POLY(ε-CAPROLACTONE) REINFORCED WITH MWCNTS AND GNPS LOADED ALIGNED ELECTROSPUN PMMA FIBRES

F.R. Lamastra[1*], D. Puglia[2], F. Madau[3], M. Monti[2], L. Peponi[4], M. Valentini[b], J.M. Kenny[2], F. Nanni[1,3*]

[1]*Italian Interuniveristy Consortium on Materials Science and Technology (INSTM),Research Unit Roma Tor Vergata, Via del Politecnico 1,00133 Rome (Italy)*
[2]*University of Perugia, Civil and Environmental Engineering Department, strada Pentima Bassa 4, 05100 Terni (Italy)*
[3] *University of Rome "Tor Vergata" Department of Industrial Engineering, Via del Politecnico 1,00133 Rome (Italy)*
[4] *Institute of Polymer Science and Technology, CSIC, Juan de la Cierva 3, 28006 Madrid (Spain)*
**fnanni@ing.uniroma2.it*

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Abstract
PCL matrix composites, reinforced by means of either PMMA, MWCNTs loaded-PMMA or GNPs loaded-PMMA aligned electrospun fibre mats, were manufactured and tested. Nanofiller dispersion in PMMA was achieved by means of sonication or centrifugation and it was checked by means of SEM analysis and Raman spectroscopy. The results show that the addition of PMMA fibres result in a clear increase of yield strength with respect to that of neat PCL, while the addition of the nanofillers in the fibres brings only a slight further increase of the mechanical properties, with the best results obtained for samples prepared starting from GNPs dispersed by centrifugation.

1 Introduction

Electrospinning is an extremely flexible, low cost and easily industrial exploiting process to manufacture continuous, randomly oriented or aligned fibres from a large range of materials [1,2]. The morphology and dimensions of electrospun fibres depend on a variety of parameters as spinning solution properties (i.e. viscosity, surface tension, conductivity), processing (i.e. needle-target distance, flow rate, applied voltage) and environmental conditions (i.e. humidity, type of atmosphere). Such fibres gained attention as reinforcing elements [3,4,5,6], since their very high surface to volume ratio can significantly promote the interaction with the matrix, with evident beneficial effect in terms of strengthening with respect to conventional fibres [7]. On the other hand, the mechanical properties of electrospun fibres and mats can be increased in by adding inorganic nanofillers within the fibres, as in the case of CNTs [8], TiO2 [9], SiO2 [10], montmorillonite [11], to cite a few.
In this paper electropsun aligned PMMA fibres either neat or loaded with MWCNT or graphene, were used as reinforcement of PCL matrix. The aim was to evaluate the effect of two different nanofillers (i.e. MWCNTs and GNPs) on the mechanical properties of the resulting composites. Such composites were produced by mans of film stacking technique, alternating electrospun fiber mats ad solvent cast PCL films. PMMA was chosen for fiber manufacturing due to its relevant mechanical properties, that were expected to reinforce those

of neat PCL. Two different carbonaceous nanofillers were used and compared, one of which, the GNPs, was chosen to its very interesting mechanical properties (the tensile modulus and strength of respectively 1100 GPa and 125 GPa [12]) and microstructure, where the sheet-like structure is expected to provide a very high surface area for good stacking with the polymer matrix [13], differently from MWCNTs where the inner nanotube surfaces are inaccessible to polymer chains [14]. GNPs is interesting in view of large scale applications, since high purity GNPs can be obtained from the abundant resource of natural graphite by means of low costs processes, if compared to other graphitic carbon nanofillers (i.e. carbon nanotubes and carbon nanofibers) the production of which usually involves expensive and complicated apparatus.

2 Materials and testing methods

PCL matrix composites reinforced with either neat or MWCNTs or GNPs loaded aligned electrospun PMMA fibre mats was made by film stacking technique. Initially PCL films were produced by solvent casting, i.e. dissolving the polymeric granules (PCL, MW= 70000-90000, Aldrich) in chloroform (6% g/ml) under stirring for 2 hours and then casting the resulting solution on a *petri* dish. The solution was air dried for 24 h at RT and the films kept in vacuum for 24 h. MWCNTs and GNPs loaded aligned PMMA fibres were produced *via* electrospinning The production involved several steps. Firstly, the nanofillers were dispersed in N,N-Dimethylformamide (DMF) (1.5 mg/ml) by means of tip sonication, with the Vibra Cell Sonics tip sonicator, mod. VC 750 (USA), for 60 minutes at room temperature. For this process, the suspension was put in a glass beaker, which was placed in a thermal bath, in order to prevent the heating of the mixture, causing the solvent evaporation. GNPs were also dispersed by centrifugation (30 minutes at 3000 rpm, labelled GNPs-c) and the effect of these two process variants (i.e. sonication and centrifugation) on the mechanical properties of the final composites was investigated. Then, PMMA granules (M_W 350000, Aldrich) (15% w/v) were dissolved in the previous prepared suspensions at RT at room temperature for 24 h. The PMMA: nanofiller weight ratio was 99:1. The mixtures were sonicated for 30 min and then electrospun in air in the following conditions: tension 12 kV, needle-target distance 15 cm, feed rate 0.5 ml/h. A grounded aluminium cylindrical target (diameter 6 cm), rotating at 2700 rpm was used to collect aligned electrospun mats. For comparison also neat PMMA solution (15% w/v) was electrospun in the same conditions. Table 1 reassumes the electrospun mats

Sample	**Type of Nanofiller (1%wt in fibres)**	**Dispersion**
PCL-PMMA	-	-
PCL/MWCNTs_PMMA	MWCNT	sonication
PCL/GNPs_PMMA	GNP	sonication
PCL/GNPc_PMMA	GNP	centrifugation

Table 1. Sample nomenclature reporting the method of nanofiller dispersion in the PMMA solution to electrospun.

PCL films and fibre mats were inserted in a Teflon mould (65x20x3 mm^3) alternating stacking 5 PCL layers and 4 reinforcement layers (PMMA or MWCNTs loaded-PMMA or GNPs loaded-PMMA or GNPs-c loaded-PMMA fibres), orientated in the main axis, to obtain an unidirectional composite. The mould, covered with a counter-mould, was then placed under pressure in an oven for 30 min at 90 °C, to insure PCL melting and flow among the fibres. Neat PCL was prepared as reference sample. Fibre volume fraction, estimated by weight of PCL films and fibre mats and the respective densities was about 7.5% in all composites.

2.4 Characterisation

A morphological characterisation of the nanofiller dispersion was carried out by transmission electron microscopy (FEG-SEM, *Leo Supra 35*) on gold sputtered samples and Raman spectroscopy (spectra were recorded at room temperature after the exposure time of 10 s using a Reflex Raman System Renishaw plc, Wotton-under-Edge, UK, employing a laser wavelength of 514.5 nm, laser power at sample = 10 mW; microscope objective = 100x). The mechanical characterisation of the composites was carried out by means of constant strain rate tensile testing (1.2 mm/min, following ASTM-D1708 standard), using a tensile machine (Lloyd RLX) equipped with 100 N load cell.

3 Results and methods

Figure 1 shows Raman spectra of the graphene nanoplatelets after the sonication process in DMF and the centrifuge, and the graphene nanoplatelets as supplied by the manufacturer. The spectra (focusing the attention on the 2D peak, that are very sensible to the number of graphene layers in a flake),revealed that supplied GNPs are characterized by more than ten layers , however after sonication GNP flakes are reduced to a stacking of few layers of graphene. The appearance of the second-order zone boundary phonon (2D) peak at ~2430 cm^{-1} together with a shoulder peak at ~2940 cm^{-1}, observed for sonicated samples, confirms the layering [15]. The D peak intensity is not related to the number of graphene layers, but only to the amount of disorder and it can be activated at the edges [15]: as a result, it is usually higher for graphene flakes with a smaller surface. Therefore, since the amplitude of D peak is lower for sonicated GNPs, we can say that the sonication process in DMF significantly reduce the surface of the graphene layers.

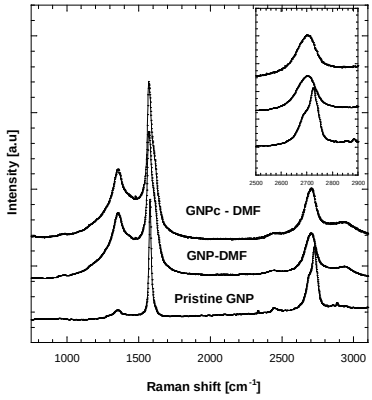

Figure 1. Raman spectra of pristine GNPs, GNPs in DMF and GNPc (centrifuged)

SEM observation of the electrospun mats revealed that they are characterized by uniform, aligned and defect-free fibres (Figure 2a) with an average diameter of 1.7 ± 0.5 μm, 1.3 ± 0.3μm and 1.0 ± 0.2 μm for neat PMMA, GNPs loaded-PMMA and MWCNTs loaded-PMMA, respectively. The results of the monotonic tensile tests (Figure 3) showed an outstanding effect of the insertion of PMMA fibres in PCL matrix on yield stress and stiffness. The addition of the nanofillers within the fibres brought to a further improvement of the yield stress despite the very low content used (1 wt% in the composite fibres, thus 0.07 wt% in the final PCL/nanofiller loaded PMMA composites). The best results were obtained for PCL/GNPs-PMMA sample, indicated that the nanofiller in the fibers produced starting from centrifugated solutions are better dispersed than those prepared via sonication (Figure 2b,c,and d). In these latter samples, though, the MWCNTs seem to provide a more efficient reinforcement than GNPs in increasing the yield stress. In any cases, when sonication is

involved, harmful aggregates (either of GNPs or MWCNTs) within the PMMA fibers were found (Figures 2b and c), that were considered responsible for the reduced reinforcing effect of the nanofillers.

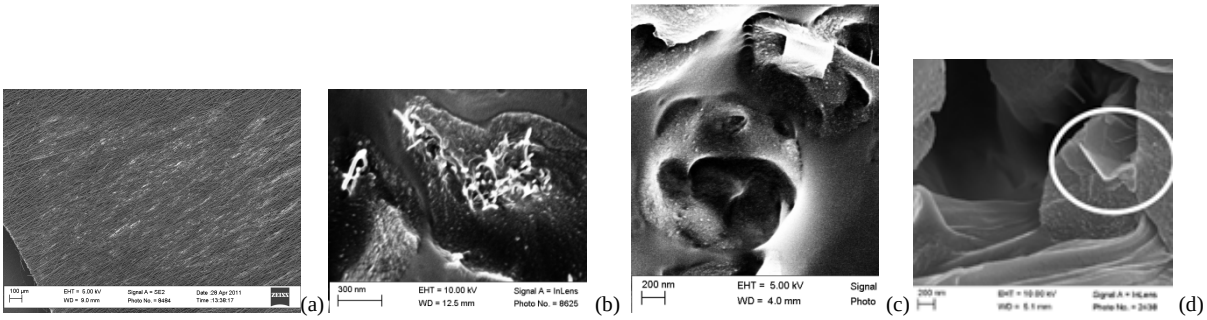

Figure 2 SEM micrographs of a) electrospun mat, b) MWCNTs and c) GNPs agglomerate into PMMA fiber, both dispersed by sonication and c) well exfoliated GNPs obtained via centrifugation at the border of a PMMA fiber

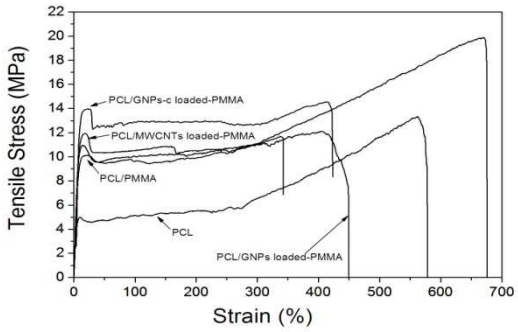

Figure 3 Typical stress-strain curves of samples manufactured by means of film stacking technique

3 Conclusion

Aligned PMMA, MWCNTs loaded-PMMA and GNPs loaded-PMMA electrospun fibre mats were obtained and used as reinforcement of PCL matrix. The composites were made by film-stacking technique. All types of electrospun mats were uniform, good aligned and constituted by defect-free fibres. Raman spectroscopy revealed that GNPs dispersed by centrifugation are well dispersed and SEM micrographs showed that they are distributed through the overall polymeric mat. GNPs and MWCNTs aggregates, starting from sonicated nanofiller dispersions, were found inside the polymeric fibres. All composites showed enhanced mechanical properties (Young's modulus and yield stress) with respect to neat PCL confirming the formation of a strong interface necessary for an efficient load transfer from the matrix to the reinforcement. The effect of PMMA fibres insertion in the PCL matrix was noteworthy, less marked was the improvement induced by the addition of the nanofillers within the polymeric fibres.

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