Title

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Journal

CIRP Annals, 66(1)

ISSN

0007-8506

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Publication Date

2017

DOI

10.1016/j.cirp.2017.04.122

Peer reviewed

CIRP Annals - Manufacturing Technology 66 (2017) 233–236

Contents lists available at ScienceDirect

CIRP Annals - Manufacturing Technology

journal homepage: http://ees.elsevier.com/cirp/default.asp

Electrospinning and characterization of polymer–graphene powder scaffolds

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ARTICLE INFO

Article history:
Available online 1 May 2017

Keywords:
Polymer
Nano structure
Electrospinning

ABSTRACT

In this paper the morphological, mechanical and electrical characteristics of fibers electrospun from a of poly-ε-caprolactone polymer solution with different percentages of graphene nanoplatelets mixed in are reported. The morphology of the fibers was studied under optical and scanning electron microscopes to investigate the interaction of the two phases within the fibers. The scaffolds were characterized to identify the effects of the graphene on the intrinsic properties of the material. The preparation of an optimized suspension of the graphene in the solution was found to be a fundamental factor for enhancing the applicability of the resulting fibers.

1. Introduction

Electrospinning from synthetic and natural polymers is widely used for the fabrication of porous structures with the aim of obtaining different polymer fiber mat morphologies [1]. Electrospinning of composite inks in general enables the integration of various types of polymers and particles to produce porous materials with wide ranges of resulting properties and length scales [2]. Moreover, electrospinning of nanofibers of mixed polymers and carbon particles enhances the mechanical properties of the resulting fiber mats and offers structural advantages as it constitutes a nonwoven mesh characterized by high surface area/unit mass and a large fraction of interconnected porosity [3]. In particular, graphene is made up of single layers of aromatic carbons and is a very promising candidate for the production of functionalized electrospun fibers due to graphene chemical and physical properties [4–6]. The peculiar surface features of graphene make it easy to suspend and then mix the material in powder form with polymers for the production of electrospinning solutions [7,8]. These composite inks are suitable for producing scaffolds for tissue engineering, sensor substrates or filters [9,10].

In this paper, the authors report on the production of composite nanofibers by electrospinning of solutions containing poly-ε-caprolactone (PCL) dissolved in a suspension of graphene powder. In particular, electrospinning tests were conducted with a solution containing a polymer–graphene mix. The aim was to better understand the role of carbon graphene particles during the electrospinning process itself and the effects of the graphene on the performances of the resulting fiber mats.

A morphology analysis was carried out by investigating the fiber diameter distribution. Moreover, the mechanical properties of each family of electrospun mats were evaluated using tensile tests and the electrical properties were investigated using a micro probe station. Finally, preliminary cell culture tests were conducted on the electrospun structures.

2. Electrospinning process

Three homogeneous solutions of 15 wt% of PCL (molecular weight 80,000 g/mol) in a 1:1 mixture of tetrahydrofuran (THF) and dimethylformamide (DMF) were prepared by stirring the polymer in the solvent for 24 h at room temperature. Subsequently, 0.5, 1 and 2 wt% graphene nanoplatelets were added to the solutions and the mixtures were sonicated for 1 h followed by further stirring.

Electrospinning experiments were carried out with the newly formulated inks and the resulting fibers were characterized to investigate the interaction between the polymer and graphene phases [11]. In particular, the polymer solutions were filled in a 5 ml plastic syringe fitted with a 20-gauge stainless steel needle. Then, electrospinning was carried out by applying a flow rate of 0.5 ml/h to the syringe and 20 kV voltage to the needle. The fibers were collected on a grounded aluminum foil (collector). The distance between the needle tip and the collector was kept at 120 mm and the experiments were performed at ambient conditions of 25 °C and relative humidity of 40%.

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http://dx.doi.org/10.1016/j.cirp.2017.04.122
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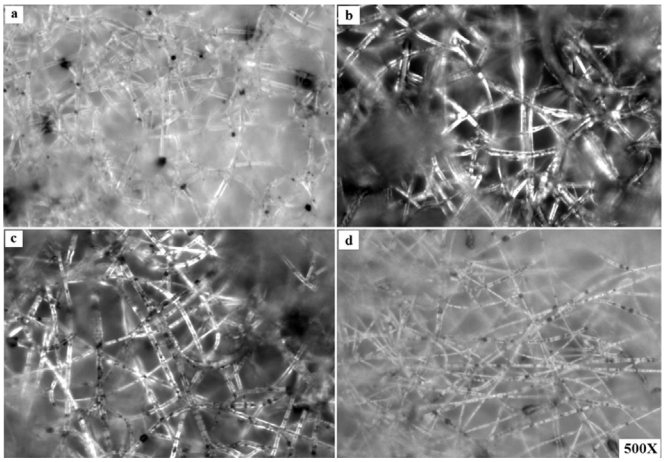

Fig. 1. Optical microscope images (500×). Comparison between preliminary dispersion tests: (a) 0.5 wt% of graphene is added to THF:DMF–PCL solution, (b) PCL is added to the THF:DMF–graphene solution with 0.5 wt% of graphene, (c) 1 wt% of graphene and (d) 2 wt% of graphene.

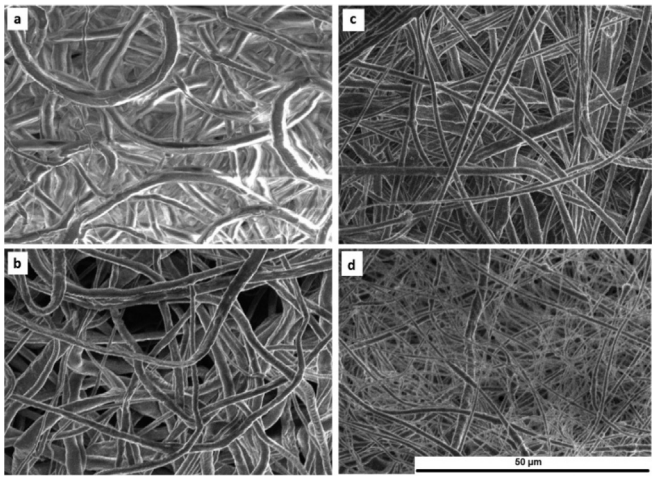

Fig. 2. SEM images (1200×). (a) THF:DMF with 0 wt% graphene, (b) THF:DMF with 0.5 wt% graphene, (c) THF:DMF with 1 wt% graphene (d) THF:DMF with 2 wt% graphene.

The electrospinning tests were carried out for 45 min in the case of the solution with 0.5 wt% of graphene, 30 min with 1 wt% of graphene and only 15 min with 2 wt% of graphene before the uniformity of the fibers started to be compromised. It was observed that the deposition area was strongly influenced by the viscosity of the solution, which in turn depends on the amount of the graphene in the polymer–graphene solution. In particular, the electrospun fibers from the solution with 2 wt% graphene were deposited on a reduced area of the collector forcing a reduction of the electrospinning exposure time.

Fig. 1a shows the preliminary results on the quality of the electrospun mat at 0.5 wt% of graphene. As it can be seen, this particular ink results in solvent droplets containing the graphene platelets particles, randomly dispersed within the network of polymer fibers. To enhance the dispersion of graphene within the solution, another graphene–polymer solution was prepared, this time by adding the graphene powder to THF:DMF solvent first, and then adding the polymer to the mixture. Fig. 1b shows that the resulting 0.5 wt% of graphene fibers have a more uniform distribution of graphene particles, demonstrating a structure in which the polymer fibers are surrounded by a linear distribution of the carbon along the axis of the fibers. The same procedure for the solution preparation was consequently followed for the inks with higher graphene content. In Fig. 1c the fibers electrospun from a solution with 1 wt% of graphene are shown. In this case, the fibers form a lower extent of structures like those observed in the previous case (0.5 wt%, Fig. 1b) where the particles surround the polymer fiber along their axis. This can be due to the fact that a higher concentration of graphene results in a possible saturation of the solution, which in turn results in less dispersion of the graphene particles in the same solution. Indeed, the fibers electrospun from the solution with 2 wt% of graphene, show a presence of graphene clusters (Fig. 1d).

3. Fibers characterization

3.1. Fibers morphology

The fibers that were manufactured using different concentrations of graphene were studied by a scanning electron microscope (SEM) at the magnification of 1200× (Fig. 2) and their diameter was measured using the open source software ImageJ [12,13]. In particular, 60 fibers were measured for each sample and data were analyzed to investigate their statistical distribution and to model the influence of the graphene on their dimensions.

Fig. 3a shows that the graphene content influences both dimension and uniformity of the fibers. In particular, as the graphene content increases, the diameter of the fibers and its scattering decrease. In fact, as graphene enhances the conductivity of the solution, it increases the current involved in the process and, therefore, the acceleration of the ejected solution. As a result, fibers are thinner and more conformed.

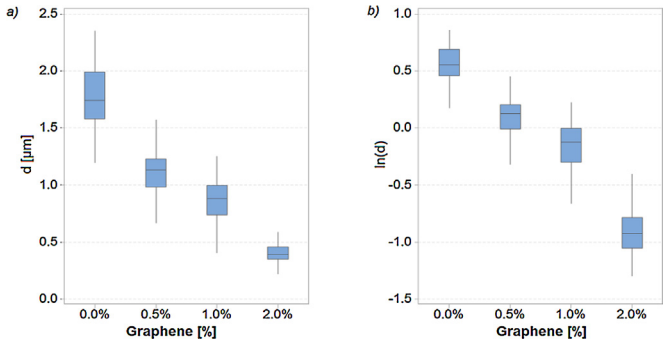

Fig. 3. Influence of the graphene content on the fiber diameter. Box plots of (a) direct measures and (b) logarithmic measures.

To further characterize the influence of the graphene on the process, fibers morphology data were analysed for identifying a statistical model that describes their distribution. In particular, Fig. 3b shows that when the logarithm of the fiber diameter is considered, the data scattering becomes more uniform and independent from the graphene content (p-Value = 0.721). Moreover, Fig. 4 shows that the diameter variability can be represented by a lognormal distribution which becomes more accurate as the

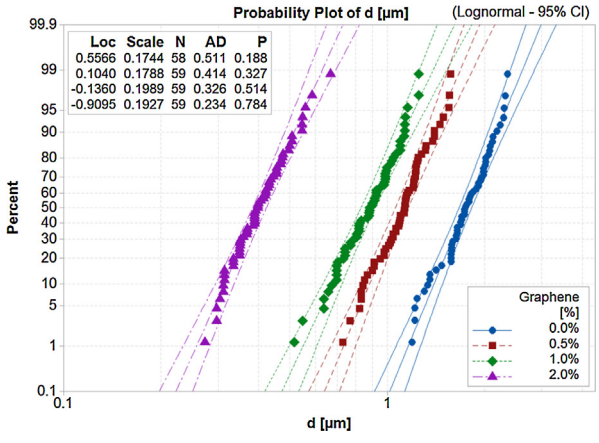

Fig. 4. Probability plots of the fiber diameter distributions using a lognormal distribution.

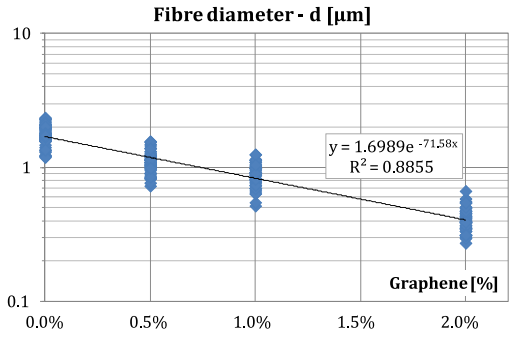

Fig. 5. Influence of the graphene content on the fiber diameter, interpolating line and correlation coefficient (R^2).

graphene content increases (p-Values from 0.188 to 0.784). Accordingly, the influence of the graphene content on the fibers diameter can be represented by an exponential function with a good accuracy (Fig. 5).

3.2. Uniaxial traction tests

The mechanical behavior of the electrospun mats was evaluated with uniaxial tensile tests carried out by applying the dynamic mechanical analyzer DMA Q800 (TA Instruments) at 23 °C. Rectangular fiber mat pieces, with length of 10 mm and a width of 5 mm, were selected from the central part of the electrospun area. The thickness of fiber specimen ranged between 0.2 to 0.4 mm. The tests were carried out with three repetitions for each specimen type. The samples were subjected to a tensile ramp under displacement control at 0.2 mm/min until failure. The stress vs. strain relationship was determined for all the materials up to final breaking point. The elastic modulus was calculated as the slope of the initial linear trend of the stress vs. strain curve. The results are reported in Fig. 6, demonstrating engineering stress vs. engineering strain curve for each material group. The curves are reported considering a maximum level of strain of 200% due to the specific ductile behavior exhibited by the composite material consisting of two or even three linear regimes at high levels of strain after a first broad transition region. For this reason, the material electrospun by a solution containing different percentages of graphene nanosheets can be considered as an elastomer, rubber-like material. Considering the high failure strain values compared with the material with 0 wt% of graphene, the viscoelasticity of the material seems to be strongly affected by the presence of the graphene. The mechanical response was primarily evaluated in terms of stiffness (Young modulus) and stress in correspondence to an elongation of 50%. The interfacial interactions between the graphene and the polymer that are causing the reduction of the fibers diameter are also responsible of

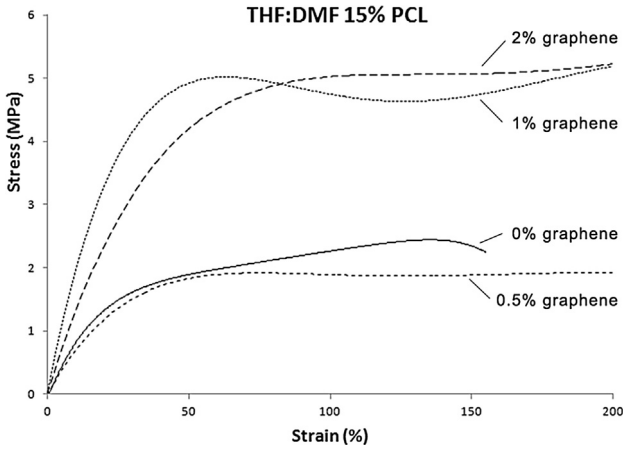

Fig. 6. Tensile engineering stress vs. engineering strain curves for the electrospun PCL with different contents of graphene nanosheets.

the changes in the composite mechanical performances. The parameters evaluated from the curves provide a quantitative description of what was already evident in the graphs: the specimens without graphene are characterized by a stiffness of 9.01 MPa and the stress at 50% of elongation is 1.87 MPa; the samples with a graphene content of 0.5 wt% show a stiffness of 7.33 MPa and the stress value at 50% of elongation is 1.86 MPa. The samples with a graphene percentage of 1 wt% and 2 wt% are characterized by a stiffness of 22.1 MPa and 14.1 MPa respectively, while the stress at 50% of elongation is 4.94 MPa and 4.06 MPa respectively. The increase of the percentage of graphene results in an increasing strength evaluated at an elongation of 50% and the material appears more ductile in terms of the plastic deformations undergoing before reaching the final break. In particular, as shown from the graphs in Fig. 6, the mechanical properties can be improved by the insertion of the graphene nanosheets under a certain percentage ($\leq$1%) to avoid any inversion of the tendency in terms of resistance and stiffness of the system.

3.3. Electrical tests

The samples were measured using a Janis ST 500 cryogenic micromanipulated probe station that can operate in air or in high vacuum ($\sim 10^{-6} \div 10^{-7}$ mbar) as a turbomolecular pumping station Edwards 75 was connected to the probe station chamber. The positioning of the probe tips onto the electrospun networks was controlled using manual micrometric positioners. The voltage across the samples is swept from −10 V to +10 V. Moreover, to evaluate the repeatability of the measurements, the same strip was evaluated three times. The line represents the last-square approximation of $I = G \times V$ where G is the conductance of the strip. The I–V curve was measured in high vacuum and in ambient (RH = 55%) under light conditions.

The current–voltage (I–V) characteristics of the PCL strips at different graphene concentrations are shown in Fig. 7. The calculated resistances are reported in the graphs in both high vacuum and ambient conditions.

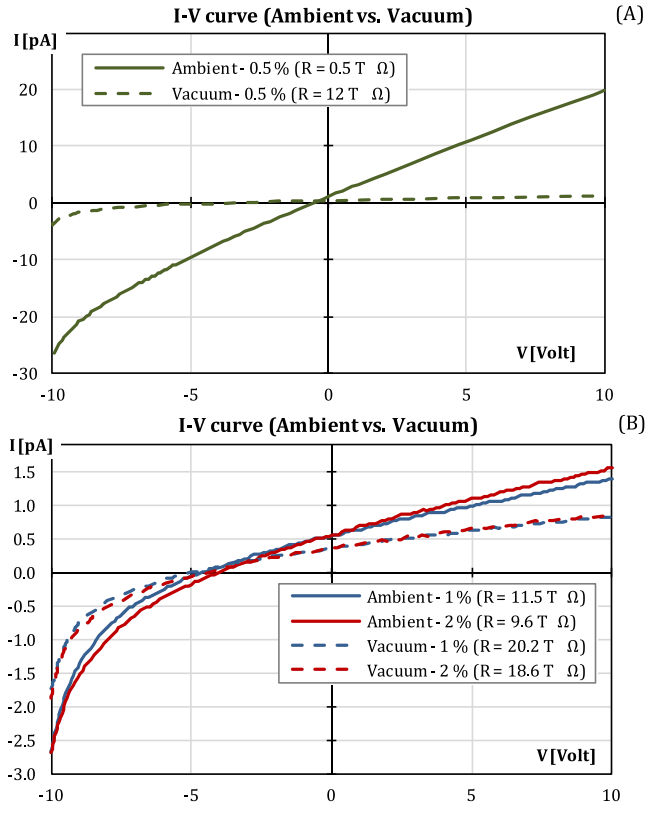

Fig. 7. (A) Voltage vs. current curves for the electrospun PCL with 0.5 wt% of graphene, (B) voltage vs. current curves for the electrospun PCL with 1 wt% and 2 wt % of graphene.

With the presence of nanoparticles, tunneling effects start occurring between neighboring graphene nanoplatelets modifying the electrical resistance (R) of the material. Results show that R raises as graphene increases from 0.5 to 1 wt% and then its variation is negligible in the 1 ÷ 2 wt% range. This can be due to the distribution of graphene: along the fiber axis at 0.5 wt% (Fig. 1b) and in increasing isolated clusters from 1 to 2 wt% (Fig. 1c and d).

Tests conducted in vacuum condition allowed to study the effects of the humidity. In particular, the humidity decreases the resistance of a factor 20 in the case of 0.5 wt% of graphene and of a factor 2 at 1 wt% and 2 wt%.

Therefore, the variation of the resistance is less significant when the graphene content is increased, revealing a threshold in the conductivity of the composite material as a function of the graphene percentage.

3.4. Biological tests

Neural stem cells (NSC) were seeded onto the polymer fibrous structures produced by the electrospinning of solutions containing pure PCL or PCL with the graphene nanosheets. The resulting networks supported cell adhesion and proliferation, being highly biocompatible. The NSC were maintained in proliferation medium for two days before adding the differentiation medium. The cells were stained after 5 days with tyrosine hydroxylase, an enzyme usually found in dopamine producing neurons. Without the graphene (Fig. 8a), the electrospun fibers were able to promote the cell differentiation into neurons but not into dopaminergic neurons. On the contrary, the electrospun structures with a graphene content of 1 wt% were able to promote the differentiation of the cells into dopaminergic neurons as reported in Fig. 8b.

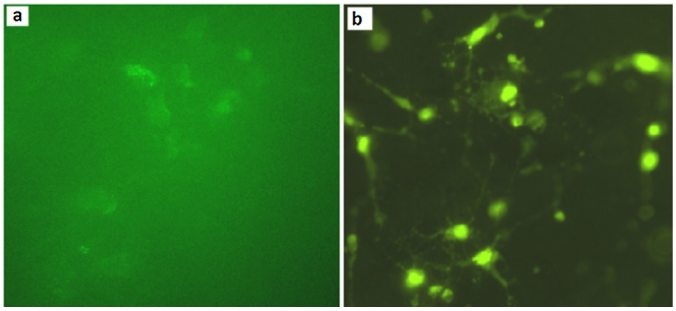

Fig. 8. Fluorescent microscope images (20×) of the stem cells differentiated in dopaminergic neurons onto (a) pure PCL and (b) PCL with a graphene content of 1 wt%.

4. Conclusion and future trends

This paper reports the morphological, mechanical and electrical characteristics of fibers electrospun from a polymer solution with different percentages of graphene platelets mixed in.

The preparation of an optimized suspension of graphene in the polymer solution was found to be the key for enhancing the applicability and quality of resulting electrospun fibers. In fact, it was shown that a good dispersion of the carbon particles leads to an ink solution for the electrospinning processes that produces well-distributed graphene within the polymer fibers.

It was also found that both the deposition area and the electrospinning time are significantly affected by the increase of the graphene content. In particular, as viscosity and conductivity of the solution are increased by the graphene content, the electrospinning process becomes more difficult and the fibers are more stretched by the electrical field, resulting in a significant reduction of the fibers diameter and scattering.

The results of tensile tests demonstrate that the mechanical behavior of the fibers (in terms of stiffness, strength, and ductility), can be strongly affected by varying the graphene content. Therefore, the mechanical performances of the composite fibers can be tailored according to the specific final application. In particular, the substrates can be used as implantable scaffolds according to the mechanical requirements of different anatomical districts.

The results of the electrical characterization show that the conductivity depends on the graphene percentage. In particular, an increase of the graphene content causes an increase of the resistance of the material probably due to a worse dispersion of the nanoparticles within the solution. Moreover, the conductivity of the composite material is function of the relative humidity and this dependence is affected by the graphene content. This latter aspect, make these mats suitable for sensoring applications.

From the biological point of view, although only preliminary cell culture tests were conducted, the results on the guided differentiation of neural stem cells are encouraging. In particular, the polymer fibers with the graphene nanoplatelets resulted in a better substrate to guide the differentiation of the stem cells in a specified phenotype in comparison to the polymer fibers.

The achieved results on fiber dimensions, mechanical, electrical and biological properties indicate that it is possible to tailor these devices according to the specific requirements. Accordingly, future research will be focused on the study of electrospun structures made of PCL–graphene nanosheets for application in sensoring and tissue engineering areas.

Acknowledgments

The authors would like to acknowledge the support and the assistance of Sunny Holmberg and Alexandra Perebikovsky at University of California, Irvine, and Prof. Fabrizio Torricelli of the University of Brescia.

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