Production and characterization of polycaprolactone/graphene powder electrospun nanofibers: effects of graphene powder content and suspension preparation

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ABSTRACT

Porous fibrous membranes having multiple scales geometries and tailored properties have become important. Because of the feasibility of incorporating graphene in electrospun nanofibres and the growing interest on these nanomaterials, the authors focused in the electrospinning of Poly (ε-Caprolactone) (PCL) solutions in the presence of different amounts of Graphene Powder (GP). Electrospinning is a process whereby ultra-fine fibers are formed in a high-voltage electrostatic field. The electrospun structure is characterized by a wide range of pore diameter distribution, high porosity and effective mechanical properties. The morphological appearance, fiber diameter, and structure of PCL nanofibers produced by the electrospinning process were studied in the presence of different concentration of GP. Moreover, the effect of a successful incorporation of GP nanosheets into PCL polymer nanofibers was analyzed. Scanning electron microscope micrographs of the electrospun fibers showed that the average fiber diameter magnitude is strongly infuenced by the presence of GP. Furthermore, the intrinsic properties developed due to the interactions of GP and PCL improved the mechanical properties of the nanofibers. The results revealed that the effect of various GP concentrations on PCL is due to the strong interfacial interactions between the two phases characterized by the good dispersion of GP nanosheets in the matrix. The functional complexity of electrospun fibers provides significant advantages over other techniques and makes the fibers suitable for many applications including air/water filters, sensors, organic solar cells, smart textiles, biocompatible scaffolds for tissue engineering and load-bearing applications. However, improved deposition efficiencies are a necessary advance needed to maintain the attractiveness of this technique.

Keywords: electrospinning, polycaprolactone, graphene powder

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1. INTRODUCTION

Electrospinning is a technique where high voltages are applied to a polymer solution to produce porous structures of varying morphologies. The fibers are collected in a nonwoven mesh characterized by high surface area/unit mass and a large fraction of interconnected porosity. This method provides the capability of integrating various types of polymers, fibers and particles to produce unique porous materials with a structural scale of the order of *nm*[1]. The present paper is intended to illustrate porous fiber mats production by electrospinning of a poly-(ε-caprolactone) (PCL) and Graphene Powder (GP) solution. The graphene, compared to carbon nanotubes, is a single layer of aromatic carbon that can be more promising in the fabrication of high-performance and functional electrospun nano-fibers due to its intrinsic extraordinary physical[2,3], electrical and biological properties[4,5]. Furthermore, graphene nanosheets can be easily mixed into a polymer solution because of their surface functionalities.

Poly (ε-caprolactone) with an average molecular weight of 80,000 g/mol was dissolved in two solutions: one consisting in 1:1 Tetrahydrofuran (THF) and Dimethylformamide (DMF) and the other consisting in only Cyclopentanone. A polymer concentration of 15% was used for the THF: DMF combination while a concentration of 23% was used for the Cyclopentanone. The solutions were prepared in bulk condition using the digital hotplate as a mixer at 40° C degrees. The solutions were poured into a 10 ml syringe, equipped with 21 Gauge needle (Inner diameter = 0.8 mm). The tests were run for 45 minutes each and the samples were observed by optical microscope and Scanning Electron Microscope (SEM). In order to analyze the effects of the process parameters on the structure of electrospun PCL, experiments were conducted under different conditions. The tests were repeated three times under the same conditions to check for the system variability based on the diameters of the fibers deposited on the collector. A first experimental trial was carried out to preliminary evaluate the process parameters to adopt. Results were evaluated in terms of process feasibility and fiber diameter (AD) and scattering. The mechanical properties of the electrospun mats were evaluated under uniaxial tensile tests.

2.MORPHOLOGICAL ANALYSIS

In this section, the process parameters were varied within ranges chosen around the values tested in a process calibration trial. In particular, the range of flow rate, voltage and tip-collector distance were 0.5÷1 ml/h, 20 kV and 12÷18 cm respectively for the THF: DMF solution and the Cyclopentanone solution. Optical microscope images are firstly reported to evaluate the effect of different GP percentages on the quality of the polymer fibers and the goodness of the interfacial interactions between the two phases. The THF: DMF solution leads to the formation of carbonized fibers even with a small amount of GP content whereas the fibers electrospun from the Cyclopentanone solution seems to be strongly affected from the GP fraction in terms of their structure (Fig. 1). In particular, core-shell fibers are deposited consisting in a polymer core surrounded by a graphene shell and the quality of the connection between the two phases is improved as the GP percentage increases (Fig. d-e-f). SEM analysis were then conducted on the samples to get high resolution images to measure the dimension of the fibers. For each test, the diameter of 70 fibers was measured using the image processing software ImageJ[6].

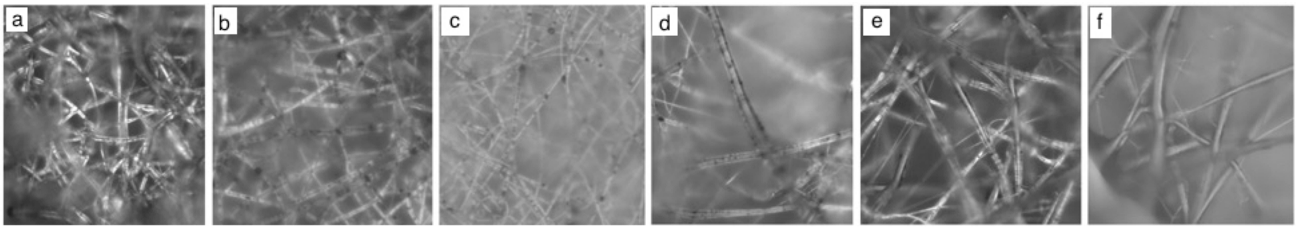

Figure 1. Optical microscope images 500x: (a) THF: DMF-PCL with 0.5% GP, (b) THF: DMF-PCL with 1% GP, (c) THF:DMF-PCL with 2% GP , (c) Cyclopentanone-PCL with 0.5% GP (e) Cyclopentanone-PCL with 1% GP, (f) Cyclopentanone-PCL with 2% GP

The electrospinning results by using the THF: DMF solution showed that a good quantity of fibers reached the collector (Fig. 2 e,f,g,h) with all the graphene percentages used. Moreover, a good fiber distribution was observed on the collector and a uniform deposition area was obtained. The diameter of the fibers was clearly influenced by the GP content. In fact, a larger amount of thinner fibers is produced as the GP fraction is increased (Fig. 3). During electrospinning of the Cyclopentanone solution, a good network of fibers was obtained although some droplets of solution appeared with a GP percentage higher then 1% (Fig. 2 c,d). Further, the deposition area on the collector was reduced as the GP content was increased. In this case, a larger amount of thicker fibers is produced as the GP percentage is increased (Fig. 3).

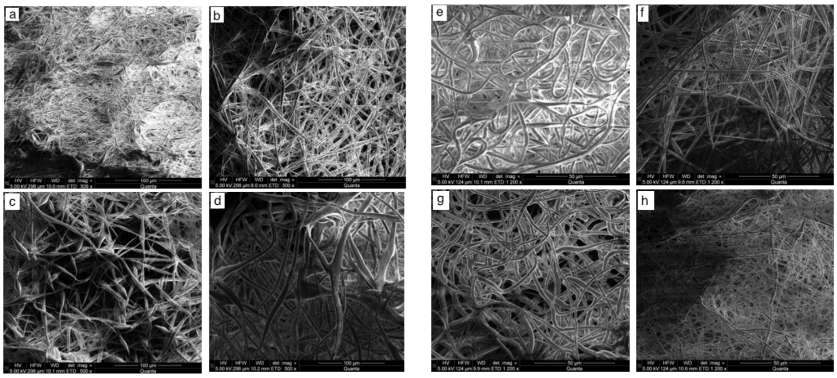

Figure 2. On the right: SEM image 500x, (a) Cyclopentanone with 0% GP, (b) Cyclopentanone with 0.5% GP, (c) Cyclopentanone-PCL with 1% GP (d) Cyclopentanone-PCL with 2% GP. On the left: SEM images 1200x, (e) THF:DMF with 0% GP, (f) THF:DMF with 0.5% GP, (g) THF:DMF with 1% GP (h) THF:DMF with 2% GP.

Figure 3 reports the trends of the Average Diameter (AD) and the related Standard Deviation (SD) calculated for all the combination of parameters involving the THF: DMF and the Cyclopentanone solutions. The uniformity of the fibers (i.e. smaller SD values) can be improved by the GP content when the THF: DMF solution is used while when Cyclopentanone is used a higher standard deviation can be easily interpreted on the basis of the “bead on string” structures observed within fibers richer in GP.

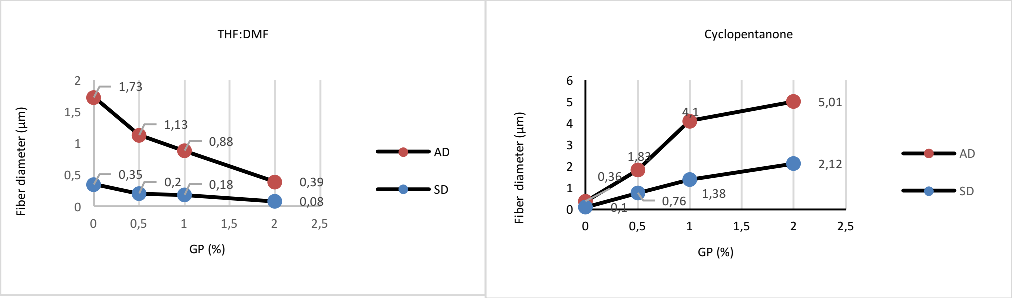

Figure 3. On the right: AD and SD *vs* GP percentage for the THF: DMF solution; on the left: AD and SD *vs* GP percentage for the Cyclopentanone solution.

3. MECHANICAL ANALYSIS

The mechanical response of the various electrospun systems was evaluated in uniaxial tensile tests, carried out at 23°C by means of the INSTRON mechanical analyzer (© Illinois Tool Works Inc.). Rectangular strips were cut from the central portion of the electrospun network, with an overall length and width of 10 mm; the thickness ranged between about 0.2÷0.8 mm in the case of the thicker systems with Cyclopentanone solvent and of about 0.2÷0.4 mm in the case of the THF: DMF systems. The tests were carried out on three specimens for each type of solution. The specimens were subjected to a tensile ramp under displacement control at 0.2 mm/sec until failure. The stress vs. strain relationship was determined for all the materials up to final break. The results are reported in Figure 4, as the most representative nominal stress vs. nominal strain curve for each material group. The results of a previous characterization of the THF: DMF solution with 15% PCL concentration are reported[7].

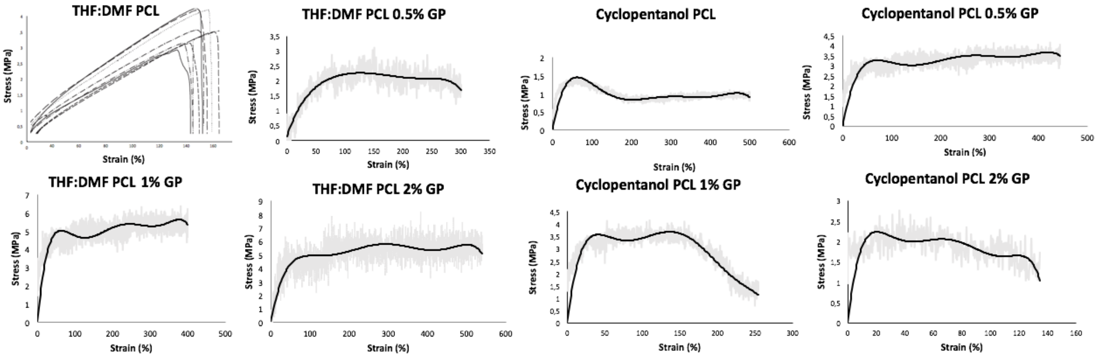

Figure 4. On the right: tensile nominal stress *vs.* nominal strain curves for the THF: DMF solutions at different GP percentages; on the left: tensile nominal stress *vs.* nominal strain curves for the Cyclopentanone solutions at different GP percentages.

The curves of the systems display a similar behavior, consisting of a first linear regime, that ranges up to strain of about 1 for the THF: DMF systems, and to about 0.2÷1 for Cyclopentanone systems, followed, after a broad transition region, by a second, and in some cases a third, linear regime at higher levels of strain. The material mechanical properties in terms of stiffness, strain at break and yield stress (evaluated as off-set yield strength corresponding to the 0.2 strain) were considered for the right interpretation of the results. The parameters evaluated from the curves provide a quantitative description of what was already evident in the graphs: for the THF: DMF solution the increase of the GP fraction leads to a more compliant and ductile systems with higher strength, evaluated in correspondence of the maximum stress. In particular, an elastic modulus of 16 MPa in correspondence of a GP content of 2% was found, compared to the 3.8 MPa found in absence of GP. The elongation at break goes up from 152.5 % to 539.7 % when the GP percentage is increased from 0 % to 2 % respectively. Whereas, for the Cyclopentanone solution, the higher stiffness shown by the fibers richer in GP content may be tentatively interpreted on the basis of their morphology, since SEM analysis suggests the development of a larger amount of thicker fibers as the GP content increases. In this case, the elastic modulus changes from 5.6 MPa, in absence of GP, to 22.5 MPa, with a GP fraction of 2%. Furthermore, the elongation at break is reduced, from 499,6 % to 134,5 %, as the GP percentage is increased from 0 % to 2 % respectively. The maximum value of the yield stress was recorded in correspondence to a GP percentage of 1% in both cases: values of 4.8 MPa and 3.23 MPa for the THF: DMF solution and the Cyclopentanone solution were calculated respectively.

4. DISCUSSION

In this analysis, PCL/GP fibers are obtained as a results of a good GP suspension in the electrospinning solution. The stability of solution is a core parameter for the repeatability of the process and to avoid a random dispersion of the GP in the electrospun polymer mat. The SEM micrographs of the electrospun fibers showed that the average fiber diameter is modified by the presence of GP by means of occurring interfacial interactions between the two phases. The diameter of the electrospun fibers increases with the GP percentage using Cyclopentanone. By contrast, the diameter of the fibers decreases with the GP percentage using the THF: DMF combination. Both the deposition area and the fiber distribution are improved by using the THF: DMF solution. Moreover, the intrinsic properties developed due to the interactions of GP and PCL improves the mechanical properties of the nano-fibers. In particular, the stiffness of the fibers increases with the GP percentage and the elongation at break and the yield stress are modified by the GP percentage differently for the two solvents. The mechanical properties of the fiber mats are strongly affected by the presence of the GP resulting in a tailored visco-elasto-plastic response. Such porous structure produced by electrospinning with high ratio between surface area and volume, are ideally useful in applications such as air/water filters, sensors, organic solar cells, smart textiles, biocompatible scaffolds for tissue engineering and load-bearing applications. The future research will be oriented on an extensive comparison study between the graphene powder and the Multi Walled Carbon Nanotubes (MWCNTs) effects on the properties of the electrospun fibers. Moreover, the effects of varying the GP percentage in Poly (acrylonitrile) electrospinning solutions will be analyzed before and after the pyrolysis treatment.

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REFERENCES

[1] Ginestra, P., Ceretti, E., Fiorentino, A. “Electrospinning of poly-caprolactone for scaffold manufacturing: experimental investigation on the process parameters influence.”, Proc. CIRP 49, 8-13, (2016).
[2] Chaoying, W. and Biqion, C., “Poly(ε-caprolactone)/graphene oxide biocomposites: mechanical properties and bioactivity”, Biomed. Mater. 6, 8pp (2011).
[3] Lee C, Wei X, Kysar J W and Hone J Measurement of the elastic properties and intrinsic strength of monolayer graphene Science 321, 385-8 (2008).
[4] Chen, H.Q., Muller, M.B., Gilmore, K.J., Wallace, G.G. and Li, D., “Mechanically strong, electrically conductive, and biocompatible graphene paper”, Adv. Mater. 20, 3557-61 (2008).
[5] Yang, W.R., Ratinac, K.R., Ringer, S.P., Thordarson, P., Gooding, J.J. and Braet, F. “Carbon nanomaterials in biosensors: should you use nanotubes or graphene?”, Angew. Chem. Int. Ed. 49, 2114-38 (2010).
[6] W.S.Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2014.

[7] Croisier, F., O van der Werf, K., Dijkstra, P.J., Bennink, M., "Mechanical testing of electrospun PCL fibers", Acta biomaterialia 8, 218-224 (2012).