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Synthesis and characterization of poly(ε-caprolactone) reinforced with aligned hybrid electrospun PMMA/nano-Al_2O_3 fibre mats by film stacking

F. Nanni · F. R. Lamastra · F. Pisa · G. Gusmano

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Abstract PMMA and PMMA/10 wt% nano-Al_2O_3 fibre mats were produced by means of electrospinning and used as reinforcing phase of poly(ε-caprolactone) matrix. The composite films were fabricated by means of film-stacking technique. SEM observations showed good wettability of PMMA-based fibres by the PCL matrix, confirming that a strong interface was formed. The Al_2O_3 nanoparticles were well-distributed along the polymeric fibres. The introduction of PMMA fibres as a reinforcement led to a clear benefit in terms of the mechanical strength (11.5 ± 0.5 MPa), the value for neat PCL being 8.2 ± 2.2 MPa. The tensile strength was further increased when the fibres were loaded with nano-Al_2O_3 (14.4 ± 0.6 MPa) due to both the presence of the ceramic filler and the smaller diameter of the composite fibres. A less marked improvement was instead found on stiffness.

Introduction

Poly(ε-caprolactone) (PCL) is a semicrystalline bioresorbable polymer that is continuously increasing its importance in view of many engineering applications. Particularly PCL is applied in controlled drug-delivery systems, medical devices as sutures, wound dressings, and contraceptive devices [1–3]. Moreover, it is attractive for use in degradable packaging [4]. PCL though suffers from scarce mechanical properties that somehow limit its application. To overcome such drawback the realization of PCL reinforced with polymethylmethacrylate (PMMA) submicrometer fibres is proposed in this article. PMMA was chosen due to its relevant mechanical properties (Young's modulus 3300 MPa and tensile strength 80–90 MPa [5]), that were expected to reinforce those of neat PCL, and to its melting point ($\geq$160 °C) that is far higher than that of PCL ($\sim$60 °C), which entails significant advantages in terms of composite processing (as in film-stacking technique, which will be proposed in the following) and recycling. Moreover PMMA was widely used in various biomedical applications as bone cement for orthopedic and dental use, contact and intraocular lens, filler for different bone cavities thus it doesn't compromise the biocompatibility but limits the PCL applications based on its biodegradable character such as controlled release of drugs and slowly degrading suture materials [6]. The PMMA fibres were produced by means of electrospinning in form of a uniformly aligned mat, to produce an unidirectional composite. Electrospinning is an extremely flexible, low cost, and easily industrial exploiting process to fabricate continuous, randomly oriented or uniaxially aligned sub-micron fibres and nanofibres, from a huge range of materials [7, 8]. Moreover electrospun fibres have much thinner diameters than those fabricated using more conventional mechanical extrusion or spinning processes, and thus present higher surface to volume ratio, that may significantly increase the interaction with the matrix, leading to an increased efficiency in strengthening with respect to conventional fibres [9]. Despite this undoubted benefit, up to now only few attempts were made to fabricate nanocomposites using electrospun fibres as reinforcing element [10]. Kim and Reneker [11] found that the

F. Nanni · F. Pisa · G. Gusmano
Department of Chemical Science and Technology, University of Rome "Tor Vergata", Via della Ricerca Scientifica, 00133 Rome, Italy

F. Nanni (✉) · F. R. Lamastra · G. Gusmano
Italian Interuniversity Consortium on Materials Science and Technology (INSTM), Research Unit Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy
e-mail: fnanni@ing.uniroma2.it

mechanical properties of a rubber film reinforced with electrospun poly(benzimidazole) nanofibres was enhanced, i.e. the Young's modulus measured for the composite was an order of magnitude greater than that for the unfilled rubber. Vancso and co-worker [12] showed that both stiffness and mechanical strength of an epoxy resin were significantly improved by using electrospun Nylon nanofibres as filler. More recently several research groups have investigated the effect of incorporation of a nanoscale filler (as CNTs [13], TiO_2 [14], SiO_2 [15], montmorillonite [16], β-tricalcium phosphate [17], nanohydroxyapatite [18], Al_2O_3 and ZrO_2 [19], to cite a few), into electrospun polymer fibres to enhance their mechanical properties, but without using such nanofiller loaded electrospun fibres as reinforcement of a matrix. To plug this gap, in this research, hybrid nano-Al_2O_3-PMMA aligned electrospun fibres, consisting of sub-micrometer PMMA fibres loaded with alumina nanoparticles, were produced and used as PCL reinforcement, to obtain a further increase of the PCL/PMMA composite resistance. As for PMMA, Al_2O_3 doesn't compromise the biocompatibility of the realized composite being a bioinert material utilized in numerous biomedical devices such as bone prostheses, dental implants, and artificial eye sockets but limits the applications based on biodegradability of PCL [20]. The results evidenced that the introduction of PMMA fibres as a reinforcement brought to a clear benefit in terms of the maximum composite strength that was even increased when nano-alumina is further added. A less marked improvement was instead found on stiffness. The measured mechanical properties were also compared with those predicted by the law of mixtures.

Materials and methods

The PCL/electrospun PMMA composites were realized by means of film stacking technique [21]. Electrospun PMMA aligned fibres are in fact in the form of a dense mat that is difficulty wet by a highly viscous liquid, as it is the melt thermoplastic PCL. However, it is well-known that, in order to get an efficient composite, it is absolutely necessary that the melt polymer gets in intimate contact with each part of the reinforcement, so to ensure the creation of a strong interface and the correct load transfer from the matrix to the reinforcement. It was therefore early clear that it was not possible to successfully produce the composite starting from melt PCL due to its high viscosity and therefore it was decided to prepare the PCL/PMMA composite by means of film-stacking. PCL films were therefore produced by means of solvent casting technique and successively alternatively stacked together with the PMMA fibre mats to form a laminate. The overall production procedure of the PMMA reinforced PCL followed these steps: 1. Neat or alumina loaded PMMA fibre mat production via electrospinning, 2. PCL film production via solvent casting and 3. Composite manufacturing by film stacking.

Preparation of PMMA and nano-Al_2O_3-PMMA fibres via electrospinning

Up to now neat PMMA was electrospun from solutions in various solvents, i.e. acetone [22] and DMF [23, 24].

In this study PMMA solution (19 wt%) was prepared dissolving the polymeric powder (PMMA, M_W 350000, Aldrich) in DMF under stirring for 24 h. Al_2O_3 nanoparticles (<50 nm particle size, Aldrich) were dispersed in DMF by sonication for 1 h, being the powder: solvent ratio 5% g/mL. The content of the ceramic powder was 10 wt% with respect to the amount of the electrospun composite fibres. The resulting suspension was stirred for 24 h and added to PMMA solution previously prepared. The mixture was sonicated for 1 h and then poured in a glass syringe (Hamilton, Carlo Erba) equipped with a 22 G needle, fixed in a digitally controlled syringe pump (KD Scientific, MA, USA). The needle was connected to a high-voltage supply (Spellman, Model SL 30, NY, USA) able to generate DC voltages up to 30 kV. A grounded aluminium cylindrical target (diameter 6 cm), rotating at 2,700 rpm was used to collect electrospun mats. The processing parameters adopted were: tension 12 kV, needle-target distance 15 cm, feed rate 0.5 mL/h. The PMMA solution was electrospun in the same conditions.

Production of PCL films

PCL was therefore produced in form of film by solvent casting, i.e. dissolving the polymeric granules (PCL, $M_W = 60000$, Aldrich) in chloroform (6% g/mL) under stirring for 2 h and then casting the resulting solution on a glass petri dish. The solution was air dried for 24 h at RT and the obtained film was kept for further 24 h in vacuum in order to eliminate residual solvent.

Production of composites

As previously mentioned, in order to ensure good matrix/fibre wettability and adhesion, both PCL/PMMA and PCL/nano-Al_2O_3-PMMA composites were manufactured by means of film stacking technique. PCL films and fibre mats were cut in order to fill a rectangular Teflon mould ($65 \times 20 \times 3$ mm^3). Then one layer of matrix film and one layer of fibre mat (PMMA or nano-Al_2O_3-PMMA) were alternatively stacked in the mould, keeping the aligned reinforcement longitudinal to the mould major axis, to obtain an unidirectional composite (Fig. 1). A sequence of six polymer and five reinforcing layers was prepared. A

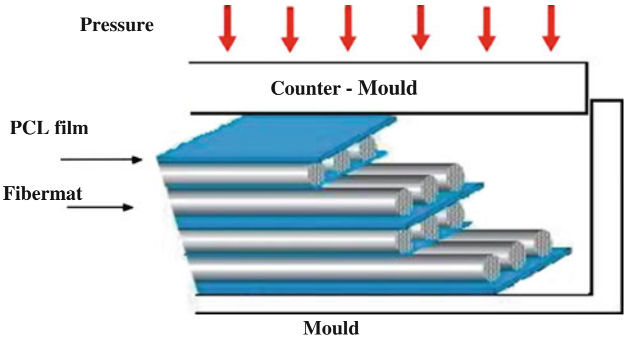

Fig. 1 Film stacking technique

counter-mould was then forced to the system that was kept in oven for 15 min at 70 °C in order to insure polymer melting and flow among the fibres and correct fibre wettability. Fibre volume fraction, estimated by the weights of PCL films and PMMA or nano-Al_2O_3-PMMA mats and the respective densities (1.145 g/cm^3 for PCL and 1.17 g/cm^3 for PMMA), for both types of composites was 7%. As reference sample, neat PCL was prepared, following the same manufacturing procedure of composites (i.e. stacking and melting 11 layers of PLC film in a mould).

Table 1 reassumes all samples realized and their nomenclature.

Characterisation

Morphology of fibre mats and composites was examined by Field Emission-Scanning Electron Microscopy (FEG-SEM, Leo Supra 35) on gold sputtered samples. In the case of fibre mats the average fibre diameter was evaluated using a CAD software (average on ~100 fibres selection).

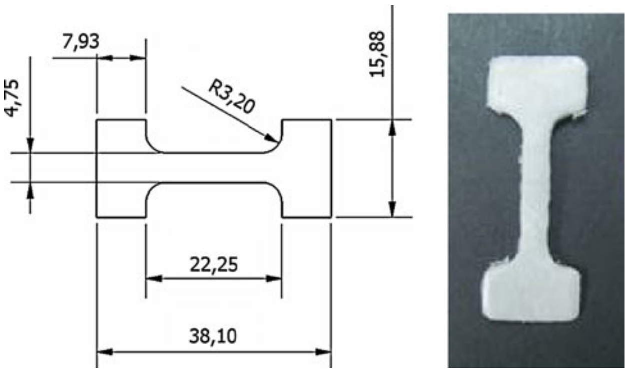

Fig. 2 Composite micro-tensile test specimen. Dimensions (mm) according to ASTM D-1708

A small part (~40 mg) of nano-Al_2O_3-PMMA fibre mat (~2.5 g) was analysed by simultaneous TG-DTA analysis (Netzsch STA 409) to check the homogeneity of the composition in terms of nanoparticle content. Measurement was performed in the following conditions: air flow 80 cm^3/min, peak temperature 800 °C, heating rate 5 °C/min. Melting temperature (T_m) and melting enthalpy (ΔH_m) of F1, Com-F1/Mat1, and Com-F1/Mat2 samples, were determined by differential scanning calorimetry (DSC) (Mettler Toledo 822e, temperature scanning in the range −60/80 °C, heating rate 20 °C/Min, N_2 flow. The degree of crystallinity (χ%) of the samples was estimated as follows:

$$\chi(\%) = \frac{\Delta H_m}{\Delta H_m^0(1-m)} \times 100 \tag{1}$$

where $(1-m)$ is the nominal weight fraction of PCL and $\Delta H_m^0 = 136$ (J/g) for 100% crystalline PCL [25].

Mechanical characterisation of the composites was carried out by means of monotonic tensile testing following ASTM-D1708 standard. Samples, whose dimensions are quoted in Fig. 2, were tested at 1.2 mm/min using a tensile machine (Lloyd RLX) equipped with 100 N load cell.

Results and discussion

Electrospun mats and composites microstructure

SEM micrograph of electrospun PMMA mat show the presence of aligned and defect-free fibres with a smooth surface and an average diameter of 990 ± 200 nm

Table 1 Summary and nomenclature of all prepared samples

Nomenclature	Matrix	Reinforcement	Nano-Al_2O_3
Film			
F1	PCL 11 layers	–	–
Electrospun aligned fibre mat			
Mat1	–	PMMA fibres	
Mat2	–	PMMA fibres	10 wt%
Composite			
Com-F1/Mat1	PCL 6 layers	Aligned electrospun PMMA mat 5 layers	–
Com-F1/Mat2	PCL 6 layers	Aligned electrospun PMMA mat 5 layers	10 wt% in PMMA

(Fig. 3a, b). The degree of alignment was estimated by means of image analysis technique in about 75% that, even though it is not fully satisfactory, still is a good value for production of quasi-unidirectional composites. Addition of nano-alumina resulted again in the production of regular, smooth surface fibres with an average diameter of 389 ± 65 nm (Fig. 3c, e) quite smaller than that of neat PMMA fibres.

The results of thermal analysis performed on 40 mg of Mat 2 are reported in Fig. 4. A weight loss of 89%, attributed to polymer removal, was observed in the temperature range 250–400 °C, showing a rather good homogeneity in composition. Moreover, higher SEM magnifications (Fig. 3e) evidence that the ceramic nanofiller is well-dispersed and distributed along each fibre. SEM observations carried out on fractured composite samples Com-F1/Mat1 and Com-F1/Mat2 revealed that pressure, time and temperature employed in composite manufacturing allowed the complete penetration of PCL melt through the porous reinforcement mats, even in the case of Mat2, where the inter-fibres voids were more numerous and narrower (Fig. 3c, d). In both cases, the final morphology results in a porous-free PCL bulk reinforced by neat or alumina loaded PMMA fibres (Fig. 5). The interesting point is that the degree of fibre alignment found in the electrospun mats is substantially kept during composite manufacturing, meaning that the flow of the viscous melt PCL during fibres impregnation did not change and deform their initial network, so that the resulting composites can be considered almost unidirectional (Fig. 5). The good impregnation of the PMMA-based fibres translates into a strong interface, as testified by the fact that debonded fibres are covered with PCL matrix (Fig. 5b, d).

Mechanical and DSC results

Monotonic tensile tests (results showed in Table 2 and Fig. 6), carried out following the previously reported procedure, evidence an outstanding effect of the insertion of PMMA fibres in PCL matrix on tensile strength that increased of about 40% with respect to neat PCL. Stiffness

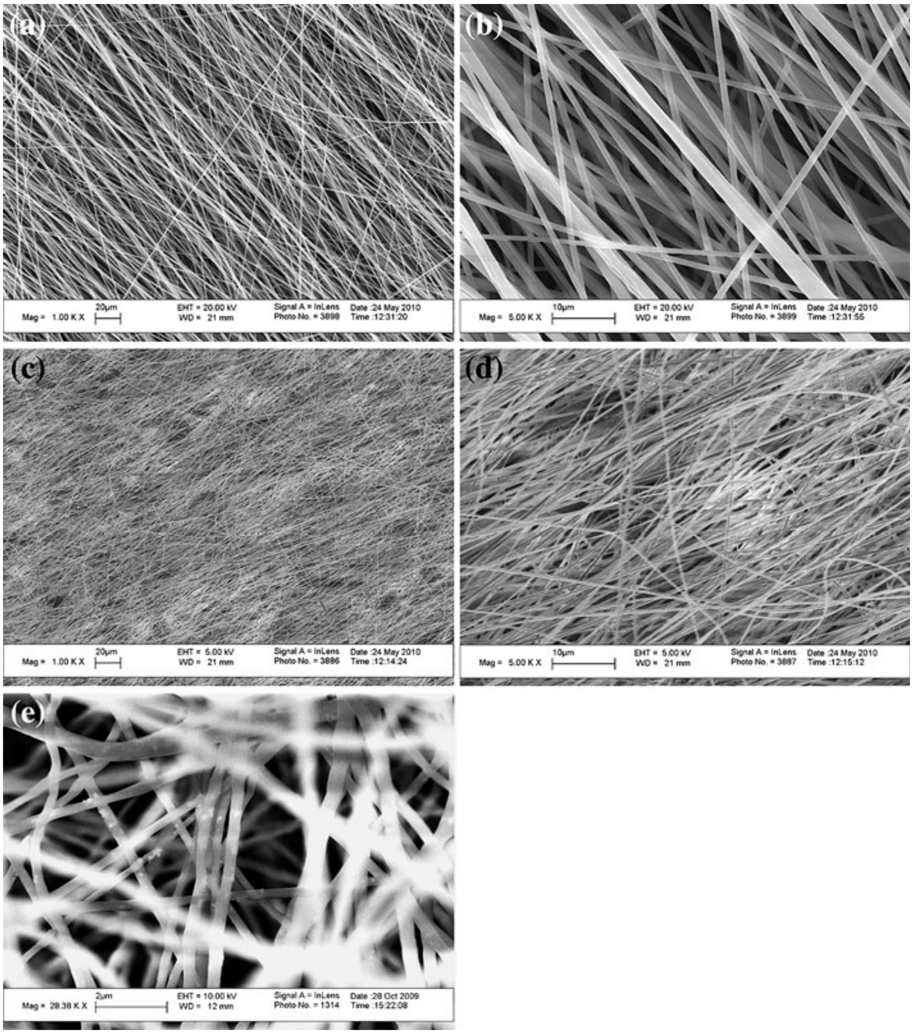

Fig. 3 SEM micrographs of electrospun mats (**a**, **b**) Mat 1 (**c**–**e**) Mat 2

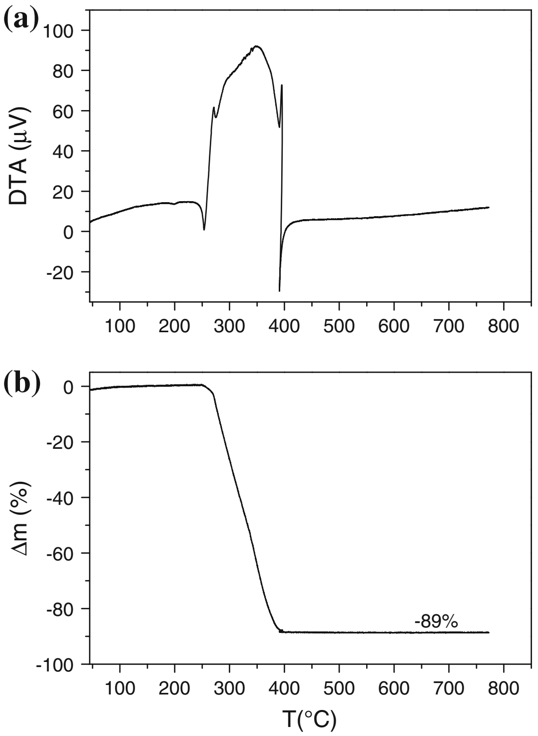

Fig. 4 DTA (**a**) and TG (**b**) curves of Mat 2

too was enhanced, with modulus E changing from 267 to 372 MPa. The addition of Al_2O_3 nanoparticles within the PMMA fibres brought to a further clear increase of tensile strength, but only a slight change of stiffness. To explain such result in the following the main features affecting the mechanical performance of the proposed composites as: fibre-matrix adhesion, degree of fibre alignment, fibre aspect ratio (l/d) and PCL crystallinity, will be shortly discussed.

Fibre-matrix adhesion and degree of alignment of the reinforcement both these features give a very important contribution to the final composite performance. The influence of the efficiency of the adhesion between the electrospun mat and the polymeric matrix as well as that of the degree of orientation of the fibres in the realized Com-F1/Mat1 composite, was indirectly estimated by means of the reinforcement efficiency factors (K_S, K_E). The former, the strength efficiency factor (K_S), was calculated from Eq. 2 [21]:

$$\sigma_c = (1 - V_f)\sigma_m + V_f K_S \sigma_f \tag{2}$$

where V_f (= 0.07) is the volume fraction of fibres; σ_c, σ_m and σ_f are the tensile strength of composite, matrix and reinforcement, respectively, taken equal to $\sigma_c = 11.5$ (measured value) MPa, $\sigma_m = 8.2$ (measured value) and $\sigma_f = 85$ MPa according to [5].

The modulus efficiency factor (K_E) that is related to the orientation of the fibres in the matrix, was instead estimated by means of Eq. 3 [21]:

$$E_c = (1 - V_f)E_m + V_f K_E E_f \tag{3}$$

with $E_c = 372$ (measured value), $E_m = 267$ MPa (measured value) and $E_f = 3300$ MPa (assumed for PMMA fibres according to [5]). The values obtained for K_S and K_E are reported in Table 2. Both K_S and K_E are dependent on several factors such as the aspect ratio (l/d), orientation

Fig. 5 SEM micrographs of fracture surface of (**a**, **b**) Com-F1/Mat1 and (**c**, **d**) Com-F1/Mat2

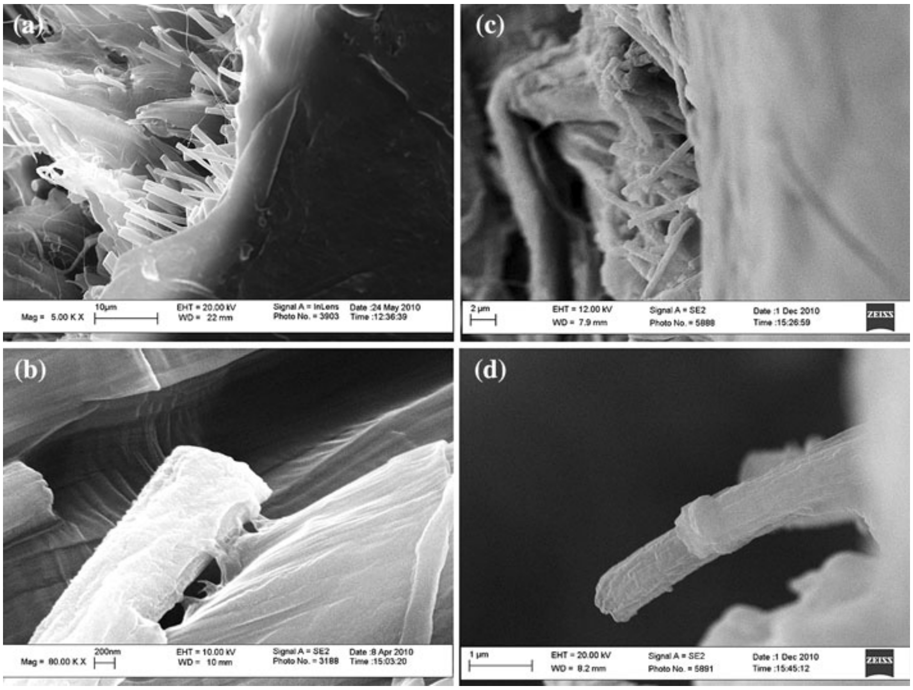

Table 2 Thermal and mechanical properties

Samples	T_m (°C)	ΔH_m (J/g)	χ (%)	Young's modulus (MPa)	Tensile strength (MPa)	Strain to break (%)	K_S	K_E
F1	65.07 ± 0.10	88.4 ± 0.5	65 ± 0.4	267 ± 44	8.2 ± 2.2	7.9 ± 0.9	–	–
Com-F1/Mat1	64.40 ± 0.08	77.6 ± 0.3	61 ± 0.3	372 ± 18	11.5 ± 0.5	6.3 ± 0.6	0.6511	0.5354
Com-F1/Mat2	62.06 ± 0.12	72.5 ± 0.5	57 ± 0.06	392 ± 11	14.4 ± 0.6	6.7 ± 0.9	–	–

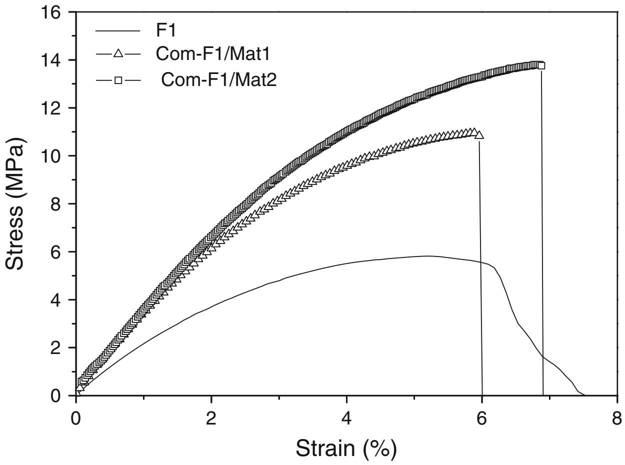

Fig. 6 Typical stress–strain curves of samples manufactured by means of film stacking technique

relative to loading direction, degree of adhesion between the fibres and the polymeric matrix, the concentration of the voids in the sample, etc. [26–29]. Among the cited factors, that most influencing the mechanical performance of the manufactured PCL-PMMA composite is the degree of adhesion, since SEM observations reported the almost complete absence of porosity and the system is composed of long fibres well wetted by the PCL matrix. Moreover, it is well-known [21] that the strength efficiency factor (K_S), can be mainly referred to both fibres orientation and effectiveness of load transfer between the fibres and the matrix, while the modulus efficiency factor (K_E) is only affected by fibres orientation within the matrix. Since K_S was found to be higher than K_E, it could be presumed that fibre/matrix adhesion is satisfactory, while a certain degree of fibre misalignment is present. Unfortunately the reinforcement efficiency factors K_S, K_E cannot be evaluated in the case of Com-F1/Mat2 samples, since the presence of the third phase (the nano-alumina), concentrated within the PMMA fibres, makes Eqs. 1 and 2 not applicable. However, since SEM micrographs of nano-alumina loaded PMMA fibres evidenced an increase of degree of fibre misalignment with respect to that neat PMMA electrospun mat, the authors hypothesized this system to be characterized by a lower K_E, which could explain the scarce effect of nano-alumina addition on the resulting composite stiffness.

Fibre aspect ratio

As already reported, the addition of nano-alumina within the PMMA reinforcement brought to a clear increase of tensile strength, with respect to Com-F1/Mat1 samples, that can be attributed both to the addition of the ceramic nanofiller, and to the decrease of nano-alumina loaded PMMA fibres diameter with respect to neat PMMA fibres, as observed in SEM micrographs (Fig. 3). This translates in the fact that the same V_f is attained with a larger number of thinner fibres that offer a larger surface area to form a bonding interface between matrix and reinforcement.

Degree of matrix crystallinity

Last but not least is the effect of PMMA fibres and nano-alumina loaded PMMA fibres on the crystallinity of PCL during its melting and subsequent cooling in composite manufacturing. Crystallinity, is known to have great influence on polymer stiffness, that is higher in high crystalline polymers. DSC results (Table 2) evidenced that sample Com-F1/Mat1 shows lower melting temperature, melting enthalpy and a slight lower crystallinity than neat PCL, due to the fact that the presence of fibres hinders the formation of crystalline areas. Moreover, the addition of nano-alumina within the PMMA fibres, resulting in a larger amount of thinner fibres, brought to a further decrease of crystallinity.

In order to conclude the discussion on the mechanical characterization, it is possible to remark that while tensile strength was found to increase from neat PCL to Com-F1/Mat1 and Com-F1/Mat2 samples, a less clear trend was found on the elastic modulus. In fact, while E increased quite markedly when PMMA fibres are added to the PCL matrix, it presented only a further slight increase in Com-F1/Mat2 samples. The reason of this latter result can be possibly ascribed to the presence of at least two features (lower crystallinity and less degree of alignment) that counterbalance the addition of ceramic nanofiller in the PMMA fibres that, per se, are expected to improve stiffness.

Conclusions

Aligned PMMA and PMMA/Al_2O_3 electrospun fibre mats were manufactured and used as reinforcement of PCL matrix. The composites were fabricated by means of film-stacking technique. The average diameter of neat polymeric fibres and PMMA/Al_2O_3 fibres was 990 ± 200 nm and 389 ± 65 nm, respectively. A homogenous distribution of Al_2O_3 nanoparticles within the fibres was observed. Both types of composites showed improved mechanical properties (i.e. tensile strength and Young's modulus) with respect to neat PCL accompanied by a decrease of the strain at break, confirming that an efficient load transfer from the matrix to the reinforcement was reached. The best results were obtained for the PCL/nano-Al_2O_3-PMMA composite due to both the presence of the ceramic nanoparticles and the smaller diameter of the fibres.

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