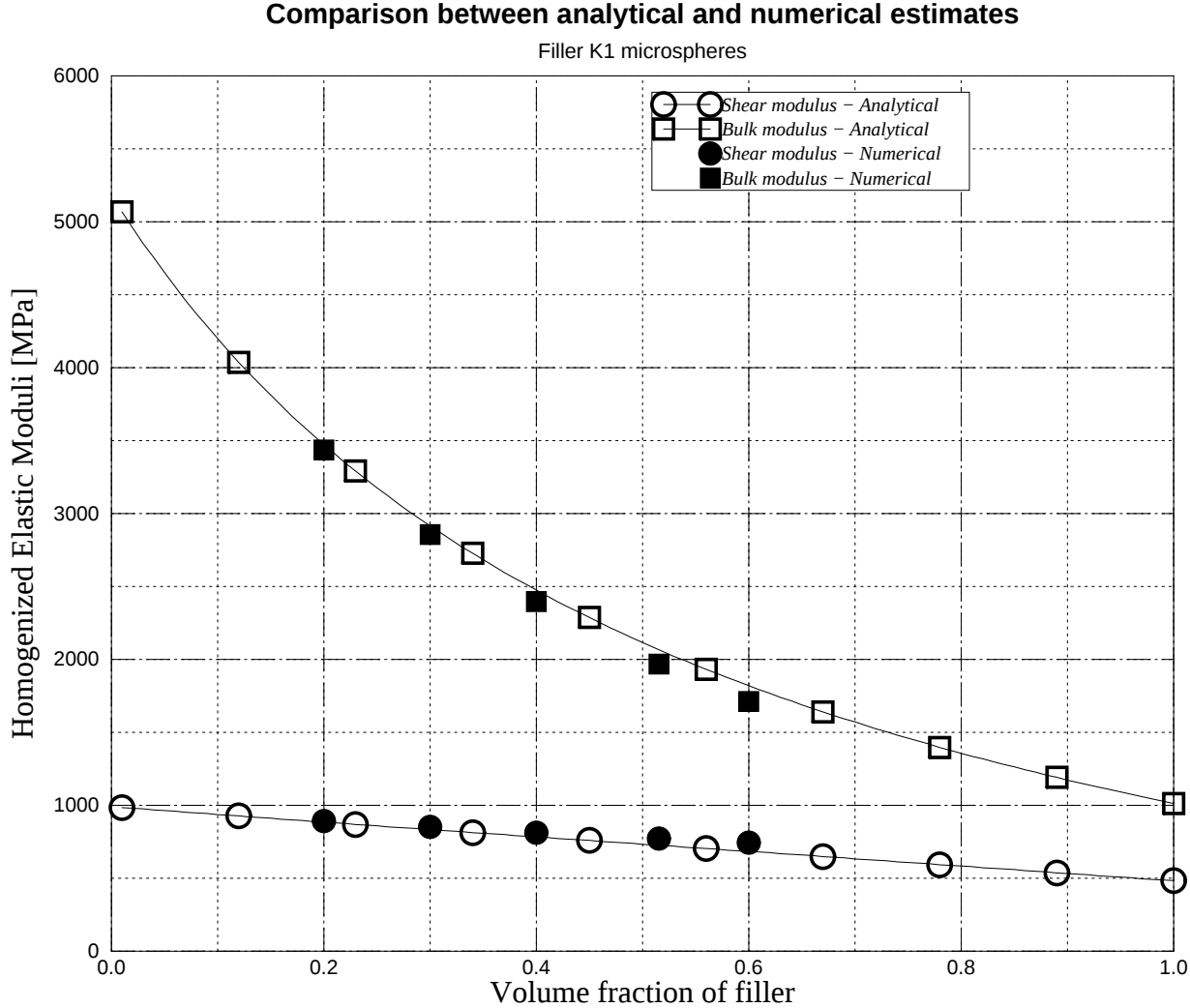


Figure 11.4: Comparison between analytical and numerical estimates of both the effective shear and bulk moduli

Chapter 12

An application: the elastic design of syntactic foamed sandwiches obtained by filling of three-dimensional sandwich-fabric panels

A non-conventional sandwich, made by a fabric panel core filled by a syntactic foam, and by resin-impregnated fiberglass skins, is studied in the elastic range, with the aim of giving guidelines to its minimum weight design. Standard homogenization techniques are employed to compute the elastic moduli of both the skins and the core; the homogenization method derived in chapter 7 is exploited to accomplish the first of the two homogenization steps needed in order to obtain the elastic moduli of the core. A simple but accurate relationship for computing the shear stiffness of the sandwich is derived and used in conjunction with well known formulae for the bending stiffness. Comparisons with both experiments and numerical predictions show the good accuracy of both the proposed homogenization methods and the overall stiffness evaluation procedure [15].

This work has been done within a research project partly supported by a grant from the “Intermarine S.p.A.” company.

12.1 Introduction

Sandwich panels are often employed in structural applications when weight is a critical issue. The quest for extreme lightness leads to the use, for instance, of honeycomb-core sandwiches, or of foamed-core sandwiches. In both cases a so-called “antiplane” sandwich is obtained, in which the purpose of the core is limited to transmitting shear stresses between the skins and to keeping the skin distance approximately constant during the deformation.

These choices, however, may introduce sources of severe structural weakness. A major one is the possibility of debonding between the core and the skins, due, in the case of

honeycomb-core sandwiches, to the small contact area between the two layers. A second one relates to strength; in antiplane sandwiches usually the average compressive strength of the core is negligible and, generally, very seldom exceeds the value of 10 MPa , whereas the compressive stress acting on the core itself may sometimes be of one order of magnitude larger. An example occurs in aircraft applications, where a core strength of the order of $30 \div 100 \text{ MPa}$ is required to carry the load acting on lightweight sandwich panels in proximity of door hinges [31]. Also the elastic stiffness of the core may be an issue.

One way to reduce the risk of delamination between core and skins has been devised in the mid-eighties, when so-called “sandwich-fabric panels” have been produced in Belgium and in Germany. These are obtained from woven, three-dimensional fabric, impregnated with resin and cured. The fabric is produced by a velvet weaving technique, by skipping the last step of cutting the fabric into 2 parts. When this fabric is impregnated with resin and cured, a solid panel is obtained, made by two thin skins of resin-impregnated fabric and a core constituted by “piles” of resin-impregnated yarns. A schematic view of this product is given in figure 12.1. A thorough description of the main features of these panels can be found in [121]. This material is a perfect example of an antiplane sandwich

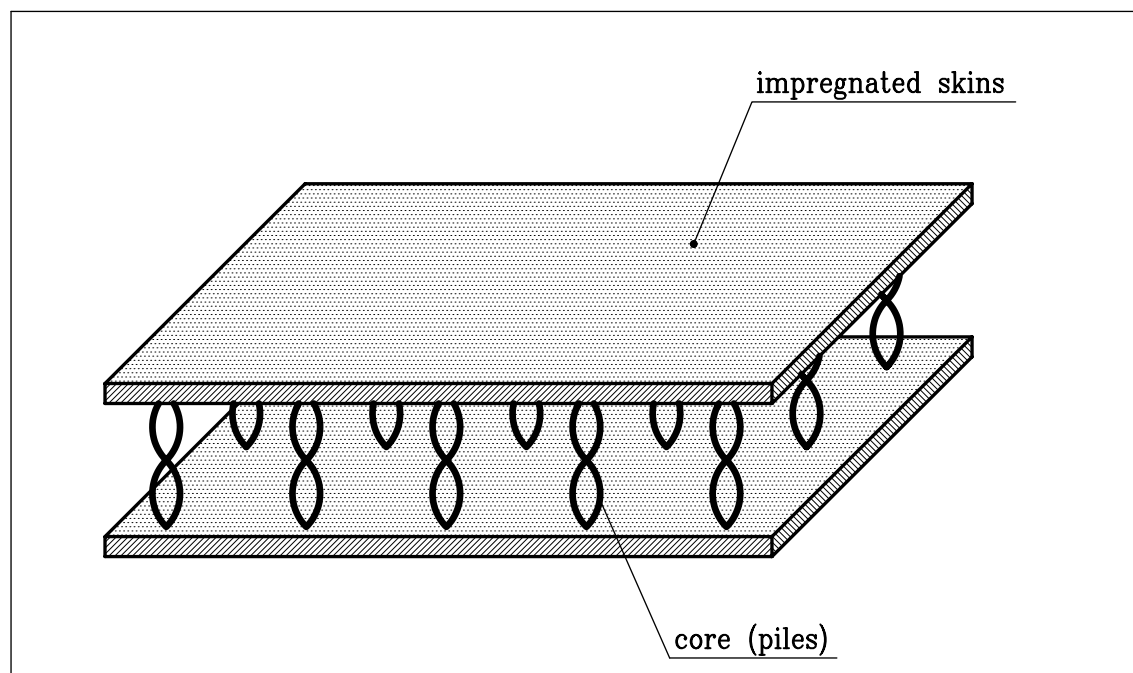


Figure 12.1: *Sandwich-fabric panel*

which does not suffer from problems of delamination as long as the piles connecting the two skins are close enough to each other, and which can function as a proper sandwich as long as the shear stiffness of the core is sufficient to transmit shear stresses and as long as the compressive stiffness of the core is sufficient to prevent relative motion of the skins in the direction orthogonal to their plane. All these conditions are difficult to be met in such a way as to obtain a sandwich usable in structural applications. Moreover, such sandwich has a core with no strength or stiffness in the directions contained in the sandwich plane.

Even filling the core of these panels with standard foams does not improve this aspect, since standard foams, as already pointed out, often do not guarantee enough stiffness or enough strength.

From these considerations the idea arises of filling the core of sandwich-fabric panels with syntactic foams.

The use of syntactic foams as a filler for the core of sandwich-fabric panels allows us to obtain a sandwich which maintains a low weight without incurring in the previously mentioned drawbacks. In this work we focus our attention on a sandwich obtained by starting from a fiberglass fabric, impregnated with standard epoxy or polyester resins; the core of the sandwich-fabric panel obtained from this fabric is filled with syntactic foams made again by standard epoxy or polyester resins and by hollow glass microspheres. Finally, the skins of the sandwich are thickened by applying on their top further layers of resin-impregnated fiberglass.

In this chapter, the linear elastic behavior of this sandwich will be illustrated, in order to understand how its rather involved morphology influences its global stiffness. To do so, a minimum weight sandwich is designed, which has a pre-defined stiffness with respect to a chosen loading condition.

The path followed implies first some elastic homogenization steps, required to reduce this highly non-conventional sandwich to a “standard” three-layered sandwich, in which each layer can be assumed as homogeneous. In particular, there is the need of computing the homogenized elastic moduli of the sandwich skins, made by fiberglass and resin, of computing the homogenized elastic moduli of the syntactic foam, and, finally, of computing the homogenized elastic moduli of the sandwich core, made by yarns of fiberglass, resin, and syntactic foam. The used homogenization methods are briefly summarized in sections 12.3 and 12.4; section 12.5 will report a comparison between the analytical estimates and some experimental results for the sandwich.

Having estimates of the elastic moduli of the three layers of the sandwich, it is possible to set up a simple weight optimization procedure following the path indicated, for instance, in Gibson and Ashby [50]. In our case, however, the situation is made difficult by two things: the fact that the sandwich is not of the antiplane type and the fact that we can not easily obtain a relationship between the density and the stiffness of the core, as done in [50]. In section 12.2 we shall describe how we have computed the sandwich stiffnesses and, in section 12.6, we shall describe the results obtained in minimizing the weight of the sandwich under a given constraint on its overall stiffness.

12.2 Elastic stiffness of a symmetric sandwich beam

Let us assume to study the elastic stiffness of a sandwich beam of total length l and width B , made by three homogeneous layers, as indicated in figure 12.2. The considered sandwich is symmetric, i.e., its external layers (skins) have identical thickness t . The thickness of the core is indicated with the symbol c . With reference to the terminology used in [3], we classify our sandwich as one with *thick skins* and a *non-antiplane core*.

The computation of the deflection of a thick skinned, non-antiplane sandwich beam can be made using different assumptions, depending on the required degree of accuracy; two possible solutions are suggested in Allen [3]. The first one is approximate and nevertheless

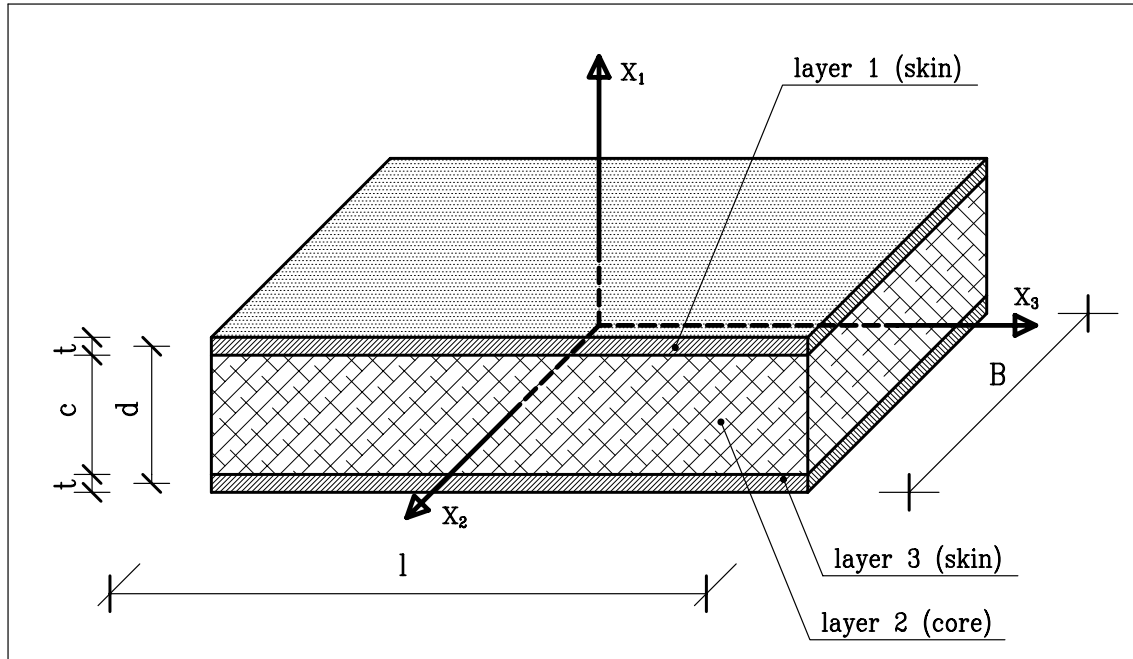


Figure 12.2: *Relevant geometrical parameters of a symmetric sandwich*

very involved, initially formulated for antiplane sandwiches, and extended to the case of non-antiplane core by Allen by adopting the further approximation that the displacement field along the sandwich core is linear. Results obtained using this method, indicated as “Allen’s method”, will be briefly commented upon later.

A second possible solution is based on the Total Potential Energy theorem, which requires the choice of an admissible displacement field along the height of the sandwich section. This approach leads rapidly to very involved computations, and in Allen it is used only in conjunction with the Ritz method, to obtain approximate solutions, and only for the antiplane core case. We have derived the “exact” solution, for the three-point bending case, using a kinematics, sketched in figure 12.3, more general than that used by Allen, and in the case of non-antiplane sandwich core. The results thus obtained will be in the following compared with others and will be denoted as “Total Potential Energy” results.

The kinematics of figure 12.3 is described by the following unknown parameters, in which v is the transverse deflection of the sandwich middle axis and λ_c and λ_s are dimensionless unknown parameters, dependent upon the dimension and the stiffness of both skins and core:

- dv/dx_3 = cross section rotation due to the bending only, equal for the core and the skins;
- γ_c = cross section rotation of the core due to the shear force;
- $\lambda_c dv/dx_3$ = total cross section rotation of the core;
- γ_s = cross section rotation of the skins due to the shear force;

- $\lambda_s dv/dx_3 = \text{total rotation of the skins.}$

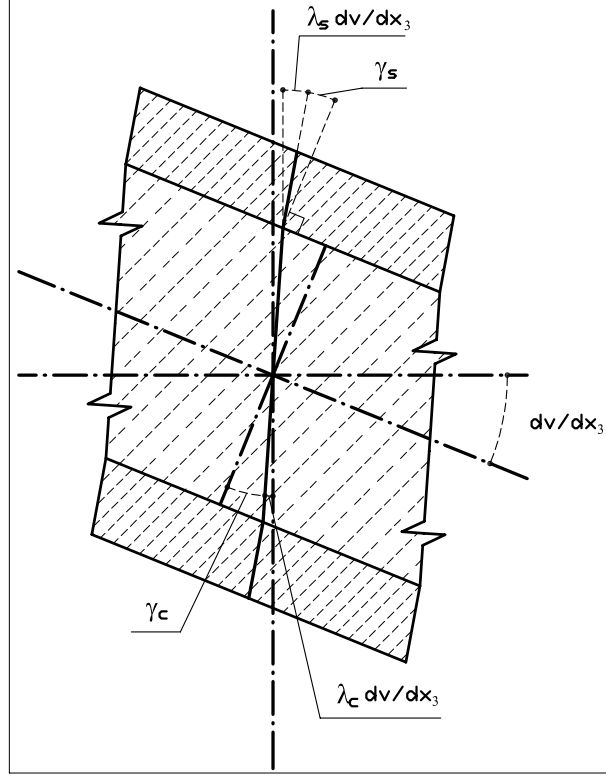


Figure 12.3: Parameters used for modeling the kinematics of a sandwich beam

These parameters are related to each other as follows:

$$\lambda_c \frac{dv}{dx_3} = \frac{dv}{dx_3} - \gamma_c \quad \lambda_s \frac{dv}{dx_3} = \frac{dv}{dx_3} - \gamma_s \quad (12.2.1)$$

where the values that λ_c can assume are bounded by $-t/c$ and 1, which correspond to the core shear stiffness G_c equal to zero or infinity respectively.

In the Total Potential Energy approach given by Allen [3], the shear compliance of the skins is always considered negligible, i.e., $G_{sk} \rightarrow \infty$, or, equivalently, $\lambda_s = 1$. This is probably a correct engineering approximation, but we shall not make it in the following computation.

Using the kinematics of figure 12.3, it is then straightforward to compute the longitudinal strain ε and the engineering shear strain γ , from which, adopting the constitutive law $\tau = G\gamma$ and $\sigma = E\varepsilon$, it is possible to derive the Total Potential Energy U for the three-point bending of a sandwich beam:

$$U = \frac{G_c Bc}{2} \int_0^l (1 - \lambda_c)^2 \left(\frac{dv}{dx_3} \right)^2 dx_3 + \frac{E_c Bc^3}{24} \int_0^l \lambda_c^2 \left(\frac{d^2v}{dx_3^2} \right)^2 dx_3 + \\ + G_{sk} Bt \int_0^l (1 - \lambda_s)^2 \left(\frac{dv}{dx_3} \right)^2 dx_3 + \frac{E_{sk} Bt}{4} \int_0^l (c\lambda_c + t\lambda_s)^2 \left(\frac{d^2v}{dx_3^2} \right)^2 dx_3 +$$

$$+ \frac{E_{sk} B t^3}{12} \int_0^l \lambda_s^2 \left(\frac{d^2 v}{dx_3^2} \right)^2 dx_3 - P \delta \quad (12.2.2)$$

in which λ_c and λ_s are taken constant (i.e., independent upon the coordinate x_3 along the longitudinal beam axis), E and G indicate the Young and shear moduli, the subscript sk refers to skin properties, the subscript c to core properties, $v(x_3)$ indicates the deformed shape of the beam, P is the force applied at the midspan of the beam, and $\delta = v(x_3 = l/2)$ is the maximum deflection.

Making U stationary with respect to the kinematic parameters, $v(x_3)$, λ_c , and λ_s , one obtains (i) the fourth-order differential equation governing the deformed shape $v(x_3)$, (ii) the natural boundary conditions, and (iii) two integral equations furnishing the value of both λ_c and λ_s . The final result is the following nonlinear integral system, in which the expression of $v(x_3)$ is defined in the interval $0 \leq x_3 \leq l/2$ (for $l/2 \leq x_3 \leq l$ one has to exploit the symmetry of $v(x_3)$):

$$v(x_3) = \frac{P \left(\alpha \cosh(\alpha \frac{l}{2}) x_3 - \sinh(\alpha x_3) \right)}{\alpha^3 \cosh(\alpha \frac{l}{2}) \left(E_{sk} B t (c \lambda_c + t \lambda_s)^2 + \frac{E_{sk} B t^3}{3} \lambda_s^2 + \frac{E_c B c^3}{6} \lambda_c^2 \right)} \quad (12.2.3)$$

$$\alpha = \sqrt{\frac{12 G_c c (1 - \lambda_c)^2 + 24 G_{sk} t (1 - \lambda_s)^2}{2 E_{sk} t \left(3 (c \lambda_c + t \lambda_s)^2 + t^2 \lambda_s^2 \right) + E_c c^3 \lambda_c^2}} \quad (12.2.4)$$

$$\lambda_c = \frac{12 G_c c \int_0^{l/2} \left(\frac{dv}{dx_3} \right)^2 dx_3 - 6 E_{sk} t^2 c \lambda_s \int_0^{l/2} \left(\frac{d^2 v}{dx_3^2} \right)^2 dx_3}{12 G_c c \int_0^{l/2} \left(\frac{dv}{dx_3} \right)^2 dx_3 + (6 E_{sk} t c^2 + E_c c^3) \int_0^{l/2} \left(\frac{d^2 v}{dx_3^2} \right)^2 dx_3} \quad (12.2.5)$$

$$\lambda_s = \frac{12 G_{sk} t \int_0^{l/2} \left(\frac{dv}{dx_3} \right)^2 dx_3 - 3 E_{sk} t^2 c \lambda_c \int_0^{l/2} \left(\frac{d^2 v}{dx_3^2} \right)^2 dx_3}{12 G_{sk} t \int_0^{l/2} \left(\frac{dv}{dx_3} \right)^2 dx_3 + 4 E_{sk} t^3 \int_0^{l/2} \left(\frac{d^2 v}{dx_3^2} \right)^2 dx_3} \quad (12.2.6)$$

The system (12.2.3)–(12.2.6) can be solved numerically by using as initial guesses for α , λ_c , and λ_s the solutions furnished by the Ritz method, for instance by choosing:

$$v(x_3) = \delta \sin \frac{x_3 \pi}{l} \quad (12.2.7)$$

After solving numerically the system (12.2.3)–(12.2.6), equation (12.2.3) furnishes, for $x_3 = l/2$, the value of the maximum deflection δ .

This method has the drawback of being very expensive and of becoming much too cumbersome for more complicated structures.

Beside their analytical complication, both the Allen method and the Total Potential Energy method have some other drawbacks, most notably that of failing to yield correct results for special cases, such as that of thin skins, or, worse, that of a homogeneous beam. For this reason a third, extremely simple approach, is here put forward, based on the classic approximate shear force treatment by Jourawsky [71] and on the Navier–Bernoulli homogeneous beam kinematics.

Within this framework, we want to compute the maximum deflection of a sandwich beam, under general loading and constraint conditions, by exploiting the well known formulae for homogeneous beams:

$$\delta = \frac{Pl^3}{Y_1 D} + \frac{Pl}{Y_2 (GA^*)} \quad (12.2.8)$$

where l is the beam length, P is the total resultant force applied to the beam, D indicates the bending stiffness, (GA^*) is the cross section shear stiffness, and Y_1 and Y_2 are numerical constants which depend on both loading and constraint conditions. For instance, in the four-point bending case and for a simply supported beam:

$$Y_1 = \frac{32}{\left(1 - \frac{l_p}{l}\right) \left[1 - \frac{1}{3} \left(1 - \frac{l_p}{l}\right)^2\right]} \quad (12.2.9)$$

$$Y_2 = \frac{4}{1 - \frac{l_p}{l}} \quad (12.2.10)$$

where l_p is the distance between the two symmetrically applied concentrated loads, each of magnitude $P/2$. In the particular case of three-point bending one has to set $l_p = 0$ in equations (12.2.9)–(12.2.10) (i.e., the force P is equal to a concentrated load applied at the beam midspan), which leads to $Y_1 = 48$ and $Y_2 = 4$.

In the case of a thick skinned, non-antiplane sandwich, the bending stiffness D includes three terms, deriving from contributions of both skins and core, written, with reference to the geometry of figure 12.2, as follows:

$$D = E_{sk} \left(\frac{Bt^3}{6} + \frac{Btd^2}{2} \right) + E_c \frac{Bc^3}{12} \quad (12.2.11)$$

where E indicates the Young modulus, subscript sk refers to skin properties, subscript c to core properties and $d = c + t$ indicates the distance between the middle planes of the two skins. This is a completely standard result [3].

A more complicated problem arises from the need of evaluating the “equivalent” sandwich shear stiffness (GA^*) . In fact, the presence of a relatively stiff core and of thick skins makes the kinematics of a sandwich beam in bending much different from that of a standard beam, which compels one to take into account the shear deformability in a rather complicated way; such phenomenon is the cause of the involved methods mentioned above.

However, if one simply assumes that a plane sandwich section remains plane during the deformation, by developing the classical beam analysis for shear stresses due to shear force one can compute the shear stresses in the three layers of the sandwich. Thereafter one can obtain the “equivalent” shear stiffness (GA^*) of the sandwich by equating the expressions of the work of deformation in the sandwich beam and in the homogeneous equivalent beam:

$$\frac{T^2}{2(GA^*)} = \frac{1}{2} \int_{A_c} \frac{\tau_c^2}{G_c} dA + \frac{1}{2} \int_{A_{sk}} \frac{\tau_{sk}^2}{G_{sk}} dA = \frac{B}{G_c} \int_0^{c/2} \tau_c^2 dx_1 + \frac{B}{G_{sk}} \int_{c/2}^{c/2+t} \tau_{sk}^2 dx_1 \quad (12.2.12)$$

where, with reference to figure 12.2, $A_{sk} = 2tB$ is the area occupied by the skins in a beam section, $A_c = cB$ is the core area, and T is the shear force applied to the sandwich cross section.

The well known Jourawsky approximation allows the shear stresses in the sandwich skins, τ_{sk} , and in the core, τ_c , to be written as:

$$\tau_{sk} = \frac{T \left(t^2 + \frac{c^2}{4} + ct - x_1^2 \right)}{2 \frac{D}{E_{sk}}} \quad (12.2.13)$$

$$\tau_c = \frac{Ttd}{2 \frac{D}{E_{sk}}} + \frac{T \left(\frac{c^2}{4} - x_1^2 \right)}{2 \frac{D}{E_c}} \quad (12.2.14)$$

By inserting equations (12.2.13) and (12.2.14) into equation (12.2.12), after some lengthy algebra the following result is thus obtained:

$$(GA^*) = \frac{\frac{5}{6}}{\frac{4}{A_{sk}G_{sk}(1+\alpha_s)} + \frac{1}{A_cG_c(1+\alpha_c)}} \quad (12.2.15)$$

in which the interaction coefficients α_s and α_c are defined as follows:

$$\alpha_s = \frac{\frac{c^6}{n^2} + \frac{12c^5t}{n} + 12c^4t^2(3 + \frac{2}{n}) + 16c^3t^3(9 + \frac{1}{n}) + 230c^2t^4 + 167ct^5 + 48t^6}{t^4(10c^2 + 25ct + 16t^2)} \quad (12.2.16)$$

$$\alpha_c = \frac{\frac{c^5t}{3n} + c^4t^2(1 + \frac{7}{3n}) + 2c^3t^3(7 + \frac{4}{3n}) + 35c^2t^4 + 32ct^5 + \frac{32t^6}{3}}{c^2 \left(\frac{c^4}{6n^2} + \frac{5c^2t(t+c)}{3n} + 5t^2(c+t)^2 \right)} \quad (12.2.17)$$

where n is the ratio between the Young moduli of skins and core:

$$n = \frac{E_{sk}}{E_c} \quad (12.2.18)$$

Despite the conceptual simplicity of this computation we have not been able to find any reference to it in the literature. In order to verify the accuracy of Allen's method, of the Total Potential Energy method, and of results (12.2.15)–(12.2.18) we have run some Finite Element simulations by means of the code ABAQUS [63], on an arbitrary geometry of three-point bending sandwich beam, for several values of both ratios n and t/c . The relevant results are shown in figure 12.4, where percentage errors given by the three approaches (Allen's, Total Potential Energy, Jourawsky), computed using the Finite Element solution as reference solution, are plotted as function of the ratio t/c for some values of coefficient n .

For the sake of completeness, here we report the formulae needed to apply the Allen method to the three-point bending case:

$$\delta = \frac{Pl^3}{48D} + \frac{Pl}{4G'A'} \left(1 - \frac{E_{sk}Bt^3}{6D} \right)^2 \left(1 - \frac{\tanh \theta}{\theta} \right) \quad (12.2.19)$$

in which

$$\theta = \frac{l}{2} \sqrt{\frac{6G'A'}{E_{sk}Bt^3 \left(1 - \frac{E_{sk}Bt^3}{6D}\right)}} \quad (12.2.20)$$

$$A' = \frac{Bd^2}{c} \quad (12.2.21)$$

$$G' = \frac{G_c}{1 + \frac{c^2}{6nt(t+c)}} \quad (12.2.22)$$

Note that for the antiplane case $G' = G_c$. It is apparent that Allen's method gives the worst results in all cases (it fails badly, in particular, for ratios $t/c \rightarrow 0$) and that even the Total Potential Energy method, in which the "exact" sandwich beam kinematics has been inserted, is not really accurate, owing to the inconsistency between the use of a trilinear kinematic model [3] and the strain field implied by Jourawsky's approach. The results given by equations (12.2.15)–(12.2.18) seem to be an acceptable approximation of Finite Element results over the whole range of variables considered.

In the following, therefore, equations (12.2.11) and (12.2.15)–(12.2.18) will be used to compute the equivalent elastic stiffnesses of a sandwich beam. In particular, we shall need them in sections 12.5 and 12.6. In section 12.6, equation (12.2.8) with the ratio δ/P treated as a known term will be prescribed as a constraint during the weight optimization of the sandwich. During this process we shall also use, as a simpler approximation, both the expression of the bending and shear stiffness, both for thin skins and antiplane core:

$$D = E_{sk} \frac{Btd^2}{2} \quad (12.2.23)$$

$$(GA^*) = G_c Bd \quad (12.2.24)$$

In figure 12.4, the results obtained by means of this formulae are compared with those of the Finite Element analyses too. It is surprising to see that this very crude approximation works better than Allen's method for high values of the skin thickness, at least in the range $1.5 \leq t/c \leq 3$ here tested.

12.3 Homogenization of the syntactic foam

The application of the equations providing the stiffness of a sandwich beam, briefly summarized in the previous section, requires the knowledge of the values of the elastic moduli of the layers of the sandwich, i.e., of the skins and of the core, seen as homogeneous materials. Since, in reality, each layer of the studied sandwich is made by a composite material, there is the need to estimate the effective elastic moduli of these layers by means of suitable homogenization techniques.

For this sandwich there is the need of homogenizing at two different geometric scales. The first one refers to the syntactic foam, which fills the space left, in the core of the sandwich, by the resin-impregnated yarns of the sandwich-fabric panel. The syntactic foam is itself a composite material, whose inclusion size is about $5 \div 100 \mu m$. The second scale is that defined by the inclusions of both skins and core; in the skins the inclusions

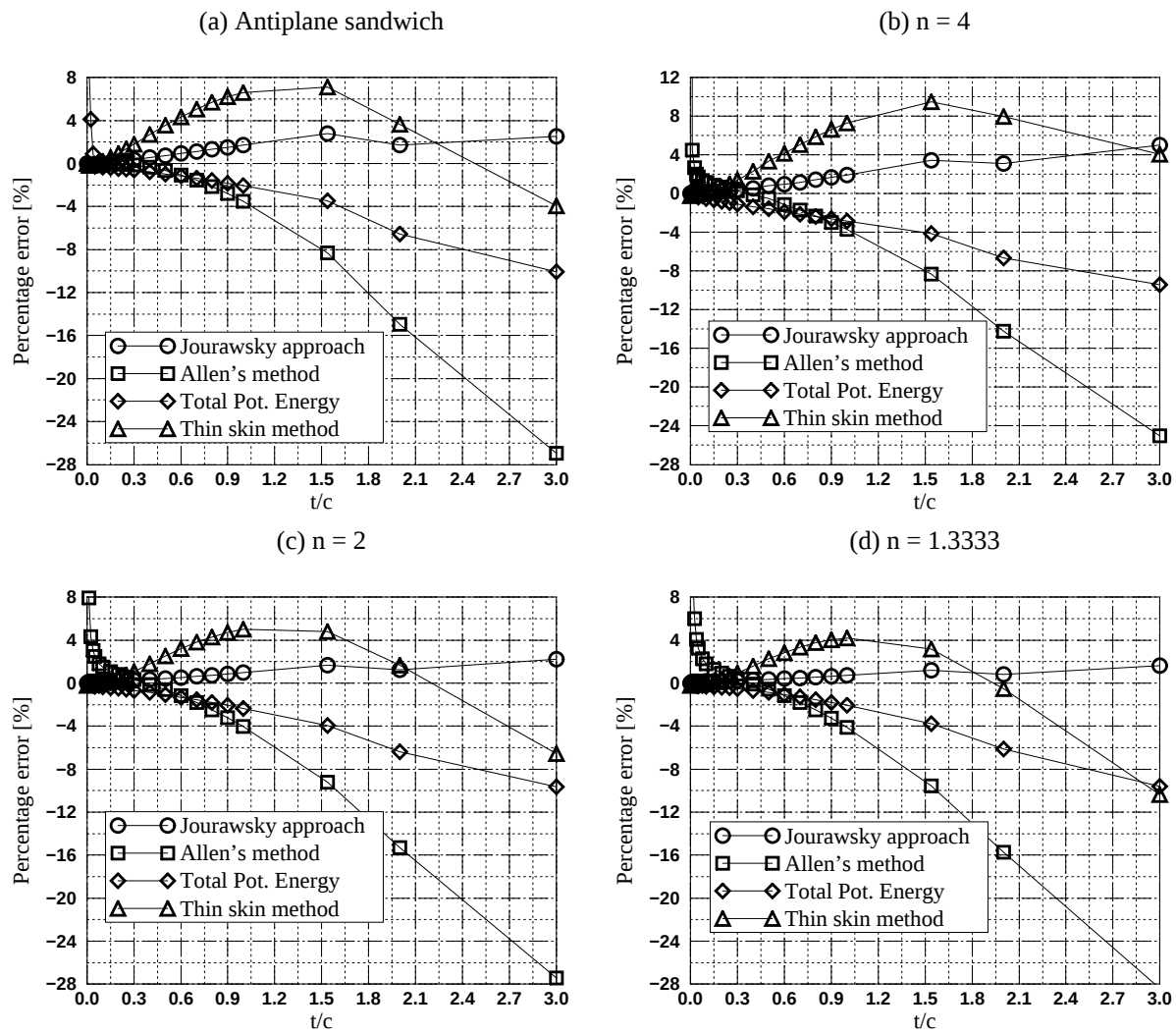


Figure 12.4: Comparison among different methods for evaluating the maximum deflection of a three-point bending sandwich beam with respect to Finite Element results

are the glass fibers, whereas in the core the inclusions are defined by the glass yarns surrounded by resin. Here, the geometric scale of the inclusion is of about the diameter of one glass yarn, i.e., according to van Vuure [121], of the order of $0.1 \div 0.5 \text{ mm}$.

Since the geometric scales of the syntactic foam and of the sandwich core are different by roughly one order of magnitude, it is possible to compute the homogenized elastic moduli of the core by means of a two-step homogenization technique: a first one, to compute the effective elastic moduli of the syntactic foam as showed in chapter 7, and a second one to compute those of the core itself. The second step will be described in the next section.

We have not tackled the study of the effect of the filler gradation on the global stiffness of the sandwich, expected to be trifling. Also, in the design of the “optimal” sandwich, we have assumed, for the sake of simplicity, that no “unwanted” voids are present into the syntactic foam. In this case, the formulae we have used to compute the homogenized elastic moduli of the syntactic foam are those given in sections 7.2 and 7.3. When comparing experimental with analytical results, however, we had to resort to the complete results reported in chapter 7, since, in this case, the presence of voids in the matrix had a significant effect and could not be neglected.

12.4 Homogenization of the fiber-reinforced resin and of the sandwich core

The computation of the effective elastic moduli of the sandwich layers, assuming to know the values of the elastic moduli of glass fibers, resin, and syntactic foam all seen as homogeneous isotropic materials, at the length scale of the sandwich, can be performed by exploiting results available in the literature. However, since the morphology of the studied sandwich is extremely complex, the use of standard results requires some interpretation.

With reference to the cartesian reference system x_1, x_2, x_3 , sketched in figure 12.2, both skins and core can be approximately considered as transversely isotropic, where every plane containing axis x_1 (or any other axis parallel to it) is a plane of material symmetry.

This statement is sufficiently accurate in the case of the core, where the geometry of the yarns connecting the two skins does not give rise to preferential directions in the plane $x_2 - x_3$ (the yarns may be placed at different distances in the warp direction and in the weft direction; a moderate in-plane anisotropy can be expected from this arrangement, but it can definitely be neglected when considering the overall behavior of the sandwich).

Actually the resin-impregnated glass yarns — the piles in the core — can be shaped in various ways, from straight, if the sandwich-fabric panel is subjected to a process called “Adhesive Foil Stretching” [121], to S-shapes and C-shapes, if the panel is not stretched. Also, the piles, during the impregnation process, group together, to form so-called “pillars”; these, depending on the production process, can be inclined with respect to axis x_1 , and are often designed on purpose with an inclination of $\pm 45^\circ$. All these possibilities complicate somewhat the geometrical description of the sandwich core; however, for most practical purposes, the assumption of considering straight pillars only can be considered acceptable.

Of the possible methods, for the computation of the homogenized elastic moduli of transversely isotropic composites, we have used that proposed by Walpole [125], which

actually considers the single phases of the composite as transversely isotropic as well.

The use of Walpole's method for our materials, however, requires some interpretation, since Walpole gives bounds for all the elastic moduli of the composite and there is the need to understand what bounds are to be chosen in relation to the morphology of both the skins and the core of the studied sandwich.

Our composite materials — both the skins and the core of the sandwich — are transversely isotropic only because of the geometrical layout of their constituents, which can be considered, individually, as isotropic. In this case the bounds given by Walpole can be applied for any possible geometrical arrangement of the single phases which, being individually isotropic, can always be imagined as having an axis of transverse isotropy coinciding with the global axis of transverse isotropy, x_1 .

For the purposes of this work we need to estimate the values of the in-plane Young and shear moduli of both skins and core, hereafter indicated by the symbols E_p and G_1 respectively.

In the core, where the stiff glass fibers are aligned with the direction of the axis of transverse isotropy, when considering the in-plane behavior ($x_2 - x_3$) the stiff inclusion phase is not connected and evidently offers little contribution to the global stiffness. For this reason we have chosen to use the lower bound given by Walpole for the Young modulus. The reasoning becomes more difficult in the case of the shear modulus; therefore, in order to get a better feeling, we also computed the analytical estimates for a transversely isotropic material given in Hervé and Zaoui [62], which apply to a material whose morphology is exactly that of the core of our sandwich (but not that of the skins). For both the Young and the shear modulus we obtained results practically coinciding with Walpole's lower bounds. Therefore, in order to avoid the description of a further set of formulae in this chapter, we decided to use Walpole's lower bounds to compute the elastic moduli of the core.

In the case of the skins the presence of a layer of fabric, lying in the skin middle planes, parallel to plane $x_2 - x_3$, introduces a moderate amount of anisotropy in the plane. Such anisotropy is shown by laboratory tests performed on the skins only (Bardella and Genna [13]), which indicate values of the Young moduli, for a particular choice of basic ingredients, in the ratio $E_2/E_3 \approx 1.20$. This ratio is closer to unity than one might expect, considering the strong orthotropy of the fiberglass fabric from which the sandwich-fabric panel is obtained; one needs to recall that, in the final sandwich, the skins are reinforced by the application, during the curing phase, of further layers of resin-impregnated fiberglass, in which the glass fibers are randomly oriented. These layers, whose thickness is significantly greater than that of the skin obtained by impregnating the original fiberglass fabric, are in themselves almost exactly transversely isotropic around axis x_1 . The final result is that, as said, of a moderate anisotropy of the skins in their plane, which contains the stress components of interest to us. However, for all practical purposes, in the sequel of this work we will assume that also the skins are transversely isotropic around axis x_1 .

For the skins, unlike the case of the core, the internal morphology sees the stiff glassy phase lying along the skin middle plane, i.e., close to a "parallel" arrangement with the matrix phase. This suggests the use of Walpole's upper bound to estimate the in-plane Young modulus of the skins.

The interpretation of the values of the shear modulus is again more difficult. Since we could not find any other reference to specific methods to compute such constant, we

decided to use, as an estimate of the value of the skin shear modulus, the average value between the lower and the upper bound. On the other hand, the value of the shear modulus of the skins has almost no relevance on the overall stiffness of the sandwich, and we do not expect this assumption to be the cause of significant errors.

A macroscopically transversely isotropic material is characterized, in the linear elastic range, by five independent elastic constants, which can be chosen in different ways. Walpole [125] gives bounds for all the following constants (the so-called Hill's moduli):

- $\kappa_{23}^{(0)}$, plane strain bulk modulus, with reference to the isotropy plane $x_2 - x_3$, defined by the following strain field: $\varphi_{11} = 0$, $\varphi_{22} = \varphi_{33} = \varphi$ and by the relationship $\sigma_{22} = \sigma_{33} = \sigma = 2\kappa_{23}^{(0)}\varphi$;
- $G_{23}^{(0)}$, shear modulus in the isotropy plane, defined by the following relationship: $\sigma_{23} = 2G_{23}^{(0)}\varphi_{23}$;
- $G_1^{(0)}$, shear modulus, defined by any of the two following relationships: $\sigma_{12} = 2G_1^{(0)}\varphi_{12}$, $\sigma_{13} = 2G_1^{(0)}\varphi_{13}$;
- $L^{(0)}$ cross modulus, as defined by Hill [65];
- $N^{(0)}$ longitudinal modulus in the direction of axis x_1 in the absence of transverse deformation,

where the superscript (0) indicates homogenized values for the equivalent homogeneous material.

The meaning of the last two constants is defined by writing a transversely isotropic constitutive law in the following way

$$\frac{1}{2}(\sigma_{22} + \sigma_{33}) = \kappa_{23}^{(0)}(\varphi_{22} + \varphi_{33}) + L^{(0)}\varphi_{11} \quad (12.4.1)$$

$$\sigma_{11} = L^{(0)}(\varphi_{22} + \varphi_{33}) + N^{(0)}\varphi_{11} \quad (12.4.2)$$

$$\sigma_{22} - \sigma_{33} = 2G_{23}^{(0)}(\varphi_{22} - \varphi_{33}), \quad \sigma_{23} = 2G_{23}^{(0)}\varphi_{23} \quad (12.4.3)$$

$$\sigma_{12} = 2G_1^{(0)}\varphi_{12}, \quad \sigma_{13} = 2G_1^{(0)}\varphi_{13} \quad (12.4.4)$$

Here, we write explicitly the specialization of Walpole's results to the case in which the single components of the composite are isotropic. In this case, each phase is characterized by two elastic constants only, instead of the five used by Walpole. In order to re-write Walpole's equations using his constants, we need to make the following replacement of elastic constants of each single phase ζ :

$$L^{(\zeta)} = \kappa_{23}^{(\zeta)} - G_{23}^{(\zeta)} \quad (12.4.5)$$

$$N^{(\zeta)} = \kappa_{23}^{(\zeta)} + G_{23}^{(\zeta)} \quad (12.4.6)$$

$$G_1^{(\zeta)} = G_{23}^{(\zeta)} \quad (12.4.7)$$

In this way a single isotropic phase ζ is characterized only by the two elastic constants $G_{23}^{(\zeta)} = G_\zeta$ and $\kappa_{23}^{(\zeta)} = \kappa_\zeta = \lambda_\zeta + G_\zeta$, where λ_ζ is the second Lamé constant.

The formulae to compute lower (superscript *low*) and upper (superscript *up*) bounds to the five elastic moduli for a transversely isotropic composite made by m isotropic phases, each of volume fraction c_r , with $\sum_{r=1}^m c_r = 1$, are the following, where to obtain lower bounds one needs (i) to replace the symbol $\star$ with the symbol *low* in the homogenized moduli and (ii) to give to the constants indicated with subscript $\star$, at the right-hand sides, the lowest values of the same constants among the single phases; to obtain upper bounds, one needs to replace the symbol $\star$ with the symbol *up* in the same way:

$$\kappa_{23}^\star = \left(\sum_{r=1}^m \frac{c_r}{\kappa_r + G_\star} \right)^{-1} - G_\star \quad (12.4.8)$$

$$G_{23}^\star = \left(\sum_{r=1}^m \frac{c_r}{G_r + \frac{G_\star \kappa_\star}{\kappa_\star + 2G_\star}} \right)^{-1} - \frac{G_\star \kappa_\star}{\kappa_\star + 2G_\star} \quad (12.4.9)$$

$$G_1^\star = \left(\sum_{r=1}^m \frac{c_r}{G_r + G_\star} \right)^{-1} - G_\star \quad (12.4.10)$$

$$L^\star = \frac{\sum_{r=1}^m \frac{c_r (\kappa_r - G_r)}{\kappa_r + G_\star}}{\sum_{r=1}^m \frac{c_r}{\kappa_r + G_\star}} \quad (12.4.11)$$

$$N^\star = \sum_{i=1}^m c_i (\kappa_i + G_i) + \frac{\sum_{r=1}^m \left(\frac{c_r (\kappa_r - G_r)}{\kappa_r + G_\star} \sum_{s=1}^m \frac{c_s (\kappa_s - G_s - \kappa_r + G_r)}{\kappa_s + G_\star} \right)}{\sum_{r=1}^m \frac{c_r}{\kappa_r + G_\star}} \quad (12.4.12)$$

Of course, for the case of the core homogenization one must set $m = 3$ (fiberglass, resin and syntactic foam) and, for the homogenization of the skins, $m = 2$ (fiberglass and resin).

The expression of the in-plane Young modulus $E_p^{(0)}$, previously defined, is the following:

$$E_p^{(0)} = \frac{4G_{23}^{(0)} \kappa_{23}^{(0)}}{\kappa_{23}^{(0)} + G_{23}^{(0)} + \frac{(L^{(0)})^2 G_{23}^{(0)}}{\kappa_{23}^{(0)} N^{(0)} - (L^{(0)})^2}} \quad (12.4.13)$$

It is not easy to understand how to combine the upper and lower bounds (12.4.8)–(12.4.12) to obtain upper and lower bounds of the in-plane Young modulus (12.4.13), since this dependence varies with the number of the phases and their relative stiffnesses. For the sandwich here studied, and for the common values of the elastic moduli of the various phases, we have found that the following relationships always give lower and upper bounds of the in-plane Young modulus E_p :

$$E_p^{low} = \frac{4G_{23}^{low} \kappa_{23}^{low}}{\kappa_{23}^{low} + G_{23}^{low} + \frac{(L^{up})^2 G_{23}^{low}}{\kappa_{23}^{low} N^{low} - (L^{up})^2}} \quad (12.4.14)$$

$$E_p^{up} = \frac{4G_{23}^{up}\kappa_{23}^{up}}{\kappa_{23}^{up} + G_{23}^{up} + \frac{(L^{low})^2 G_{23}^{up}}{\kappa_{23}^{up} N^{up} - (L^{low})^2}} \quad (12.4.15)$$

Owing to the microstructural arrangement of the core and of the skins of the sandwich under investigation, for the reasons illustrated at the beginning of this chapter, we shall use the lower bound (12.4.14) as an estimate of Young modulus of the core, and the upper bound (12.4.15) as an estimate of Young modulus of the skins.

An indication about the accuracy of this choice has been sought both for the skins alone and for the core of the sandwich. For the skins experimental results have been obtained by means of uniaxial tension tests performed in our laboratory (Bardella and Genna [13]). The skins were made by the epoxy resin SP Ampreg 20TM described in chapters 2 and 3 (here, we adopt the approximate values $E_r = 3700 \text{ MPa}$ and $\nu_r = 0.4$), with a volume fraction $f_g = 0.342$ of fibers of glass type “E”, which have Young modulus $E_g = 73000 \text{ MPa}$ and Poisson coefficient $\nu_g = 0.23$. The average values of the in-plane Young moduli for this material are $E_p^a = 13720 \text{ MPa}$ in the warp direction and $E_p^e = 16360 \text{ MPa}$ in the weft direction; with the same data the upper bound estimate (12.4.15) is $E_p = 16300 \text{ MPa}$, in reasonable agreement with the experimental results.

We could not perform any experimental test on the core material of the sandwich, made up of syntactic foam mixed with the resin-impregnated glass yarns. Therefore we have tested the accuracy of the predictions given by the lower bound (12.4.14) by means of numerical simulations, performed on a three-dimensional unit cell of the material. The glass yarn, surrounded by resin, has been considered as a cylindrical element of circular cross section; its inner part is made by glass, and a circular ring of resin has been added around it; the volume fraction of glass, in this cylindrical element, has been taken equal to that of the glass in the skins, i.e., $f_g = 0.342$.

The unit cell is prismatic, of height equal to c (thickness of the core) and square basis, whose side has been chosen equal to the average distance between the piles in the sandwich-fabric panel. Periodicity boundary conditions have been prescribed on the vertical sides of the prism. The materials here are the same resin and glass used for the skins, and microspheres taken from the 3M industrial batch of the type K1 [1].

Figure 12.5 shows the used mesh, and figure 12.6 compares both the analytical predictions (12.4.14) and (12.4.15) with the numerical results, for volume fractions of impregnated glass fibers (“pillars”) in the core ranging from $f_p = 0$ to $f_p = 0.2$; actual values of this parameter, for the studied sandwiches, are of the order of $f_p \approx 0.05$. As expected, there is a reasonable agreement of the numerical results with the lower bound estimates.

12.5 Verification of the sandwich model by comparison with experimental results

The homogenization methods described in the previous sections give the values of the elastic moduli of both the skins and the core of the sandwich, considered as homogeneous materials, as function of the geometric and material parameters of their constituents. Therefore, we can treat the sandwich, from now on, as a standard sandwich, and use the relationships summarized in section 12.2 to compute its stiffness in bending.

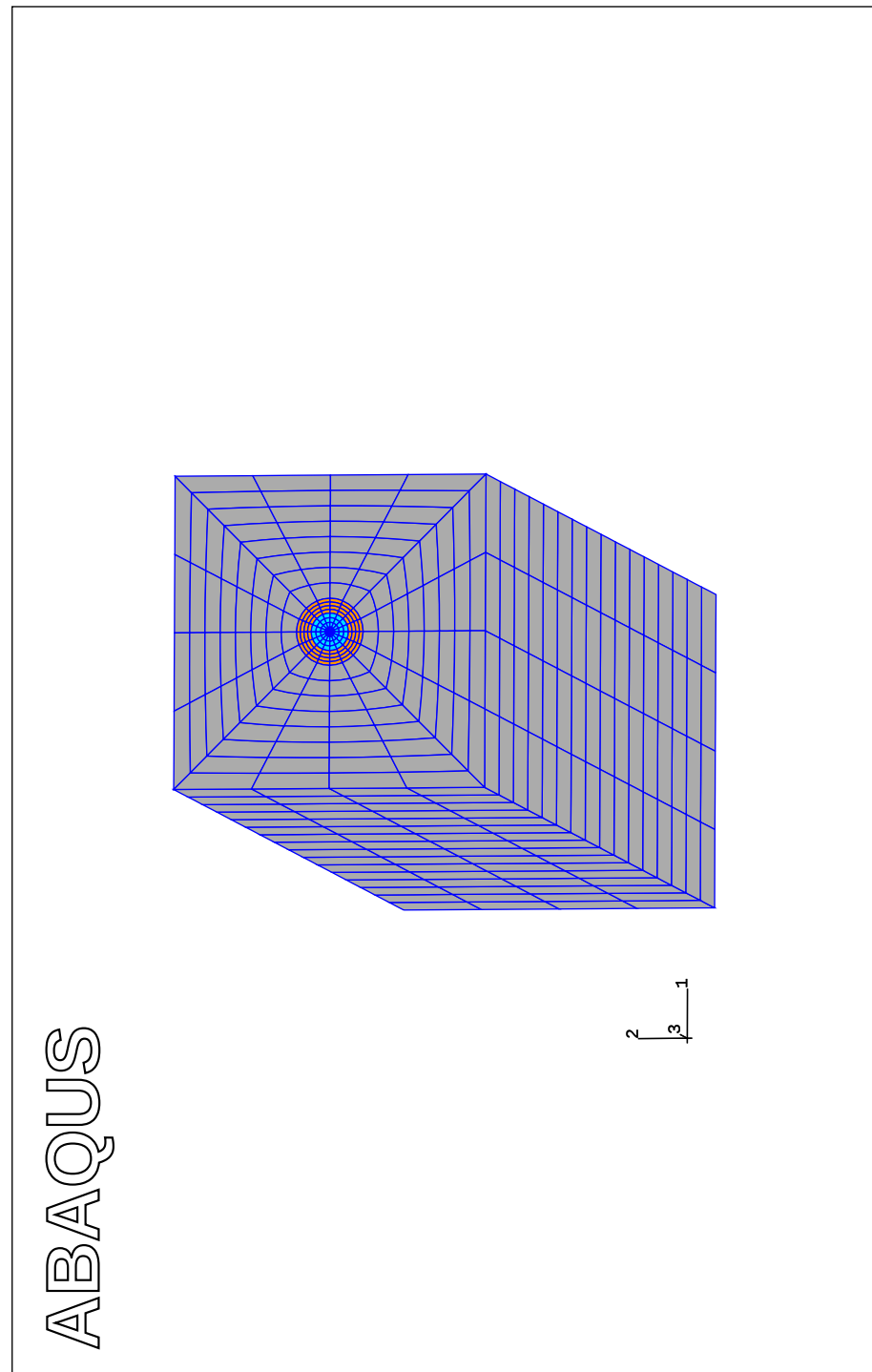


Figure 12.5: *The unit cell model of the sandwich core*

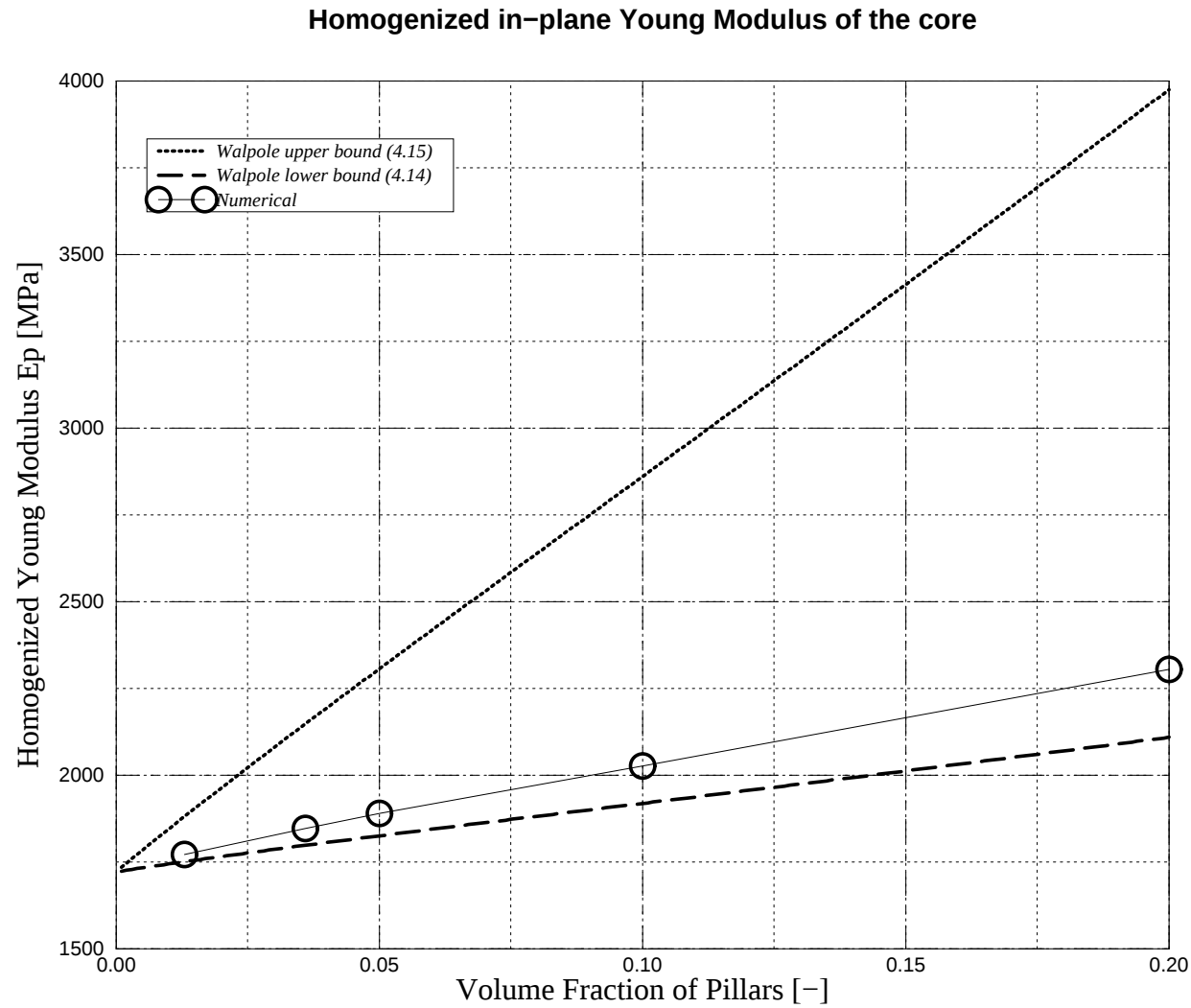


Figure 12.6: *Effective in-plane Young modulus of the core*

In this section we compare the results of the analytical predictions with some experimental results obtained at the Politecnico of Milano [86]. These results refer to a single type of sandwich, and to two different testing modalities: three-point bending and four-point bending.

The basic materials of the sandwich — resin and glass — are of the type already described in the previous section:

- epoxy resin, Young modulus $E_r = 3700 \text{ MPa}$, Poisson coefficient $\nu_r = 0.4$, density $\rho_r = 1.15 \text{ g/cm}^3$;
- glass type “E”, Young modulus $E_g = 73000 \text{ MPa}$, Poisson coefficient $\nu_g = 0.23$, density $\rho_g = 2.6 \text{ g/cm}^3$.

The sandwich-fabric panel is made by resin and glass fibers with volume fraction of glass $f_g = 0.342$. After impregnation of the glass fabric with resin, and after curing, a panel is obtained with skin thickness $t \approx 0.35 \text{ mm}$ and with core thickness c varying in the range $5 \leq c \leq 20 \text{ mm}$. Depending on the desired core thickness, various pillar shapes are obtained, and each pillar, made by many impregnated glass yarns, has a quite variable cross section geometry. Here, the geometry of the “average” pillar, among those observed by us, has always been considered, it has been kept fixed to that of a cylinder, of circular cross section of radius $R = 0.2142 \text{ mm}$. The density of pillars in the core is also variable from one type to the other of sandwich-fabric panel; the most common cases have a density of 25 pillars per square centimeter.

During the curing process of this panel, as said, further layers of impregnated glass fibers are used to thicken the skins, which may reach thicknesses of the order of $1 \div 3 \text{ mm}$. The layers are made by the same glass fibers and resin as the starting panel, with the same volume fractions.

The syntactic foam used to fill the voids in the core of the sandwich-fabric panel is made with the same resin as the panel, and with hollow glass microspheres of the type K1, taken from the industrial batch produced by 3M [1]. These spheres have average diameter $\Phi = 70 \text{ }\mu\text{m}$, and ratio a/b between inner and outer radius equal to $a/b = 0.9836$.

We could compare estimates of the stiffness of such sandwich, as given by the assemblage of the techniques illustrated above, with some experimental results obtained in three- and four-point bending described in [86]. The sandwich beam had length $l = 60 \text{ mm}$, width $B = 30 \text{ mm}$, skin thickness $t \approx 2 \text{ mm}$ and core thickness $c \approx 11 \text{ mm}$.

In computing the analytical predictions of the sandwich deflection we have taken into account the “unwanted” void content in the syntactic foam. In fact, owing to the production modalities of both the syntactic foam and the final sandwich, the sandwich core contained a significant quantity of “unwanted” voids, some of which were clearly visible. The source of the experimental results [86] does not report explicitly the void content of their specimens, but it does give some information, apparently about the same sandwich, referred to different types of testing. According to these data, the average void content of the sandwich core is 30%. Using this information, we could determine the volume fraction of the K1 microspheres present in the syntactic foam filling the core, equal to $f = 0.3877$, and then the effective elastic moduli of the syntactic foam filling the core (using the equations derived in chapter 7): $E_s = 1190 \text{ MPa}$ and $G_s = 456 \text{ MPa}$.

Tables 12.1 and 12.2 summarize the experimental results given in [86]. For the

Specimen	Load P [N]	Displacement δ [mm]	δ/P [mm/N] * 10^4
BBPL2	4991	0.93	1.863
BBPL3	4998	0.54	1.080
BBPC2	4998	0.79	1.581
BBPC3	4989	0.94	1.884
AAPL2	4998	1.36	2.721

Table 12.1: *Three-point bending experimental results [86]*

Specimen	Load P [N]	Displacement δ [mm]	δ/P [mm/N] * 10^4
BBPL2	7988	0.85	1.064
BBPL3	7991	0.75	0.939
BBPC2	7999	1.27	1.588
BBPC3	8003	0.77	0.962
AAPL2	8000	0.89	1.113

Table 12.2: *Four-point bending experimental results [86]*

three-point bending case, the estimate given by the set of analytical tools described in the previous sections furnishes the value $\delta/P = 1.239 \times 10^{-4} \text{ mm/N}$, whereas, for the four-point bending case, the analytical estimate is $\delta/P = 0.9213 \times 10^{-4} \text{ mm/N}$. The experimental results exhibit some dispersion, whose causes are not easily explained (and no attempt at doing that is found in [86]). The analytical results tend to overestimate the stiffness of the sandwich with reference to all the tests, by an average value of about 32% for the three-point bending case, and of 17% for the four-point bending case. Among the possible causes of this discrepancy, beside the uncertainty about the material and geometry data, is the brittleness of the very thin and large K1 spheres, which might break during the production stage of the syntactic foam, thus increasing the “weak phase” content. Another possible explanation lies in the orthotropy of the skins in their plane, neglected by our model, which assumes, as the Young modulus of the skins, a value coincident with the maximum experimental value (in the weft direction — see section 12.4). In any case, considering the complication of the morphology of this sandwich, the obtained results can be considered acceptable from an engineering viewpoint.

12.6 Design of minimum weight panels

We can now turn to the design of an “optimum” sandwich with respect to its elastic stiffness, considering the possibility of changing all the involved geometry and material parameters. We have explored a choice of both resin and microsphere types, by considering, among the design variables, the resin material parameters and the microsphere geometry, defined, for our purposes, only by the ratio a/b . These variables are all discrete variables, taken from a “catalog”. For the resin, we have considered four different materi-

als, whose properties are summarized in Table 12.3. For the microspheres we have made

Resin type	E_r [MPa]	ν_r [–]	ρ_r [g/cm ³]
1	3700	0.4	1.15
2	2800	0.4	1.18
3	4890	0.4	1.24
4	3500	0.4	1.10

Table 12.3: *Resin properties*

reference to the data given by 3M, reported in [1], and summarized, for the part here of interest, in Table 12.4. We have always considered a “perfect” syntactic foam, i.e., one in which neither extra voids are present nor the filler particles break during the production process or under the action of the loads. On the basis of these data, we have explored the

Sphere type	Median diameter [μ m]	a/b [–]	ρ_{sph} [g/cm ³]
K1	70	0.9836	0.125
K15	70	0.9802	0.15
K20	60	0.9734	0.20
S22	40	0.9709	0.22
K25	55	0.9667	0.25
S32	45	0.9569	0.32
K37	50	0.9501	0.37
S38	45	0.9489	0.38
K46	50	0.9376	0.46
S60	30	0.9175	0.60

Table 12.4: *Sphere properties, from 3M Italia [1]*

influence, on the weight of the sandwich, of a number of basic variables:

- resin material parameters, considered as a discrete variable taken from the above “catalog” (Table 12.3); we assume to have used the same resin for producing both the sandwich-fabric panel and the syntactic foam;
- microsphere material parameters, considered as a discrete variable taken from the above “catalog” (Table 12.4);
- volume fraction f of microspheres in the syntactic foam; this is a continuous variable, varied in the interval $0.4 \leq f \leq 0.6$; the lower limit is based on engineering considerations, whereas the upper one is the technological packing limit of the microsphere–resin mix;
- we have kept fixed the volume fraction of glass fibers in the skins and in the pillars of the core to the value $f_g = 0.342$; this constraint, however, could easily be removed in this theoretical analysis;

- core thickness c , continuously varying in the interval $5 \leq c \leq 100 \text{ mm}$;
- skin thickness t , continuous variable, constrained to be smaller than c ;
- distance between the pillars in warp direction, b_a , and in weft direction, b_e , continuous variables constrained to be larger than the diameter of one pillar for obvious reasons. As already said, the diameter of one pillar has been kept fixed in this analysis, to the value $2R = 0.4284 \text{ mm}$; also this information could easily be considered as a design variable.

We then want to find the set of the preceding values which minimizes the total weight W of a sandwich beam of length l and width B (such as schematically shown in figure 12.2)

$$W = gBl \left[2\rho_{sk}t + \frac{\rho_p \pi R^2 c}{b_a b_e} + \rho_s \left(c - \frac{\pi R^2 c}{b_a b_e} \right) \right] \quad (12.6.1)$$

where g is gravity's acceleration, ρ_p is the pillar density (in our case equal to the skin density, and computed on the basis of the resin density indicated in Table 12.3, the glass density $\rho_g = 2.6 \text{ g/cm}^3$ and the prescribed volume fraction of glass in the composite, $f_g = 0.342$) and ρ_s is the density of the syntactic foam, computed on the basis of the resin and particle densities and on the sphere volume fraction f .

We have here chosen to perform the minimization under the constraint given by equation (12.2.8), i.e., in such a way that the final sandwich has a constant stiffness with respect to the three and four-point bending test. Extending this constraint to more general loading and geometry conditions requires the knowledge of relationships analogous to (12.2.8)–(12.2.10), valid, for instance, for bending of plates, etcetera. The overall beam geometry here considered is $l = 200 \text{ mm}$ and $B = 50 \text{ mm}$; we have started with the three-point bending case, i.e., by setting $l_p = 0$ in equations (12.2.9)–(12.2.10).

The minimization of the total weight (12.6.1) is obviously nonlinear, and can not be performed by means of standard procedures. We have therefore both studied the objective function as a function of some of the design variables, in order to understand what type of minima are to be sought, and subsequently implemented a very simple search algorithm, able to compute a global minimum at a rather high cost. The algorithm requires, at each step, having chosen a set of independent variables, the following computations:

- elastic moduli of the skins, based on equations (12.4.10) and (12.4.15);
- elastic moduli of the syntactic foam, based on the equations reported in chapter 7;
- elastic moduli of the core, based on equations (12.4.10) and (12.4.14);
- bending stiffness of the sandwich (equation (12.2.11));
- shear stiffness of the sandwich (equations (12.2.15)–(12.2.18));
- solution of the nonlinear equation (12.2.8), where the ratio δ/P is assumed as a given datum; in our computations it has been kept fixed at the value $\delta/P = 0.001 \text{ mm/N}$. This operation, rather involved owing to the strong nonlinearity of the problem, allows us to eliminate one design variable from the variable set; we have here chosen to eliminate the skin thickness t ;

- computation of the weight of the sandwich and selection of the minimum among all those computed previously.

It is obvious that even a single optimization step requires a considerable effort. For this reason, before performing the optimization, we have studied the behavior of the objective function keeping fixed several design variables and varying the remaining ones. The results of this preliminary analysis are shown in figures 12.7 to 12.12.

Figure 12.7 illustrates the variation of the sandwich weight consequent to the variation of the resin choice, for all the microspheres used in the analysis. In this case the resin material parameters have been considered as continuous variables; the density has been taken as an independent variable and the Young modulus has been correlated linearly to the density, as a first approximation on the safe side, on the basis of results given in Ashby [7], by means of the following relationship

$$E_r = 4750\rho_r - 1848, \quad 0.5 \leq \rho_r \leq 2.5 \quad (12.6.2)$$

in which the Young modulus is expressed in MPa and the density in g/cm^3 . All the other variables (with the exception of t) are set fixed at their “optimum” values, which we will comment about later in this section.

It is apparent from figure 12.7 that the “best” sandwich, with respect to the stiffness constraint (12.2.8), is always found using the lightest resin and the lightest microspheres. We will see in a moment that this tendency carries out with respect to more or less all the other design variables.

Figure 12.8 illustrates the effect of varying the volume fraction of microspheres in the syntactic foam, for the four resin types here considered and for the lightest and heaviest sphere types. Again, the best sandwich is always that made up of the lightest ingredients, which means the maximum possible volume fraction of the lightest microspheres in the lightest resin.

Figure 12.9 relates to the choice of the microsphere stiffness, as if it were a continuous variable. We have computed the sandwich weight, always under constraint (12.2.8), as function of the ratio a/b ; values of a/b smaller than 0.7 result in unfeasible solutions. It can be seen that, in this case, there is an optimum inclusion stiffness, given by ratios a/b very close to the unity, without being equal to 1 (which would mean standard foams, with void inclusions). This indicates that even with the objective of minimum weight syntactic foams are preferable to standard foams. In the case of sandwiches which may be employed in underwater applications standard foams are to be avoided in any case.

In figure 12.10 we have explored the influence of a variable which has actually been kept fixed in the analysis, for the said reasons, i.e., the radius of a pillar in the core. It can be seen that, again, the lightest internal microstructure always gives the best sandwich, in our situation. The chosen value $R = 0.2142 \text{ mm}$ is not optimal, but definitely close to it.

Figure 12.11 shows the influence on the sandwich weight of the pillars density in the core. It is readily seen that the smaller is the number of pillars the lighter is the resulting structure, even if the stiffness constraint (12.2.8) is always prescribed. This conclusion, however, can not be taken into too much consideration, owing to the delamination problems mentioned in section 12.1, which will be briefly re-addressed later on. In our analysis

we have set, as a lower limit to the pillar density, the value of 25 pillars per square centimeter, which means, for equal spacing in the warp and weft directions, $b_a = b_e = 2 \text{ mm}$.

Finally, figure 12.12 shows the effect of the variation of the core thickness (related to that of the skin thickness by the constraint (12.2.8)) on the sandwich weight. Despite all the nonlinearities of the problem we have here a well defined single, absolute minimum for all the resins and the microspheres examined. On the basis of these results it is possible to set up a very much reduced optimization procedure of the sandwich than the general one previously illustrated. One can in fact choose the lightest resins and microspheres, use the highest possible volume fraction of spheres and use the lightest possible sandwich-fabric panel (the smallest pillar density compatible with delamination risks), and thus eliminate several design variables from his problem, which is reduced to two variables only, the thicknesses of the core c and of the skins t .

It is then possible to operate at different levels of approximation. If one computes the stiffness of the sandwich as indicated (i.e., using equation (12.2.8) and (12.2.15)–(12.2.18)) one obtains the “exact” result. A first approximation, which we indicate as approximation 1, may consist of choosing the much simpler expression (12.4.10) for the shear stiffness. In this case it is possible to express the variable t as function of c , using the approximation $d \approx c$ and always considering the three-point bending case $l_p = 0$, through equation (12.2.8), obtaining

$$t(c) = -\frac{c}{2} - \frac{\sqrt[3]{cE_{sk}^2 \left(l - 4BcG_c \frac{\delta}{P}\right)^2 \left[c^2lE_{sk} - c^2lE_c - l^3G_c + 4Bc^3E_cG_c \frac{\delta}{P} - 4Bc^3E_{sk}G_c \frac{\delta}{P}\right]}}{2E_{sk} \left(l - 4BcG_c \frac{\delta}{P}\right)} \quad (12.6.3)$$

Inserting expression (12.6.3) into equation (12.6.1) and equating to zero the derivative of the result with respect to c one obtains a nonlinear equation in c which can be solved through Newton’s method. We will comment about results in a moment.

A cruder approximation (approximation 2) can be obtained by adopting both the thin skins and the antiplane core expressions for both the bending and the shear stiffness, i.e., equations (12.4.9) and (12.4.10). Again, setting $d \approx c$, $l_p = 0$ and solving equation (12.2.8) for t one gets

$$t(c) = \frac{G_c l^3}{6E_{sk} c \left(4BcG_c \frac{\delta}{P} - l\right)} \quad (12.6.4)$$

and, inserting this result into (12.6.1) and making it stationary with respect to c , one obtains a fourth-order algebraic equation in c which can be solved in closed-form.

We can finally discuss the obtained results. As said, the best sandwich is essentially the lightest one, even if not necessarily made with the stiffest materials. The set of “optimum” parameters, as given by the “exact” optimization procedure, is the following:

- resin type 4 of Table 12.3;
- microspheres type K1 of Table 12.4;
- $c^{opt} = 16.21 \text{ mm}$;

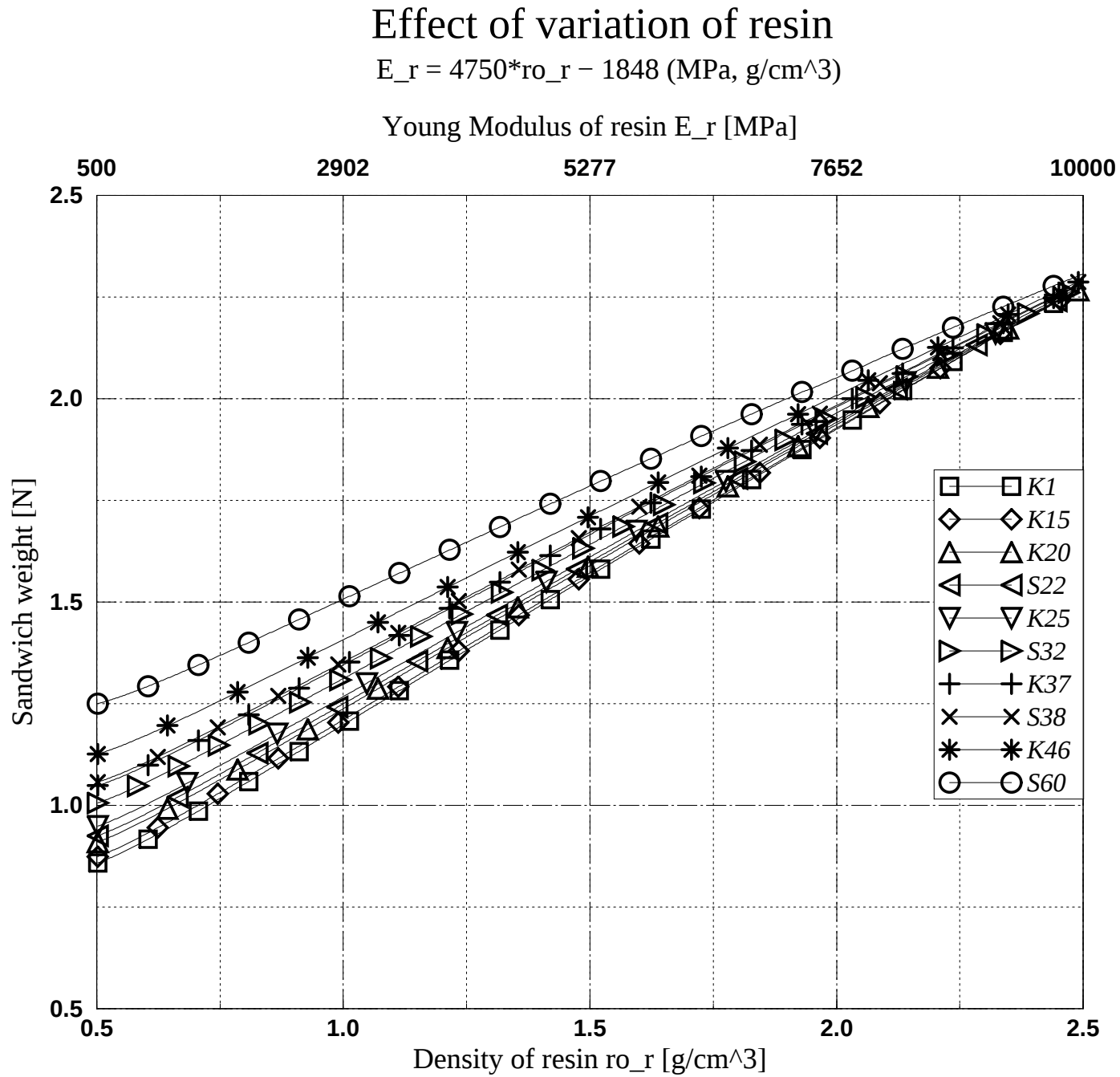


Figure 12.7: Effect of the resin on the sandwich weight

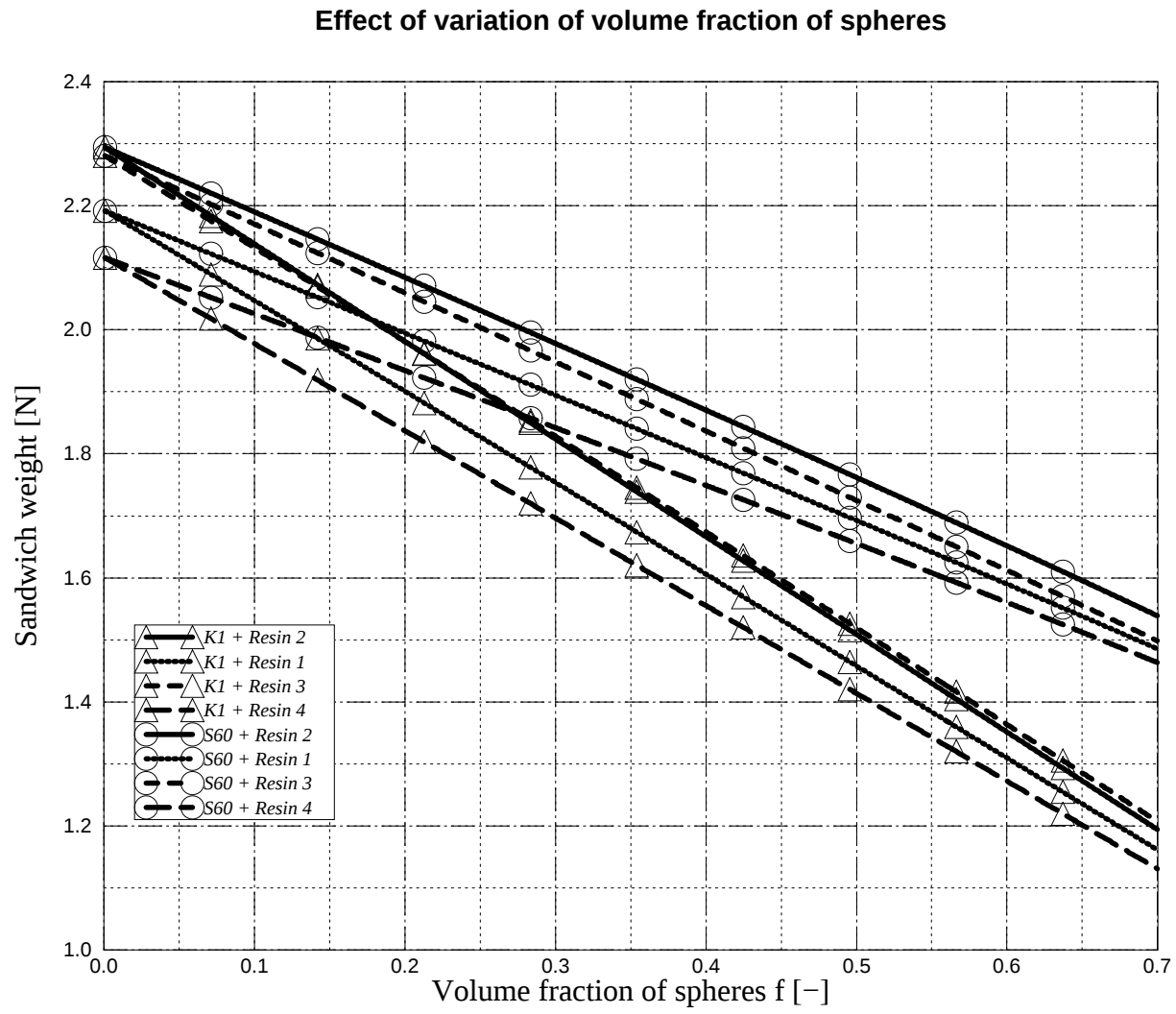


Figure 12.8: Effect of the volume fraction of spheres on the sandwich weight

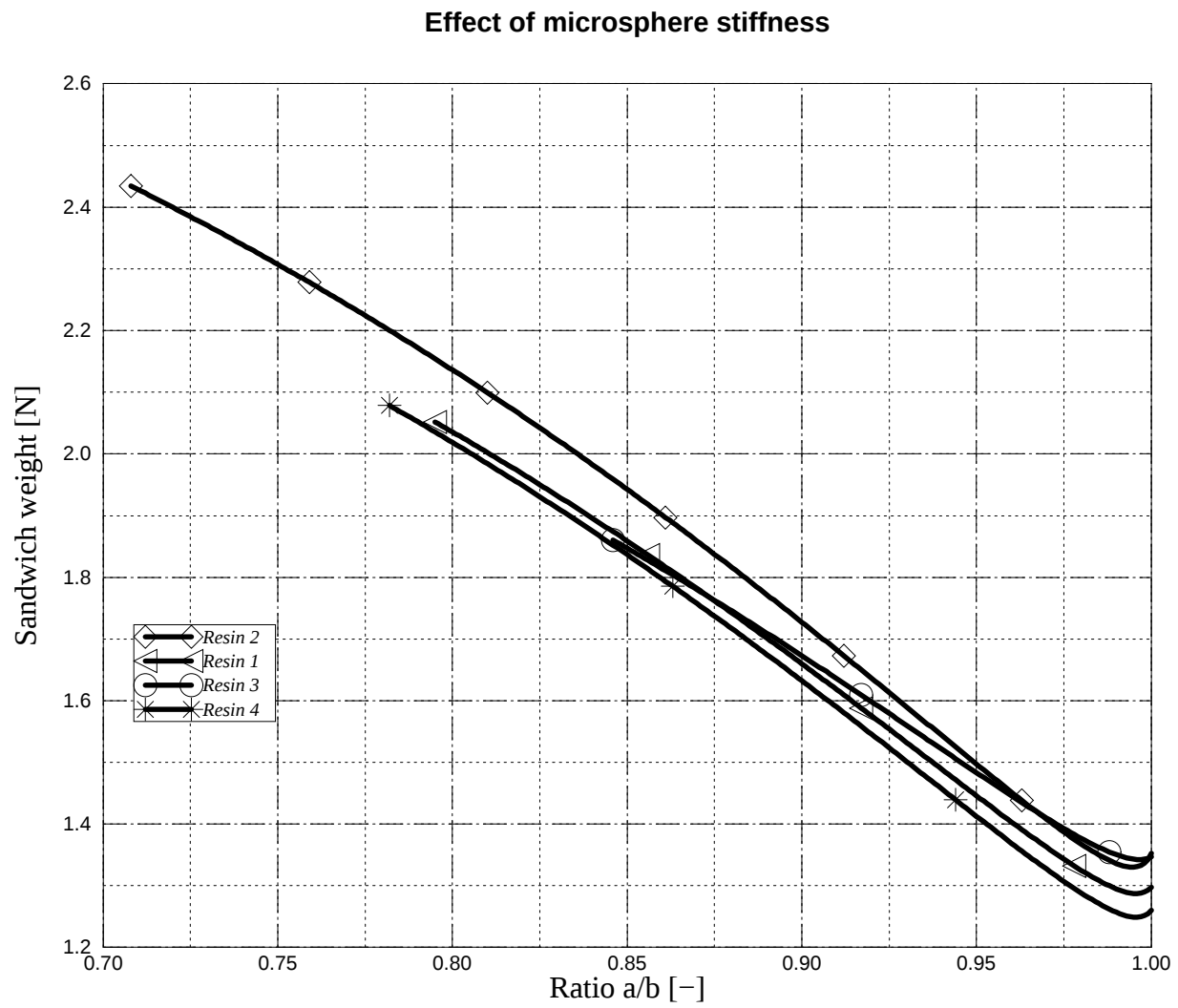


Figure 12.9: *Effect of the hollow sphere geometry on the sandwich weight*

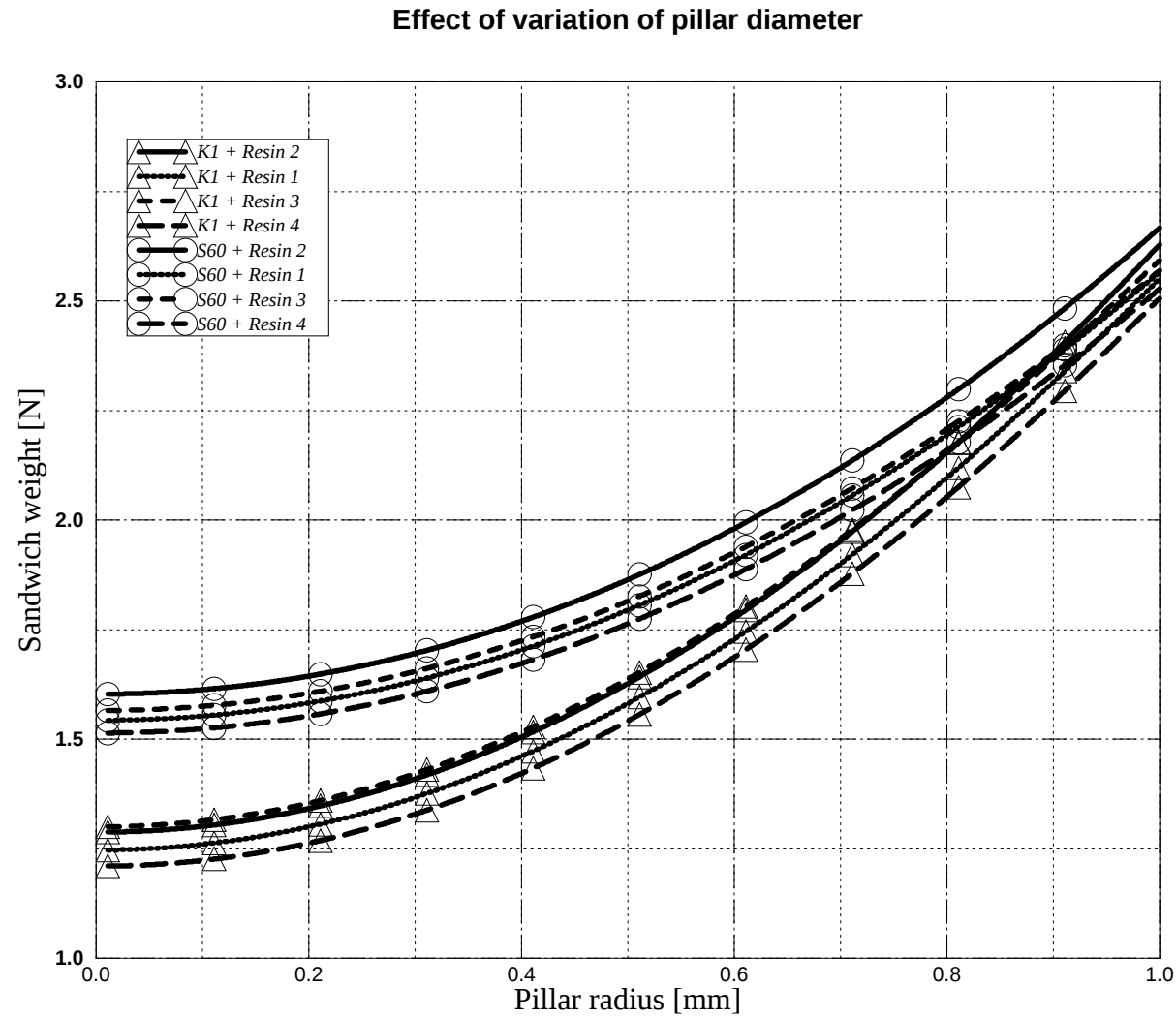


Figure 12.10: Effect of the pillar diameter on the sandwich weight

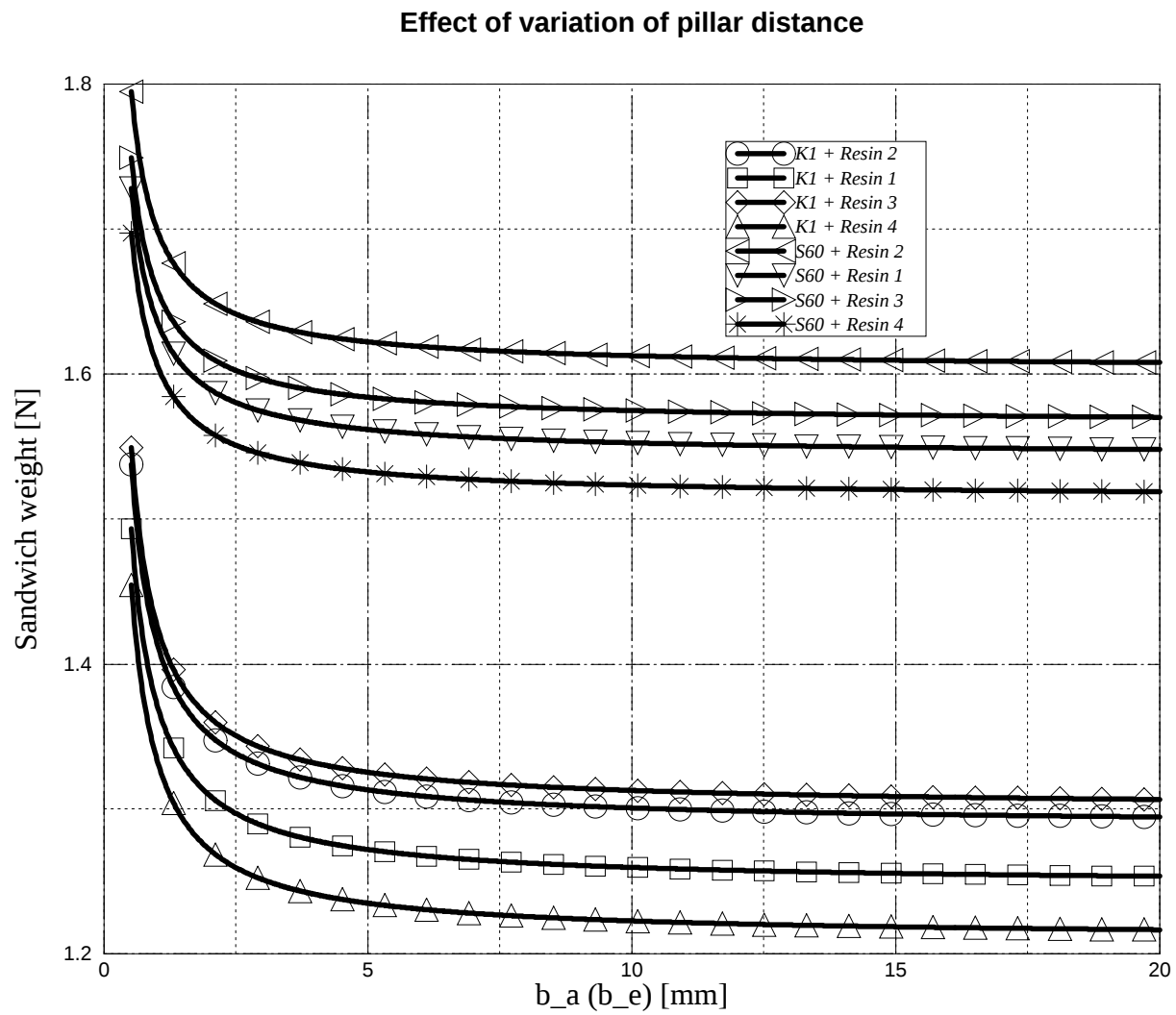


Figure 12.11: *Effect of the pillar distance on the sandwich weight*

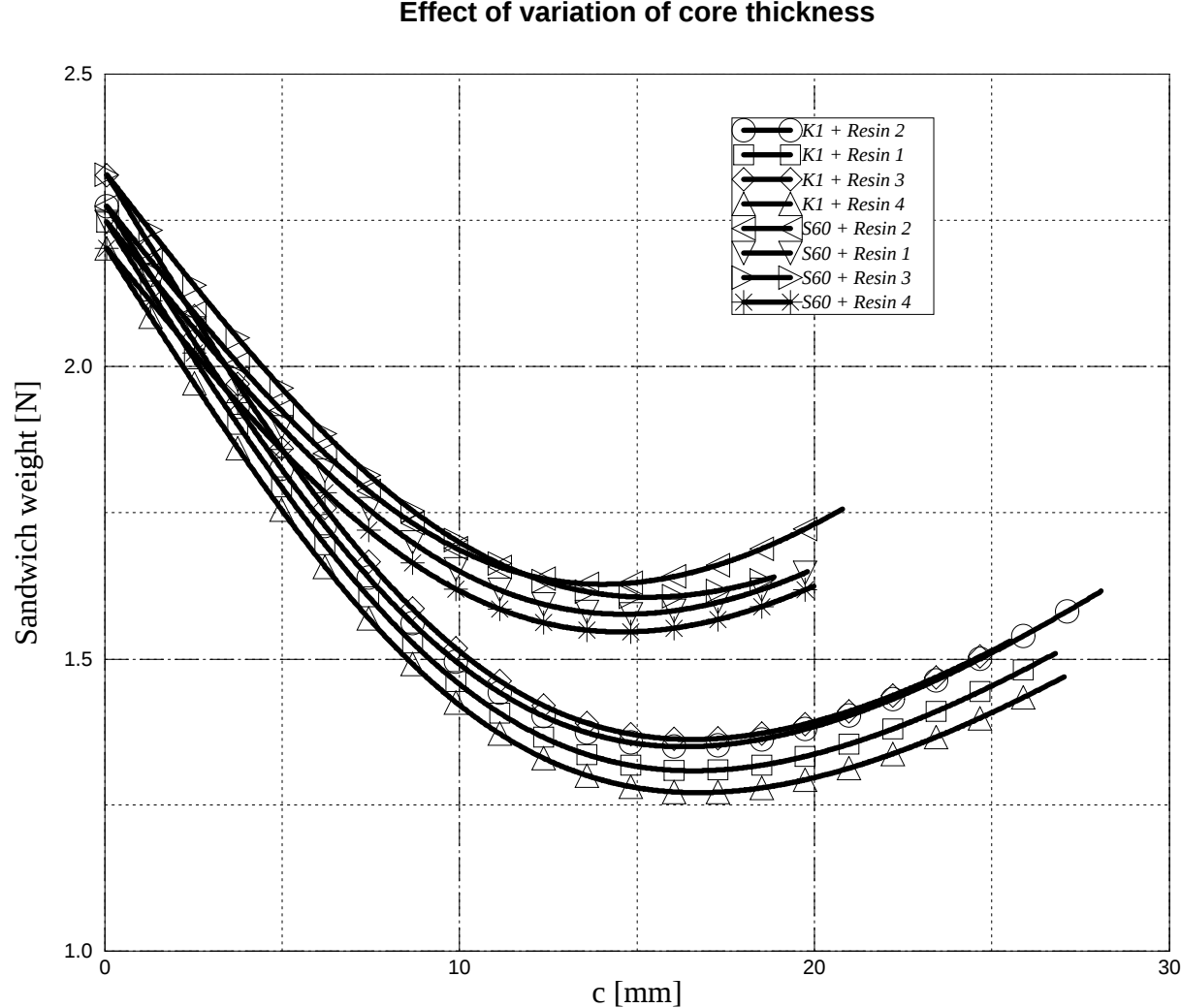


Figure 12.12: Effect of the core thickness on the sandwich weight

- $t^{opt} = 1.16 \text{ mm}$;
- $f^{opt} = 0.6$ (maximum value allowed during the analysis);
- $b_a^{opt} = b_e^{opt} = 2.0 \text{ mm}$ (maximum values allowed during the analysis);
- skin properties: $E_{sk} = 16060 \text{ MPa}$; $G_{sk} = 4852 \text{ MPa}$;
- syntactic foam properties: $E_s = 2076 \text{ MPa}$; $G_s = 783 \text{ MPa}$;
- core properties: $E_c = 2160 \text{ MPa}$; $G_c = 811 \text{ MPa}$;
- beam stiffnesses: $D = .179 \times 10^9 \text{ N mm}^2$; $(GA^*) = .723 \times 10^6 \text{ N}$.

The sandwich weight is then $W_{min} = 1.249 \text{ N}$, which corresponds to a sandwich density $\rho = 0.687 \text{ g/cm}^3$. To give an idea of the save in weight, with respect to a conventional beam, we may say that a beam of same length and width, made by a standard fiberglass reinforced resin ($E = 16000 \text{ MPa}$, $\rho = 1.8 \text{ g/cm}^3$), in order to exhibit the same stiffness needs a height $h = 14 \text{ mm}$ and a weight of about 2.5 N .

The two approximate optimization methods described above, applied by using the homogenized Young moduli of the “optimum” sandwich, yield the following results:

- 1. approximation 1: $t^{opt} = 1.13 \text{ mm}$, $c^{opt} = 16.4 \text{ mm}$;
- 2. approximation 2: $t^{opt} = 1.452 \text{ mm}$, $c^{opt} = 17.535 \text{ mm}$.

Only the first result can be considered reasonable from the engineering viewpoint; it is clear that the most important error is introduced, for this sandwich, by the assumption of thin skins and antiplane core in the bending stiffness D (approximation 2), and not by the use of the simple formula (12.4.10) for the shear stiffness instead of the more complex (12.2.15)–(12.2.18).

We conclude this section by adding the results for the four-point bending case, in order to give an example of how the loading condition affects the design of the sandwich. By setting $l_p = l/3$ as the distance between the points of application of the concentrated forces in equations (12.2.8)–(12.2.11), one obtains the following “exact” results:

- resin type 4 of Table 12.3;
- microspheres type K1 of Table 12.4;
- $c^{opt} = 15.205 \text{ mm}$;
- $t^{opt} = 1.1 \text{ mm}$;
- $f^{opt} = 0.6$ (maximum value allowed during the analysis);
- $b_a^{opt} = b_e^{opt} = 2.0 \text{ mm}$ (maximum values allowed during the analysis);
- beam stiffnesses: $D = .149 \times 10^9 \text{ N mm}^2$; $(GA^*) = .679 \times 10^6 \text{ N}$.

The approximate results exhibit the same type of error as in the three-point bending case.

The sandwich weight is in this case $W_{min} = 1.175 \text{ N}$, which corresponds to a sandwich density $\rho = 0.688 \text{ g/cm}^3$. The same “conventional” fiberglass reinforced resin beam described above, designed to exhibit the same stiffness in four-point bending, has height $h = 12.87 \text{ mm}$ and weighs 2.32 N . In both loading cases the save in weight is of the order of 50%.

12.7 Open issues and conclusions

The optimization procedure outlined in this chapter can be seen only a first step in the design of a sandwich which may be produced for a large-scale utilization. There is a number of problems still to be addressed, and even in the elastic range the conclusions indicated by this first analysis can not be accepted without further scrutiny.

We can immediately observe that optimization is possible with respect to several other loading and geometry conditions; it is well known that different optimal microstructures are required depending on the stress type — axial loading versus beam bending or plate bending or fully three-dimensional stress states. The extension of the analysis procedure followed here to all these loading conditions does not pose, however, conceptual difficulties.

Another issue to be addressed is the influence of the pillar shape on the overall sandwich behavior. This parameter is of the utmost importance in the behavior of the sandwich-fabric panel alone, as shown in [121]. It is however very likely that in the filled sandwich this aspect loses some significance; in fact, in the sandwich, owing also to the extremely low volume fraction of the pillars (of the order of 5%), the core properties, with reference to the sandwich bending and shear stiffness, are essentially those of the syntactic foam (this is confirmed also by the very small difference between the elastic moduli of the foam and those of the homogenized core given as “optimal” in the previous section). Such analysis, in any case, would require microstructural techniques more sophisticated than the simple homogenization methods used in this work.

As said, the conclusions reached with respect to the elastic stiffness can not be accepted without some reserve. The optimum sandwich, with reference to its elastic stiffness only, is made by the lightest ingredients, i.e., the lightest resin and the maximum possible volume fraction of the lightest K1 microspheres, with the lowest possible density of pillars in the core. All these choices have of course some drawbacks, which need careful examination when designing a sandwich. The light K1 glassy microspheres, for instance, tend to break during the production process of the syntactic foam, thus introducing both a degradation of the stiffness and a path for permeability. This reason alone may be sufficient to reconsider such choice.

The quest for a light core might suggest the use of non-glassy inclusions, or even to mix particulate inclusions with air. These are possible solutions which need careful examination, outside the scope of this work. A possible solution might be the use of phenolic microspheres, as done in Bunn and Mottram [31]; we have presently no experience of such materials.

Also the density of pillars creates conflicting indications. As said, the pillars give almost no contribution, in bending and in shear, to the elastic stiffness, but they are essential to guarantee the absence of risk of delamination between skins and core. This brings us to issues of strength, not addressed here. The only result obtained so far with reference to delamination indicates that, for standard beam applications, a minimum density of pillars (i.e., the 25 pillars per square centimeter already used in the production of the prototype sandwich) is more than enough to guarantee the ability of carrying the shear stress arising in three-point bending (Bardella and Genna [13]).

Nothing has been done so far in the field of nonlinear analysis of the final sandwich (whose internal complexity poses a rather formidable problem), with the exception of what addressed in this thesis about the nonlinear behavior of syntactic foams. We are aware of

some research done on the nonlinear behavior of woven fabric composites (see, for instance, [109] and references therein quoted), but in all cases on two-dimensional fabric.

The results described in section 12.6 indicate that, despite the remarkable internal complexity of this sandwich, its minimum weight design, with respect to the elastic behavior only and with reference to specific geometry and loading conditions, does not require sophisticated optimization techniques. This conclusion should help practicing engineers in designing such sandwiches for large-scale production.

Chapter 13

Effective thermal expansion coefficient

The fundamental hypothesis for homogenizing the thermal expansion coefficient consists of assuming steady state heat conduction (i.e., we neglect the transient states and account for the quasi-static case of uniform temperature distribution only), which implies that when a temperature increment ΔT is imposed at the RVE boundary, the same temperature increment affects all the phases. Besides, the thermal and mechanical behaviors are uncoupled.

More details about the here exploited theory can be for instance found in [43] (see also section 17.4 in which the general Transformation Field Analysis will be briefly described).

By letting the properties of each phase being dependent upon the absolute temperature T , the local thermoelastic behavior of a heterogeneous material subjected to a temperature increment ΔT is defined by the constitutive relations:

$$\sigma_{ij}(\mathbf{x}) = L_{ijkl}(\mathbf{x}, T)\varepsilon_{kl}(\mathbf{x}) + l_{ij}(\mathbf{x}, T)\Delta T \quad (13.0.1)$$

$$\varepsilon_{ij}(\mathbf{x}) = M_{ijkl}(\mathbf{x}, T)\sigma_{kl}(\mathbf{x}) + m_{ij}(\mathbf{x}, T)\Delta T \quad (13.0.2)$$

in which, as in equation (6.1.17), the local stiffness $L_{ijkl}(\mathbf{x}, T)$ reads

$$L_{ijkl}(\mathbf{x}, T) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) L_{ijkl}^{(r)}(T) \quad (13.0.3)$$

and the local *thermal stress vector* $l_{ij}(\mathbf{x}, T)$ and the local *thermal strain vector* $m_{ij}(\mathbf{x}, T)$ read:

$$l_{ij}(\mathbf{x}, T) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) l_{ij}^{(r)}(T) \quad (13.0.4)$$

$$m_{ij}(\mathbf{x}, T) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) m_{ij}^{(r)}(T) \quad (13.0.5)$$

being, for each isotropic phase r :

$$m_{ij}^{(r)}(T) = \alpha^{(r)}(T)\delta_{ij} \quad (13.0.6)$$

and

$$l_{ij}^{(r)}(T) = -L_{ijkl}^{(r)}(T)m_{kl}^{(r)}(T) \quad (13.0.7)$$

where $\alpha^{(r)}(T)$ is the thermal expansion coefficient of the phase r , generally also dependent on the temperature T .

The goal is to estimate, for a macroscopically isotropic medium, the overall thermal expansion coefficient $\alpha^{(0)}(T)$ which enters into the global constitutive law through the effective thermal stress and strain vectors ($l_{ij}^{(0)}(T)$ and $m_{ij}^{(0)}(T)$ respectively):

$$\Sigma_{ij} = L_{ijkl}^{(0)}(T)E_{kl} + l_{ij}^{(0)}(T)\Delta T \quad (13.0.8)$$

$$E_{ij} = M_{ijkl}^{(0)}(T)\Sigma_{kl} + m_{ij}^{(0)}(T)\Delta T \quad (13.0.9)$$

$$m_{ij}^{(0)}(T) = \alpha^{(0)}(T)\delta_{ij} \quad (13.0.10)$$

$$l_{ij}^{(0)}(T) = -L_{ijkl}^{(0)}(T)m_{kl}^{(0)}(T) \quad (13.0.11)$$

The Levin equations (Levin [81]) allow us to estimate the effective thermal stress and strain vectors after having evaluated the strain localization and the stress concentration tensors averaged over each phase by means of a suitable homogenization method (e.g., one of either those reviewed in chapter 6 or, for syntactic foams, those proposed in chapter 7):

$$m_{ij}^{(0)}(T) = \sum_{r=1}^N c_r m_{kl}^{(r)}(T) \bar{B}_{klij}^{(r)}(T) \quad (13.0.12)$$

$$l_{ij}^{(0)}(T) = \sum_{r=1}^N c_r l_{kl}^{(r)}(T) \bar{A}_{klij}^{(r)}(T) \quad (13.0.13)$$

Since, as above outlined, we are interested in isotropic local and overall properties (such as syntactic foams have), we can simplify equations (13.0.10)–(13.0.13) into:

$$\alpha^{(0)}(T) = \frac{1}{3K^{(0)}(T)} \sum_{r=1}^N c_r K^{(r)}(T) \alpha^{(r)} \bar{A}_{ijij}^{(r)}(T) \quad (13.0.14)$$

in which both subscripts i and j have to be saturated.

By exploiting equations (7.3.11) and (7.3.12) of section 7.3 and the method proposed in section 7.4, equation (13.0.14) can be written for the general case of a syntactic foam in which both the filler gradation and the “unwanted” voids have to be accounted for:

$$\alpha^{(0)} = \frac{1}{K^{(0)}} \left((1-f) K^{(m)} \alpha^{(m)} \sum_{\lambda=1}^N f_{\lambda} P_1^{(\lambda)}(\theta=1) + f K^{(i)} \alpha^{(i)} \sum_{\lambda=1}^N f_{\lambda} \left(1 - \frac{a_{\lambda}^3}{b_{\lambda}^3}\right) J_1^{(\lambda)}(\theta=1) \right) \quad (13.0.15)$$

in which we have neglected the temperature dependence for simplicity of notation and the dimensionless coefficients $P_1^{(\lambda)}(\theta=1)$ and $J_1^{(\lambda)}(\theta=1)$ are obtained by solving the system (7.3.5)–(7.3.10), for each MRP λ , in which the imposed isotropic deformation θ has to be set equal to 1.

Note that to solve equation (13.0.15) there is the need of computing the effective bulk modulus first. If the syntactic foam can be characterized by one composite sphere only,

equation (13.0.15) becomes very simple, since in that case the bulk modulus homogenization is uncoupled from the shear modulus homogenization and, therefore, only equation (7.3.14) for $K^{(0)}$ is needed.

From Ashby [7], we can see that the coefficient of linear thermal expansion of the glass, $\alpha^{(i)}$, ranges from $3.5 \times 10^{-6} \text{ K}^{-1}$ to $9. \times 10^{-6} \text{ K}^{-1}$, whereas that of epoxy resins, $\alpha^{(m)}$, ranges from $5. \times 10^{-5} \text{ K}^{-1}$ to $10. \times 10^{-5} \text{ K}^{-1}$; these values depend on the materials but not on the temperature, which is taken constant at room conditions. Therefore, we can now evaluate the value of the effective coefficient of thermal expansion of syntactic foams type 1 and 6 described in chapters 4 and 9. By taking the elastic moduli of the glass as $E^{(i)} = 77500 \text{ MPa}$ and $\nu^{(i)} = 0.23$ and, for the epoxy resins, those of the DGEBA DER 332 cured with DDM 32950, i.e. $E^{(m)} = 2800 \text{ MPa}$ and $\nu^{(m)} = 0.41$, one can obtain the graphic plotted in figure 13.1, which is nearly linear between the extreme values $\alpha^{(m)} = 5. \times 10^{-5} \text{ K}^{-1}$ and $\alpha^{(i)} = 5. \times 10^{-6} \text{ K}^{-1}$ (reached for volume fraction of filler tending to 1; note that a free hollow sphere expands like a solid one). Figure 13.1 refers to the fillers K37 and H50, characterized by the data reported in Tables 10.1 and 10.2; anyway, the evaluation of equation (13.0.15) by means of one mean composite sphere only furnishes almost identical results in this case. It is interesting to note that the effective linear thermal expansion coefficient appears to be almost independent upon the microsphere thickness.

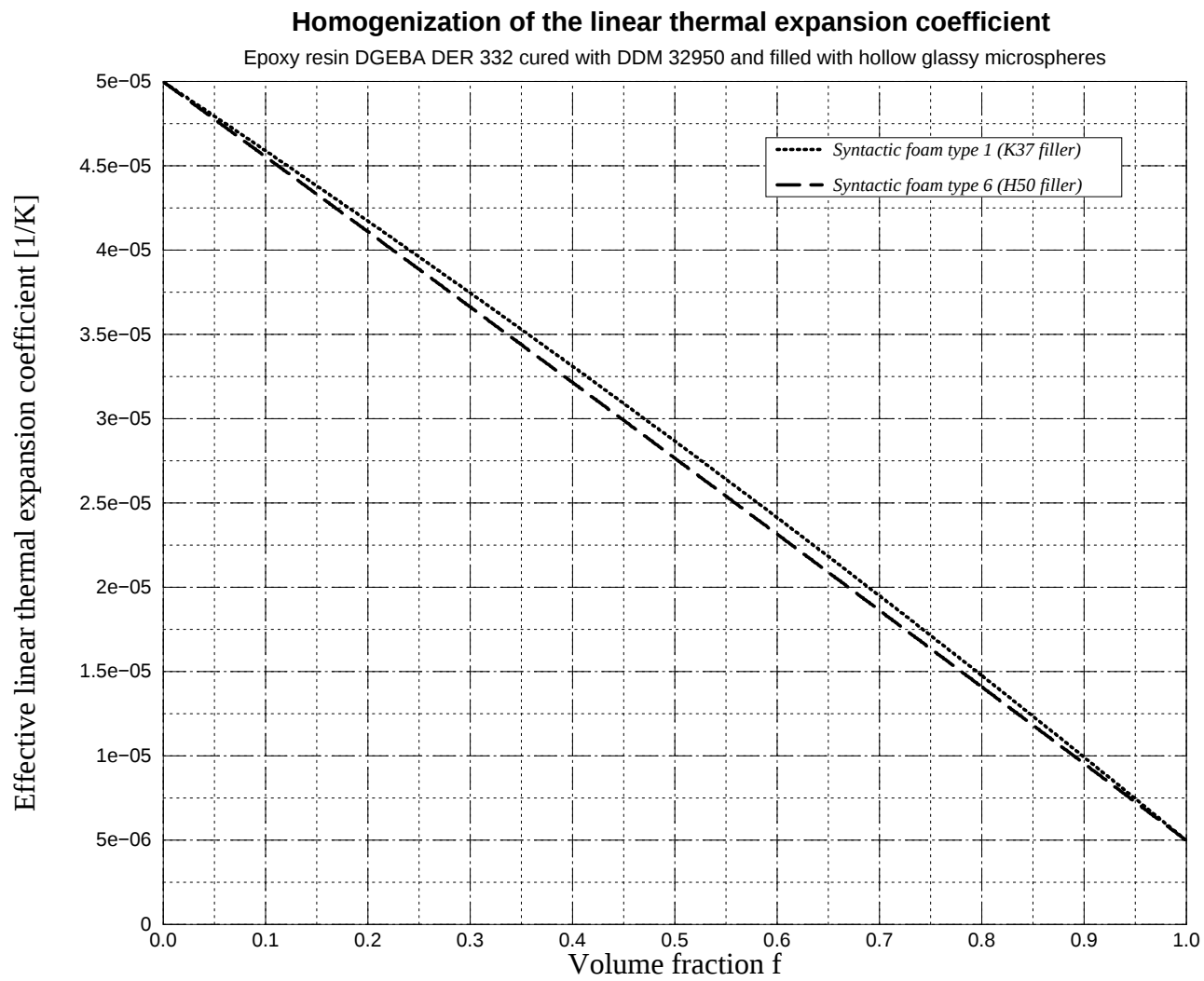


Figure 13.1: *Effective thermal expansion coefficient*

Part III

Inelastic and nonlinear behavior

Chapter 14

Introduction

The analysis of the syntactic foam behavior outside the linear elastic range can be tackled by means of several different approaches.

One could develop a phenomenological constitutive law, based on the experimental evidence, for any particular syntactic foam, seen as a homogeneous material, made up of particular phases at fixed volume fraction. This kind of approach has been followed in [101], where a bimodulus constitutive law of the Drucker–Prager type has been identified in order to fit the experimental data for the syntactic foam type 5, whose average elastic moduli have been reported in section 4.5. This “phenomenological method” has the crucial drawback that it furnishes constitutive models whose expressions look completely unrelated to both the mechanical properties and the geometrical data of the phases. Thus, it can not be used to design the composite. Furthermore, if constitutive models are needed for different syntactic foams, it is necessary to identify a macroscopic constitutive law, operation which may involve a lot of work, for any different syntactic foam composition, after corresponding experimental results are made available.

Here, we shall focus on the micromechanical approach based on the homogenization theory which, in principle, can provide constitutive models able to predict the final macroscopic properties of the composite as functions of its constituents. This capability, for instance, allows one to design the best composite for a given application (see previous chapter 12 for an example in the linear elastic range).

In our case of epoxy resins filled with glassy microspheres, since the filler is taken linear elastic until failure, it is necessary to have an accurate constitutive law for epoxy resins. Since we could not find in the literature a constitutive law suitable for epoxy resins, we have developed a model to predict their viscoelastic nonlinear behavior prior to yield (chapter 16). This constitutive model, partly based on a statistical interpretation of the kinematics of the epoxy macromolecule, will be derived in order to be representative of the experimental results obtained in chapter 3. In particular, it will be shown to be able to predict the most salient features of the epoxy resin cyclic behavior. Then, this constitutive model will be used to investigate the syntactic foams behavior before failure by means of unit cell analyses (section 16.6).

In the first attempt of accomplishing an analytical homogenization of the syntactic foam behavior beyond the linear elastic range (see next chapter 15), we shall take the instance of a linear viscoelastic matrix (in a linear elastic filler), which might be the case of some real polymeric binder subjected to a low stress level. This case is interesting

since it allows the use of the correspondence principle which furnishes an “exact” inelastic homogenization as long as the linear elastic homogenization procedure which it is based on can accurately predict the dependence of the effective linear elastic moduli on the mechanical and geometrical data of the phases for the real RVE. The main problem of such a method is that the analytical manipulations may require some difficult complex analysis. Anyway, for a simple but meaningful case, we shall derive a result useful to comment other homogenization methods later either reviewed specifically derived.

Chapter 17 will be devoted to reviewing some homogenization methods for composites in the nonlinear or inelastic range. In particular, we shall deal with the “direct approach” credited to Suquet [108], two different variational approaches ([96] and [110]), and the Transformation Field Analysis [42]. Among them, the methods suitable to homogenize syntactic foams will be applied in chapter 18, where a new homogenization method for syntactic foams will be both proposed and tested. In order to accomplish these analytical homogenizations, a strongly simplified constitutive law for epoxy resins will be employed.

Some preliminary results about the epoxy resin behavior have already been presented in [10] and [98].

Chapter 15

Linear viscoelastic matrix

The results of this chapter will not be applied to the syntactic foams concerned in chapter 4 but they will be referenced later in discussing others homogenization method (see subsections 17.5.2 and 18.2.1).

The case in which the matrix behavior is linear viscoelastic can be treated by exploiting the *correspondence principle* (Alfrey [2]). Since the differential equation governing the matrix behavior is linear, the Laplace transform can be used to obtain an equivalent linear elastic problem in the transformed space just by replacing the elastic moduli with the Laplace transform of their viscoelastic counterpart; it is then possible to compute the effective elastic properties in the transformed space and then, antitransforming their expression, the time-dependent composite behavior searched for is obtained.

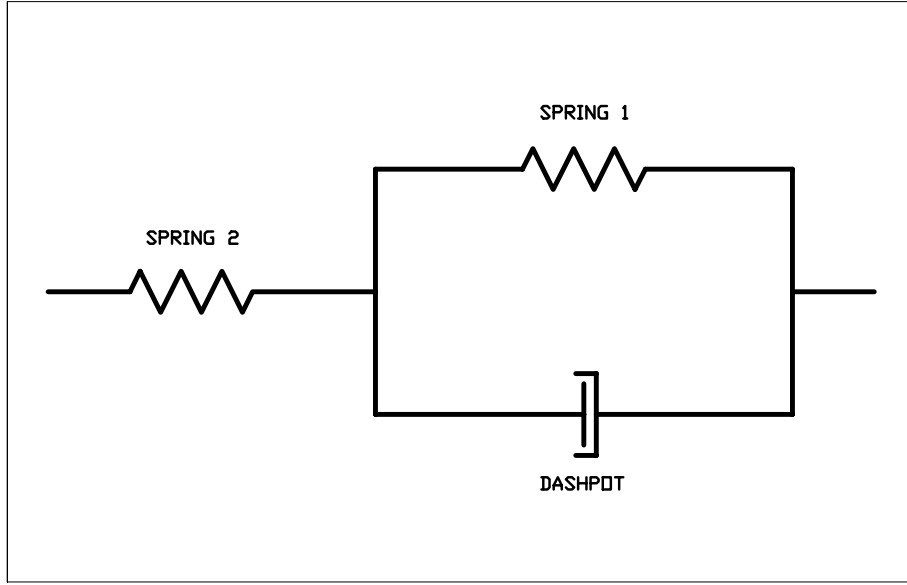
It is worth noting that also nonlinear viscoelastic matrixes, like the epoxy resins described in chapter 3, when subjected to low intensity loads, can often be modeled as linear viscoelastic solids.

One of the most common linear viscoelastic constitutive law can be obtained by means of the rheological model sketched in figure 15.1, often called “standard linear solid”, in which only the deviatoric behavior of the material is taken as time-dependent. It consists of a Kelvin model (i.e., a dashpot, characterized by a constant coefficient of viscosity η , connected in parallel with a linear elastic spring — the spring 1 in figure 15.1) connected in series with a linear elastic spring element (the spring 2 in figure 15.1). It is well known that this kind of model allows us, unlike the Kelvin model, to have a linear elastic response at the instant in which a load is applied and, when subjected to a constant force, it gives, unlike the simpler Maxwell model, strains that approach asymptotically finite values when the time t tends to infinity. The material volumetric behavior is linear elastic and governed by one parameter only: the bulk modulus $K^{(m)}$; its Laplace transform, $\hat{K}^{(m)}(p)$, turns out to be the following function of the complex variable p :

$$\hat{K}^{(m)}(p) = \frac{K^{(m)}}{p} \quad (15.0.1)$$

The differential equation governing the global behavior of this rheological model reads

$$\frac{G_1 + G_2}{G_2} s_{ij}^{(m)} + \frac{\eta}{2G_2} \dot{s}_{ij}^{(m)} = 2G_1 e_{ij}^{(m)} + \eta \dot{e}_{ij}^{(m)} \quad (15.0.2)$$

Figure 15.1: *The rheological model*

in which G_1 and G_2 are the shear moduli of the springs 1 and 2 respectively, $s_{ij}^{(m)}$ is the stress deviator, $e_{ij}^{(m)}$ is the strain deviator, and a superimposed dot $\dot{}$ indicates the derivative with respect to the time.

Laplace transforming both sides of equation (15.0.2), the following relation, dependent upon the complex variable p , is obtained:

$$\frac{G_1 + G_2}{G_2} \hat{s}_{ij}^{(m)} + \frac{\eta}{2G_2} p \hat{s}_{ij}^{(m)} = 2G_1 \hat{e}_{ij}^{(m)} + \eta p \hat{e}_{ij}^{(m)} \quad (15.0.3)$$

where the superimposed symbol $\hat{}$ indicates transformed quantities.

The shear viscous kernel of the matrix, $G^{(m)}(t)$, can be defined by means of the classical representation of the hereditary linear viscoelastic constitutive law [34] as:

$$s_{ij}^{(m)}(t) = 2G^{(m)}(t)e_{ij}^{(m)}(0) + 2 \int_0^t G^{(m)}(t - \tau) d e_{ij}^{(m)}(\tau) \quad (15.0.4)$$

It is then straightforward to compute the transformed shear viscous kernel of the matrix. From equation (15.0.3), we obtain:

$$\hat{G}^{(m)}(p) = \frac{\hat{s}_{ij}^{(m)}}{2p \hat{e}_{ij}^{(m)}} = \frac{(2G_1 + \eta p)G_2}{(2(G_1 + G_2) + \eta p)p} \quad (15.0.5)$$

Substituting the symbols $K^{(m)}$ and $G^{(m)}$ with the right-hand sides of equations (15.0.1) and (15.0.5) respectively into the homogenization procedure described in chapter 7 and antitransforming the so obtained results, it is theoretically possible to compute the effective viscoelastic behavior of syntactic foams made by the viscoelastic matrix here above described. Any, even more complicated, linear viscoelastic model for the syntactic foam

phases can be treated in the same way, but antitransforming might be analytically entangled. Even for the simple viscoelastic behavior here concerned, the computation of the effective shear viscous kernel of a syntactic foam homogenized by means of the Self-Consistent estimate based on one composite sphere only, $G_0^{SC}(t)$, needs a lot of lengthy algebra to write down the coefficients of equation (7.2.33) in the transformed space as functions of the complex variable p ; moreover, the antitransformation of the significant root $\hat{G}_0^{SC}(p)$ is not trivial at all (see [136] for the simpler case in which the Generalized Self-Consistent Scheme of Christensen and Lo is used as homogenization technique for composite filled with solid spheres). Finally, if there is the need of employing the more complicated homogenization method accounting for the filler gradation described in chapter 7, only numerical methods seem to be suitable for evaluating both the effective bulk and shear viscous kernel.

In the following, as an example, the effective bulk viscous kernel, $K_0^{est}(t)$, is given for a syntactic foam made by a linear elastic filler and a viscoelastic matrix such as the one described above (figure 15.1). The effective bulk viscous kernel rules the volumetric time-dependent macroscopic behavior:

$$\Sigma_{kk}(t) = 3K_0^{est}(t)E_{kk}(0) + 3 \int_0^t K_0^{est}(t - \tau) dE_{kk}(\tau) \quad (15.0.6)$$

Exploiting equations (7.3.14) and (7.3.15), i.e., assuming that the filler might be characterized by one composite sphere only, it is straightforward to observe that the effective bulk modulus in the transformed space can be written as:

$$\hat{K}_0^{est}(p) = K^{(m)} \frac{Ap^2 + Bp + C}{p(Dp^2 + Ep + F)} \quad (15.0.7)$$

in which A , B , C , D , E , and F are coefficients dependent on the geometrical and mechanical parameters characterizing the syntactic foam:

$$A = \delta K^{(m)} \eta + \frac{4b^3}{3c^3} \delta G_2 \eta \quad (15.0.8)$$

$$B = 2\delta K_m(G_1 + G_2) + \frac{4}{3} \left(1 - \frac{b^3}{c^3}\right) \kappa G_2 \eta + \frac{8b^3}{3c^3} \delta G_1 G_2 \quad (15.0.9)$$

$$C = \frac{8}{3} \left(1 - \frac{b^3}{c^3}\right) \kappa G_1 G_2 \quad (15.0.10)$$

$$D = \left(1 - \frac{b^3}{c^3}\right) \delta K^{(m)} \eta \quad (15.0.11)$$

$$E = \frac{4}{3} \kappa G_2 \eta + \frac{b^3}{c^3} \kappa K^{(m)} \eta + 2 \left(1 - \frac{b^3}{c^3}\right) \delta K^{(m)} (G_1 + G_2) \quad (15.0.12)$$

$$F = \frac{8}{3} \kappa G_1 G_2 + 2 \frac{b^3}{c^3} \kappa K^{(m)} (G_1 + G_2) \quad (15.0.13)$$

where κ and δ are defined in equation (7.3.15).

If the quadratic equation $Dp^2 + Ep + F = 0$ has two distinct non-zero roots p_1 and p_2 , $K_0^{est}(t)$ reads

$$K_0^{est}(t) = H(t) \left(\frac{C}{F} + \sum_{i=1}^2 \exp(p_i t) \frac{Ap_i^2 + Bp_i + C}{3Dp_i^2 + 2Ep_i + F} \right) \quad (15.0.14)$$

in which $H(t)$ is the Heaviside function.

It is interesting to note that the effective bulk modulus K_0^{est} is time-dependent, even if the bulk moduli of both matrix and filler are not. In subsection 17.5.2, this result will be useful in discussing an approximate homogenization technique.

Finally, it is important to remark that, as pointed out for instance by Christensen [35], when the correspondence principle is applied together with homogenization procedures which furnish bounds for linear elastic composite (e.g., the “classical” Hashin–Shtrikman ones), the antitransformation, in general, makes those procedures lose the property of yielding bounds, and only estimates of the effective viscoelastic properties can be obtained.

Chapter 16

A phenomenological constitutive law for the nonlinear viscoelastic behavior of epoxy resins in the glassy state

16.1 Introduction

This chapter is concerned with the derivation of a phenomenological constitutive model for epoxy resins in the deformation regime prior to yielding. Such a model, based on the experimental results of chapter 3, can then for instance be used for analysing the mechanical behavior of the syntactic foams described in chapters 4 and 9.

For this purpose, we are interested in the behavior of epoxy resins in the glassy state, i.e., for temperatures below their glass transition temperature T_g . Polymers in the glassy state are often said to be in the amorphous state (that is the state in which polymers enter after cooling down from the molten state), to make the difference evident with the crystalline state which is mostly characteristic of metals. Actually, such a strict discrimination does not exist, since in glassy polymers a completely random molecules packing can not occur (Ward [127]) and they can even show high crystallinity grade. Indeed, the molecular chains of a polymer arrange themselves in space aiming at the configuration of minimum Potential Energy with respect to their own geometry and the topology of their neighbors, which affects both the orientation and the crystallinity [127].

The chance of a molecular chain of changing its conformation is dependent upon (i) the magnitude of the energy barrier ΔG which has to be got over to move towards a new configuration, (ii) the thermal energy of any possible conformation, and (iii) other perturbing effects such as an applied stress state.

Even if macromolecule convolutions are mostly immobilized in the glassy state, there are several possible limited local molecular motions, the so-called rotational isomerisms, which affect the macroscopic viscoelastic properties of glassy polymers (Ferry [47]). The viscoelasticity of these materials may be nonlinear even for relatively small strains (of the order of few percent).

The glassy polymer behavior differs from that of elastomers (also called rubbers, which

are polymers at a temperature greater than T_g), whose characteristic nonlinearity appears for relatively high strains.

Epoxy resins are *thermoset* materials. Thermosets are those polymers whose long chain molecules are linked to each other by covalent bonds; they are so discriminated from *thermoplastic* polymers whose bonds among their long chain molecules are of the van der Waals type only (therefore weaker than those present in thermosets). This fact makes the thermoplastic behavior strongly affected by the temperature: unlike thermosets, thermoplastics can easily be plastically deformed when the temperature increases. In spite of this, in both [135] and [77] experimental results have been found (already mentioned in section 3.1) which show the similarity in deformation mechanism below T_g between thermoplastics and thermosets.

Both thermosets and thermoplastics are characterized by a rather complex microstructure (at the molecular scale length) whose investigation is often very difficult. Furthermore, thermosets can most of the time be represented only in average through a “mean” chemical composition [122]. This is for instance the case of the epoxy resin SP Ampreg 20TM cured with the hardener UltraSlow which consists, as already mentioned in chapter 2, of a mixture of different curing agents: this fact makes the resin molecular structure unknown. Even when the chemistry of a resin is exactly known, as for the epoxy resin DGEBA DER 332 hardened with DDM 32950, its microstructure is not deterministic, for the reasons already explained in section 2.1 (Oleinik [92]).

16.2 Constitutive law derivation

The time-dependent deformation field that develops over random microstructures, like those characterizing the above mentioned kind of polymers, when somehow subjected to external stresses, can be described on the basis of the theory due to Eyring [46] of *thermally activated* rate processes. These are stochastic processes which can be formulated in terms of the probability that a molecule gets over an energy barrier $\Delta\mathcal{G}$, given by the Boltzmann factor $\exp(-\Delta\mathcal{G}/k_B T)$, and the effective rate of crossing the energy barrier, equal to $k_B T/h_P$, in which $\Delta\mathcal{G}$ is the Gibbs free energy barrier height per molecule, k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23} \text{ J/K}$), T is the absolute temperature, and h_P is the Planck constant ($h_P = 6.6262 \times 10^{-34} \text{ Js}$). This statistical interpretation leads to the well-known Arrhenius equation which expresses the angular frequency of molecular jumps between two rotational isomeric states as follows:

$$\omega = \omega_0 \exp \frac{-\Delta\mathcal{G}}{k_B T} \quad (16.2.1)$$

where

$$\omega_0 = 2\pi \frac{k_B T}{h_P} \quad (16.2.2)$$

The Gibbs free energy $\mathcal{G}$ can be written in terms of the temperature T , the entropy $\mathcal{S}$, the internal energy $\mathcal{U}$, and the thermodynamic tensions τ_i which are conjugated to the substate variables ν_i ($i = 1, \dots, N$) (Malvern [87]):

$$\mathcal{G} = \mathcal{U} - ST - \tau_i \nu_i = \mathcal{H} - ST \quad (16.2.3)$$

in which $\mathcal{H} = \mathcal{U} - \tau_i \nu_i$ is the enthalpy. To make the meaning of thermodynamic tensions and substate variables clear, let us mention the trivial case of a perfect gas, for which the enthalpy is expressed as $\mathcal{H} = \mathcal{U} - pV$ since it is assumed that the only thermodynamic tension acting on the material is the pressure $p = \sigma_{kk}/3$, which is conjugated to the total volume V .

Taking both the temperature T and the substate variables ν_i constant over the energy activated deformation process, the increment in the Gibbs free energy, i.e. the energy barrier, reads:

$$\Delta\mathcal{G} = \Delta\mathcal{U} - T\Delta\mathcal{S} - \nu_i\Delta\tau_i = \Delta\mathcal{H} - T\Delta\mathcal{S} \quad (16.2.4)$$

in which $\Delta\mathcal{U}$ and $\Delta\mathcal{H}$ are integrals of the perfect differentials of $\mathcal{U}$ and $\mathcal{H}$ respectively, taken with respect to the independent variables $\mathcal{S}$ and τ_i .

The Eyring model assumes that the thermodynamic tensions consist of the tensor components of the applied stress field which are conjugated with properly defined *activation volumes*. Therefore, the enthalpy part of the energy barrier is shifted by an external applied stress field.

The effect of the application of a uniaxial stress σ is to increase the probability of a molecular transformation in the direction of the applied stress (“forward”) and to decrease the probability of a molecular transformation in the opposite direction (“backward”); this causes a net molecule flow in the forward direction [127] given by:

$$\omega_{net} = \omega_f - \omega_b = \omega_0 \exp \frac{-\Delta\mathcal{G}}{k_B T} \sinh \frac{\sigma v}{k_B T} \quad (16.2.5)$$

in which v is the activation volume associated with the uniaxial stress σ (see section 16.4 for some information about the physical meaning of the activation volume). Note that in equation (16.2.5) the stress contribution to the free energy barrier has not been included in the symbol $\Delta\mathcal{G}$, which in fact represents the energy barrier when no mechanical action is applied; this is in order to single out the dependence of the resulting law on the applied stress σ . Furthermore, equation (16.2.5) is affected by the approximation of assuming that the activation energy, $\Delta\mathcal{G}$, is the same for the forward transformation and the reverse one when the polymer is not subjected to any external stress field.

The fundamental hypothesis in deriving the Eyring model is to relate the net flow ω_{net} to the viscoelastic strain rate $\dot{\epsilon}$ through the dimensionless constant ϵ , thus getting:

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp \frac{-\Delta\mathcal{G}}{k_B T} \sinh \frac{\sigma v}{k_B T} \quad (16.2.6)$$

in which $\dot{\epsilon}_0 = \epsilon\omega_0$ becomes a material parameter. Let us remind that Prandtl [99] was the first one to suggest a dependence of the viscoelastic strain rate on the applied stress through the hyperbolic sine; this was done so as to describe the steady creep rate, in particular to model the secondary creep stage.

Here, we are interested in three-dimensional stress states, therefore we assume that the equivalent strain rate $\dot{\epsilon}_{eq}$, defined as

$$\dot{\epsilon}_{eq} = \sqrt{\frac{2}{3} \dot{\epsilon}_{ij} \dot{\epsilon}_{ij}}, \quad (16.2.7)$$

can be directly related to the equivalent stress σ_{eq} , defined as

$$\sigma_{eq} = \sqrt{\frac{3}{2}s_{ij}s_{ij}}, \quad (16.2.8)$$

through the following equation, formally similar to equation (16.2.6):

$$\dot{\varepsilon}_{eq} = \dot{\varepsilon}_0 \exp \frac{-\Delta\mathcal{G}}{k_B T} \sinh \frac{\sigma_{eq} v}{k_B T} \quad (16.2.9)$$

In the preceding equation e_{ij} and s_{ij} are the deviatoric strain and stress tensors respectively and the symbols $\Delta\mathcal{G}$, $\dot{\varepsilon}_0$, and v have been kept to indicate the material parameters even if equation (16.2.9) refers to a general stress state and, on the contrary, equation (16.2.6) refers to uniaxial stress states. Note that equation (16.2.9) implies that the viscosity affects only the epoxy change of shape. The volumetric behavior is assumed to be linear elastic and it is characterized by the instantaneous bulk modulus K_2 . In a moment, we shall show that equation (16.2.9) can be used to successfully derive a triaxial constitutive law to model the nonlinear viscoelastic behavior of epoxy resins.

In chapter 3, it has been shown that the asymptotic behavior of epoxy resins subjected to creep tests is nonlinear. Therefore, the rheological model of figure 15.1 seems to be suitable to describe the epoxy resin behavior if the spring in parallel with the dashpot (spring 1) is assumed to be nonlinear. The serial spring 2 is instead taken linear elastic and characterized by the instantaneous bulk and shear moduli K_2 and G_2 . Later, we shall give more insight about the choice of such a rheological model. Moreover, since we limit the analysis of the epoxy resin inelastic behavior to the viscoelasticity, which has been shown in chapter 3 to be the most important effect before the material strength is reached, the nonlinear spring in parallel with the dashpot is taken to be reversible.

Owing to the lack of an ad hoc model for the nonlinear elasticity prior to yield of epoxy resins in the glassy state (see section 16.7 for more comments on this), here, for the sake of simplicity, we adopt the Ramberg–Osgood constitutive law, which links the deviatoric stress and strain acting on the spring 1 (whose stress is marked with the superscript (1)) as follows:

$$s_{ij}^{(1)} = \frac{2G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} e_{ij}^{(v)} \quad (16.2.10)$$

where G_1 , α , σ_0 , and n are material constants and $e_{ij}^{(v)}$ is the viscoelastic (deviatoric) strain present both in the spring 1 and in the dashpot.

A constitutive law of the Ramberg–Osgood type has been used in [82] to fit the stress–strain curve obtained from the uniaxial tension of the Araldite 502 epoxy resin cured with HY955 hardener (both prepolymer and curing agent produced by Ciba Geigy). The match between the experimental results and the analytical prediction has been in this case good only in the monotonic deformation range prior to softening.

As said, we assume that the nonlinear epoxy behavior is deviatoric, i.e., that both the spring 1 and the Eyring dashpot are incompressible. In other words, the volumetric part of the constitutive law is linear elastic and governed by the spring 2 only:

$$p = K_2 \varepsilon_{kk} \quad (16.2.11)$$

p , ε_{kk} , and K_2 being the total pressure ($p = \sigma_{kk}/3$), the volumetric strain, and the bulk modulus respectively.

Finally, to write down the constitutive equation based on the rheological model of figure 15.1, in which the dashpot and the spring 1 are governed by equation (16.2.9) and equation (16.2.10) respectively, we need to derive the tensorial stress-strain law related to the dashpot. To this purpose, we first invert equation (16.2.9) (by the way adding the superscript (v) to indicate the stress acting on the dashpot):

$$\sigma_{eq}^{(v)} = \frac{k_B T}{v} \operatorname{arcsinh} \left(\frac{\dot{\varepsilon}_{eq}^{(v)}}{\dot{\varepsilon}_0} \exp \frac{\Delta \mathcal{G}}{k_B T} \right) \quad (16.2.12)$$

then, we compute the deviatoric stress tensor components, $s_{ij}^{(v)}$, acting on the dashpot by means of the following definitions:

$$s_{ij}^{(v)} = n_{ij} \sigma_{eq}^{(v)} \quad (16.2.13)$$

$$n_{ij} = \frac{2\dot{e}_{ij}^{(v)}}{3\dot{\varepsilon}_{eq}^{(v)}} \quad (16.2.14)$$

Note that the definitions (16.2.13)-(16.2.14) imply that $s_{ij}^{(v)} \dot{e}_{ij}^{(v)} = \sigma_{eq}^{(v)} \dot{\varepsilon}_{eq}^{(v)}$. Later, we shall give more insight on the reason why we chose such definitions.

At this point, we can write the searched constitutive relation:

$$s_{ij} = \frac{2G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} e_{ij}^{(v)} + \frac{2\dot{e}_{ij}^{(v)}}{3\dot{\varepsilon}_{eq}^{(v)}} \frac{k_B T}{v} \operatorname{arcsinh} \left(\frac{\dot{\varepsilon}_{eq}^{(v)}}{\dot{\varepsilon}_0} \exp \frac{\Delta \mathcal{G}}{k_B T} \right) \quad (16.2.15)$$

in which

$$e_{ij}^{(v)} = e_{ij} - \frac{s_{ij}}{2G_2} \quad (16.2.16)$$

$$\dot{e}_{ij}^{(v)} = \dot{e}_{ij} - \frac{\dot{s}_{ij}}{2G_2} \quad (16.2.17)$$

and $\sigma_{eq}^{(1)}$ has to be computed by means of the implicit relation:

$$\sigma_{eq}^{(1)} = \frac{3G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} \varepsilon_{eq}^{(v)} \quad (16.2.18)$$

where

$$\varepsilon_{eq}^{(v)} = \sqrt{\frac{2}{3} e_{ij}^{(v)} e_{ij}^{(v)}} \quad (16.2.19)$$

The particularization of equation (16.2.15) to a uniaxial stress state reads

$$\sigma_l = \frac{2G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} \left(\varepsilon_{dev} - \frac{\sigma_l}{2G_2} \right) + \frac{k_B T}{v} \operatorname{arcsinh} \left(\frac{2}{3\dot{\varepsilon}_0} \left(\dot{\varepsilon}_{dev} - \frac{\dot{\sigma}_l}{2G_2} \right) \exp \frac{\Delta \mathcal{G}}{k_B T} \right) \quad (16.2.20)$$

$$\sigma_{eq}^{(1)} = |\sigma_l^{(1)}| = \frac{2G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} \left| \varepsilon_{dev} - \frac{\sigma_l}{2G_2} \right| \quad (16.2.21)$$

where σ_l is the uniaxial (longitudinal) stress and

$$\varepsilon_{dev} = \varepsilon_l - \varepsilon_t \quad (16.2.22)$$

$$\dot{\varepsilon}_{dev} = \dot{\varepsilon}_l - \dot{\varepsilon}_t \quad (16.2.23)$$

in which ε_l and ε_t are the longitudinal and transversal strains respectively.

It is now important to note that the definitions (16.2.13)–(16.2.14), together with the fact that the $\operatorname{arcsinh}$ function preserves the sign of its argument, allow us to preserve the sign of $\dot{\varepsilon}_{eq}^{(v)}$ inside the $\operatorname{arcsinh}$ function in its uniaxial particularization (16.2.20); this is a crucial point to be able to model the flex characterizing cyclic uniaxial tests (see chapter 3). Indeed, in the unloading stage of a uniaxial cyclic test, the nonlinear spring 1 tends to recover elastically the viscous strain, whereas the Eyring dashpot tends to develop more viscous longitudinal strain of the same sign of the applied stress, even if the absolute stress value is decreasing. Thus, to satisfy the compatibility condition which has to exist between the Ramberg–Osgood spring and the dashpot, it turns out that the stress acting on the dashpot has to strongly decrease, even changing sign with respect to the overall applied stress. This last extreme situation corresponds to the flex in the unloading stress–strain curve.

Of course, this model capability is not only dependent on how the Eyring dashpot has been extended for triaxial stress states (equations (16.2.9), (16.2.13), and (16.2.14)), but it is also dependent on the choice of rheological model sketched in figure 15.1. This choice can be justified both by means of the already mentioned phenomenological reasons and from the molecular viewpoint. Indeed, as observed by Oleinik [92], the epoxy resin instantaneous linear elastic behavior is determined by van der Waals intermolecular forces and the deformation of the chemical network, which then behaves viscously, does not affect the elastic moduli. This means that it is sensible to describe the linear and nonlinear effects of the epoxy resins behavior by a serial scheme, as in the rheological model of figure 15.1. Furthermore, the fact that the dashpot and the nonlinear spring have been put in parallel in the employed rheological model can be explained by considering that the nonlinear elastic spring describes the behavior of the main macromolecule backbone chains, whereas the dashpot simulates the delayed behavior due to the encumbering macromolecule side groups, as the aromatic rings, which protrude from the backbone chains, whose relative positions change in time depending on the stress acting on the network. However, this explanation would require to be supported by a deeper study of the epoxy macromolecule behavior.

Let us now further discuss the ground of the chosen rheological model by comparing it with the alternative, equally complex rheological model sketched in figure 16.1, in which, with respect to the rheological model of figure 15.1, the linear elastic element (spring 2) has been put in parallel with the Ramberg–Osgood nonlinear spring. This allows us to obtain the following relation between stress and strain deviatoric tensors:

$$s_{ij} = \frac{2G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} e_{ij} + \frac{2\dot{\varepsilon}_{ij}^{(v)}}{3\dot{\varepsilon}_{eq}^{(v)}} \frac{k_B T}{v} \operatorname{arcsinh} \left(\frac{\dot{\varepsilon}_{eq}^{(v)}}{\dot{\varepsilon}_0} \exp \frac{\Delta \mathcal{G}}{k_B T} \right) \quad (16.2.24)$$

This model, of easier implementation than the first one, has the advantage of allowing

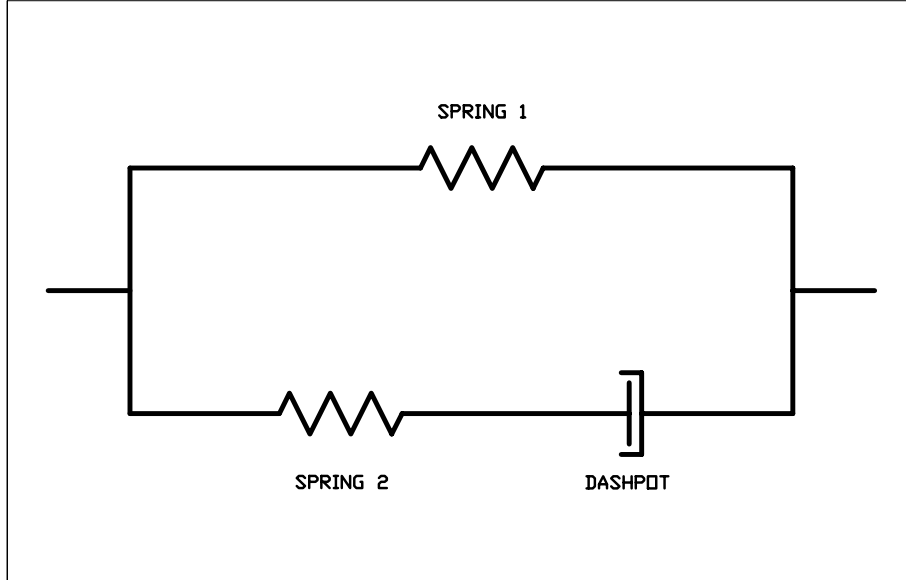


Figure 16.1: *An alternative rheological model for the constitutive modeling of epoxy resins*

nonlinear elastic strains to develop upon instantaneous loading. On the other hand, it is likely that this model could hardly catch the epoxy resin cyclic behavior, because, when unloading, the linear elastic spring can recover the elastic strains that the Ramberg–Osgood one recovers, thus probably preventing, in the Eyring dashpot, the change in the stress sign which allows the flex to be caught. In spite of this conjecture, Bergström and Boyce [20] successfully employed the rheological model of figure 16.1 to describe the hysteretic behavior of rubbers, whose unloading has some likeness with that of epoxy resins. Anyway, all the three elements in the Bergström and Boyce rheological model were specifically derived for elastomers.

Going back to the proposed model (16.2.15), note that, to better characterize the epoxy behavior, we should replace the linear elastic spring with a more complex element which could account for the time-independent nonlinear effects. Furthermore, a failure criterion should be incorporated in the nonlinear spring 1 and plastic strains should be taken into account too (e.g., by means of either the Argon [5] or the Bowden model [27] — see next section 16.3 to get some more insight into this subject). In this case, since, as already said, plastic deformations are assumed to develop after the material strength is reached, there would most likely be the need of employing a finite strain theory. In addition, many more tests would be needed to try to discriminate the plastic deformations from the viscoelastic ones. Unfortunately, the model (16.2.15) is already rather involved and, therefore, we shall not make it more complicated by adding further nonlinearities and parameters. Moreover, let us highlight once again that we are interested in modeling the epoxy resin behavior prior to yielding.

16.3 Comments on other literature constitutive models involving the Eyring equation

Models somehow similar to the one proposed in the previous section are available in the literature.

The large recoverable extension of thermoplastic polymers below their T_g has been modeled by Haward and Thackray [54] by means of the same rheological model as the one sketched in figure 15.1. However, Haward and Thackray limited their analysis to the uniaxial stress state and chose as nonlinear spring 1 a Langevin spring, which is actually suitable for elastomers; this suggests that they were interested in studying polymers not too far from T_g . Anyway, Wu and van der Giessen [134] showed that models for rubbers can be successfully employed for representing the behavior of some glassy polymers too, in particular for thermoplastics. This fact is based on the assumption that glassy polymers can exhibit large inelastic strains if they overcome two physically distinct sources of resistance (see [54], [28], and [134]). In this view, first, the network must be stressed to allow molecular chains to rotate; then, after molecular alignment has occurred, another internal resistance to flowing arises, called orientational hardening, which is due to the attempt of altering the configurational entropy of the material. We shall come back in a moment on this.

Let us first discuss the fact that Haward and Thackray approximated the Eyring dashpot by replacing the function $\sinh$ with the simpler $\exp$. They justified this simplification by noting that for high stress values the hyperbolic sine and the exponential tend to coincide. Haward and Thackray were indeed dealing with high stress states. Unfortunately, the dashpot resulting from this simplification has a few drawbacks, first of all that of predicting non-zero viscous flow for zero stress; moreover, as already pointed out by Hasan and Boyce [55], simplifying the $\sinh$ with the $\exp$, i.e., neglecting the backward term in the derivation of the Eyring model, is equivalent to disregard the thermoreversible nature of the transformation, which implies a very poor performance of the model in predicting non-monotonic loading. It is possible to show that this simplification produces a physically meaningless creep behavior. It is indeed expected, as shown in figures 3.12 and 3.25, that the relaxation modulus be, at a fixed time, a decreasing function of the constant stress imposed in a creep test: this is the contrary of what happens if the $\sinh$ is replaced by the $\exp$ in the Eyring equation. To prove this statement, let us focus on the rheological model of figure 15.1 in which both the springs be taken as linear elastic; this simplification leads to the following uniaxial constitutive law:

$$\sigma_l = 2G_1 \left(\varepsilon_l - \varepsilon_t - \frac{\sigma_l}{2G_2} \right) + \frac{\Delta\mathcal{G}}{v} + \frac{k_B T}{v} \ln \left(\frac{2}{3\dot{\varepsilon}_0} \left(\dot{\varepsilon}_l - \dot{\varepsilon}_t - \frac{\dot{\sigma}_l}{2G_2} \right) \right) \quad (16.3.1)$$

Since we are focusing our attention to creep tests, we may set σ_l constant (i.e., $\dot{\sigma}_l = 0$). Using the symbol x to indicate the difference between the longitudinal and transversal strains, we obtain the following differential equation:

$$A = Bx + \ln \dot{x} \quad (16.3.2)$$

in which

$$A = \frac{G_1 + G_2}{G_2} \frac{\sigma_l v}{k_B T} - \frac{\Delta\mathcal{G}}{k_B T} - \ln \frac{2}{3\dot{\varepsilon}_0} \quad (16.3.3)$$

$$B = \frac{2G_1v}{k_BT} \quad (16.3.4)$$

Equation (16.3.2) can be integrated in closed-form:

$$x(t) = \frac{A}{B} + \frac{1}{B} \ln(B(t+C)) \quad (16.3.5)$$

C being the integration constant to be determined by imposing the condition:

$$x(t=0) = \frac{\sigma_l}{2G_2} \quad (16.3.6)$$

which furnishes:

$$C = \frac{k_BT}{3G_1v\dot{\epsilon}_0} \exp \frac{\Delta\mathcal{G} - \sigma_lv}{k_BT} \quad (16.3.7)$$

We now want to evaluate the variation of the “relaxation shear modulus”, here defined as

$$G(\sigma_l, t) = \frac{\sigma_l}{2x(t)}, \quad (16.3.8)$$

with respect to the applied stress σ_l . To this purpose we have to discuss the sign of the following expression:

$$\frac{1}{x} - \frac{\sigma_l}{x^2} \frac{dx}{d\sigma_l} \quad (16.3.9)$$

that should be always negative to be “physically sensible”. After some algebra (and noting that x and σ_l must always have the same sign and that all the parameters $\Delta\mathcal{G}$, v , G_1 , and $\dot{\epsilon}_0$ must be positive), equations (16.3.2)–(16.3.5), (16.3.7), and (16.3.9) allow us to find that the negativeness of expression (16.3.9) is equivalent to the positiveness of the following:

$$-D \exp D + \frac{\Delta\mathcal{G}}{v} F(t) - \frac{k_BT}{v} F(t) \ln F(t) \quad (16.3.10)$$

where

$$D = \frac{\Delta\mathcal{G} - \sigma_lv}{k_BT} \quad (16.3.11)$$

$$F(t) = \frac{3G_1v}{k_BT} \dot{\epsilon}_0 t + \exp D \quad (16.3.12)$$

Since $F(t)$ is linear in t and $F(t) \ln F(t)$ goes to infinity faster than $F(t)$, expression (16.3.10), for $t \rightarrow \infty$, is always negative, which is physically meaningless. This shows that the Eyring dashpot in which the sinh function is replaced with the exp function can not be suitable to correctly model any nonlinear viscoelastic behavior, at least in the context of the rheological model of figure 15.1.

Hasan and Boyce [55] focused their attention on the viscous behavior of thermoplastic materials; they employed an Eyring dashpot more refined than that here adopted (equation (16.2.5)), obtained by adding a parameter giving asymmetry in the backward and forward transformations when computing the net flow. The Hasan and Boyce model has anyway been derived for uniaxial stress states only and it is simply based on a Maxwell-type rheological model (i.e., the inelastic strain can indefinitely increase for any stress level) in which the spring is taken linear elastic.

The material behavior which Hasan and Boyce investigated, as well as that of the polymers on which Haward and Thackray worked [54], is anyway different from the one we want to predict with the here proposed model, which consists of the nonlinear viscoelasticity preceding yielding. In fact, all these researchers developed models whose main purpose was to predict the uniaxial stress–strain curve in the softening range and for high deformations (even if, because of the uniaxial condition of both stresses and strains, they used small strains in deriving their constitutive laws), in order to establish the dependence of the strength (defined as the highest stress value in the uniaxial test) on both the temperature and the strain rate. This softening behavior is not distinctive of the epoxy resin DGEBA DER 332 hardened with DDM 32950 tested by us, whereas it can be partly appreciated in the uniaxial compressive tests carried out on the epoxy resin SP Ampreg 20TM cured with UltraSlow hardener (see chapter 3). Beside the fact that epoxy resins are thermoset materials, while Hasan and Boyce and Haward and Thackray were concerned with thermoplastics, a reason for explaining these different mechanical behaviors can be found in how much T_g of each polymer is close to the test temperature, i.e., how the tested polymer is far from the rubbery state. For instance, Hasan and Boyce modeled the PMMA behavior at temperatures up to 50°C , and the T_g of the PMMA is of about 100°C , value very close to the T_g of the epoxy resin SP Ampreg 20TM cured with UltraSlow hardener, which indeed shows some softening. Instead, the T_g of the epoxy resin DGEBA DER 332 hardened with DDM 32950 is of about 170°C . Furthermore, note that our tests were all performed at room temperature ($\approx 23^\circ\text{C}$). Most likely, this last temperature value is too low to allow our epoxy resins to overcome the physical source of resistance which prevents the plastic flow to occur.

Moreover, another important issue to keep in mind is that we are referring our reasoning mostly to the uniaxial compressive tests, since our specimens tested in uniaxial tension (see section 2.2 and chapter 3) were too brittle to develop any yielding. As pointed out in [77] and [82] and already mentioned in chapter 3, to obtain any result from tests on the epoxy resins after yield has been occurred, it is essential to suppress both crack propagation (in tension) and buckling (in compression) by means of suitable test modalities (e.g., by performing plane strain compressive tests).

Summing up, one of the main differences between the model proposed here and those put forward in [54] and [55] consists of the different interpretation of the Eyring dashpot: we use it for describing viscoelastic deformations, whereas in [54] and [55] it is used to deal with viscoplastic deformations. Let us specify that the term viscoplastic is in this context used to mean a theory in which plastic strains are constantly accumulated (i.e., there is no yield surface or, that is the same, the current stress state always lies on the yield surface). As pointed out in [17], the term viscoplastic should be more appropriately used to mean constitutive laws in which plastic strains develop only depending on a yield criterion, at a different deformation regime from that which rules the viscoelastic deformations. Indeed, in the context of the Hasan and Boyce work [55], even if the Maxwell rheological model allows permanent deformations after a cyclic loading, the irreversible nature of these deformations is only apparent since they can always be recovered by applying a stress of opposite sign. This fact limits the use of such a kind of models.

Furthermore, in the theories characterized by two distinct deformation regimes, the material parameters governing the yield criterion can be dependent on the strain rate, which is the case of the so-called rate dependent plasticity. In this last context, Ward

[127] and Lesser and Kody [80], among other authors, made use of an Eyring dashpot as the one defined in equation (16.2.9), actually extended to account for the pressure but often simplified by replacing the hyperbolic sine with the exponential; as said, this kind of Eyring model has been used to derive rate sensitive yield criteria.

Fotheringham and Cherry [48] made the Eyring model even more complicated than that here used by adding a further material parameter m , basing their reasoning on the so-called “co-operative jump processes”. The resulting Eyring model looks like equation (16.2.6) in which the hyperbolic sine function is raised to the m^{th} power. In the Finite Element code ABAQUS, this kind of Eyring model is available in a constitutive law in which it is simply combined in series with a hookean spring. As already said, this constitutive law (which can be seen as the triaxial extension of the Hasan and Boyce model), being based on a Maxwell-type rheological model, does not allow one to describe the cyclic behavior of epoxy resins.

Finally, let us mention that in the already quoted papers [77], [28], and [134], among many others, the Eyring model has not been employed and the so-called Argon model [5], has been used instead. This model, which, as the Eyring one, is based on macromolecular thermally activated processes, furnishes the plastic strain rate in glassy polymers as function of the current stress and some material parameters. By the way, [28] and [134] were concerned, as the paper of Haward and Thackray [54], with viscoplasticity in its “one deformation regime” acceptance. Yamini and Young [135] found that the Bowden model [27], again based on the theory of the thermally activated processes, works better than the Argon model for the epoxy resins tested by them.

16.4 Material parameters identification and comparison with experimental results

The material parameters of the model described by equation (16.2.15) have been identified by means of the tests reported in chapter 3; since those tests are uniaxial, the relevant constitutive equations are (16.2.20)–(16.2.23).

The parameter identification can be simplified by subdividing it in three different stages. First, it is possible to determine the linear elastic parameters E_2 and ν_2 (and then G_2 and K_2 by exploiting the well-known connections among the linear elastic moduli of isotropic materials) as averages of the values obtained from linear regressions over all the available tests on the longitudinal strain versus the longitudinal stress plot and on the longitudinal strain versus the opposite of the transversal strain plot respectively. As already said, the elastic constants have been here defined by taking the linear regressions in the longitudinal strain range spanning from 0 to 0.004, independently upon the applied load rate; this way of determining the linear elastic constants produces results which are in principle affected by the viscoelastic effects, but the time-dependent behavior has been experimentally shown to be trifling for such a small longitudinal strain and for the chosen crosshead displacement rates.

After having identified G_2 , it is possible to determine the parameters characterizing the nonlinear spring, G_1 , n , α , and σ_0 , by exploiting the creep tests (note that one of either α or σ_0 is redundant); they indeed furnish the strain asymptotic values, which correspond to the rheological model in which the hookean spring and the Ramberg–Osgood spring

are connected in series (i.e., the viscoelastic strain rate is zero and, then, there is no stress acting in the dashpot). Dependently also on how many asymptotic values are available (in our case, for both the epoxy resin tested, we measured 5 values, approximately corresponding to uniaxial constant stresses of 14 MPa, 21 MPa, 43 MPa, 63 MPa, and 86 MPa), the determination of the Ramberg–Osgood parameters may have some degrees of freedom; among different choices of G_1 , n , α , and σ_0 which nearly satisfy the asymptotic behavior, the best one must be determined in conjunction with the identification of the remaining parameters, which characterize the Eyring dashpot. These last material constants have to be chosen in such a way as to best fit both the cyclic behavior and the time–strain curve in the creep tests (the linear elastic constants G_2 and K_2 set the strain values $\varepsilon(t = 0)$ at the initial instant, the Ramberg–Osgood parameters then determine the strain values for $t \rightarrow \infty$, and, finally, the Eyring constants influence the way the strains evolve from $\varepsilon(t = 0)$ to $\varepsilon(t \rightarrow \infty)$).

In order to validate the proposed model, it is useful to be able to estimate some material constants in a different way from the analytical parameter identification. To this purpose, it is interesting to mention the physical meaning associated with the activation volume. As stated in [54], the activation volume “represents the volume of the polymer segment which has to move as a whole in order for flow to take place”. Haward and Thackray [54] showed that the activation volume can be underestimated up to an order of magnitude by evaluating the volume of the “statistical link”, i.e., the ratio between the body volume and the number of primary bonds contained in it. This concept is useful to check the value of the activation volume calibrated as above explained and the “statistical link” size may be even used as initial guess in an empirical calibration procedure. Anyway, as Haward and Thackray finally pointed out, “for the empirical success of the model [...] it is only necessary that the Eyring equation should represent the results”.

The relevant constitutive law (16.2.20)–(16.2.23) has been implemented with the purpose of identifying the material parameters. The tested specimens are assumed to be subjected, where the deformations have been measured, to perfectly uniform stress and strain fields and, therefore, the uniaxial tests have been simulated by integrating the constitutive law on one material point only; in other words, the numerical integration of the uniaxial particularization (16.2.20)–(16.2.23) does not need to be implemented into a material subroutine for a suitably open Finite Element code, because the input for the material subroutine is trivially known without solving the compatibility and equilibrium equations.

Two different implementations are needed: one for modeling the cyclic uniaxial tests, carried out at controlled displacement rate; the other for simulating the creep tests, carried out at imposed constant load; in the first case (hereafter called “strain-driven”) we know the measured longitudinal and transversal strains and, then, we can use their difference as a datum to compute the longitudinal stress according to equations (16.2.20)–(16.2.23); in the case of creep tests, the tests are “stress-driven” and the datum is the constant longitudinal stress from which we want to compute the longitudinal strain. Note that the boundary condition consisting of imposing zero tractions to the lateral specimen surface has already been accounted for in deriving equations (16.2.20)–(16.2.23).

The Crank–Nicholson integration scheme (also called Midpoint Rule) is known to be, among the trapezoidal methods, the only second-order accurate to integrate parabolic differential equations (see, for instance, Hughes [69]). We shall here adopt the Central

Difference Scheme, which is coincident with the Crank-Nicholson scheme for linear viscoelasticity and consists of replacing the current value of any time-dependent function, $f(t + \Delta t)$, with its value at the middle of the time step increment Δt :

$$f(t + \frac{1}{2}\Delta t) = f(t) + \frac{1}{2}\Delta f \quad (16.4.1)$$

and

$$\dot{f} = \dot{f}(t + \frac{1}{2}\Delta t) = \frac{\Delta f}{\Delta t} \quad (16.4.2)$$

The little advantage of using this integration scheme lies in the fact that the resulting nonlinear algebraic function to solve is independent upon the rates at the beginning of the increment.

The material parameters have been identified in [98] by means of a constrained least squares method for the epoxy resin DGEBA DER 332 cured with the hardener DDM 32950. To this purpose, the cyclic test on sample 8 and the creep tests on samples 15–19 on that resin have been used (see section 3.2). The bulk modulus value has been taken $K_2 = 5185 \text{ MPa}$ according to the Young modulus and Poisson ratio values measured in section 3 ($E_2 = 2800 \text{ MPa}$ and $\nu = 0.41$). The following values of the other parameters have been obtained (setting $\sigma_0 = 60 \text{ MPa}$ and $\dot{\epsilon}_0 = 1 \text{ sec}^{-1}$ — since we kept constant temperature in our tests, it turns out that, in the identification procedure, one of either $\Delta\mathcal{G}$ or $\dot{\epsilon}_0$ is redundant): $G_2 = 1004 \text{ MPa}$, $G_1 = 7042 \text{ MPa}$, $n = 3.17$, $\alpha = 3.07$, $v = 1536 \text{ \AA}^3$, and $\Delta\mathcal{G} = 6.343 \times 10^{-10} \text{ N\AA}$.

It is interesting to observe that the activation volume value which better fits the experimental data is very close to the values computed by Kurata and Stockmayer [76] (quoted in [54]) by means of the Treloar equation [118], based on measurements of molecular properties, such as the molecular weight and length.

The match between the experimental and analytical results is shown in figure 16.2 in which the five creep tests and the cyclic test on sample 8 already reported in chapter 3.2 are compared with the analytical predictions. Note that to simulate the creep tests, the longitudinal stress, computed by means of the experimentally recorded load and transversal strain, has been used as input to compute the difference between the longitudinal and transversal strains; in figure 16.2, this quantity is labeled as “strain difference”.

The greatest differences between experimental and analytical results can be seen in the creep tests at load values equal to 10, 15, and 60 kN ; they are due to the fact that, unfortunately, the samples used to carry out these tests were significantly stiffer, even in the linear elastic range, than this epoxy resin in average is. However, for the creep test at prescribed load of 60 kN the asymptotic behavior predicted by the model tends to get close to the experimental one, whereas for the creep tests at prescribed load of 10 and 15 kN the disagreement between experimental and analytical results is quite large (up to $\approx 30\%$) for any time.

The above differences are also due to the adopted identification strategy [98]: the only creep test data used to identify the material parameters have been the strain values at the end of the tests, which were arbitrarily incremented by 5% to estimate the asymptotic values. Furthermore, the used identification procedure does not consider on an equal footing all the stress levels, weighing more high stress levels; this is the reason why the simulated asymptotic values in the creep tests performed at low stress level are slightly different from the experimental ones.

Epoxy Resin DGEBA DER 332 cured with DDM 32950: comparison between experimental and analytical results

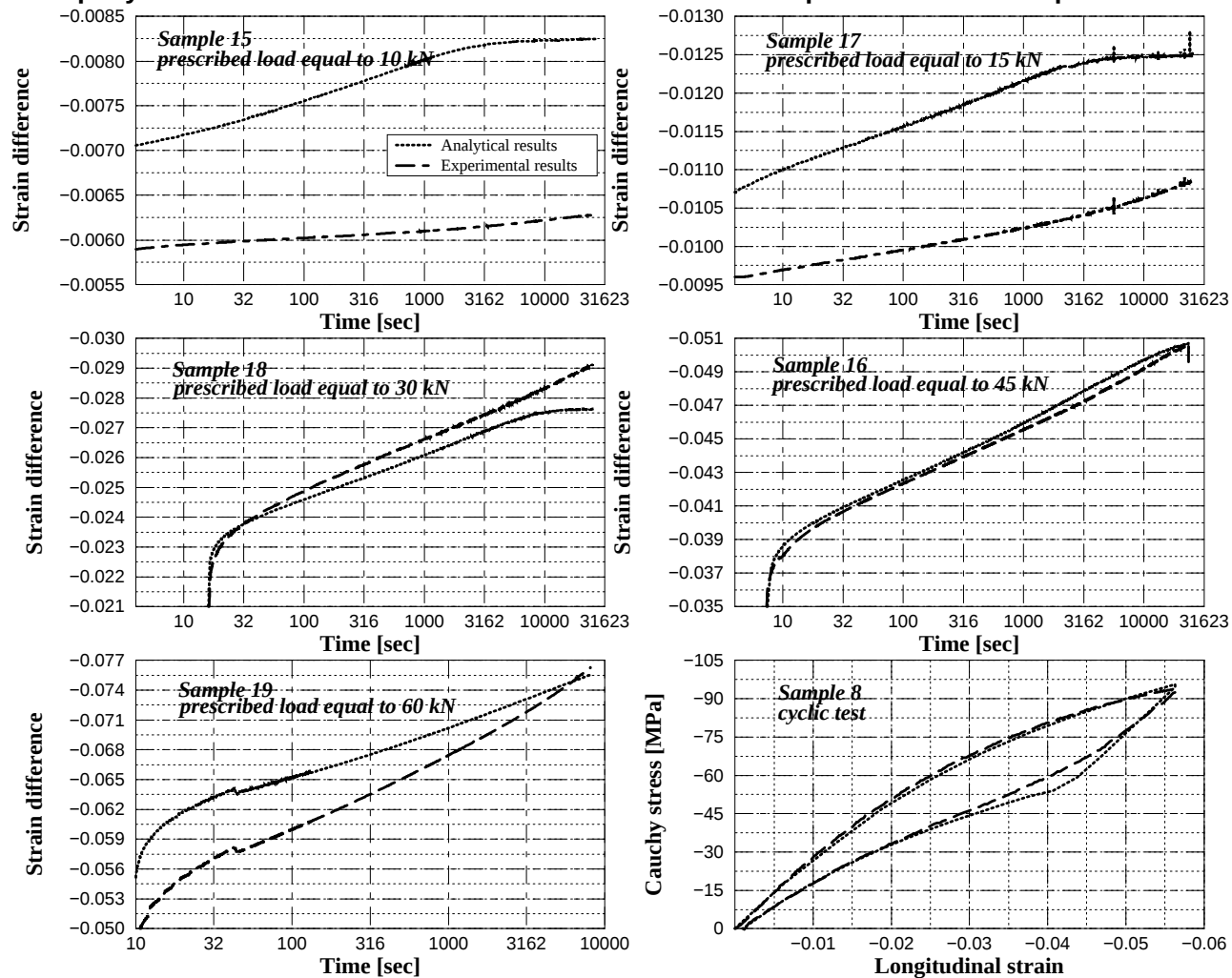


Figure 16.2: Comparison between experimental and analytical results

The analytical predictions concerning the remaining three tests (i.e., the creep tests performed at prescribed load of 30 and 45 kN and the cyclic test on sample 8) are very close to the experimental evidence. In particular, the model proposed here is able to catch the concavity change which appears in the stress–strain curve when unloading.

16.5 Three-dimensional implementation

The constitutive law (16.2.15)–(16.2.19) has been implemented into a User Material subroutine (UMAT) for the Finite Element code ABAQUS. The numerical integration, as for the uniaxial case, has been accomplished by means of the Central Difference Scheme, obtaining the following algebraic nonlinear system to be solved for the incremental stress deviator Δs_{ij} , where the superscript (t) indicates the beginning of the increment, when both stresses and strains are known:

$$\Delta s_{ij} = 2 \left(\frac{2G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} e_{ij}^{(v)} + \frac{2\Delta e_{ij}^{(v)} k_B T}{3\Delta \varepsilon_{eq}^{(v)} v} \operatorname{arcsinh} \left(\frac{\Delta \varepsilon_{eq}^{(v)}}{\Delta t \dot{\varepsilon}_0} \exp \frac{\Delta \mathcal{G}}{k_B T} \right) - s_{ij}^{(t)} \right) \quad (16.5.1)$$

in which

$$e_{ij}^{(v)} = e_{ij}^{(t)} + \frac{1}{2} \Delta e_{ij} - \frac{s_{ij}^{(t)} + \frac{1}{2} \Delta s_{ij}}{2G_2} \quad (16.5.2)$$

$$\Delta e_{ij}^{(v)} = \Delta e_{ij} - \frac{\Delta s_{ij}}{2G_2} \quad (16.5.3)$$

$$\Delta \varepsilon_{eq}^{(v)} = \sqrt{\frac{2}{3} \Delta e_{ij}^{(v)} \Delta e_{ij}^{(v)}} \quad (16.5.4)$$

and equations (16.2.18) and (16.2.19) hold. After guessing an initial attempt for Δs_{ij} , equation (16.2.18) has to be solved for $\sigma_{eq}^{(1)}$.

Let us now define $f_{ij}(\Delta \mathbf{s})$ as the difference between the right-hand side and the left-hand side of equation (16.5.1); to solve equation (16.5.1) for Δs_{ij} is equivalent to make every component of f_{ij} vanish. The relevant jacobian to solve the related Newton loop reads:

$$\frac{df_{ij}(\Delta \mathbf{s})}{d\Delta s_{kl}} = -\frac{1}{2G_2} \left(A e_{ij}^{(v)} e_{kl}^{(v)} + (2G_2 + B) I_{ijkl} + C \Delta e_{ij}^{(v)} \Delta e_{kl}^{(v)} \right) \quad (16.5.5)$$

where

$$A = -\frac{12 \frac{\alpha(n-1)}{\sigma_0^2} \left(\frac{G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} \right)^3 \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-3}}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1} + 9 \frac{\alpha(n-1)}{\sigma_0^2} \left(\frac{G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} \right)^2 \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-3} (\varepsilon_{eq}^{(v)})^2} \quad (16.5.6)$$

$$B = \frac{2G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} + \frac{4}{3\Delta\varepsilon_{eq}^{(v)}} \frac{k_B T}{v} \operatorname{arcsinh} \left(\frac{\Delta\varepsilon_{eq}^{(v)}}{\Delta t \dot{\varepsilon}_0} \exp \frac{\Delta\mathcal{G}}{k_B T} \right) \quad (16.5.7)$$

$$C = \frac{8}{9(\Delta\varepsilon_{eq}^{(v)})^3} \frac{k_B T}{v} \left(\frac{\frac{\Delta\varepsilon_{eq}^{(v)}}{\Delta t \dot{\varepsilon}_0} \exp \frac{\Delta\mathcal{G}}{k_B T}}{\sqrt{\left(\frac{\Delta\varepsilon_{eq}^{(v)}}{\Delta t \dot{\varepsilon}_0} \exp \frac{\Delta\mathcal{G}}{k_B T} \right)^2 + 1}} - \operatorname{arcsinh} \left(\frac{\Delta\varepsilon_{eq}^{(v)}}{\Delta t \dot{\varepsilon}_0} \exp \frac{\Delta\mathcal{G}}{k_B T} \right) \right) \quad (16.5.8)$$

Since the Finite Element code ABAQUS at the beginning of any analysis passes in the material subroutine zero total and incremental strains, to make the UMAT subroutine working, it is also important to compute the limits of the coefficient B and the tensor $C\Delta e_{ij}^{(v)}\Delta e_{kl}^{(v)}$ for $\Delta\mathbf{e}^{(v)} \rightarrow \mathbf{0}$:

$$\lim_{\Delta\mathbf{e}^{(v)} \rightarrow \mathbf{0}} B(\Delta\mathbf{e}^{(v)}) = \frac{2G_1}{1 + \alpha \left(\frac{\sigma_{eq}^{(1)}}{\sigma_0} \right)^{n-1}} + \frac{4 \exp \frac{\Delta\mathcal{G}}{k_B T}}{3\Delta t \dot{\varepsilon}_0} \frac{k_B T}{v} \quad (16.5.9)$$

$$\lim_{\Delta\mathbf{e}^{(v)} \rightarrow \mathbf{0}} C(\Delta\mathbf{e}^{(v)})\Delta e_{ij}^{(v)}\Delta e_{kl}^{(v)} = 0 \quad \forall ijkl \quad (16.5.10)$$

Moreover, the above limits are useful any time the incremental viscous strains are numerically too small to obtain an accurate evaluation of the coefficients B and C by means of equations (16.5.7) and (16.5.8).

Finally, the consistent jacobian (Simo and Taylor [105]) to be computed in the UMAT to assure the quadratic convergence in solving the global equilibrium equation by means of the Newton method reads:

$$\frac{d\Delta\sigma_{ij}}{d\Delta\varepsilon_{kl}} = \frac{d\Delta s_{ij}}{d\Delta e_{mn}} K_{mnkl} + 3K_2 J_{ijkl} \quad (16.5.11)$$

in which the fourth-order tensor $\frac{d\Delta s_{ij}}{d\Delta e_{kl}}$ can be expressed in terms of $\frac{df_{ij}(\Delta\mathbf{s})}{d\Delta s_{kl}}$:

$$\frac{d\Delta s_{ij}}{d\Delta e_{kl}} = - \left(\frac{df_{ij}(\Delta\mathbf{s})}{d\Delta s_{mn}} \right)^{-1} \left(A e_{mn}^{(v)} e_{kl}^{(v)} + B I_{mnkl} + C \Delta e_{mn}^{(v)} \Delta e_{kl}^{(v)} \right) \quad (16.5.12)$$

16.6 Application to syntactic foams

The aim of this section is to simulate the syntactic foam behavior beyond the linear elastic range by means of Finite Element analyses on unit cell models similar to that employed in chapter 11 to numerically compute the effective elastic moduli.

More specifically, we want to simulate the cyclic behavior of the syntactic foams tested by us. To this purpose, we shall refer our analyses to sample 1 of syntactic foam type 1 (section 4.1) and to sample 7 of syntactic foam type 6 (section 4.6). This choice is related to the fact that the matrix of these syntactic foams consists of the epoxy resin DGEBA DER 332 cured with DDM 32950, whose material parameters have been identified in section 16.4.

The glass is taken as linear elastic with Young modulus $E^{(i)} = 77500 \text{ MPa}$ and Poisson ratio $\nu^{(i)} = 0.23$; these values have indeed been found in sections 9.2 and 9.7 to be the most likely for the fillers employed in the syntactic foams produced by us.

It is expected that the nonlinear and inelastic behavior of these syntactic foams, for stresses below the strength limit, could be described by means of the constitutive law for epoxy resins derived in this section 16.2.

All the analyses have been run on the Finite Element code ABAQUS, in which the constitutive law for epoxy resins has been implemented by means of a user material subroutine based on the algorithm derived in the previous section 16.5.

Since the unit cell analyses involve both three-dimensional stress states and high stress gradients, their match with the experimental results can also be seen as an indirect way to test the constitutive law for epoxy resins developed in this chapter.

In figure 16.3 the experimental and the numerical results are compared. The match is quite satisfactory, even in terms of the unloading part.

In order to better appreciate these results, let us remind both the already discussed sources of uncertainty affecting the material parameters of both the epoxy resin and the glass and the approximations intrinsic to the unit cell model (see chapter 11).

16.7 Open issues and conclusions

The proposed model seems to be able to describe the viscoelastic behavior of epoxy resins, which is nonlinear and rules the epoxy mechanical behavior prior to yield.

The work on the identification procedure is in progress and, in the near future, it will be applied to the epoxy resin SP Ampreg 20TM cured with UltraSlow Hardener too.

As conjectured in section 16.2, it is perhaps worth to investigate the behavior of the different rheological model sketched in figure 16.1.

It would be good to replace the phenomenological Ramberg–Osgood element with a spring based on the epoxy macromolecule behavior. As mentioned in section 16.3, models which have been proposed for the large stretch behavior of rubbery elastic materials (e.g., see [6]), have also found an application in describing the post–yield behavior of glassy polymers ([54], [28], and [134]). These nonlinear elastic models for elastomers are based on approximate spatial distributions of the molecular chains, which may be used to represent the epoxy network too. On the other hand, if it is not of interest to predict the epoxy behavior after yielding, as for instance in the micromechanical investigation of the viscoelastic behavior of syntactic foams, it is desirable to employ simpler models. This important issue will be hopefully addressed after a careful examination of the models for rubbers available in the literature.

Moreover, the extension of the model here put forward in order to catch other material phenomena like plasticity would probably require the use of stress and strain definitions which can take finite strains into account.

It would be interesting to test epoxy resins at different temperatures, still in the glassy state, to see whether the dependence on the temperature of the Eyring dashpot can model the thermoviscoelastic behavior. Most likely, there would be the need of determining the dependence of some of the material parameters on the temperature too. More details about the temperature dependence of the Eyring model can be found in Ward [127].

Syntactic foams type 1 and 6 (DGEBA/DDM + different 3M fillers, $f = 0.5153$)

Comparison between experimental and numerical results

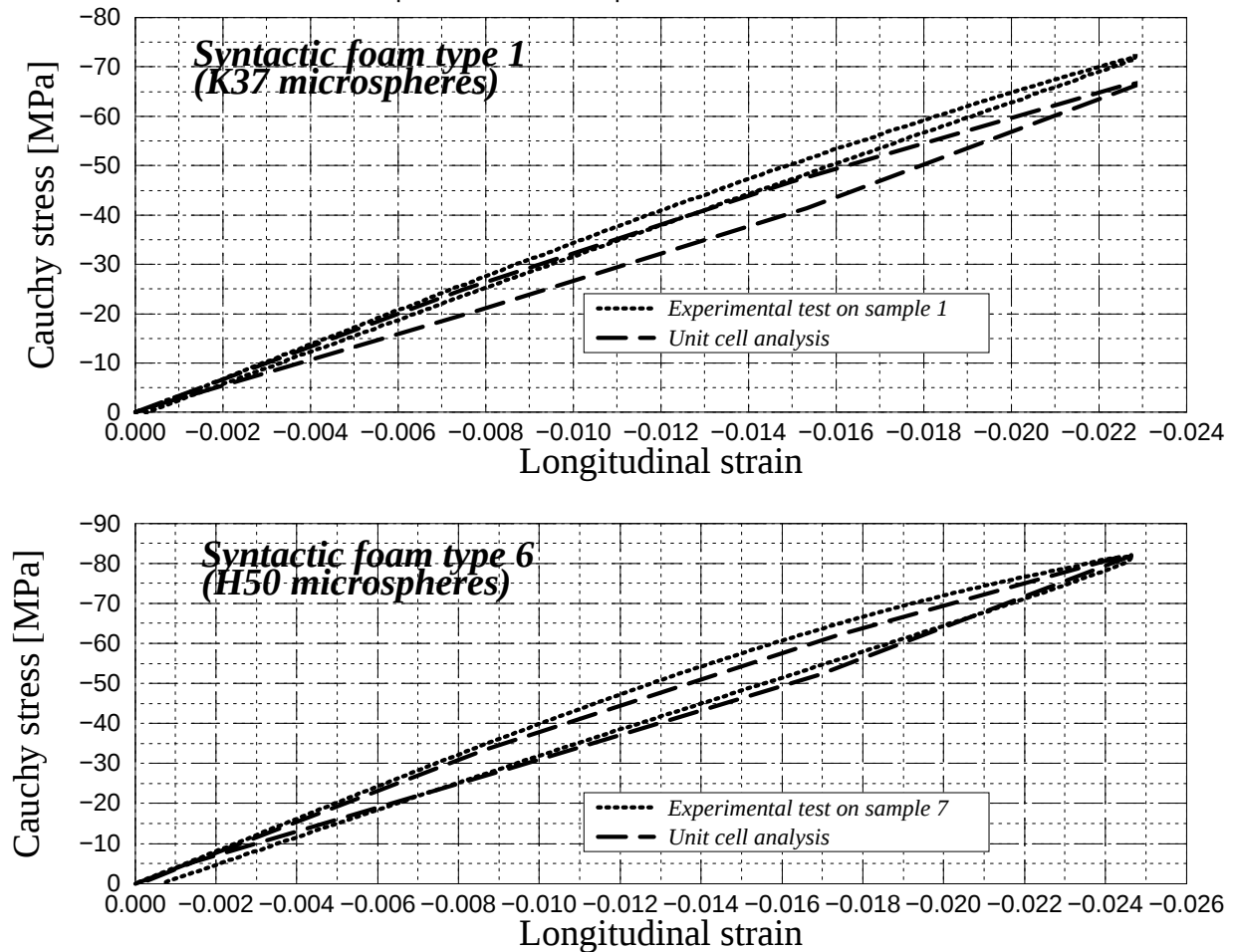


Figure 16.3: Syntactic foams: comparison between experimental and numerical results

Finally, as already pointed out in section 16.4, there is the need of carrying out more experimental tests than those reported in chapter 3, mostly involving multiaxial stress states, both to get more insight into the epoxy resin behavior beyond the linear elastic range and to test the here developed constitutive law.

Chapter 17

Review of some nonlinear homogenization methods

17.1 Introduction

Among several approaches put forward to homogenize composites in the nonlinear range, in this chapter we shall focus on the researches of Dvorak, Ponte Castañeda, Suquet, Willis, and their coworkers.

Dvorak [41] and Dvorak and Benveniste [43] founded the so-called “*Transformation Field Analysis*” (reported in section 17.4), which is in principle useful to estimate the overall properties of composites exhibiting inelastic deformation (this kind of heterogeneous materials will be hereafter called *inelastic composites*).

Ponte Castañeda and Willis (see, for instance, [96]) have first of all developed variational approaches to deal with *nonlinear composites*, i.e., heterogeneous materials whose phases are nonlinear elastic; however, under quite heavy assumptions, these variational approaches can somehow account also for inelastic behavior (see section 17.3.3). The starting point of these methods, which will be briefly reviewed in section 17.3, was the Willis extension (see [132] and Talbot and Willis [110]) of the “classical” Hashin–Shtrikman variational principle.

Here, we first focus on the “direct approach” (Suquet, [108]), which is quite general, can be used to deal with both nonlinear and inelastic composites, and can be linked with the Ponte Castañeda variational approach (see subsections 17.2.4 and 17.3.3).

17.2 The Incremental, Secant, and Modified Secant methods

17.2.1 Approach philosophy

In Suquet [108] three methods are compared to homogenize the behavior of heterogeneous media beyond the linear elastic range: the Incremental Method, the Secant Method, and the Modified Secant Method. The Incremental Method was first proposed by Hill [67], whereas the Secant Method has been introduced by Berveiller and Zaoui [21]; Suquet himself [107] put forward the use of the Modified Secant Method. All these three methods can

be used to homogenize nonlinear composites and the first one can deal with irreversibility as well. Each of them needs the choice of a linear elastic homogenization procedure (LEHP) to be applied repeatedly. In principle, any LEHP can be adopted which is suitable to model the composite we are dealing with; anyway, as it will be made clear in the following, technical difficulties may arise in applying the chosen LEHP within this context.

In the following, we shall refer our discussion to the displacement approach, corresponding to the boundary conditions (6.1.5), but similar arguments hold for the dual force approach, in which the RVE is loaded with the tractions (6.1.6).

The essence of all the three above mentioned methods consists of imposing to the RVE the homogeneous boundary conditions step-by-step (this discretization can be seen as a continuous loading path if the steps are chosen small enough). At each step, the effective composite nonlinear behavior is modeled by exploiting the chosen LEHP, accounting for the stiffness change of the phases due to the strain growth in each phase. The main problem of this approach lies in the determination of the local strain; indeed, only the averages of the strain field over each phase are usually available, and their estimation is dependent on the chosen LEHP. In both the Incremental and Secant methods, these first-order strain averages are used to evaluate, by means of the constitutive law of each phase, the elastic moduli which have to be given as data to the LEHP in the current step of the nonlinear homogenization procedure. Unfortunately, such a kind of strain localization, in general, leads to overestimate the overall composite stiffness [108].

To improve the estimate of the composite behavior, it is in principle possible to subdivide every homogeneous phase into many *subdomains* over which one can compute the strain average at each step, obtaining a more accurate strain distribution. Note that the chance of computing different strain averages over different subdomains of the same phase is dependent on the LEHP. For those LEHPs based on the “classical” Eshelby solution (for which the local fields are homogeneous), it is not possible to get different strain averages over different subdomains belonging to the same phase, at least if each subdomain has the same shape. This is not the case for LEHPs, such as those derived in chapter 7 for syntactic foams, based on the MRP theory, in which the local fields are not homogeneous. Furthermore, the choice of the shape of each subdomain is restricted by the need of being able to solve the corresponding Eshelby problem at each step. This, for instance, means that if we want to apply this subdomain discretization to the case of syntactic foams, according to the LEHPs derived in chapter 7, any phase must be discretized in subdomains shaped as spherical shells, in such a way as to obtain multilayered composite spheres, for which the related Eshelby problem can still be solved (as done in Hervé and Pellegrini [60]). Unfortunately, this subdomain discretization in spherical shells is not, in general, very good to characterize the local strain gradient by computing the strain averages over each subdomain at each step (see, for instance, Bornert et al. [25]).

This subdomain discretization does not represent a theoretical improvement, but it is just a cumbersome and brute-force approach which will not be exploited in the homogenization of the nonlinear behavior of syntactic foams (see chapter 18).

17.2.2 The Incremental Method

Adopting the same notation employed in chapter 6, the rigorous incremental formulation reads:

$$\dot{\varepsilon}_{ij}(\mathbf{x}) = \frac{1}{2}(\dot{u}_{i,j}(\mathbf{x}) + \dot{u}_{j,i}(\mathbf{x})) \quad (17.2.1)$$

$$\dot{\sigma}_{ij,i}(\mathbf{x}) = 0 \quad (17.2.2)$$

$$\dot{u}_i(\Gamma) = \dot{E}_{ij}x_j \quad \text{or} \quad \dot{t}_j(\Gamma) = \dot{\Sigma}_{ij}n_i \quad (17.2.3)$$

$$\dot{\sigma}_{ij}(\mathbf{x}) = L_{ijkl}^{(t)}(\boldsymbol{\varepsilon}(\mathbf{x}))\dot{\varepsilon}_{kl}(\mathbf{x}) \quad (17.2.4)$$

in which

$$L_{ijkl}^{(t)}(\boldsymbol{\varepsilon}(\mathbf{x})) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) L_{ijkl}^{(r,t)}(\boldsymbol{\varepsilon}^{(r)}(\mathbf{x})) \quad (17.2.5)$$

where $L_{ijkl}^{(r,t)}(\boldsymbol{\varepsilon}^{(r)}(\mathbf{x}))$ is the tangent stiffness of the phase r . We want to compute the overall tangent stiffness $L_{ijkl}^{(0,t)}$, defined by

$$\dot{\Sigma}_{ij} = L_{ijkl}^{(0,t)} \dot{E}_{kl} \quad (17.2.6)$$

The Incremental Method assumes that the tangent stiffness $L_{ijkl}^{(r,t)}$ of each phase ($r = 1, \dots, N$) is dependent only upon the strain average over the phase:

$$L_{ijkl}^{(r,t)} = L_{ijkl}^{(r,t)}(\bar{\boldsymbol{\varepsilon}}^{(r)}) \quad (17.2.7)$$

This approximation makes the nonlinear homogenization possible for instance if a LEHP is available which furnishes the value of $\bar{\boldsymbol{\varepsilon}}_{ij}^{(r)}$ at each step:

$$\bar{\boldsymbol{\varepsilon}}_{ij}^{(r)} = \bar{A}_{ijkl}^{(r)} \dot{E}_{kl} \quad (17.2.8)$$

Furthermore, the current tangent stiffness $L_{ijkl}^{(r,t)}$ can be computed by simply deriving the constitutive law of the phase r and, therefore, the Incremental Method does not add nonlinear equations to solve to those required by the LEHP, if it is the case.

As pointed out by Suquet [108], in very particular cases (for instance, there is at least the need of assuming reversible mechanical behavior for each phase), equation (17.2.6) can be integrated along the history obtaining the effective nonlinear constitutive law in closed form.

One of the toughest problems in applying the Incremental Method is that, in general, the nonlinearity makes the tangent tensors $L_{ijkl}^{(r,t)}$ anisotropic and, then, the adopted LEHP has to be able to estimate the effective linear elastic behavior (isotropic or not it does not matter) of a composite made by anisotropic phases. The Willis extension of the Hashin-Shtrikman bounds [129] meets these requirements at least if all the phases are transversely isotropic about the same axis (which can be a priori assumed if the condition of axisymmetric loading holds).

By assuming the heavy hypothesis of *proportional loading* all along the loading path (i.e., the plastic flow directions remain constant over the loading process in each local point; we shall come back on this in subsection 17.2.5 and section 18.3), González and Llorca [52] were able to write the tangent stiffness tensor in isotropic form for isotropic elastoplastic phases following the incremental J_2 -flow theory of plasticity. Therefore, they could exploit the “classical” Self-Consistent Scheme for isotropic phases as LEHP.

17.2.3 The Secant Method

In the rigorous secant formulation equations (17.2.1)–(17.2.3) hold, but equations (17.2.4) and (17.2.5) are replaced with:

$$\sigma_{ij}(\mathbf{x}) = L_{ijkl}^{(s)}(\boldsymbol{\varepsilon}(\mathbf{x}))\varepsilon_{kl}(\mathbf{x}) \quad (17.2.9)$$

and

$$L_{ijkl}^{(s)}(\boldsymbol{\varepsilon}(\mathbf{x})) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) L_{ijkl}^{(r,s)}(\boldsymbol{\varepsilon}^{(r)}(\mathbf{x})) \quad (17.2.10)$$

where $L_{ijkl}^{(r,s)}(\boldsymbol{\varepsilon}^{(r)}(\mathbf{x}))$ is the secant stiffness of the phase r . The homogenization problem consists of computing the overall secant stiffness, defined by

$$\Sigma_{ij} = L_{ijkl}^{(0,s)} E_{kl} \quad (17.2.11)$$

As for the Incremental Method, the Secant Method assumes constant secant stiffness tensor in each phase r according to:

$$L_{ijkl}^{(r,s)} = L_{ijkl}^{(r,s)}(\bar{\boldsymbol{\varepsilon}}^{(r)}) \quad (17.2.12)$$

In general, the Secant Method, with respect to the Incremental Method, has the advantage of allowing one to write the secant tensor in isotropic form, at least for a wide class of nonlinear elastic constitutive laws called “power law materials” [97]. Unfortunately, this is not the case of the J_2 -flow theory of plasticity, for which the definition of an isotropic secant stiffness needs the same heavy hypothesis as that assumed when dealing with the Incremental Method; we shall give more details on this in subsection 17.2.5.

A drawback which typically affects the Secant Method is that in order to determine the secant stiffness tensors from equation (17.2.12) a nonlinear equation has to be solved for each phase.

Moreover, if the nonlinear homogenization procedure is implemented in a material subroutine for a Finite Element code, the Incremental Method is more convenient than the Secant Method since the first one directly gives the consistent jacobian (in the sense of Simo and Taylor [105]), whereas if one employs the Secant Method there is the need of specifically computing the tangent stiffness to assure the quadratic convergence in solving the nonlinear equilibrium equations by means of the Newton method.

The Incremental Method estimates an effective constitutive law stiffer than that obtainable by the Secant Method; for composites in which the phases are nonlinear *elastic*, this is because the Incremental Method, at a general current step, does not update the strains, already computed on the basis of the previous loading history, by accounting for the decrease in the phase stiffness due to the load growth.

17.2.4 The Modified Secant Method

As said, both the Incremental and the Secant methods in general overestimate the overall stiffness of nonlinear composites because of the approximations introduced with equations (17.2.7) and (17.2.12) respectively [108]. Furthermore, Girolmini [51] has proved that if these methods are employed in conjunction with the “classical” Self-Consistent Method,

the obtained estimates might even violate rigorous bounds for nonlinear composites (discussed in section 17.3).

The Modified Secant Method improves both those methods by assuming that the secant tensors of each phase are dependent upon the “second-order moment” of the strain field over the phase, i.e.:

$$L_{ijkl}^{(r,s)} = L_{ijkl}^{(r,s)}(\bar{\varepsilon}_{eq}^{(r)}) \quad (17.2.13)$$

in which

$$\bar{\varepsilon}_{eq}^{(r)} = \sqrt{\frac{1}{|\Omega_r|} \int_{\Omega_r} \varepsilon_{eq}^2(\mathbf{x}) d\Omega_r} \quad (17.2.14)$$

ε_{eq} being the Mises equivalent strain, related to the deviatoric strain e_{ij} as follows:

$$\varepsilon_{eq} = \sqrt{\frac{2}{3} e_{ij} e_{ij}} \quad (17.2.15)$$

This nonlinear localization method can be applied to the Secant Method only, since, if applied to the Incremental Method, it would furnish results senselessly dependent upon the load discretization, for instance such as to give the sum of the localized incremental strains generally different from the localized total strains. Furthermore, this second-order localization can be exploited for invariant quantities only, otherwise giving results which would be frame dependent; in other words, this method may not be used if there is the need of localizing all the strain components, thus limiting the choice of the constitutive laws of the individual phases. The local constitutive models fitting into this method always furnish an isotropic jacobian and typically consist of power laws.

Moreover, let us note that this second-order localization, if extended to the first and third invariants, would not be able to account for their sign. A spontaneous way for overcoming this problem might consist of assigning to the first and the third invariants, localized by means of their second-order moments, the sign obtained from their first-order averages. As far as we know, in the literature there are not examples of homogenization involving the second-order localization of the first and third invariants.

However, beside all the above mentioned limitations, the Modified Secant Method may be made difficult by the computation of equation (17.2.14), the local fields being usually unavailable. One way to accomplish it consists of exploiting the following theorem (Kreher [74] or Buryachenko [32], as quoted in [108]):

Consider a composite constituted by N linear elastic phases. Let (K, G) denote the set of $2N$ elastic moduli $(K^{(r)}, G^{(r)})$, $r = 1, \dots, N$, characterizing the mechanical behavior of all the phases. Let $L_{ijkl}^{(0)}(K, G)$ be the effective stiffness of the composite as a function of the elastic bulk and shear moduli of all the individual phases. Then

$$\bar{\varepsilon}_{eq}^{(r)} = \sqrt{\frac{1}{3c_r} E_{ij} \frac{\partial L_{ijkl}^{(0)}(K, G)}{\partial G^{(r)}} E_{kl}} \quad (17.2.16)$$

The idea behind the definition (17.2.14) can be applied to define the second-order moment of $\vartheta^{(r)} = \varepsilon_{kk}^{(r)}/3$:

$$\bar{\vartheta}^{(r)} = \sqrt{\frac{1}{|\Omega_r|} \int_{\Omega_r} \vartheta^2(\mathbf{x}) d\Omega_r} \quad (17.2.17)$$

and a theorem equivalent to (17.2.16) can be easily proved to obtain the following relation:

$$\bar{\bar{\vartheta}}^{(r)} = \sqrt{\frac{1}{9c_r} E_{ij} \frac{\partial L_{ijkl}^{(0)}(K, G)}{\partial K^{(r)}} E_{kl}} \quad (17.2.18)$$

The simple, but apparently new, result (17.2.18) will not be applied in the following since, in order to homogenize the syntactic foam behavior (see next chapter 18), the stiffness of each phase will be taken to be dependent on the second strain invariant only.

For macroscopically isotropic composites, equation (17.2.16) can be rewritten as:

$$\bar{\bar{\varepsilon}}_{eq}^{(r)} = \sqrt{\frac{1}{c_r} \left(\frac{\partial G_0(K, G)}{\partial G^{(r)}} E_{eq}^2 + 3 \frac{\partial K_0(K, G)}{\partial G^{(r)}} \langle \vartheta \rangle^2 \right)} \quad (17.2.19)$$

where

$$E_{eq} = \sqrt{\frac{2}{3} \mathcal{E}_{ij} \mathcal{E}_{ij}} \quad \langle \vartheta \rangle = \frac{E_{kk}}{3} \quad (17.2.20)$$

$\mathcal{E}_{ij}$ being the deviatoric part of the strain E_{ij} applied to the RVE.

The use of this theorem makes the knowledge of the localization tensors unnecessary. In other words, the Modified Secant Method can be used in conjunction with any LEHP, even if not based on the knowledge of any local fields.

Suquet has shown that the Modified Secant Method significantly improves both the Incremental and Secant methods [108] and proved that it coincides with the Ponte Castañeda variational procedure [107]; this also implies that the estimate obtained by means of the Modified Secant Method, when used in conjunction with a LEHP which furnishes a proper bound of $L_{ijkl}^{(0)}$, enjoys the property of being a bound too (see subsection 17.3.3 for more details). Moreover, the Modified Secant Method predictions, unlike those obtainable by means of the Incremental and Secant methods, can be shown to derive from an elastic potential.

It is perhaps worth a comment that $L_{ijkl}^{(0)}$ in equations (17.2.16) and (17.2.18) does not need to be the *true* effective stiffness, usually unknown and replaced by an estimate or a bound of it. Therefore, the obtained second-order moments of the relevant fields turn out to be those of the fictitious composite whose microstructure is in accordance with the used estimate of $L_{ijkl}^{(0)}$.

In section 18.2, we shall comment more upon this method and we shall put forward a slightly different method, which will be shown to be useful to homogenize the mechanical behavior of composites whose suitable LEHPs are based on the MRP theory.

Other ways to modify the Secant Method

Thébaud et al. [113] (as quoted in [25]) proposed a different nonlinear way to localize the strains to modify the Secant Method in such a way as to make it less stiff. The method has been proposed for composites whose nonlinear phase behavior depends on the Mises equivalent strain only and consists of computing the equivalent local strain $\varepsilon_{eq}(\mathbf{x})$ first, and then evaluating its first-order average; the secant stiffness of each nonlinear phase is assumed to be dependent on such an average only. If variable local fields are available, as when the adopted LEHP is based on the MRP theory, this is in principle a good

localization method, but, unfortunately, as pointed out in [25], the average operation is in general not feasible in closed-form because of the presence of the square root operator inside the integral; therefore, the only way to deal with this method is to perform a very expensive numerical integration.

Bornert et al. [25] proposed one more method for defining the secant shear tensor, $G^{(r,s)}$, which rules the nonlinear behavior of the generic phase r . It consists of computing an “equivalent secant shear modulus” after having averaged over the phase the product of the deviatoric strain e_{ij} times the secant shear modulus distribution $G^{(s)}(\mathbf{e})$:

$$G^{(r,s)} = \sqrt{\frac{\overline{G^{(s)}(\mathbf{e})e_{ij}}^{(r)} \overline{G^{(s)}(\mathbf{e})e_{ij}}^{(r)}}{\overline{e_{kl}}^{(r)} \overline{e_{kl}}^{(r)}}} \quad (17.2.21)$$

This method, which is appropriate for instance for the MRP theory where e_{ij} is in general available as a variable field over any phase, needs the solution of the local constitutive law for $G^{(s)}(\mathbf{e}(\mathbf{x}))$ for the continuously variable field $e_{ij}(\mathbf{x})$. This operation may be very expensive, $G^{(s)}(\mathbf{e})$ being often nonlinear; if closed-form solutions for $G^{(s)}(\mathbf{e})$ are not available, equation (17.2.21) can be solved only numerically. Moreover, this kind of localization is dependent on the chosen constitutive law for the phase over which a mean strain has to be computed and, then, it does not allow one to derive general formulae related to a particular LEHP. Unfortunately, this method has not been tested even in [25].

It is worth remarking that the variable fields employed with the here mentioned methods, i.e., those available from the MRP-based LEHP, are not in general the real ones, even in a RVE whose microstructure is such that the effective elastic moduli are exactly equal to those predicted by the LEHP. In other words, the variable fields, furnished by the Eshelby problem of a heterogeneous inclusion in a MRP-based LEHP, are, in general, just useful to indirectly account for some morphological feature in computing the effective elastic moduli. On the contrary, equations (17.2.16) and (17.2.18) allow one to indirectly account for the true local fields present in the RVE whose effective stiffness is furnished by the chosen LEHP. We shall examine closely this point in section 18.2.

17.2.5 Particularization to the J_2 -flow theory of plasticity

Finally, it is important to show how the J_2 -flow theory of plasticity can be used to describe the local phase behavior in composites which need to be homogenized by means of a LEHP which is not able to account for the phase anisotropy due to the strain growth. This is for instance the case of syntactic foams, whose LEHPs described in chapter 7 are based on elastic solutions which require every phase to be isotropic. This problem can be solved for all the three methods described in the previous sections by assuming the so-called *proportional loading condition*, which means that the plastic strain and the stress tensors have components which keep all over the loading history the same proportions one each other (actually, for the stress tensor this is true only after the yield stress is reached for the first time); in other words, we can directly compute the local plastic strain in the phase r from the equation

$$\varepsilon_{ij}^{(r,pl)} = \frac{3\varepsilon_{eq}^{(r,pl)} s_{ij}^{(r)}}{2\sigma_{eq}^{(r)}} \quad (17.2.22)$$

in which $\varepsilon_{eq}^{(r,pl)}$ is the equivalent plastic strain, defined as the following second invariant of the plastic strain tensor (deviator):

$$\varepsilon_{eq}^{(r,pl)} = \sqrt{\frac{2}{3} e_{ij}^{(r,pl)} e_{ij}^{(r,pl)}} \quad (17.2.23)$$

and $\sigma_{eq}^{(r)}$ is the equivalent stress, related as follows to the stress deviator $s_{ij}^{(r)}$:

$$\sigma_{eq}^{(r)} = \sqrt{\frac{3}{2} s_{ij}^{(r)} s_{ij}^{(r)}} \quad (17.2.24)$$

This assumption allows us to represent both the tangent and the secant stiffnesses of the phase r governed by the J_2 -flow theory with isotropic hardening as isotropic fourth-order tensors:

$$L_{ijkl}^{(r,t)} = 2G^{(r)} \left(1 - \frac{1}{1 + \frac{H'(r)}{3G^{(r)}}} \right) K_{ijkl} + 3K^{(r)} J_{ijkl} \quad (17.2.25)$$

$$L_{ijkl}^{(r,s)} = \frac{2G^{(r)}}{1 + \frac{3G^{(r)} \varepsilon_{eq}^{(r,pl)}}{\sigma_{eq}^{(r)}}} K_{ijkl} + 3K^{(r)} J_{ijkl} \quad (17.2.26)$$

in which $H'(r)$ is the first derivative of the strain hardening function $(\sigma_Y^{(r)}(\varepsilon_{eq}^{(r,pl)})) = \sigma_0^{(r)} + H^{(r)}(\varepsilon_{eq}^{(r,pl)})$, $\sigma_0^{(r)}$ and $\sigma_Y^{(r)}$ being the initial and current yield stress of the phase r respectively) with respect to the equivalent plastic strain $\varepsilon_{eq}^{(r,pl)}$.

The derivation of expression (17.2.26) is quite straightforward [108], whereas the slightly more involved derivation of (17.2.25) can be found in [52].

17.3 Variational methods for nonlinear composites

Most of this section and part of its quotations are taken from [97] and [96].

17.3.1 Behavior of the phases and basic results

Talbot and Willis [110] provided the first extension of the Hashin–Shtrikman variational principle for nonlinear composites. This principle works, as well as that of Ponte Castañeda (see, for instance, [96] and [97]) which will be reported later, for composites whose individual N phases are governed by the strain energy functions $w^{(r)}(\boldsymbol{\varepsilon})$ ($r = 1, \dots, N$), convex in $\boldsymbol{\varepsilon}$, such that:

$$\sigma_{ij}^{(r)} = \frac{\partial w^{(r)}(\boldsymbol{\varepsilon})}{\partial \varepsilon_{ij}} \quad (17.3.1)$$

or, dually, by the stress energy functions $u^{(r)}(\boldsymbol{\sigma})$, convex in $\boldsymbol{\sigma}$, such that:

$$\varepsilon_{ij}^{(r)} = \frac{\partial u^{(r)}(\boldsymbol{\sigma})}{\partial \sigma_{ij}} \quad (17.3.2)$$

For the purpose of deriving bounds, it is useful to note that the strain and stress energy functions, since convex, are linked by means of the Legendre–Fenchel transform:

$$u^{(r)}(\boldsymbol{\sigma}) = \left(w^{(r)}(\boldsymbol{\varepsilon})\right)^{\star} = \sup_{\boldsymbol{\varepsilon}^{(r)}} \left\{ \sigma_{ij}^{(r)} \varepsilon_{ij}^{(r)} - w^{(r)}(\boldsymbol{\varepsilon}) \right\} \quad (17.3.3)$$

in which the superscript $\star$ indicates the so-called convex dual function (or convex polar).

The local potentials over the whole RVE read:

$$w(\mathbf{x}, \boldsymbol{\varepsilon}) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) w^{(r)}(\boldsymbol{\varepsilon}) \quad (17.3.4)$$

$$u(\mathbf{x}, \boldsymbol{\sigma}) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) u^{(r)}(\boldsymbol{\sigma}) \quad (17.3.5)$$

where $\chi^{(r)}(\mathbf{x})$ is the characteristic function of the phase r .

If the boundary conditions (6.1.5) are applied to the RVE, the minimum Potential Energy principle states that the displacement field $u_i(\mathbf{x})$ is the solution of the following problem, which also defines the effective strain energy potential $W(\mathbf{E})$:

$$W(\mathbf{E}) = \inf_{\mathbf{v} \in \mathcal{K}(\mathbf{E})} \langle w(\mathbf{x}, \boldsymbol{\varepsilon}(\mathbf{v})) \rangle \quad (17.3.6)$$

in which $\mathcal{K}(\mathbf{E})$ is the following set of displacement fields $v_i(\mathbf{x})$:

$$\mathcal{K}(\mathbf{E}) = \left\{ v_i(\mathbf{x}) \mid \varepsilon_{ij} = \frac{1}{2}(v_{i,j} + v_{j,i}) \text{ and } v_i(\mathbf{x}) = E_{ij}x_j \ \forall \mathbf{x} \in \Gamma \right\} \quad (17.3.7)$$

Dually, the minimum Complementary Energy principle allows one to conclude that $\sigma_{ij}(\mathbf{x})$ is the solution of the problem, which also defines the effective stress energy potential $U(\boldsymbol{\Sigma})$:

$$U(\boldsymbol{\Sigma}) = \inf_{\boldsymbol{\tau} \in \mathcal{S}(\boldsymbol{\Sigma})} \langle u(\mathbf{x}, \boldsymbol{\tau}) \rangle \quad (17.3.8)$$

in which $\mathcal{S}(\boldsymbol{\Sigma})$ is the following set of stress fields $\tau_{ij}(\mathbf{x})$:

$$\mathcal{S}(\boldsymbol{\Sigma}) = \left\{ \tau_{ij}(\mathbf{x}) \mid \tau_{ij,i}(\mathbf{x}) = 0 \ \forall \mathbf{x} \in \Omega \text{ and } \langle \tau_{ij} \rangle = \Sigma_{ij} \right\} \quad (17.3.9)$$

where Σ_{ij} is the effective stress related to the imposed effective strain E_{ij} .

If the boundary conditions (6.1.6) are assumed, the definitions of $\mathcal{K}(\mathbf{E})$ and $\mathcal{S}(\boldsymbol{\Sigma})$ become

$$\mathcal{K}(\mathbf{E}) = \left\{ v_i(\mathbf{x}) \mid \varepsilon_{ij} = \frac{1}{2}(v_{i,j} + v_{j,i}) \text{ and } \langle \varepsilon_{ij}(\mathbf{v}) \rangle = E_{ij} \right\} \quad (17.3.10)$$

where E_{ij} is the effective strain related to the imposed effective stress Σ_{ij} , and

$$\mathcal{S}(\boldsymbol{\Sigma}) = \left\{ \tau_{ij}(\mathbf{x}) \mid \tau_{ij,i}(\mathbf{x}) = 0 \ \forall \mathbf{x} \in \Omega \text{ and } \tau_{ij}(\mathbf{x})n_i = \Sigma_{ij}n_i \ \forall \mathbf{x} \in \Gamma \right\} \quad (17.3.11)$$

Note that both the definitions of the effective strain potential $W(\mathbf{E})$ under the displacement boundary conditions (6.1.5) and of the effective stress potential $U(\boldsymbol{\Sigma})$ under the force boundary conditions (6.1.6) follow straightforwardly from the classical principles of the

Total Potential Energy and the Complementary Energy respectively, whereas the derivations of the above definitions of $W(\mathbf{E})$ under the boundary conditions (6.1.6) and of $U(\mathbf{\Sigma})$ under the boundary conditions (6.1.5) need some convex analysis [96].

Under the further assumption that $w^{(r)}(\boldsymbol{\varepsilon})$ and $u^{(r)}(\boldsymbol{\sigma})$ are strictly convex, the two types of boundary conditions (6.1.5) and (6.1.6) furnish exactly the same results for the overall properties [97].

It is important to highlight that the definitions (17.3.6) and (17.3.8) imply, through Hill's lemma (6.1.8), that [64]

$$\Sigma_{ij} = \frac{\partial W(\mathbf{E})}{\partial E_{ij}} \quad (17.3.12)$$

and

$$E_{ij} = \frac{\partial U(\mathbf{\Sigma})}{\partial \Sigma_{ij}} \quad (17.3.13)$$

Furthermore, the convexity of $w^{(r)}(\boldsymbol{\varepsilon})$ and $u^{(r)}(\boldsymbol{\sigma})$ guarantees that both $W(\mathbf{E})$ and $U(\mathbf{\Sigma})$ are convex potentials and that

$$U(\mathbf{\Sigma}) = \left(W(\mathbf{E}) \right)^* = \sup_{\mathbf{E}} \left\{ \Sigma_{ij} E_{ij} - W(\mathbf{E}) \right\} \quad (17.3.14)$$

The minimum energy principles (17.3.6) and (17.3.8) can be used to obtain the so-called Taylor [112] and Sachs [102] bounds which are, for nonlinear composites, the corresponding to the Voigt and Reuss ones in the linear elastic range (see section 6.4); by taking uniform strain or stress trial fields all over the RVE and by exploiting equation (17.3.14), we indeed get

$$\left(\sum_{r=1}^N c_r u^{(r)} \right)^* (\mathbf{E}) \leq W(\mathbf{E}) \leq \left(\sum_{r=1}^N c_r w^{(r)} \right) (\mathbf{E}) \quad (17.3.15)$$

These rigorous bounds were found also by Bishop and Hill ([23] and [24]) for rigid perfectly plastic polycrystals and by Drucker [40] for particulate composites whose matrix is elastic perfectly plastic. Unfortunately, as for linear elasticity, these bounds are not of much use since they are not sharp enough, particularly for composites with high contrast.

17.3.2 The Talbot and Willis variational principle

The Talbot and Willis [110] extension of the Hashin–Shtrikman upper bound [57] consists, as for linear elasticity, of properly choosing a *homogeneous linear elastic comparison medium* of stiffness $L_{ijkl}^{(R)}$, to which the “reference potential” $w^{(R)}(\boldsymbol{\varepsilon}) = (1/2)\varepsilon_{ij}L_{ijkl}^{(R)}\varepsilon_{kl}$ can be associated; this choice must be taken in such a way that the potential difference $w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon})$ is a concave function of $\boldsymbol{\varepsilon}$, whose so-called concave polar is defined as follows and denoted by means of the subscript $\star$:

$$\left(w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon}) \right)_{\star} (\mathbf{x}, \boldsymbol{\tau}) = \inf_{\boldsymbol{\varepsilon}} \left\{ \tau_{ij} \varepsilon_{ij} - \left(w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon}) \right) \right\} \quad (17.3.16)$$

in which $\tau_{ij}(\mathbf{x})$ is the so-called “polarization field”¹ that consists of the local stresses arising in the fictitious RVE governed by the potential $w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon})$ and subjected

¹The term “polarization field” has been introduced by Hashin and Shtrikman [57] to mean the independent field in their variational principle.

to the local strain field $\varepsilon_{ij}(\mathbf{x})$ of the actual RVE to which the macroscopic strain E_{ij} is imposed at the boundary.

Since $w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon})$ is concave in $\boldsymbol{\varepsilon}$, by taking its concave polar twice we obtain it again:

$$w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon}) = \left(w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon}) \right)_{\star\star} = \inf_{\boldsymbol{\tau}} \left\{ \tau_{ij} \varepsilon_{ij} - \left(w - w^{(R)} \right)_{\star}(\mathbf{x}, \boldsymbol{\tau}) \right\} \quad (17.3.17)$$

where every subscript $\star$ means that the concave polar is taken of the subscripted function.

Substituting this last relation into equation (17.3.6), after some convex analysis, it is possible to get

$$W(\mathbf{E}) = \inf_{\boldsymbol{\tau}} \left\{ \inf_{\mathbf{v} \in \mathcal{K}(\mathbf{E})} \left\langle w^{(R)}(\boldsymbol{\varepsilon}(\mathbf{v})) + \tau_{ij} \varepsilon_{ij} \right\rangle - \left\langle \left(w - w^{(R)} \right)_{\star}(\mathbf{x}, \boldsymbol{\tau}) \right\rangle \right\} \quad (17.3.18)$$

Taking the polarization field τ_{ij} in the inner infimum problem as given, the displacement field v_i can be obtained by exploiting the Green function $G_{ij}^{(R)}$ of the reference medium:

$$\varepsilon_{ij}(\mathbf{x}) = E_{ij} - \int_{\Omega} \Gamma_{ijkl}^{(R)}(\mathbf{x}, \mathbf{x}') \left(\tau_{kl}(\mathbf{x}') - \langle \tau_{kl} \rangle \right) d\Omega' \quad (17.3.19)$$

in which

$$\Gamma_{ijkl}^{(R)}(\mathbf{x}, \mathbf{x}') = \frac{\partial^2 G_{ik}^{(R)}}{\partial x_j \partial x'_l} \Big|_{(ij), (kl)} \quad (17.3.20)$$

where the parentheses enclosing the subscripts denote symmetric parts with respect to the enclosed subscripts [129].

Since it is not feasible to compute the Green function $G_{ij}^{(R)}$ for any bounded region Ω , the kernel $\Gamma_{ijkl}^{(R)}$ is usually approximated by the kernel deriving from the infinite body Green function.

The “outer” infimum problem in (17.3.18) can be solved only in terms of piecewise constant polarization fields. This produces the form

$$W(\mathbf{E}) \leq \inf_{\substack{\boldsymbol{\tau}^{(t)}, \\ t=1, \dots, N}} \left\{ w^{(R)}(\mathbf{E}) + \langle \tau_{ij} \rangle E_{ij} - \sum_{r=1}^N c_r \left(w^{(r)} - w^{(R)} \right)_{\star}(\boldsymbol{\tau}^{(r)}) - \frac{1}{2} \sum_{r=1}^N \sum_{s=1}^N \tau_{ij}^{(r)} \Gamma_{ijkl}^{(rs)} \tau_{kl}^{(s)} \right\} \quad (17.3.21)$$

in which the operator $\Gamma_{ijkl}^{(rs)}$ accounts for the composite microstructure:

$$\Gamma_{ijkl}^{(rs)} = \left\langle \int_{\Omega} \chi^{(r)}(\mathbf{x}) \left(\chi^{(s)}(\mathbf{x}') - c_s \right) \Gamma_{ijkl}^{(R)}(\mathbf{x}, \mathbf{x}') d\Omega' \right\rangle \quad (17.3.22)$$

Finally, the solution for the N constant polarization fields consists of the following N tensorial equations:

$$\frac{\partial}{\partial \tau_{ij}^{(r)}} \left(w^{(r)} - w^{(R)} \right)_{\star}(\boldsymbol{\tau}^{(r)}) + \frac{1}{c_r} \sum_{s=1}^N \Gamma_{ijkl}^{(rs)} \tau_{kl}^{(r)} = E_{ij} \quad r = 1, \dots, N \quad (17.3.23)$$

and the overall stress turns out to be

$$\Sigma_{ij} = L_{ijkl}^{(R)} E_{kl} + \langle \tau_{ij} \rangle \quad (17.3.24)$$

By choosing $L_{ijkl}^{(R)}$ in such a way that $w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon})$ is convex, it is possible to obtain a similar formulation to produce lower bounds. Furthermore, the dual variational principle involving the stress energy function instead of the strain energy function can be similarly derived.

For composites whose phases are linear elastic, it is in principle possible to choose $L_{ijkl}^{(R)}$ in such a way that $w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon})$ is either concave or convex, then obtaining both upper and lower bounds: the choices of section 6.5 permit to recover the “classical” Hashin–Shtrikman bounds. In this case, indeed, the evaluation of (17.3.21) is simple, because the following relation holds:

$$\left(w^{(r)} - w^{(R)}\right)_\star(\boldsymbol{\tau}^{(r)}) = \frac{1}{2} \sum_{r=1}^N c_r \tau_{ij}^{(r)} \left(L_{ijkl}^{(r)} - L_{ijkl}^{(R)}\right)^{-1} \tau_{kl}^{(r)} \quad (17.3.25)$$

Unfortunately, for nonlinear composites $w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\boldsymbol{\varepsilon})$ is typically neither concave nor convex and, therefore, the equality in equation (17.3.18) must be replaced by an inequality. In general, depending on the growth of $w(\mathbf{x}, \boldsymbol{\varepsilon})$ with respect to $\boldsymbol{\varepsilon}$, it is not possible to find both upper and lower bounds, but only one of them. Note that the formulation in the stress energy function furnishes exactly the same bounds. To always get both lower and upper bounds, Talbot and Willis [111] suggested to replace the homogeneous linear elastic comparison medium with a nonlinear one.

An approach similar to that summarized here has been followed by Bisegna and Luciano [22] to specifically derive the Hashin–Shtrikman bounds for nonlinear composite materials with periodic microstructure and to discuss their variational nature.

17.3.3 The Ponte Castañeda variational principle

The variational approach of Ponte Castañeda ([94], [95], and [96]) is based on a *linear comparison composite* and, beside being able to reduce itself to the Talbot and Willis extension of the Hashin–Shtrikman bounding procedure, it has the advantage, with respect to the Talbot and Willis approach, of allowing the generation of bounds and estimates, for nonlinear composites, corresponding to any suitable linear elastic homogenization procedure (LEHP).

The local constitutive behavior, defined in subsection 17.3.1 by means of the local potential, has to be further restricted to be nonlinearly dependent on the Mises equivalent strain $\varepsilon_{eq}^{(r)}$ only. This requirement constrains the local potential to have the following form:

$$w(\mathbf{x}, \boldsymbol{\varepsilon}) = \frac{1}{2} \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) K^{(r)} \varepsilon_{kk}^2(\mathbf{x}) + f(\mathbf{x}, \varepsilon_{eq}^2(\mathbf{x})) \quad (17.3.26)$$

in which

$$f(\mathbf{x}, \varepsilon_{eq}^2(\mathbf{x})) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) f^{(r)}(\varepsilon_{eq}^2(\mathbf{x})) \quad (17.3.27)$$

$f^{(r)}(\varepsilon_{eq}^2(\mathbf{x}))$ being the potential functions characterizing the deviatoric behavior of the phases.

Ponte Castañeda took the reasonable assumption that the deviatoric part of $w(\mathbf{x}, \boldsymbol{\varepsilon})$ has weaker-than-quadratic growth in ε_{eq} , which is then equivalent to prescribe that $f(\mathbf{x}, \varepsilon_{eq}^2(\mathbf{x}))$

has weaker-than-linear growth in ε_{eq}^2 and it is thus concave; for some materials this turns out to imply that a concave f corresponds to a convex w . Recall that the concavity of f implies $f = f_{**}$.

Let us here omit several details concerning the derivation of the following results, which can be obtained by means of both some convex analysis similar to that exploited by Talbot and Willis to extend the Hashin–Shtrikman bounds (see previous subsection 17.3.2) and the following starting point.

The introduction of a linear comparison composite (with completely general microstructure, even continuously variable in the space) whose strain energy function reads

$$w^{(R)}(\mathbf{x}, \boldsymbol{\varepsilon}) = \frac{1}{2} \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) K^{(r)} \varepsilon_{kk}^2(\mathbf{x}) + \frac{3}{2} G^{(R)}(\mathbf{x}) \varepsilon_{eq}^2(\mathbf{x}) \quad (17.3.28)$$

allows the following representation of the local potential w :

$$w(\mathbf{x}, \boldsymbol{\varepsilon}) = \inf_{G^{(R)}(\mathbf{x}) \geq 0} \left\{ w^{(R)}(\mathbf{x}, \boldsymbol{\varepsilon}) + \nu(\mathbf{x}, G^{(R)}(\mathbf{x})) \right\} \quad (17.3.29)$$

where

$$\nu(\mathbf{x}, G^{(R)}(\mathbf{x})) = \sup_{\boldsymbol{\varepsilon}} \left\{ w(\mathbf{x}, \boldsymbol{\varepsilon}) - w^{(R)}(\mathbf{x}, \boldsymbol{\varepsilon}) \right\} \quad (17.3.30)$$

Finally, the effective potential reads

$$W(\mathbf{E}) = \inf_{G^{(R)}(\mathbf{x}) \geq 0} \left\{ \inf_{\boldsymbol{\varepsilon}(\mathbf{x}) \in \mathcal{K}(\mathbf{E})} \left\langle w^{(R)}(\mathbf{x}, \boldsymbol{\varepsilon}) \right\rangle + \left\langle \nu(\mathbf{x}, G^{(R)}(\mathbf{x})) \right\rangle \right\} \quad (17.3.31)$$

Note that, under the assumption of concavity of $f(\mathbf{x}, \varepsilon_{eq}^2(\mathbf{x}))$, this representation follows directly from equation (17.3.6). The problem is in this case solved by minimizing with respect to the shear modulus distribution $G^{(R)}(\mathbf{x})$; its solution is the *secant* modulus distribution $\hat{G}^{(R)}(\mathbf{x})$ whose knowledge allows one to write:

$$\sigma_{ij}(\mathbf{x}) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) K^{(r)} \varepsilon_{kk}(\mathbf{x}) \delta_{ij} + 2 \hat{G}^{(R)}(\mathbf{x}) e_{ij}(\mathbf{x}) \quad (17.3.32)$$

As for the Talbot and Willis approach, the formulation (17.3.31) can be shown to be completely equivalent to its dual involving the stress energy function, provided that w and u can be related by the Legendre–Fenchel transformation. Therefore, also this approach suffers the limitation of providing, if any at all, only one bound (upper or lower depending on the potential growth).

A suitable way to solve approximately the problem (17.3.31) is to take $G^{(R)}(\mathbf{x})$ piecewise constant as follows:

$$G^{(R)}(\mathbf{x}) = \sum_{r=1}^N \chi^{(r)}(\mathbf{x}) G^{(R,r)} \quad (17.3.33)$$

This allows the “inner” minimum problem in (17.3.31) to be solved by exploiting any suitable LEHP, which predicts $L_{ijkl}^{(est,0)}(G^{(R,1)}, G^{(R,2)}, \dots, G^{(R,N)})$ as elastic tensor for the actual composite microstructure. Obviously, the global variational problem (17.3.31), when solved, can in this case furnish an upper bound to the effective nonlinear behavior if a LEHP is used which gives an upper bound to the effective elastic moduli; moreover,

this method can not preserve the bounding nature of LEHPs which furnish lower bounds and it overestimates the effective nonlinear behavior if any LEHP as the Self-Consistent or the Mori-Tanaka ones are employed.

The “outer” minimization produces a system of N equations, whose solution consists of the N local secant moduli $\hat{G}^{(R,r)}$.

The final form of the overall nonlinear behavior can then be expressed in the following secant form, in which the nonlinearity is given by the dependence of $\hat{G}^{(R,r)}$ on the applied strain E_{ij} :

$$\Sigma_{ij} = L_{ijkl}^{(est,0)}(\hat{G}^{(R,1)}, \hat{G}^{(R,2)}, \dots, \hat{G}^{(R,N)})E_{kl} \quad (17.3.34)$$

The Ponte Castañeda variational approach here summarized has been shown by Suquet [108] to be coincident with the Modified Secant Method (see section 17.2); i.e., the Modified Secant Method can be used to produce bounds to the overall nonlinear elastic behavior of composites.

The application to syntactic foams of either the Ponte Castañeda variational principle or the Modified Secant Method is not straightforward at all; indeed, at least two difficulties arise: the first one consists of the necessity of employing a LEHP chosen among those developed in chapter 7 (this is because those LEHPs seem to be the only accurate enough to homogenize syntactic foams), which, by the way, do not furnish any bound, but a direct estimate. Unfortunately, to incorporate them into nonlinear methods like those here mentioned is, to say the least, cumbersome. Secondly, the real constitutive behavior of the epoxy resins used by us as matrixes (see chapter 16) does not fit into the hypotheses on the mechanical behavior for the individual phases. This last problem can anyway be tentatively overcome by approximating the epoxy resin behavior with some nonlinear elastic constitutive law; this will be done in the next section 18.3.

The above derivation works exactly in the same way if the strain tensors are replaced with the strain rate tensors, which even allows the use of finite strains. This, i.e., means that we can deal with constitutive laws like the following one, which, if it is the case, would replace equation (17.3.1):

$$\sigma_{ij}^{(r)} = \frac{\partial v^{(r)}(\dot{\varepsilon}_{eq})}{\partial \dot{\varepsilon}_{ij}} \quad (17.3.35)$$

in which $v^{(r)}(\dot{\varepsilon}_{eq})$ is the potential of the phase r and $\dot{\varepsilon}_{ij}$ and σ_{ij} represent the Eulerian strain rate and the Cauchy stress respectively.

Starting from this observation, Kailasam and Ponte Castañeda [72] (interested in accounting for the microstructure evolution in porous metals) developed an approximate way to model plasticity by means of the Ponte Castañeda variational principle. The approximation consists of uncoupling the determination of the elastic strains from that of the plastic strains and computing the latter by integrating their rates, which are described for each phase by means of an equation like (17.3.35). This method gives accurate results if the elastic strains are small in comparison to the plastic ones. This approximation is needed since the Ponte Castañeda variational principle does not work for potentials which are functions of both strain and strain rate tensors. In general, as it will be shown in the next section 17.4, one of the problems in considering composites made up of elastoplastic phases is that the macroscopic elastic and plastic strains, in general, can not be obtained as averages of the analogous local fields, owing to the lack of individual compatibility.

17.4 Transformation Field Analysis

Let us now introduce the Transformation Field Analysis (see, for instance, Dvorak and Bahei-El-Din [42]). This method is based on the use of the so-called eigenstrain and eigenstress fields. Eigenstrains are stress-free and not necessarily compatible strain fields; they are said stress-free in the sense that they cause residual stress fields, independent on the applied mechanical load, only if the body is properly constrained. Dually, eigenstresses are deformation-free and generally non-equilibrated stress fields. These fields are useful to model many kinds of linear and nonlinear mechanical phenomena such as the inhomogeneity effect in the Eshelby problem (Hill [66]), the thermoelasticity, and any inelastic behavior. Since this section is concerned with nonlinear elasticity and/or plasticity, we limit the general Transformation Field theory to this case.

The behavior of each phase r can be always written in terms of the linear elastic stiffness if the inelastic (eigen)strain $\varepsilon_{ij}^{(r,in)}(\mathbf{x})$ or the relaxation (eigen)stress tensor $\sigma_{ij}^{(r,re)}(\mathbf{x})$ (which is the elastic corrector for irreversible constitutive laws) are employed:

$$\sigma_{ij}^{(r)}(\mathbf{x}) = L_{ijkl}^{(r)} \left(\varepsilon_{kl}^{(r)}(\mathbf{x}) - \varepsilon_{kl}^{(r,in)}(\mathbf{x}) \right) = L_{ijkl}^{(r)} \varepsilon_{kl}^{(r)}(\mathbf{x}) + \sigma_{ij}^{(r,re)}(\mathbf{x}) \quad (17.4.1)$$

in which

$$\sigma_{ij}^{(r,re)}(\mathbf{x}) = -L_{ijkl}^{(r)} \varepsilon_{kl}^{(r,in)}(\mathbf{x}) \quad (17.4.2)$$

Because of the presence over the composite of the eigenstrain distribution $\varepsilon_{ij}^{(in)}(\mathbf{x})$, the strain localization can be written as:

$$\varepsilon_{ij}(\mathbf{x}) = A_{ijkl}(\mathbf{x}) E_{kl} + \int_{\Omega} D_{ijkl}(\mathbf{x}, \mathbf{x}') \varepsilon_{kl}^{(in)}(\mathbf{x}') d\Omega(\mathbf{x}') \quad (17.4.3)$$

in which $D_{ijkl}(\mathbf{x}, \mathbf{x}')$ is a Green-type influence function that furnishes the compatible strain at $\mathbf{x}$ due to a unitary eigenstrain at $\mathbf{x}'$ (i.e., $D_{ijkl}(\mathbf{x}, \mathbf{x}')$ does not account for the strain at $\mathbf{x}$ due to the boundary conditions (6.1.5) or (6.1.6)). Actually, the approach followed in order to derive equation (17.4.3) is somehow similar to that proposed much earlier by Colonnetti [38], who was mostly interested in metal plasticity.

In general, the problem of determining $D_{ijkl}(\mathbf{x}, \mathbf{x}')$ is impossible to solve, since we can not know the elastic solution for a *random* RVE subjected to any kind of loading condition. Even if the composite microstructure were exactly known (i.e., if the linear elastic problem were deterministic), in general, only a numerical set of linear elastic solutions approximating the tensor $D_{ijkl}(\mathbf{x}, \mathbf{x}')$ could be obtained, but this operation might be too expensive.

Therefore, an approximation has to be introduced. The one proposed in [41] consists of discretizing the RVE into M subdomains and taking the eigenstrain constant over each subdomain s (note that the roughest discretization corresponds to choosing each subdomain coincident with a single phase, i.e., $M = N$). Then, equation (17.4.3) simplifies into:

$$\varepsilon_{ij}(\mathbf{x}) = A_{ijkl}(\mathbf{x}) E_{kl} + \sum_{s=1}^M D_{ijkl}^{(s)}(\mathbf{x}) \bar{\varepsilon}_{kl}^{(s,in)} \quad (17.4.4)$$

in which $D_{ijkl}^{(s)}(\mathbf{x})$ furnishes the strain at $\mathbf{x}$ due to a unitary eigenstrain over the subdomain s and $\bar{\varepsilon}_{kl}^{(s,in)}$ is the eigenstrain average over that subdomain. Averaging equation (17.4.4)

over the subdomain r , we get the mean strain over that subdomain:

$$\bar{\varepsilon}_{ij}^{(r)} = \bar{A}_{ijkl}^{(r)} E_{kl} + \sum_{s=1}^M D_{ijkl}^{(rs)} \bar{\varepsilon}_{kl}^{(s,in)} \quad (17.4.5)$$

where $D_{ijkl}^{(rs)}$ are the so-called *transformation influence functions* which give the strain field average over the subdomain r due to the unitary eigenstrain over the subdomain s . These functions can be exactly related to the localization tensors and the stiffness of the phases for a two-phase composite discretized into two subdomains coincident to the phases (see, for instance, [42]); for multi-phase heterogeneous materials, the transformation influence functions can instead be only estimated, by means of a suitable LEHP which has to furnish the effective stiffness and the localization tensors (see, for instance, [41]):

$$D_{ijkl}^{(rs)} = (I_{ijmn} - \bar{A}_{ijmn}^{(r)}) (L_{mnpq}^{(r)} - L_{mnpq}^{(0)})^{-1} (\delta_{rs} I_{pqtv} - c_s \bar{A}_{tvpq}^{(s)}) L_{tvkl}^{(s)} \quad (17.4.6)$$

As shown by Dvorak and Benveniste [43], equation (17.4.6) holds at least for both the Mori–Tanaka and the Self–Consistent methods. The numerical computation of $D_{ijkl}^{(rs)}$ by means of the Finite Element Method or the Boundary Element Method is sensible when the composite is representable with a simple unit cell model (therefore, the composite has to be, or is assumed to be, periodic); actually, in that case, since the mechanical problem is deterministic and since unit cell analyses are not too expensive, one could just simulate the composite behavior by running some Finite Element analyses in the nonlinear range. Anyway, in principle, it is possible to compute the transformation influence functions once for all by means of a sufficient number of linear elastic Finite Element analyses on the unit cell and then one may exploit the eigenstrain approach to simulate at low cost the composite behavior.

After the transformation influence functions are computed, the homogenization goal is to find the overall stress Σ_{ij} acting on the RVE subjected to the overall strain E_{ij} , whose effective elastic stiffness $L_{ijkl}^{(0)}$ is already known by means of the chosen LEHP:

$$\Sigma_{ij} = L_{ijkl}^{(0)} (E_{kl} - E_{kl}^{(in)}) = L_{ijkl}^{(0)} E_{kl} + \Sigma_{kl}^{(re)} \quad (17.4.7)$$

in which the overall eigenstrain $E_{ij}^{(in)}$ is given by the following Levin equation [81], completely similar to equation (13.0.12) for thermoelasticity:

$$E_{ij}^{(in)} = \sum_{r=1}^N c_r \bar{\varepsilon}_{kl}^{(r,in)} \bar{B}_{kl ij}^{(r)} \quad (17.4.8)$$

in which $\bar{B}_{ijkl}^{(r)}$ is the averaged stress concentration tensor of the phase r . At this point, the eigenstrain averages over each phase are still unknown, but we may assume that they can be computed by means of the constitutive behavior of each phase, that is known and can in general furnish the inelastic strain tensor as a function of the stress and the history. Besides, assuming that such a kind of constitutive relation holds for the field averages over the subdomain s , we have:

$$\bar{\varepsilon}_{ij}^{(s,in)} = f_{ij}^{(s)}(\bar{\sigma}^{(s)}) \quad (17.4.9)$$

Since $\bar{\sigma}_{ij}^{(r)} = L_{ijkl}^{(r)} (\bar{\varepsilon}_{kl}^{(r)} - \bar{\varepsilon}_{kl}^{(r,in)})$, equations (17.4.5) and (17.4.9) furnish a nonlinear system in the eigenstrains $\bar{\varepsilon}_{ij}^{(r,in)}$.

17.5 Other nonlinear homogenization methods

17.5.1 A method based on the Fast Fourier Transform

Moulinec and Suquet [89] proposed a numerical method based on the Fast Fourier Transform (FFT) to compute the response of nonlinear composites. This method is suitable to solve the unit cell problem and, since it makes direct use of digital images of the real microstructure (obtained, for instance, by Scanning Electron Microscopy), it can account for any kind of microstructure complexity, at least in two dimensions. This procedure overcomes the problem of meshing the microstructure, has the advantage of taking the unit cell periodicity conditions automatically into account, and, being based on the Green function of a linear elastic and homogeneous comparison material, can easily handle, if it is the case, the incompressibility constraint. The worst drawback of the method consists of its failure if the composite contrast is infinite; therefore, this method is not suitable for predicting the mechanical behavior of syntactic foams, in which, as said, the presence of a void phase makes the contrast to be infinite.

17.5.2 An approximate method for particulate composites made up of a linear elastic filler into a nonlinear matrix

In the case in which a particulate composite consists of a linear elastic filler into a nonlinear matrix, it might seem sensible to assume that the macroscopic behavior would be affected by the same kind of nonlinearity as that of the matrix. This strategy has been for instance adopted by van der Sluis et al. [120] to homogenize the behavior of particulate composites whose matrix is ruled by the Perzyna constitutive law and the filler is made up of spherical linear elastic inclusions. The starting assumption, however, may be false. For example, in chapter 15, it has been shown that, in a syntactic foam filled with a linear elastic inclusions, a deviatoric viscoelastic matrix behavior makes the volumetric macroscopic behavior viscoelastic too. This result is based on the LEHPs derived in chapter 7 and on the correspondence principle, which, for linear viscoelasticity, is “exact” in the sense that it does not introduce any approximation beside, if it is the case, those intrinsic into the employed LEHP. Since the LEHPs derived in chapter 7 have been shown to well describe the linear elastic behavior of syntactic foams, it seems to us that the above assumption needs at least to be carefully verified case by case by means of experimental or numerical tests.

For the sake of understanding how this approximate homogenization method could be formulated for syntactic foams, and since the syntactic foams produced by us have always been filled with glassy (linear elastic) inclusions, let us anyway examine the results of this assumption in the following of this subsection.

Application to syntactic foams

We can try and describe the overall syntactic foam behavior by just rewriting the matrix constitutive law derived in section 16.2 in which all the material parameters have to be homogenized:

$$\Sigma_{kk} = 3K_2^{(0)} E_{kk} \quad (17.5.1)$$

$$S_{ij} = \frac{2\bar{G}_1}{1 + \bar{\alpha}\left(\frac{\Sigma_{eq}^{(1)}}{\bar{\sigma}_0}\right)^{\bar{n}-1}} \mathcal{E}_{ij}^{(v)} + \frac{2\dot{\mathcal{E}}_{ij}^{(v)}}{3\dot{E}_{eq}^{(v)}} \frac{k_B T}{\bar{v}} \operatorname{arcsinh} \left(\frac{\dot{E}_{eq}^{(v)}}{\bar{\varepsilon}_0} \exp \frac{\bar{\Delta\mathcal{G}}}{k_B T} \right) \quad (17.5.2)$$

where Σ_{ij} , E_{ij} , S_{ij} , and $\mathcal{E}_{ij}$ are the overall stress and strain tensors and their deviatoric parts respectively and the subscript eq indicates the Mises equivalent stress or strain, defined as in equations (16.2.7) and (16.2.8).

As in chapter 16, we have:

$$\mathcal{E}_{ij}^{(v)} = \mathcal{E}_{ij} - \frac{S_{ij}}{2G_2^{(0)}} \quad (17.5.3)$$

$$\dot{\mathcal{E}}_{ij}^{(v)} = \dot{\mathcal{E}}_{ij} - \frac{\dot{S}_{ij}}{2G_2^{(0)}} \quad (17.5.4)$$

and $\Sigma_{eq}^{(1)}$ has to be computed by means of the implicit relation:

$$\Sigma_{eq}^{(1)} = \frac{3\bar{G}_1}{1 + \bar{\alpha}\left(\frac{\Sigma_{eq}^{(1)}}{\bar{\sigma}_0}\right)^{\bar{n}-1}} E_{eq}^{(v)} \quad (17.5.5)$$

where, as for instance pointed out in [106] with reference to the Mises equivalent stress, note that

$$E_{eq}^{(v)} = \sqrt{\frac{2}{3} \mathcal{E}_{ij}^{(v)} \mathcal{E}_{ij}^{(v)}} = \sqrt{\frac{2}{3} \langle e_{ij}^{(v)} \rangle \langle e_{ij}^{(v)} \rangle} \leq \langle \varepsilon_{eq}^{(v)} \rangle \quad (17.5.6)$$

It is important to make it clear that the effective material constants have been here discriminated from the analogous matrix parameters in two different ways according to how they can be evaluated: the effective elastic moduli $G_2^{(0)}$ and $K_2^{(0)}$ have been distinguished by adopting the superscript (0) because they can be directly estimated by means of one of the LEHPs proposed in chapter 7, whereas for the remaining material parameters $\bar{G}_1$, $\bar{\alpha}$, $\bar{\sigma}_0$, $\bar{n}$, $\bar{v}$, $\bar{\varepsilon}_0$, and $\bar{\Delta\mathcal{G}}$ we have used the overline to mean that we can not evaluate them by means of a “true” homogenization method, but we have to resort to an identification procedure of experimental results.

If experimental tests are not available, a way to deal with the estimation of these last parameters is to run Finite Element analyses on the unit cell model (as done in section 16.6) to produce as many numerical simulations of experimental tests as we need to identify all the material constants. The identification procedure would work exactly as explained in section 16.4 for epoxy resins. This identification procedure is poorer than a homogenization since the resulting parameters are just numbers which do not give any information about their dependence on the composite microstructure.

Finally, it is important to note that if numerical solutions are available, the identification of the “overlined” parameters can be ennobled by constraining them to satisfy the following relations between macro and micro fields:

- the effective stress definition:

$$S_{ij} = \langle s_{ij} \rangle \quad (17.5.7)$$

- the equality between the effective dissipation and the average of the local dissipation (Gurson [53]):

$$S_{ij}\dot{\mathcal{E}}_{ij}^{(v)} = \langle s_{ij}\dot{e}_{ij}^{(v)} \rangle \quad (17.5.8)$$

- if the assumption of periodical microstructure is taken (unit cell analyses), the weak form of the equilibrium equations reduces to [133]:

$$\langle \dot{\sigma}_{ij}\varepsilon_{ij} \rangle = 0 \quad \langle \sigma_{ij}\varepsilon_{ij} \rangle = 0 \quad (17.5.9)$$

Chapter 18

Homogenization of the syntactic foam inelastic and nonlinear behavior

18.1 Introduction

In chapters 6 and 7, we have shown the ineffectiveness of the “classical” Hashin–Shtrikman LEHP in bounding the linear elastic moduli of syntactic foams. This is because of the presence of a void phase, which makes null the “classical” Hashin–Shtrikman lower bound; furthermore, the “classical” Hashin–Shtrikman upper bound predicts elastic moduli which are too stiff with respect to the actual ones. Therefore, here, we shall not apply the Talbot and Willis variational approach (see section 17.3.2), which would furnish the extension of the “classical” Hashin–Shtrikman bounds to the nonlinear range. In principle, the Ponte Castañeda variational procedure (section 17.3.3) could be used in conjunction with the “composite sphere”-based Hashin–Shtrikman (or even Voigt) upper bound (see chapter 7) to obtain an upper bound to the nonlinear behavior of syntactic foams. Actually, because of the complicated form of the LEHPs derived in chapter 7, that derivation would be, to say the least, too expensive. Furthermore, rather than in obtaining bounds, we are anyway more interested in testing whether the LEHPs which have given the best estimates of the effective elastic moduli of syntactic foams can accurately predict the nonlinear behavior too, if used together with some nonlinear techniques among those reported in chapter 17. Hence, the Ponte Castañeda variational principle will be only indirectly used by exploiting the Modified Secant Method (see sections 17.2.4 and 17.3.3) and only the Self-Consistent and the Mori–Tanaka “composite sphere”-based estimates will be adopted as LEHPs.

Beside applying the suitable methods among those reported in the chapter 17, in the next sections we shall propose and test a different way to compute the local field averages, relevant to estimate the current stiffness of the phases, in the context of the “direct approach” reviewed in section 17.2.

18.2 The Second Order Secant Method

Let us first propose one more method, which may be framed in the “direct approach” (see section 17.2), to compute mean values of local fields which the secant stiffness of each composite phase is dependent on.

The “exact” way of computing the second-order moment of the equivalent strain field which the Modified Secant Method is based on (see equation (17.2.16)) in general furnishes different results with respect to those obtainable from the application of definition (17.2.14) directly to the approximated fields available from the LEHP exploited to predict the effective stiffness $L_{ijkl}^{(0)}$. This fact can be shown by for instance reasoning on the “classical” estimates and bounds based on the Eshelby solution of the homogeneous inclusion (see chapter 6). Since, for most inclusion shapes, the Eshelby solution implies constant fields over the inclusion, the application of definition (17.2.14) to those fields furnishes exactly the same results as those obtainable through the first-order average; instead, let us highlight once again that if the elastic moduli obtained by means of the same “classical” LEHP are put into equation (17.2.16), in general we find different results from those given by the first order estimates, the first ones being “exact” in the sense that they are the second-order moments of the local fields in the fictitious composite whose unknown microstructure corresponds to the used estimate of $L_{ijkl}^{(0)}$ (see, for instance, the explicit formulae based on the “classical” Hashin–Shtrikman lower bound in [108]).

For LEHPs based on the Eshelby problem of a heterogeneous inclusion, as those derived in chapter 7 for syntactic foams, where variable local fields (whose averages allow us to estimate the effective elastic moduli) are available, the direct application of definition (17.2.14) in general gives results different from both those deriving from the first-order average and those obtainable by means of equation (17.2.16).

All of this can be obviously extended to the first invariant localization (see equations (17.2.17) and (17.2.18)), but note that Suquet called “Modified Secant Method” the method which makes use of equation (17.2.16) only; all the properties proved by Suquet himself and reported in subsection 17.2.4 are strictly referred to this procedure.

The direct use of definitions (17.2.14) and (17.2.17) to localize the relevant fields will be in the following called *Second Order Secant Method*; of course, there is no reason at all to think that the Second Order Secant Method would enjoy the useful properties of the Modified Secant Method, except that it should furnish better estimates of the local fields than those obtained by means of the first-order averages, in order to evaluate the current stiffness of the phases. Of course, the Second Order Secant Method is of use only if a LEHP which furnishes variable local fields is available.

As far as we know, no one has ever highlighted the difference between the Modified Secant Method and the here introduced Second Order Secant Method.

In the next subsection, we shall derive the equations arising from the application of the Second Order Secant Method to syntactic foams (and to any other composite whose LEHP is based on a similar linear elastic solution — see [37] and [60]).

18.2.1 The Second Order Secant Method for syntactic foams

Let us focus on the case in which the matrix only is nonlinear, that corresponds to the most likely situation of a syntactic foam filled with glassy hollow spheres. However, starting

from the equations that we shall here provide, the extension to account for a nonlinear filler is definitely straightforward.

As said in the previous section, in order to derive the relevant equations for the Second Order Secant Method we directly start from the local strain expression in the matrix, available after solving the corresponding Eshelby problem (i.e., the linear elastic problem on the four-phase model), to apply definitions (17.2.14) and (17.2.17). In the case of syntactic foams, the Second Order Secant Method has the advantage, with respect to the Modified Secant Method, of avoiding the cumbersome analytical derivation of the formulae derived in chapter 7. Moreover, since, in the case in which either the filler gradation or the “unwanted” voids have to be accounted for, those formulae have been given leaving two linear systems to be solved, the only straightforward way to use the Modified Secant Method is the very expensive one consisting of computing the derivative (17.2.16) numerically.

Thus, we need to know the local strain field due to general displacement boundary conditions (7.1.2) applied to the four-phase model (which has then to be related to the boundary conditions applied to the RVE, as explained in chapters 6 and 7). Representing the homogeneous strain tensor as the superposition of its simple shear components ($E_{12}^{(R)}$, $E_{23}^{(R)}$, and $E_{31}^{(R)}$) and $\theta = E_{kk}^{(R)}/3$, we can solve the linear elastic problem by means of the solutions reported in chapter 7.

The local value of ϑ turns out to be:

$$\vartheta^{(m)}(\mathbf{x}) = \left(\frac{5\alpha_2^{(m)}}{3} + 4 \frac{1}{a^2} M_3 - 2 \frac{a^3}{r^5} M_4 \right) \left(E_{12}^{(R)} x_1 x_2 + E_{23}^{(R)} x_2 x_3 + E_{31}^{(R)} x_3 x_1 \right) + P_1 \theta \quad (18.2.1)$$

The first direct strain component reads

$$\begin{aligned} \varepsilon_{11}^{(m)}(\mathbf{x}) = & \left(-15 \frac{a^5}{r^7} M_2 + 2(\alpha_2^{(m)} + 1) \frac{1}{a^2} M_3 + (2\alpha_{-3}^{(m)} - 13) \frac{a^3}{r^5} M_4 \right) (E_{12}^{(R)} x_1 x_2 + E_{31}^{(R)} x_3 x_1) + \\ & + \left(-5 \frac{a^5}{r^7} M_2 + \alpha_2^{(m)} \frac{1}{a^2} M_3 + (\alpha_{-3}^{(m)} - 5) \frac{a^3}{r^5} M_4 \right) E_{23}^{(R)} x_2 x_3 + \\ & + \left(35 \frac{a^5}{r^9} M_2 + 5(5 - \alpha_{-3}^{(m)}) \frac{a^3}{r^7} M_4 \right) \left(E_{12}^{(R)} x_1 x_2 + E_{23}^{(R)} x_2 x_3 + E_{31}^{(R)} x_3 x_1 \right) x_1^2 + \\ & + P_1 \theta + P_2 \left(\frac{a^3}{r^3} - 3 \frac{a^3}{r^5} x_1^2 \right) \theta \end{aligned} \quad (18.2.2)$$

whereas equation (7.2.16), which has been derived in the case $E_{23}^{(R)} = E_{31}^{(R)} = 0$, becomes

$$\begin{aligned} \varepsilon_{12}^{(m)}(\mathbf{x}) = & \left(M_1 + \frac{a^5}{r^5} M_2 + \frac{r^2}{a^2} M_3 + \frac{a^3}{r^3} M_4 \right) E_{12}^{(R)} + \frac{1}{2} \left(-10 \frac{a^5}{r^7} M_2 + \right. \\ & + (\alpha_2^{(m)} + 2) \frac{1}{a^2} M_3 + (\alpha_{-3}^{(m)} - 8) \frac{a^3}{r^5} M_4 \left. \right) \left(E_{12}^{(R)} (x_1^2 + x_2^2) + E_{23}^{(R)} x_3 x_1 + E_{31}^{(R)} x_2 x_3 \right) + \\ & + \left(35 \frac{a^5}{r^9} M_2 + 5(5 - \alpha_{-3}^{(m)}) \frac{a^3}{r^7} M_4 \right) \left(E_{12}^{(R)} x_1 x_2 + E_{23}^{(R)} x_2 x_3 + E_{31}^{(R)} x_3 x_1 \right) x_1 x_2 + \\ & - 3 P_2 \frac{a^3}{r^5} \theta x_1 x_2 \end{aligned} \quad (18.2.3)$$

in which the constants P_1 , P_2 , M_1 , M_2 , M_3 , and M_4 have to be computed from the systems (7.2.17)–(7.2.26) and (7.3.2)–(7.3.10) in which $S_1 = 1$ and $T_1 = 1$. The formulae for $\varepsilon_{22}^{(m)}(\mathbf{x})$, $\varepsilon_{33}^{(m)}(\mathbf{x})$, $\varepsilon_{23}^{(m)}(\mathbf{x})$, and $\varepsilon_{31}^{(m)}(\mathbf{x})$ follow from obvious index permutation.

Let us use the superscript $\dagger$, instead of the double overline employed to indicate the “exact” second-order moments (see subsection 17.2.4), to mean the second-order moments obtained from the application of their definitions, given by equations (17.2.14) and (17.2.17), to the local fields available from the elastic solutions on which the LEHP is based.

After some lengthy algebra, the second-order moment of $\vartheta^{(m)}(\mathbf{x})$ finally reads:

$$\begin{aligned} \vartheta^{\dagger(m)} = & \left(\left(\frac{c^7 - b^7}{420a^4(c^3 - b^3)}(4 + 5\alpha_2^{(m)})^2 M_3^2 - \frac{a(c^2 - b^2)}{10(c^3 - b^3)}(4 + 5\alpha_2^{(m)})M_3M_4 + \right. \right. \\ & \left. \left. + \frac{a^6}{5b^3c^3}M_4^2 \right) E_{eq}^{(R)2} + P_1^2\theta^2 \right)^{\frac{1}{2}} \end{aligned} \quad (18.2.4)$$

whereas the second-order moment of the equivalent strain over the matrix reads:

$$\begin{aligned} \varepsilon_{eq}^{\dagger(m)} = & \left(\left(M_1^2 + \frac{6a^{10}(c^7 - b^7)}{b^7c^7(c^3 - b^3)}M_2^2 + \frac{2(c^5 - b^5)}{5a^2(c^3 - b^3)}(5 + \alpha_2^{(m)})M_1M_3 + \right. \right. \\ & + \frac{c^7 - b^7}{210a^4(c^3 - b^3)}(278 + 128\alpha_2^{(m)} + 17\alpha_2^{(m)2})M_3^2 + \frac{12a^8(c^5 - b^5)}{5b^5c^5(c^3 - b^3)}(5 - \alpha_{-3}^{(m)})M_2M_4 + \\ & - \frac{a(c^2 - b^2)}{10(c^3 - b^3)}(2 + \alpha_2^{(m)})(2 + \alpha_{-3}^{(m)})M_3M_4 + \\ & \left. \left. + \frac{a^6}{10b^3c^3}(72 - 28\alpha_{-3}^{(m)} + 3\alpha_{-3}^{(m)2})M_4^2 \right) E_{eq}^{(R)2} + \frac{4a^6}{b^3c^3}P_2^2\theta^2 \right)^{\frac{1}{2}} \end{aligned} \quad (18.2.5)$$

$$E_{eq}^{(R)} = \sqrt{\frac{2}{3}\mathcal{E}_{ij}^{(R)}\mathcal{E}_{ij}^{(R)}} \quad (18.2.6)$$

$\mathcal{E}_{ij}^{(R)}$ being the deviatoric part of the strain $E_{ij}^{(R)}$ applied to the four-phase model.

Note that these expressions can be reduced in the Mori–Tanaka case, for which $M_3 = 0$ and $M_1 = 1$; on the other hand, the Self-Consistent Method has the little advantage of directly giving $E_{ij} = E_{ij}^{(R)}$. Moreover, in the Mori–Tanaka case we, of course, still have $\bar{\varepsilon}_{eq}^{(m)} = E_{eq}^{(R)}$, but note that the relation $\varepsilon_{eq}^{\dagger(m)} = E_{eq}^{(R)}$ does not hold, $\varepsilon_{eq}^{\dagger(m)}$ (and $\vartheta^{\dagger(m)}$ too, if it is the case) being only used in order to compute the local stiffness of the matrix according to

$$L_{ijkl}^{(r,s)} = L_{ijkl}^{(r,s)}(\varepsilon_{eq}^{\dagger(r)}) \quad (18.2.7)$$

completely similar to equation (17.2.13).

Again, the Second Order Secant Method, contrary to the other LEHP extensions to the behavior beyond the linear elastic range reviewed in chapter 17, furnishes different predictions for the two micromechanical models based on the Mori–Tanaka approximation which have been shown, in appendix 7.C, to provide the same effective elastic moduli. In particular, the use of the model introduced in appendix 7.C, in which the syntactic foam is seen as a two phase particulate composite in which the filler is a “heterogeneous

phase”, does not allow us to obtain, by applying the Second Order Secant Method, any improvement with respect Secant Method, because the matrix local fields are in this case trivially homogeneous and equations (18.2.4) and (18.2.5) do not hold; this is not the case if the more expensive four-phase model is employed, for which the above expressions (18.2.4) and (18.2.5) apply and furnish different estimates of the local fields with respect to the first-order average. This is not trivial as it might seem, since the Modified Secant Method, which, as the Second Order Secant Method, bases its nonlinear prediction on the second-order average of some local field, furnishes exactly the same results if applied to the two Mori–Tanaka LEHPs above mentioned, being dependent on the final expression of the effective elastic moduli only.

Still about the Mori–Tanaka approximation based on the four-phase model, let us finally note that the use of this LEHP together with the Second Order Secant Method gives rise to some theoretical problem if more than one composite spheres are needed in order to describe the composite microstructure. This is because in this case, at a generic step of the nonlinear homogenization, we get different current stiffness values of the matrix surrounding different composite spheres, thus making the choice of the reference unbounded medium not unique. One way to deal with this problem consists of taking a different reference medium for any different four-phase model, by choosing as elastic moduli of each four-phase model those of the matrix in the corresponding composite sphere.

It is important to highlight that both $\nu^{\dagger(m)}$ and $\varepsilon_{eq}^{\dagger(m)}$ depend on both $E_{eq}^{(R)}$ and θ , which is what one might expect, because it means, for instance, that the effective volumetric behavior can be nonlinear even if the bulk behavior of all the phases is linear elastic, and this agrees with the analogous result found in chapter 15 in the context of linear viscoelasticity by means of the “exact” correspondence principle. This desirable dependence in the homogenization of the mechanical behavior beyond the linear elastic range does not appear in both the Incremental and Secant methods (see the first order localization formulae reported in sections 7.2 and 7.3).

Finally, we may add the comment that equations (18.2.4) and (18.2.5) can be easily adapted to be used for homogenizing the behavior of any composite whose LEHP is based on the Eshelby problem of a multilayered hollow spherical inclusions [60]. The particularization to the case of composites filled with solid spherical inclusions (see [37] and, for the extension to the multilayered case, [61]) can be accomplished as well, but it exhibits difficulties similar to those highlighted in section 7.2 about the particularization of the formulae there derived to the Christensen and Lo solution [37].

18.3 Application of the Incremental, Secant, Second Order Secant, and Modified Secant methods to syntactic foams

In this section, the Incremental, Secant, Second Order Secant, and Modified Secant methods will be applied to the syntactic foams types 1 and 6 described in chapter 4. The only nonlinear phase of this composite is the matrix, which consists of the epoxy resin DGEBA DER 332 cured with the hardener DDM 32950. In chapter 16 we have proposed a constitutive law for epoxy resins, which, since its current stiffness in general needs to be

expressed by means of an anisotropic fourth-order tensor, can not be used in conjunction with any of the LEHPs derived in chapter 7, which can deal with isotropic phases only. Therefore, here we shall use the J_2 -flow theory of plasticity for describing the monotonic epoxy resin behavior, with the purpose of modeling the monotonic syntactic foam behavior only. The following equations rule the J_2 -flow theory of plasticity with the isotropic strain hardening here adopted for the matrix (for simplicity of notation, the superscript m is hereafter omitted which would indicate that we are dealing with stress and strain fields over the matrix phase):

- the additiveness of small elastic and plastic strain rates:

$$\dot{\varepsilon}_{ij} = \dot{\varepsilon}_{ij}^{(el)} + \dot{\varepsilon}_{ij}^{(pl)} \quad (18.3.1)$$

- the constitutive law can be expressed either in terms of the linear elastic stiffness and the incremental elastic strain or in terms of the tangent tensor and the total strain increment:

$$\dot{\sigma}_{ij} = L_{ijkl} \dot{\varepsilon}_{kl}^{(el)} = L_{ijkl}^{(t)} \dot{\varepsilon}_{kl} \quad (18.3.2)$$

- the associated flow rule:

$$\dot{\varepsilon}_{ij}^{(pl)} = \frac{3\dot{\varepsilon}_{eq}^{(pl)} s_{ij}^{(r)}}{2\sigma_{eq}^{(r)}} \quad (18.3.3)$$

- the yield condition:

$$\sigma_{eq} \leq \sigma_Y(\lambda^{(pl)}) \quad (18.3.4)$$

in which $\lambda^{(pl)}$ is a scalar representing the current amount of plastic strains developed:

$$\lambda^{(pl)} = \int_{history} \dot{\lambda}^{(pl)} dt \quad \dot{\lambda}^{(pl)} \equiv \dot{\varepsilon}_{eq}^{(pl)} \quad (18.3.5)$$

- the consistency condition:

$$\left(\dot{\sigma}_{eq} - \dot{\sigma}_Y(\lambda^{(pl)}) \right) \dot{\varepsilon}_{eq}^{(pl)} = 0 \quad (18.3.6)$$

- the strain hardening rule:

$$\begin{aligned} \sigma_Y(\lambda^{(pl)}) &= \sigma_0 + H\lambda^{(pl)\alpha} \quad \text{if } \sigma_Y \leq \sigma_L \\ \sigma_Y &= \sigma_L \quad \text{otherwise} \end{aligned} \quad (18.3.7)$$

- further constraints:

$$\left(\sigma_{eq} - \sigma_Y(\lambda^{(pl)}) \right) \dot{\varepsilon}_{eq}^{(pl)} = 0 \quad (18.3.8)$$

$$\text{if } \sigma_{eq} = \sigma_Y(\lambda^{(pl)}) \quad \text{then} \quad \dot{\sigma}_{eq} - \dot{\sigma}_Y(\lambda^{(pl)}) \leq 0 \quad (18.3.9)$$

in which the equivalent stress σ_{eq} has already been defined in equation (17.2.24), σ_0 is the initial yield stress, σ_L is the limit stress, and H and the exponent α are constant hardening parameters which define the current yield stress σ_Y .

This constitutive law has been integrated by means of the Backward Euler scheme and then implemented into a User Material subroutine (UMAT) for the Finite Element code ABAQUS. Let us report the relevant nonlinear algebraic equation to be solved, for instance by means of the Newton method, in the UMAT when the material hardening is strain driven:

$$\sigma_Y(\lambda^{(pl)}) - 3G(\varepsilon_{eq} - \Delta\varepsilon_{eq}^{(pl)}) = 0 \quad (18.3.10)$$

This equation will be of some use later, in comparing the Incremental and Secant methods.

Note that if the *proportional loading condition* is assumed (see subsection 17.2.5) we have

$$\lambda^{(pl)} \equiv \varepsilon_{eq}^{(pl)} \quad (18.3.11)$$

$\varepsilon_{eq}^{(pl)}$ being defined in equation (17.2.23).

The material parameters have been calibrated in such a way as to obtain a uniaxial stress-strain law similar to that which characterizes the epoxy resin DGEBA behavior under monotonic loading; they have been set as follows: $E = 2800 \text{ MPa}$, $\nu = 0.41$, $\sigma_0 = 30 \text{ MPa}$, $H = 200 \text{ MPa}$, $\alpha = 0.315$, and $\sigma_L = 100 \text{ MPa}$. The match with the experimental test carried out on sample 5 (see previous figure 3.3) is shown in figure 18.1. Obviously, the use of this constitutive law makes the matrix volumetric behavior linear elastic. The glass has been taken as linear elastic, with elastic moduli $E^{(i)} = 77500 \text{ MPa}$ and $\nu^{(i)} = 0.23$.

Since the LEHPs of chapter 7 have been derived from the displacement approach (i.e., by subjecting the RVE to the boundary conditions (6.1.5)), to simulate a syntactic foam uniaxial test, we have imposed to the RVE the following uniform strain field, properly discretized into steps:

$$E_{ij} = \begin{bmatrix} E_{11} & 0 & 0 \\ 0 & -\nu_0 E_{11} & 0 \\ 0 & 0 & -\nu_0 E_{11} \end{bmatrix} = E_{11} \frac{1 - 2\nu_0}{3} \delta_{ij} + E_{11} \frac{1 + \nu_0}{3} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (18.3.12)$$

Assuming that the matrix keeps isotropic properties at each step, the deviatoric part of the uniaxial strain field (18.3.12) localizes according to equation (7.2.28), if the first-order averages are used; this is because the second term of the right-hand side of equation (18.3.12) can always be seen as a superposition of three simple shear fields.

Obviously, to get the right overall behavior, many implicit problems have to be solved by a suitable implementation. First of all, let us highlight the fact that even the boundary conditions (18.3.12) are not a priori known, since the homogenized Poisson ratio ν_0 is dependent on both the LEHP and the magnitude of the current overall strain E_{11} . Actually, the boundary conditions describing our uniaxial tests are mixed in displacements and stresses (see chapter 6), but we found it convenient to impose to the surface whose normal is orthogonal to the axis x_1 the radial displacements resulting from the strain $-\nu_0 E_{11}$, instead of imposing it to be stress-free; this trick is useful to treat the uniaxial test simulation with the homogenization displacement approach. Note that here we keep the term “Poisson ratio” to mean the sign opposite of the ratio between the current transversal and longitudinal strains, even if we are dealing with inelastic strains.

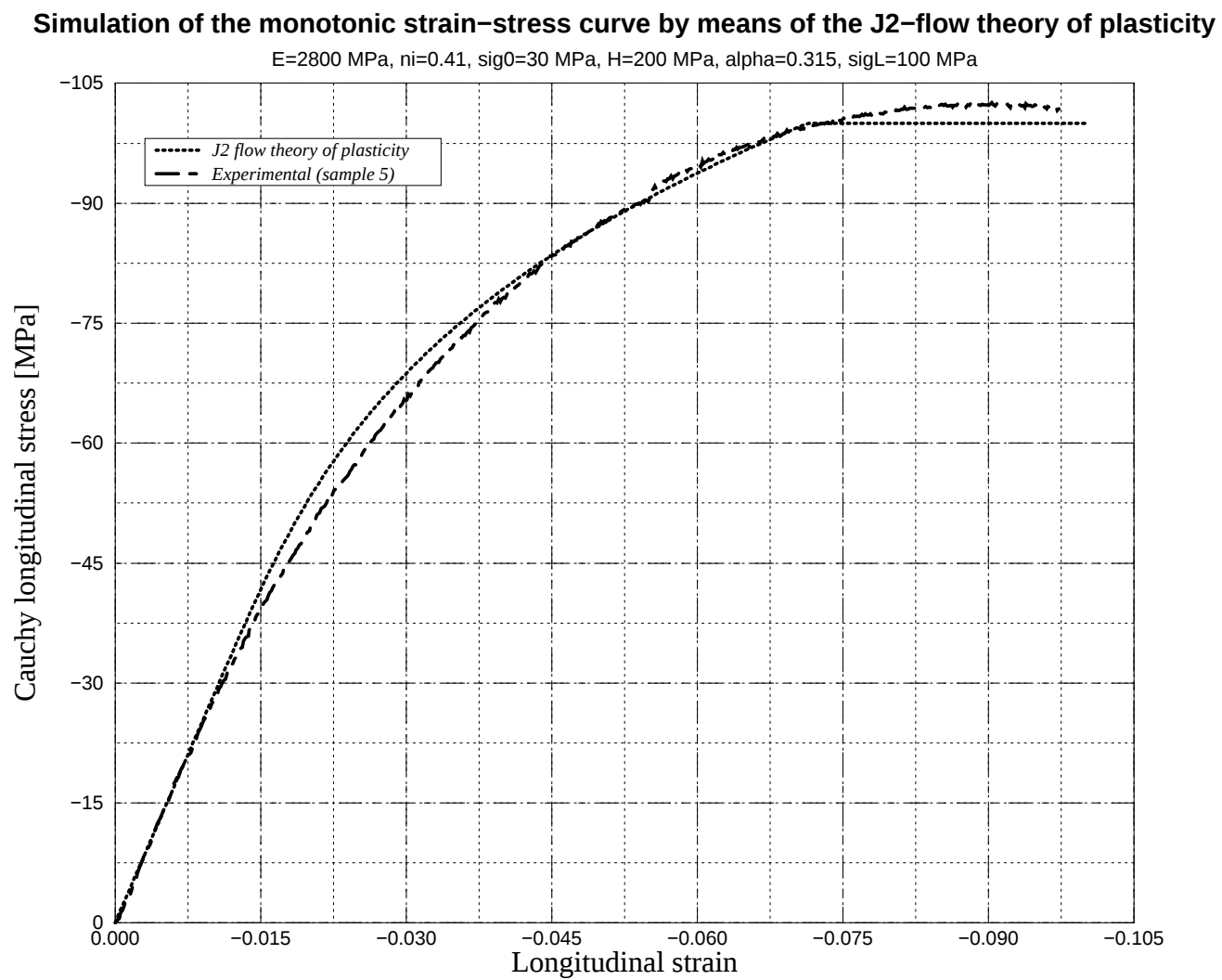


Figure 18.1: Material parameters calibration for the epoxy resin

Equations (17.2.25) and (17.2.26) have to be employed for the matrix to make it isotropic at any homogenization step. Anyway, it is important to note that, as a first attempt, the hypothesis of proportional loading, which allows us to express both the tangent stiffness and the secant stiffness as isotropic fourth-order tensors, has been kept in assembling the jacobian only. This means that at each step the incremental stress average computed over the matrix has been integrated by means of the above mentioned J_2 -flow theory material routine without any restriction on the direction of the plastic flow; in other words, both the stress integration and the computation of the plastic strains are inconsistent with the use of equations (17.2.25) and (17.2.26).

It is perhaps worth to point out that there is a mismatch between the use of the secant homogenization methods and the choice of modeling the matrix behavior by means of the J_2 -flow theory of plasticity, which is in principle an incremental constitutive law. This problem can be overcome, in order to obtain a macroscopic secant (nonlinear elastic) formulation, by integrating, at each step, the whole total strain in the matrix. This can be done in two ways, both of them resulting in making the matrix constitutive behavior reversible. The first one consists of integrating at each step the whole matrix strain by properly subincrementing it to exploit the above described incremental algorithm to integrate the J_2 -flow theory of plasticity (see, e.g., equation (18.3.10)). This is quite expensive, since at each increment of the macroscopic boundary conditions, the matrix stresses must be re-integrated step-by-step.

A second possibility is to re-write the algorithm for the J_2 -flow theory of plasticity by keeping the hypothesis of proportional loading in the stress integration and in the plastic strain computation too. This is equivalent to replace equation (18.3.3) with equation (17.2.22). If isotropic strain hardening is adopted, the relevant nonlinear equation to be solved for $\varepsilon_{eq}^{(pl)}$ reads

$$\sigma_Y(\varepsilon_{eq}^{(pl)}) - 3G(\varepsilon_{eq} - \varepsilon_{eq}^{(pl)}) = 0 \quad (18.3.13)$$

instead of solving equation (18.3.10) step-by-step. This different material routine has the advantage of being consistent with the use of the isotropic stiffness (17.2.26), even if the total strain average over the matrix does not in general keep its components with the same proportions at each step. This second method allows us to obtain a faster code, but, in principle, it should integrate the plasticity less accurately than the first one. Both these methods have been tested.

In the cases here simulated of uniaxial tests on syntactic foams types 1 and 6, the effective nonlinear behaviors resulting from the two integration schemes coincide. Likely, this is because in this particular case the hypothesis of proportional loading is almost satisfied at every material point, i.e., the plastic flow direction does not significantly depend on the magnitude of the load.

A Finite Element analysis has also been run by means of the code ABAQUS on the unit cell model (see chapter 11) in which the matrix constitutive law was given by the UMAT in which the J_2 -flow theory (18.3.1)–(18.3.9) has been implemented. It is interesting to compare this numerical simulation with the theoretical homogenization procedures, also because the unit cell analysis is not affected by the hypothesis of proportional loading condition and the matrix can develop any kind of anisotropy consistent with both the chosen local constitutive laws and the composite microstructure.

In figures 18.2 and 18.3 the results from the compressive tests on both sample 2 of syntactic foam type 1 (see figure 4.7) and sample 2 of syntactic foam type 6 (see figure 4.23) are compared with those obtained by means of the unit cell analyses and the theoretical homogenizations. All the four methods described in this chapter have been used in conjunction with both the Self-Consistent “composite sphere”-based estimate (chapter 7) and the Mori-Tanaka “composite sphere”-based estimate (appendix 7.C, interpreted in the sense of the four-phase micromechanical model to overcome the problem highlighted in subsection 18.2.1 for what concerns the Second Order Secant Method). Note that the Modified Secant Method has been implemented by computing the derivative (17.2.16) numerically. This last method has been employed to extend to the nonlinear range the Reuss “composite sphere”-based estimate and the Hashin-Shtrikman “composite sphere”-based upper bound too. All the exploited LEHPs have been always used in their versions which can account for many composite spheres, by using the data reported in Tables 10.1 and 10.2; for the Self-Consistent estimate, this is in principle important to try to catch the different strain localization that indeed happens in the matrix embedding different glass microspheres. Actually, in the case here treated, the difference has always been found trifling between the estimates accounting for the whole graded filler and those in which only a characteristic composite sphere is used; this is because of the particular gradation of the filler here employed (actually not much scattered at all) and it is *not* a general result (see chapter 10).

Considering all the possible sources of uncertainty regarding the material parameters (see, for instance, chapter 4), it seems that all the employed homogenization techniques are accurate enough to catch the mild syntactic foam nonlinearity before failure; the Second Order and the Modified Secant methods furnish a too soft behavior for syntactic foam type 1, whereas the Incremental and Secant methods are slightly too stiff in predicting the behavior of syntactic foam type 6. Overall, the closest estimate to the behavior predicted by the unit cell calculations is the Mori-Tanaka “composite sphere”-based one extended by means of the Second Order Secant Method, even if it seems that the Self-Consistent “composite sphere”-based estimate used in conjunction with the Modified Secant Method has the advantage of being able to predict the stress-strain slope after the perfectly plastic plateau has been reached in some point in the matrix.

Recall now that the Modified Secant Method is coincident with the Ponte Castañeda variational principle (see subsections 17.2.4 and 17.3.3); this implies that the Modified Secant Method should produce nonlinear estimates somehow stiffer than the analogous direct estimates of the effective elastic moduli furnished by LEHPs as the Self-Consistent or the Mori-Tanaka schemes. Unfortunately, the predictions furnished by the Second Order Secant Method lie above the corresponding Modified Secant Method estimates. The Hashin-Shtrikman “composite sphere”-based upper bound is an upper bound of the elastic moduli for the chosen morphology (CSA) and the Modified Secant Method preserves its bounding nature also in the nonlinear range. Both the Self-Consistent “composite sphere”-based estimates extended with the Secant and Incremental methods violate that upper bound for some volume fraction. Note that the Reuss “composite sphere”-based estimate extended with the Modified Secant Method is not a lower bound.

It is also worth noting that once the matrix has become fully perfectly plastic, the Incremental Method predicts zero overall stiffness, in agreement with the matrix property of being the connected phase and with its tangent jacobian which is null in the fully

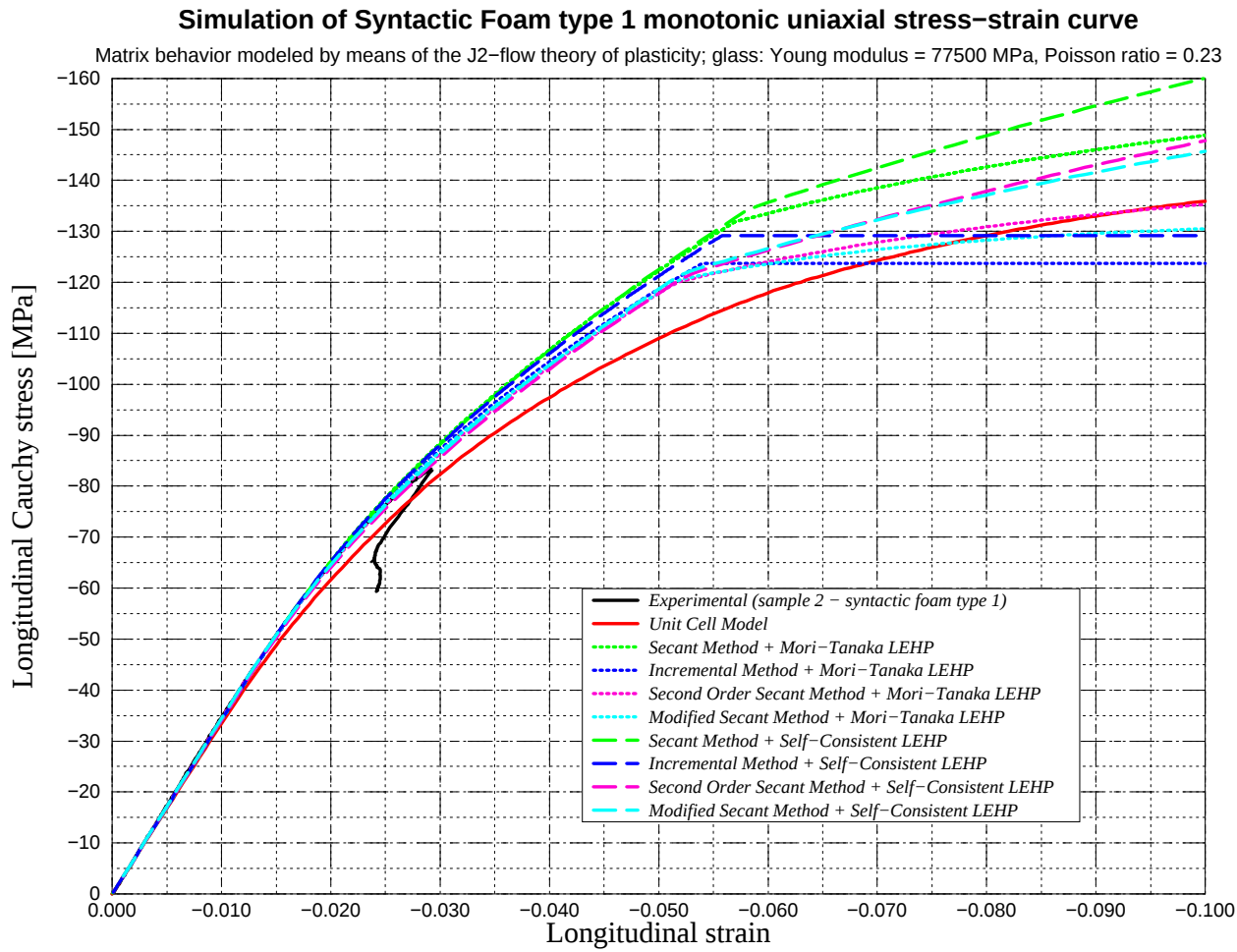


Figure 18.2: Comparison among experimental results and analytical and numerical homogenization techniques

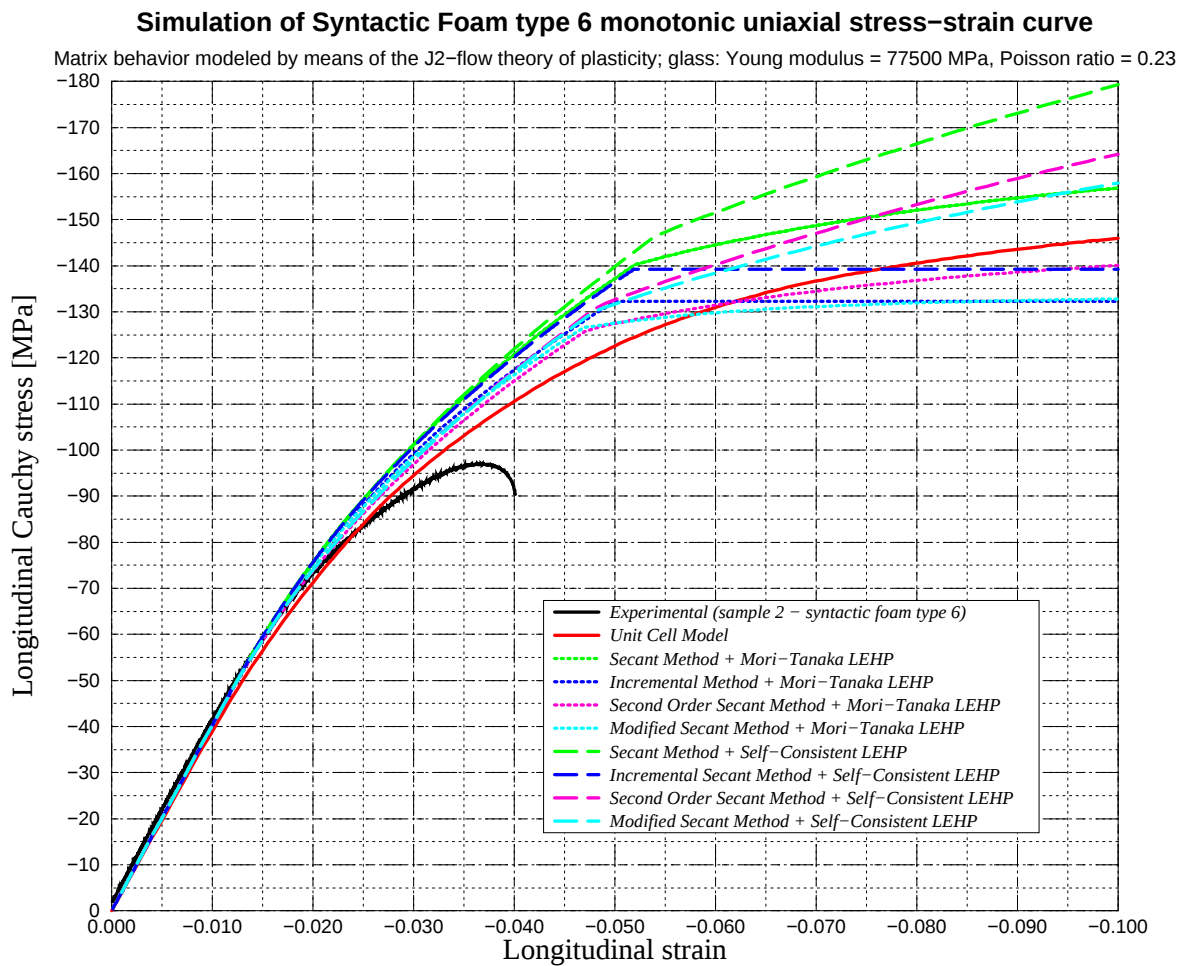
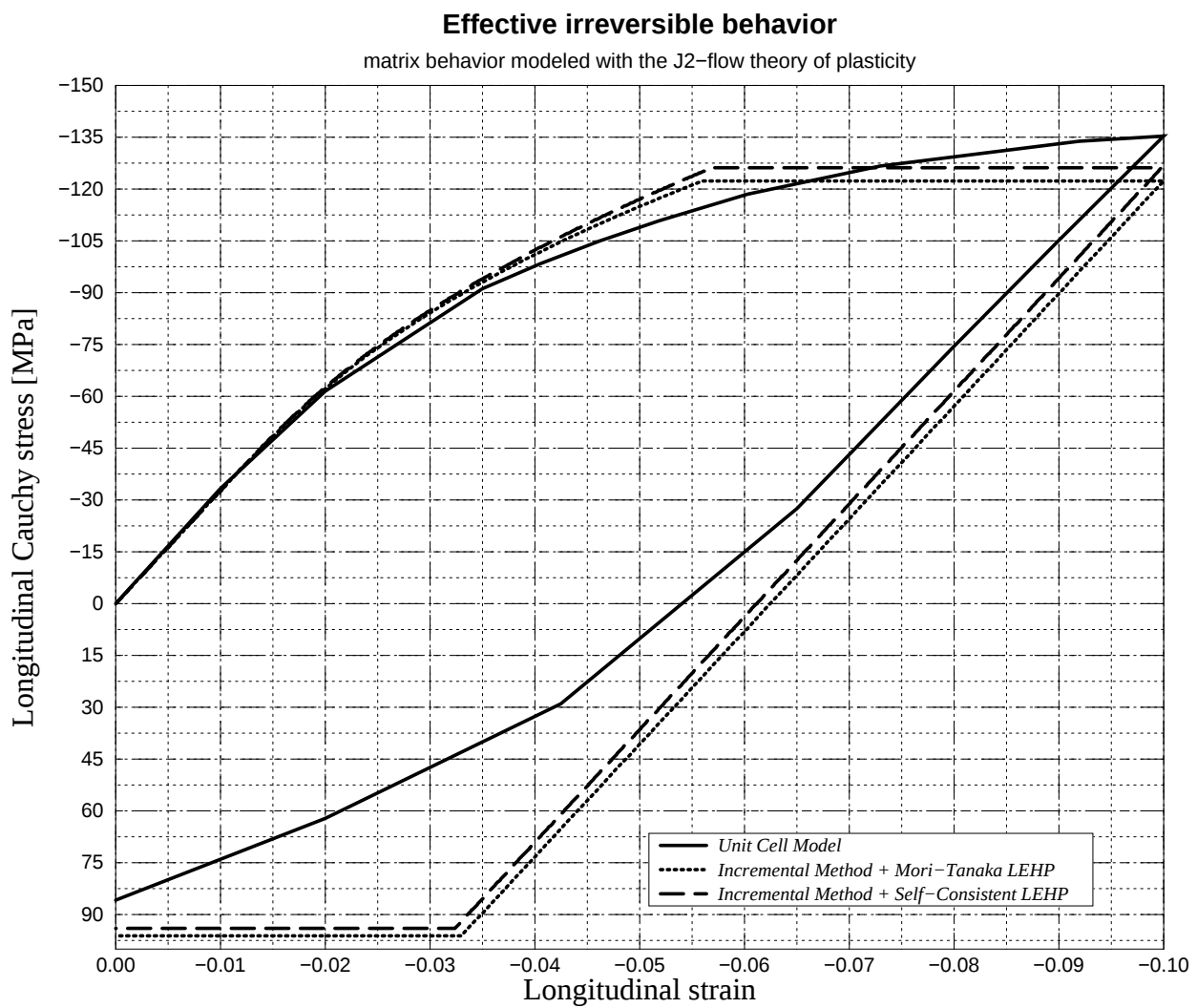


Figure 18.3: Comparison among experimental results and analytical and numerical homogenization techniques

perfectly plastic range; this is not the case with the secant methods which never deal with a null jacobian for the matrix.

It was theoretically expected that both the Incremental and Secant methods would predict an overstiff behavior. Figures 18.2 and 18.3 on the contrary show a good agreement between the analytical and numerical estimates. The reason of this partial disagreement with the general theory probably lies in the approximation of taking isotropic jacobians, which, evidently, made in this case those predictions softer than usual (the same has been found in [52] too).

The J_2 -flow theory of plasticity employed for modeling the epoxy behavior is an inelastic constitutive law which allows us to simulate irreversibility upon unloading if the Incremental Method is used, even if the requirement of proportional loading necessary to obtain an isotropic jacobian is in this case hardly met. A J_2 -flow theory cyclic behavior is not interesting for the syntactic foams tested by us, whose matrix irreversible behavior has nothing to do with Mises plasticity, but, for the sake of understanding how the theoretical homogenization procedures work, it may be interesting to compare the results found by applying them with those from the unit cell analyses, which are then taken as the “exact” ones. Figure 18.4 does that by applying the Incremental Method together with both the Mori–Tanaka and the Self–Consistent “composite sphere”–based LEHPs. The results are reasonably good, except that the theoretical homogenization can not catch the nonlinearity when unloading before reaching the plateau. The main reason of this is that the analytical homogenization can only account for the local field averages: this implies that, unlike the Finite Element simulation, it can not take the stress redistribution into account. Therefore, in the analytical homogenization, since the limit stress σ_L has already been reached in the loading path, the nonlinear effect due to the strain hardening is lost when unloading.

Figure 18.4: *Effective cyclic behavior*

Chapter 19

Closure

19.1 Conclusions

In this thesis, we have studied the mechanical behavior of syntactic foams made up of epoxy resins filled with glassy hollow microspheres.

In order to get an insight into the mechanical behavior of these materials, both syntactic foams and plain epoxy resins have been produced and tested. We have carried out uniaxial, torsional, and biaxial (torsion in conjunction with tension or compression) tests.

The epoxy resin behavior is mostly nonlinear viscoelastic before the material strength is reached; this last can then be considered, as usually assumed in the literature, coincident with the initial yield stress. This nonlinear viscoelastic behavior, which affects the syntactic foam behavior until failure, causes a peculiar cyclic behavior characterized by a flex in the unloading stress–strain curve.

The experimental results show a brittle-elastic behavior of the studied syntactic foams.

We have developed an accurate homogenization technique in order to estimate the elastic moduli of “real” syntactic foams. This technique is able to account for (i) the presence of air bubbles entrapped in the matrix (“unwanted” voids), (ii) the actual geometrical details of the hollow microspheres, and (iii) fillers possibly made by different materials. The technique is based on analytical results obtained by Hervé and Pellegrini [60], and extends their homogenization method by means of the MRP theory [26].

This homogenization technique has been applied to the linear elastic design of sandwich panels made up of a syntactic foamed core into fiber-reinforced epoxy skins. We have then made available an optimization procedure which, under some technological constraints, furnishes the lightest sandwich that satisfies a given stiffness constraint.

We have derived a constitutive law able to predict the epoxy resin nonlinear viscoelastic behavior. This model is essentially based on the Eyring statistical interpretation of the molecular motion [46]. In particular, the model appears to be suitable to predict both the most salient features of the cyclic behavior and the creep behavior. We have implemented this constitutive law into a User Material for the Finite Element code ABAQUS, in order to simulate the syntactic foam behavior before failure by means of unit cell analyses. The comparison between experimental and numerical results has shown the good accuracy of both the constitutive law for epoxy resins and the unit cell model.

Finally, we have extended the proposed linear elastic homogenization procedure, in

both its Self-Consistent and Mori-Tanaka versions, to both the nonlinear and inelastic cases. In order to accomplish this task, we have employed a strongly simplified constitutive law for epoxy resins, because the employed linear elastic homogenization technique can deal only with constitutive laws for the phases which furnish isotropic jacobians, even if inelastic deformations develop. The extension to the behavior beyond the linear elastic range has been accomplished by means of both suitable methods available in the literature and a technique specifically derived for syntactic foams which is expected to work for a wider class of composites.

The comparison of the proposed homogenization techniques with both experimental and numerical results indicates that

- for the considered materials, the actual gradation of the hollow microspheres seems to have little influence on the overall properties of the syntactic foam. The filler geometry seems to be described well enough by the average value of the ratio between the inner and outer radii, to be computed by means of the particle density and the glass density;
- the presence of “unwanted” voids has a significant effect on the homogenized elastic moduli of the composite and, then, on the behavior beyond the linear elastic range too;
- the Self-Consistent “composite sphere”-based estimate, based on a model similar to that of Christensen and Lo [37] and relevant extension by Hervé and Pellegrini [60], gives results in good agreement with both experimental and numerical results. The analogous Mori-Tanaka estimate is, for the fillers and matrixes considered in this research, very accurate too and much less expensive. The equations describing the homogenized values of the elastic moduli of the composite have a rather involved aspect, but they are simple in essence, and therefore can be relatively easily implemented into a computer code;
- the obtained results suggest that the developed method should provide an effective tool for designing syntactic foams.

19.2 Open issues

A lot of work has still to be done, apart from what already said in the “Open issues and conclusions” sections 12.7 and 16.7, regarding the sandwich-fabric panel design and the constitutive law for epoxy resins respectively.

An open area for research concerns the analysis of the interface between filler and matrix. In this thesis, we have always assumed that the glassy inclusions are perfectly bonded to the epoxy binder. If this is true for low stress levels, approaching failure it might be not. The disconnection between filler and matrix can even be the principal reason of collapse for some syntactic foam under particular stress states. Furthermore, a faulty interface adhesion affects the nonlinear inelastic behavior and may be the source of some damage. However, as pointed out in sections 2.1 and 4.2, the glassy filler can be silanized in order to obtain a strong chemical bond with the matrix. Some new generation of glassy

hollow spheres is even directly silanized by the producer, like the hollow microspheres H50 employed to fill the syntactic foam type 6 (see section 4.6).

The filler silanization may in case change the matrix properties around the filler particles because of the imperfect chemical match between the silane agent and the epoxy resin (Al-Moussawi, Drown, and Drzal [4]). In particular, a spherical shell of matrix around each glass hollow microsphere (the so-called interphase) may have more compliant elastic moduli than those of the plain matrix. Once the mechanical properties of the silane/epoxy shell are determined by means of experimental tests on the plain polymer affected by the silane, this interphase effect can be straightforwardly incorporated into the homogenization techniques developed in this thesis.

A major research area which we have not dealt with is that concerning the composite failure modalities. In particular, it would be interesting to both investigate the stress state which brings the composite to fail and understand where the fracture unstable propagation starts from (matrix, filler, or interface).

To get an insight into this subject there is the need to carry out many more tests, mostly under multiaxial stress states, as well as to analyze the microscale composite behavior by means of proper numerical simulations. The first step towards this direction is to have accurate constitutive laws (and failure criteria) for the single phases. We have done some work in this direction by developing a constitutive law for epoxy resins (chapter 16), but nothing has been said about rupture.

The unit cell Finite Element analyses in which such a constitutive model is employed (section 16.6) may be a useful tool to start this research. In fact, by applying to the unit cell the same boundary conditions as those, experimentally observed, which bring the material about to fail, it is possible to try and identify the reason for rupture. Then, this analysis may in some case be able to give an insight into the kind of microstructural defects which cause the failure, making it clear whether the flaws which drive the composite failure are either in the matrix or in the glass (the interface analysis is also possible).

Some preliminary simulations of the compressive uniaxial behavior of the syntactic foam type 1 (material described in section 4.1) have shown that, when the macroscopic longitudinal strain which corresponds to the composite failure is reached, the direct stress component normal to the plane along which the fracture has been experimentally observed is of about 700 MPa in some inclusion points. This value is coincident with that employed, but not justified, in [128] as the strength for glassy hollow spheres of similar dimensions. Therefore, this unit cell analysis seems to be able to explain that the fracture in uniaxial compression for the syntactic foam type 1 is filler driven. This does not seem to be the case for the syntactic foam type 5 (see section 4.5), for which 45° shear bands have been observed [86]. This different failure modality is likely due both to the presence of “unwanted” voids and to the lightness of the K1 microspheres employed.

A crude indication about the glass strength at this size can be obtained as follows. The glass fracture toughness can be taken as $K_{IC} \approx 0.7 \div 0.8 \text{ MN}/\text{m}^{3/2}$ [7]. The well known Griffith relation furnishes the unstable fracture propagation stress σ_0 of an unbounded panel with a flaw of length $2a_f$:

$$\sigma_0 = \frac{K_{IC}}{\sqrt{\pi a_f}} \quad (19.2.1)$$

If we adopt it to approximately evaluate the strength of a glassy hollow sphere subjected to some tensile loading, by setting $a_f = 0.2 \text{ } \mu\text{m}$, more or less one tenth of the average

wall thickness of the K37 microspheres used to fill the syntactic foam type 1, we obtain $\sigma_0 \approx 900 \text{ MPa}$. This tensile strength evaluation procedure is strongly approximate, since it takes neither the real geometry (sphere curvature and flaw shape) nor the real stress state in the hollow sphere into account; furthermore, it assumes that Linear Elastic Fracture Mechanics holds. However, the most difficult and influential problem arises in the determination of a meaningful flaw depth, which, if arbitrarily chosen, would make the evaluation of the glass strength meaningless. An indirect but perhaps efficient way to obtain the glass strength at the microsphere size could consist of testing, in uniaxial compression, different syntactic foams without “unwanted” voids and made up of the same suitable filler, possibly sifted in order to have accurate information on its geometry, in different volume fractions and into different matrixes. Then, if numerical simulations on unit cell models of all these syntactic foams could prove that the failure is glass driven and also furnished similar values of the maximum tensile stress in the inclusion, we could obtain a reliable indirect estimate of the glass strength.

The problem of determining the epoxy resin tensile strength is even more difficult, both its geometry and flaw distribution inside the composite being completely unknown. Also, the epoxy fracture toughness is not exactly known: [7] gives $K_{IC} \approx 0.6 \div 1 \text{ MN/m}^{3/2}$, whereas we found $K_{IC} \approx 6 \text{ MN/m}^{3/2}$ (see section 3.3).

Note that unit cell analyses are not suitable to simulate the failure observed in the tensile tests reported in chapter 4, in which the rupture is triggered by macroscopic superficial flaws which the unit cell can not account for. Furthermore, we did not investigate by means of numerical tools the collapse of the syntactic foams types 2–5, since they have “unwanted” voids and, then, the axisymmetric unit cell model, as that exploited in chapter 11, is impossible to use. Among the other tested composites, we focused first our attention on the syntactic foam type 1 only, because the dog-bone specimens (DB3, see section 4.6) used to perform the uniaxial compressive test on the syntactic foam type 6 became unstable, and unit cell analyses can not take the equilibrium bifurcation into account.

“Unwanted” voids, boundary conditions, or geometrical effect could be accounted for by Finite Element analyses on the whole composite (meshing, for instance, a tested specimen), seen as homogeneous but in which the constitutive law accounts for the microstructure through a homogenization technique. We have obtained some preliminary results by applying the Incremental Method to both the Self-Consistent and Mori-Tanaka “composite sphere”-based estimates (see section 18.3). We got, as expected, good results for what concerns the simulation of the global nonlinearity before failure, but we found the following difficulties.

The User Material, in which a nonlinear homogenization technique among those developed in this thesis is implemented, is quite expensive. We just implemented the Incremental method, even if it is not the most accurate among those proposed in section 18.3, because it directly furnishes the consistent jacobian, whereas all the other secant methods need either a lot of algebra or a very expensive numerical computation to obtain it. Furthermore, as explained in section 18.3, we could not incorporate the accurate model for epoxy resins, developed in chapter 16, into a homogenization technique since, in general, it furnishes an anisotropic jacobian. We have not yet tried to see whether some assumption (as that of proportional loading) might allow us to express that jacobian as an isotropic tensor.

Another problem concerns the localization of the overall fields in order to have a meaningful measure of either the local stresses or the local strains to be used in the failure criterion of each phase. In the case of brittle materials, after having established the strength of each phase (operation which, as said, is not trivial at all), one possible, but still unexplored, way to deal with this problem is to assume the overall nonlinearity/inelasticity dependent on a different average definition from that used to evaluate the significant stress to be compared with the local material strength. For instance, a possible measure for this last purpose is the maximum (positive) stress value. Such a measure can be tentatively evaluated by means of the elastic solutions reported in sections 7.2 and 7.3.

Another research field only partly explored is that concerning the asymmetric linear elastic behavior of some syntactic foams. This is the case of our syntactic foams types 2 and, most of all, 5. For the latter a bimodulus Drucker–Prager constitutive model has been macroscopically identified in [101] in order to fit the experimental data. Some preliminary Finite Element analyses on unit cell models have shown that this asymmetric behavior in the macroscopic, apparently linear, elastic range, which consists of a uniaxial behavior in compression softer than in tension, can be ascribed to nonlinear geometrical effects at the microscale. Indeed, the presence of “unwanted” voids, together with the use of the very light K1 microspheres, can make some inclusions unstable in compression if the “unwanted” voids are at the interface between matrix and filler.

It would also be useful to obtain a closed-form solution for the homogenized nonlinear behavior of syntactic foams. This appears to be feasible only by (i) exploiting the Mori–Tanaka estimate based on just one “composite sphere”, (ii) introducing some simplifying assumptions on the phase behavior, and (iii) using the theorem (17.2.16). For instance, if we take the matrix to be incompressible, the derivative (needed to localize the equivalent strain or stress) of the effective bulk modulus (given by equation (7.3.14)) with respect to the matrix shear modulus simply reads:

$$\frac{\partial K_0^{est}}{\partial G^{(m)}} = \frac{4(1-f)}{3f} \quad (19.2.2)$$

The computation of the other relevant derivative $\frac{\partial G_0^{MT}}{\partial G^{(m)}}$ needs the solution of the system reported in appendix 7.C in which the incompressibility constraint has to be somehow imposed. After having checked whether this computation provides a tractable expression for $\frac{\partial G_0^{MT}}{\partial G^{(m)}}$ too, a proper nonlinear constitutive law for the matrix has to be chosen (the filler being linear elastic) in order to see if it is possible to obtain the desired closed-form solution.

Finally, it would be interesting to investigate about the residual stress field remaining into syntactic foams due to the cool-down from the melting state in the hardening process. Even if it is known that the presence of a gas-filled filler makes this phenomenon in syntactic foams less important than in other composites, it appears worthwhile to go more deeply into this subject. Its knowledge would be useful also to analyze the interface behavior. To pursue this aim, there is the need of an accurate constitutive law for epoxy resins, working for temperatures ranging from the room temperature up to the glass transition temperature (we could not yet test the model developed in chapter 16 for temperatures different from the room temperature). Note that it is possible to neglect what happens in the composite when the matrix is still either liquid or soft enough because, in this case,

every stress can be relaxed owing to the high viscosity ruling the binder behavior. If such a model for epoxy resins is made available, numerical simulations of the cool-down can be accomplished by means of unit cell models. The analytical investigation through the homogenization theory can be in principle done, with the help of the results of chapter 13, but, as already discussed, it is not straightforward to make the constitutive law for epoxy resins fitting into the homogenization theoretical frame.

Bibliography

- [1] 3M Italia (1993) *ScotchliteTM Glass Bubbles. Informazioni di prodotto* (in Italian), private communication.
- [2] Alfrey T. (1944) Non-homogeneous stresses in viscoelastic media *Quarterly of Applied Mathematics* **II** (2), 113–119.
- [3] Allen H. G. (1969) *Analysis and Design of Structural Sandwich Panels*, Pergamon Press Ltd., Oxford, UK.
- [4] Al-Moussawi H., Drown E. K., and Drzal L. T. (1993) The silane/sizing composite interphase *Polymer Composites* **14** (3), 195–200.
- [5] Argon A. S. (1973) A theory for the low-temperature plastic deformation of glassy polymers *Philosophical Magazine* **28**, 839–865.
- [6] Arruda E. M. and Boyce M. C. (1993) A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials *Journal of the Mechanics and Physics of Solids* **41** (2), 389–412.
- [7] Ashby M. F. (1989) On the engineering properties of materials, Overview No. 80, *Acta Metallurgica* **37** (5), 1273–1293.
- [8] Asaro R. J. and Barnett D. M. (1975) The non-uniform transformation strain problem for an anisotropic ellipsoidal inclusion *Journal of the Mechanics and Physics of Solids* **23**, 77–83.
- [9] Bardella L. (1999) Mechanical behaviour of syntactic foams: experimental results and estimates of the effective elastic moduli. Technical Report N. 14/1999, Department of Civil Engineering, University of Brescia, Italy.
- [10] Bardella L. (2000) A phenomenological constitutive law for epoxy resins *Proceedings, XIII Convegno Italiano di Meccanica Computazionale, Brescia, 13–15 novembre 2000*.
- [11] Bardella L., Carini A., and Genna F. (1999) Analisi delle proprietà chimiche, fisiche e micromeccaniche di un materiale composito in sandwich di schiuma sintattica e fibra di vetro preimpregnata. Analisi delle caratteristiche meccaniche di resine base della schiuma sintattica (in Italian). Technical Report N. 6/1999, Department of Civil Engineering, University of Brescia, Italy.

- [12] Bardella L. and Genna F. (1999) Analisi delle proprietà chimiche, fisiche e micromeccaniche di un materiale composito in sandwich di schiuma sintattica e fibra di vetro preimpregnata. Analisi micromeccanica della schiuma sintattica (in Italian). Technical Report N. 7/1999, Department of Civil Engineering, University of Brescia, Italy.
- [13] Bardella L. and Genna F. (1999) Analisi delle proprietà chimiche, fisiche e micromeccaniche di un materiale composito in sandwich di schiuma sintattica e fibra di vetro preimpregnata. Analisi di alcune caratteristiche elastiche di un sandwich in “sandwich-fabric panel” e schiuma sintattica (in Italian). Technical Report N. 8/1999, Department of Civil Engineering, University of Brescia, Italy.
- [14] Bardella L. and Genna F. (2000) Approximate computation of the elastic shear stiffness of a sandwich beam *Proceedings, XIII Convegno Italiano di Meccanica Computazionale, Brescia, 13–15 novembre 2000*.
- [15] Bardella L. and Genna F. (2001) Elastic design of syntactic foamed sandwiches obtained by filling of three-dimensional sandwich-fabric panels *International Journal of Solids and Structures* **38** (2), 307–333.
- [16] Bardella L. and Genna F. (2001) On the elastic behavior of syntactic foams *International Journal of Solids and Structures* to be published.
- [17] Bardenhagen S. G., Stout M. G., and Gray G. T. (1997) Three-dimensional, finite deformation, viscoplastic constitutive models for polymeric materials *Mechanics of Materials* **25**, 235–253.
- [18] Benveniste Y. (1987) A new approach to the application of Mori–Tanaka’s theory in composite materials *Mechanics of Materials* **6**, 147–157.
- [19] Benveniste Y., Dvorak G. J., and Chen T. (1991) On diagonal and elastic symmetry of the approximate effective stiffness tensor of heterogeneous media *Journal of the Mechanics and Physics of Solids* **39**, 927–946.
- [20] Bergström J. S. and Boyce M. C. (1998) Constitutive modeling of the large strain time-dependent behavior of elastomers *Journal of the Mechanics and Physics of Solids* **46**, 931–954.
- [21] Berveiller M. and Zaoui A. (1979) An extension of the Self–Consistent Scheme to plastically–flowing polycrystals *Journal of the Mechanics and Physics of Solids* **26**, 325–344.
- [22] Bisegna P. and Luciano R. (1999) Consistent Hashin–Shtrikman bounds on the effective properties of periodic materials *Journal of Applied Mechanics, Transactions of the ASME* **66**, 858–866.
- [23] Bishop J. F. W. and Hill R. (1951) A theory of the plastic distortion of a polycrystalline aggregate under combined stress *Philosophical Magazine* **42**, 414–427.
- [24] Bishop J. F. W. and Hill R. (1951) A theoretical derivation of the plastic properties of a polycrystalline face-center metal *Philosophical Magazine* **42**, 1298–1307.

- [25] Bornert M., Hervé É., Stolz C., and Zaoui A. (1994) Self-Consistent approaches and strain heterogeneities in two-phase elastoplastic materials *Applied Mechanics Reviews* **47** (1), Part 2, S66–S76.
- [26] Bornert M., Stolz C., and Zaoui A. (1996) Morphologically Representative Pattern-based bounding in elasticity *Journal of the Mechanics and Physics of Solids* **44**, 307–331.
- [27] Bowden P. B. and Jukes J. A. (1972) The plastic flow of isotropic polymers *Journal of Material Science* **7**, 52–63.
- [28] Boyce M. C., Parks D. M., and Argon A. S. (1988) Large inelastic deformation of glassy polymers. Part I: rate dependent constitutive model *Mechanics of Materials* **7**, 15–33.
- [29] Brandt A. M. (1995) *Cement-based Composites. Materials, Mechanical Properties and Performance* E & FN SPON, London.
- [30] Budiansky B. (1965) On Elastic Moduli of Some Heterogeneous Materials *Journal of the Mechanics and Physics of Solids* **13**, 223–227.
- [31] Bunn P. and Mottram J. T. (1993) Manufacture and compression properties of syntactic foams *Composites* **24** (7), 565–571.
- [32] Buryachenko V. (1993) Effective strength properties of elastic physically nonlinear composites. In Marigo J. and Rousselier G. (Eds.) *Micromechanics of Materials*. Eyrolles, 567–578.
- [33] Calò G. and Guizzetti I. (1998) *Analisi elastica del comportamento meccanico di schiume sintattiche* (in Italian). Laurea thesis, University of Brescia, Italy.
- [34] Carini A. and De Donato O. (1992) Fundamental solutions for linear viscoelastic continua *International Journal of Solids and Structures* **29**, 2989–3009.
- [35] Christensen R. M. (1979) *Mechanics of composite materials* Krieger Publishing Company, Malabar, Florida.
- [36] Christensen R. M. (1990) A critical evaluation for a class of micromechanics models *Journal of the Mechanics and Physics of Solids* **38**, 379–404.
- [37] Christensen R. M. and Lo K. H. (1979) Solutions for effective shear properties in three phase sphere and cylinder models *Journal of the Mechanics and Physics of Solids* **27**, 315–330.
- [38] Colonnetti G. (1955) *L'équilibre des corps déformables* Dunod, Paris.
- [39] De Runtz J. A. Jr. and Hoffman O. (1969) The static strength of syntactic foams *Journal of Applied Mechanics, Transactions of the ASME* **36** (E4), 551–557.
- [40] Drucker D. C. (1966) The continuum theory of plasticity on the macroscale and the microscale *Journal of Materials* **1**, 873–910.

- [41] Dvorak G. J. (1992) Transformation field analysis of inelastic composite materials *Proceedings of the Royal Society, London* **A437**, 311–327.
- [42] Dvorak G. J. and Bahei-El-Din Y. A. (1997) Inelastic composite materials: transformation analysis and experiments. In Suquet P. (Ed.) *Continuum Micromechanics*. CISM Lecture Notes 377, Springer-Verlag, Wien, 1–60.
- [43] Dvorak G. J. and Benveniste Y. (1992) On transformation strains and uniform fields in multiphase elastic media *Proceedings of the Royal Society, London* **A437**, 291–310.
- [44] Dvorak G. J. and Srinivas M. V. (1999) New estimates of overall properties of heterogeneous solids *Journal of the Mechanics and Physics of Solids* **47**, 899–920.
- [45] Eshelby J. D. (1957) The determination of the elastic field of an ellipsoidal inclusion, and related problems *Proceedings of the Royal Society, London* **A241**, 376–396.
- [46] Eyring H. (1936) Viscosity, plasticity and diffusion as examples of absolute reaction rates *Journal of Chemistry and Physics* **4**, 283–291.
- [47] Ferry J. D. (1980) *Viscoelastic Properties of Polymers*, 3rd ed., John Wiley & Sons, New York.
- [48] Fotheringham D. G. and Cherry B. W. (1978) The role of recovery forces in the deformation of linear polyethylene *Journal of Materials Science* **13**, 951–964.
- [49] Gamba A. and Marini S. (1998) *Analisi sperimentale del comportamento meccanico di resine epossidiche* (in Italian). Laurea thesis, University of Brescia, Italy.
- [50] Gibson L. J. and Ashby M. F. (1988) *Cellular Solids*, Pergamon Press, New York.
- [51] Girolmini P. (1996) A critical evaluation of various nonlinear extensions of the Self-Consistent model. In Pineau A. and Zaoui A. (Eds.) *Micromechanics of Plasticity and Damage of Multiphase Materials*. Kluwer Academic Publishers, Dordrecht, The Netherlands, 67–74.
- [52] González C. and Llorca J. (2000) A Self-Consistent approach to the elasto-plastic behaviour of two-phase materials including damage *Journal of the Mechanics and Physics of Solids* **48**, 675–692.
- [53] Gurson A. L. (1977) Continuum theory of ductile rupture by void nucleation and growth: part I — Yield criteria and flow rules for porous media *Journal of Engineering Materials and Technology* **99**, 2–15.
- [54] Haward R. N. and Thackray G. (1968) The use of a mathematical model to describe isothermal stress-strain curves in glassy thermoplastics *Proceedings of the Royal Society, London* **A302**, 453–472.
- [55] Hasan O. A. and Boyce M. C. (1995) A constitutive model for the nonlinear viscoelastic viscoplastic behavior of glassy polymers *Polymer Engineering and Science* **35**, 331–344.

- [56] Hashin Z. (1962) The elastic moduli of heterogeneous materials *Journal of Applied Mechanics, Transactions of the ASME* **29**, 143–150.
- [57] Hashin Z. and Shtrikman S. (1962) On some variational principles in anisotropic and nonhomogeneous elasticity *Journal of the Mechanics and Physics of Solids* **10**, 335–342.
- [58] Hashin Z. and Shtrikman S. (1963) A variational approach to the theory of the elastic behaviour of multiphase materials *Journal of the Mechanics and Physics of Solids* **11**, 127–140.
- [59] Hazanov S. and Huet C. (1994) Order relationships for boundary conditions effect in heterogeneous bodies smaller than the representative volume *Journal of the Mechanics and Physics of Solids* **42** (12), 1995–2011.
- [60] Hervé É. and Pellegrini O. (1995) The elastic constants of a material containing spherical coated holes *Archives Mechanics* **47** (2), 223–246.
- [61] Hervé É. and Zaoui A. (1993) n-layered inclusion-based micromechanical modelling *International Journal of Engineering Science* **31** (1), 1–10.
- [62] Hervé É. and Zaoui A. (1995) Elastic behavior of multiply coated fibre-reinforced composites *International Journal of Engineering Science* **33** (10), 1419–1433.
- [63] Hibbitt, Karlsson & Sorensen (1999) *ABAQUS User's & Theory Manuals* Release 5.8, Pawtucket, USA.
- [64] Hill R. (1963) Elastic properties of reinforced solids: some theoretical principles *Journal of the Mechanics and Physics of Solids* **11**, 357–372.
- [65] Hill R. (1964) Theory of mechanical properties of fiber-strengthened materials: I. Elastic behavior *Journal of the Mechanics and Physics of Solids* **12**, 199–212.
- [66] Hill R. (1965) A Self-Consistent mechanics of composite materials *Journal of the Mechanics and Physics of Solids* **13**, 213–222.
- [67] Hill R. (1965) Continuum micro-mechanics of elastoplastic polycrystals *Journal of the Mechanics and Physics of Solids* **13**, 89–101.
- [68] Huang J. S. and Gibson L. J. (1993) Elastic moduli of a composite of hollow spheres in a matrix *Journal of the Mechanics and Physics of Solids* **41**, 55–75.
- [69] Hughes T. J. R. (1987) *The Finite Element Method* Prentice-Hall, Inc., New Jersey.
- [70] Hull D. (1981) *An Introduction to Composite Materials* Cambridge University Press, Cambridge, UK.
- [71] Jourawsky M. (1856) Sur la résistance d'un corps prismatiques et d'une pièce composée en bois ou en tôle de fer à une force perpendiculaire à leur longueur *Annales des Ponts and Chaussées* **12**, 328–351.

- [72] Kailasam M. and Ponte Castañeda P. (1998) A general constitutive theory for linear and nonlinear particulate media with microstructure evolution *Journal of the Mechanics and Physics of Solids* **46**, 427–465.
- [73] Kinra V. K. and Ker E. (1982) Effective elastic moduli of a thin-walled glass microsphere/PMMA composite *Journal of Composite Materials* **16**, 117–138.
- [74] Kreher W. (1990) Residual stresses and stored elastic energy of composites and polycrystals *Journal of the Mechanics and Physics of Solids* **38**, 115–128.
- [75] Kröner E. (1977) Bounds for effective elastic moduli of disordered materials *Journal of the Mechanics and Physics of Solids* **25**, 137–155.
- [76] Kurata M. and Stockmayer W. H. (1963) Intrinsic viscosities and unperturbed dimensions of long chain molecules *Advances in Polymer Science* **3**, 196–312.
- [77] Lee S. M. (1988) Plastic deformations in epoxy resins. In Dickie R. A., Labana S. S., and Bauer R. (Eds.) *Cross-linked Polymers: Chemistry, Properties, and Applications*. ACS Symposium series no 367, American Chemical Society, Washington D. C., 136–144.
- [78] Lee A. and McKenna G. B. (1990) The physical ageing response of an epoxy glass subjected to large stresses *Polymer* **31**, 423–430.
- [79] Lee K. J. and Westmann R. A. (1970) Elastic properties of hollow-sphere-reinforced composites *Journal of Composite Materials* **4**, 242–253.
- [80] Lesser A. J. and Kody R. S. (1997) A generalized model for the yield behavior of epoxy networks in multiaxial stress states *Journal of Polymer Science: Polymer Physics Edition* **35**, 1611–1619.
- [81] Levin V. M. (1967) *Mekhanika Tvergo Telo* **2**, 88–94 (English translation — On the coefficients of thermal expansion in heterogeneous materials *Mechanics of Solids* **2**, 58–61).
- [82] Liang Y.-M. and Liechti K. M. (1996) On the large deformation and localization behavior of an epoxy resin under multiaxial stress states *International Journal of Solids and Structures* **33** (10), 1479–1500.
- [83] Love A. E. H. (1944) *A Treatise on the Mathematical Theory of Elasticity* Dover Publications, Inc., New York.
- [84] Luciano R. and Willis J. R. (2000) Bounds on non-local effective relations for random composites loaded by configuration-dependent body forces *Journal of the Mechanics and Physics of Solids* **48**, 1827–1849.
- [85] McLaughlin R. (1977) A study of the differential scheme for composite materials *International Journal of Engineering Sciences* **15**, 237–244.

- [86] Maier G. (1998) *Analisi delle proprietà chimiche, fisiche e micromeccaniche di un materiale composito in sandwich di schiuma sintattica e fibra di vetro preimpregnata. Studio del comportamento meccanico di un materiale composito a sandwich di schiuma sintattica e fibra di vetro* (in Italian), private communication.
- [87] Malvern E. L. (1969) *Introduction to the Mechanics of a Continuous Medium* Prentice-Hall, Inc., New Jersey.
- [88] Mori T. and Tanaka K. (1973) Average stress in matrix and average energy of materials with misfitting inclusions *Acta Metallurgica* **21**, 571–574.
- [89] Moulinec H. and Suquet P. (1997) A numerical method for computing the overall response of nonlinear composites with complex microstructure *Computer Methods in Applied Mechanics and Engineering* **157**, 69–94.
- [90] Mura T. (1987) *Micromechanics of defects in solids* Second Edition, Martinus Nijhoff Publisher, Dordrecht, The Netherlands.
- [91] Nielsen L. E. (1983) Elastic modulus of syntactic foams *Journal of Polymer Science: Polymer Physics Edition* **22**, 1567–1568.
- [92] Oleinik E. F. (1986) Epoxy-aromatic amine networks in the glassy state: structures and properties *Advances in Polymer Science* **80**, 49–99.
- [93] Palumbo M. and Tempesti E. (1998) On the nodular morphology and mechanical behaviour of a syntactic foam cured in thermal and microwave fields *Acta Polymerica* **49**, 482–486.
- [94] Ponte Castañeda P. (1991) The effective mechanical properties of nonlinear isotropic composites *Journal of the Mechanics and Physics of Solids* **39**, 45–71.
- [95] Ponte Castañeda P. (1992) New variational principles in plasticity and their application to composite materials *Journal of the Mechanics and Physics of Solids* **40**, 1757–1788.
- [96] Ponte Castañeda P. (1997) Nonlinear composite materials: effective constitutive behavior and microstructure evolution. In Suquet P. (Ed.) *Continuum Micromechanics*. CISM Lecture Notes 377, Springer-Verlag, Wien, 131–195.
- [97] Ponte Castañeda P. and Suquet P. (1998) Nonlinear composites *Advances in Applied Mechanics* **34**, 172–302.
- [98] Prandini M. and Bardella L. (2000) Identification of a constitutive model for epoxy resins *Proceedings, XIII Convegno Italiano di Meccanica Computazionale, Brescia, 13–15 novembre 2000*.
- [99] Prandtl L. (1928) Ein Gedankenmodell zur kinetischen Theorie der festen Körper *Zeitschrift für Angewandte Mathematik und Mechanik* **8**, 85.
- [100] Reuss A. (1929) Calculation of the flow limits of mixed crystals on the basis of the plasticity of mono-crystals *Zeitschrift für Angewandte Mathematik und Mechanik* **9**, 49–58.

- [101] Rizzi E., Papa E., and Corigliano A. (2000) Mechanical behavior of a syntactic foam: experiments and modeling *International Journal of Solids and Structures* **37**, 5773–5794.
- [102] Sachs G. (1928) Zur Ableitung einer Fließbedingung *Zeitschrift des Vereines Deutscher Ingenieur* **72**, 734–736.
- [103] Samuelli G. (2000) *Analisi del comportamento non lineare di compositi particolati* (in Italian). Laurea thesis, University of Brescia, Italy.
- [104] Shutov F. A. (1986) Syntactic polymer foams *Advances in Polymer Science* **73/74**, 63–123.
- [105] Simo J. C. and Taylor R. L. (1985) Consistent tangent operators for rate-independent elastoplasticity *Computer Methods in Applied Mechanics and Engineering* **48**, 101–118.
- [106] Suquet P. (1987) Elements of homogenization for inelastic solid mechanics. In Sanchez-Palencia E. and Zaoui A. (Eds.) *Homogenization Techniques for Composite Media*. Lecture Notes in Physics, Springer Verlag, **272**, 193–278.
- [107] Suquet P. (1995) Overall properties of nonlinear composites: a modified secant moduli theory and its link with Ponte Castañeda’s nonlinear variational procedure *Comptes Rendus de l’Académie des Sciences, Paris — Série IIB* **320**, 563–571.
- [108] Suquet P. (1997) Effective properties of nonlinear composites. In Suquet P. (Ed.) *Continuum Micromechanics*. CISM Lecture Notes 377, Springer-Verlag, Wien, 197–264.
- [109] Tabiei A. and Jiang Y. (1999) Woven fabric composite material model with material nonlinearity for nonlinear finite element simulation *International Journal of Solids and Structures* **36**, 2757–2771.
- [110] Talbot D. R. S. and Willis J. R. (1985) Variational principles for inhomogeneous nonlinear media *IMA Journal of Applied Mathematics* **35**, 39–54.
- [111] Talbot D. R. S. and Willis J. R. (1995) Upper and lower bounds for the overall properties of a nonlinear elastic composite. In Parker D. E. and England A. H. (Eds.) *Anisotropy, inhomogeneity and nonlinearity in solid mechanics*. Kluwer Academic Publishers, Dordrecht, The Netherlands, 409–414.
- [112] Taylor G. I. (1938) Plastic strains in metals *Journal of the Institute of Metals* **62**, 307–324.
- [113] Thébaud F., Michel J. C., Hervé É., Suquet P., and Zaoui A. (1992) Modeling nonlinear behavior of composites with imperfect interfaces *Proceedings of the 13th Risø International Symposium on Materials Science*, Andersen S.I. (Eds.) 467–472.
- [114] Tempesti E. (1998) *Analisi delle proprietà chimiche, fisiche e micromeccaniche di un materiale composito in sandwich di schiuma sintattica e fibra di vetro preimpregnata*. (in Italian), private communication.

- [115] Terada K., Hori M., Kyoya T., and Kikuchi N. (2000) Simulation of the multi-scale convergence in computational homogenization approaches *International Journal of Solids and Structures* **37**, 2285–2311.
- [116] Timoshenko S. P. and Goodier J. N. (1970) *Theory of Elasticity* Third Edition, McGraw-Hill International Editions, London, UK.
- [117] Torquato S. (1991) Random heterogeneous media: microstructure and improved bounds on effective properties *Applied Mechanics Reviews* **44** (2), 37–76.
- [118] Treloar L. R. G. (1975) *The physics of rubber elasticity* Second Edition, Oxford University Press, UK.
- [119] Tvergaard V. (1982) On localization in ductile materials containing spherical voids *International Journal of Fracture* **18** (4), 237–252.
- [120] van der Sluis O., Schreurs P.J.G., Brekelmans W.A.M., and Meijer H.E.H. (2000) Overall behaviour of heterogeneous elastoviscoplastic materials: effect of microstructural modelling *Mechanics of Materials* **32**, 449–462.
- [121] van Vuure A. W. (1997) *Composite panels based on woven sandwich-fabric preforms*. PhD Thesis, Katholieke Universiteit Leuven, Belgium.
- [122] Vargiu S. (1986) Polimeri termoindurenti *Macromolecole — Scienza e Tecnologia* (in Italian) **1**, 507–529, Pacini Editore, Pisa.
- [123] Voigt W. (1889) Ueber die Beziehung zwischen den beiden Elasticitäts-constanten isotroper Körper *Annalen der Physik (Leipzig)* **38** (3), 573–587.
- [124] Walpole L. J. (1966) On bounds for the overall elastic moduli of inhomogeneous system — I *Journal of the Mechanics and Physics of Solids* **14**, 151–162.
- [125] Walpole L. J. (1969) On the overall elastic moduli of composite materials *Journal of the Mechanics and Physics of Solids* **17**, 235–251.
- [126] Walpole L. J. (1981) Elastic behavior of composite materials: theoretical foundations *Advances in Applied Mechanics* **21**, 169–242.
- [127] Ward I. M. (1990) *Mechanical Properties of Solid Polymers*, 2nd ed., John Wiley & Sons, New York, NY, USA.
- [128] Wei D., Baptiste D., Bompard Ph., and François D. (1989) A damage micromechanics approach to a heterogeneous material. In Mazars J. and Bažant Z. P. (Eds.) *Cracking and Damage, Strain Localization and Size Effect* Elsevier, New York, 128–139.
- [129] Willis J. R. (1977) Bounds and Self-Consistent estimates for the overall properties of anisotropic composites *Journal of the Mechanics and Physics of Solids* **25**, 185–202.
- [130] Willis J. R. (1978) Variational principles and bounds for the overall properties of composites. In Provan J. (Ed.) *Continuum models and discrete systems (CMDS 2)* Univ. Waterloo Press, Waterloo, ON Canada, 185–202.

- [131] Willis J. R. (1981) Variational and related methods for the overall properties of composites *Advances in Applied Mechanics* **21**, 1–78.
- [132] Willis J. R. (1983) The overall response of composite materials *Journal of Applied Mechanics, Transactions of the ASME* **50**, 1202–1209.
- [133] Wu X. and Ohno N. (1999) A homogenization theory for time-dependent nonlinear composites with periodic internal structures *International Journal of Solids and Structures* **36**, 4991–5021.
- [134] Wu P. D. and van der Giessen (1993) On improved network models for rubber elasticity and their applications to orientation hardening in glassy polymers *Journal of the Mechanics and Physics of Solids* **41** (3), 427–456.
- [135] Yamini S. and Young R. J. (1980) The mechanical properties of epoxy resins. Part I: mechanism of plastic deformation *Journal of Material Science* **15**, 1814–1822.
- [136] Zaoui A. (1997) Structural Morphology and Constitutive Behaviour of Microheterogeneous Materials. In Suquet P. (Ed.) *Continuum Micromechanics*. CISM Lecture Notes 377, Springer-Verlag, Wien, 291–347.
- [137] Zimmermann R. W. (1991) Elastic moduli of a solid containing spherical inclusions *Mechanics of Materials* **12**, 17–24.