MONOFILAMENT COMPOSITES WITH CARBON NANOTUBES AND CO-CONTINUOUS POLYAMIDE12 / POLY (METHYL METHACRYLATE) BLENDS

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Introduction

Co-continuous bi-polymer composites with carbon nanotubes (CNT) were prepared and mono-filaments were produced at different drawing ratios. The blends were obtained by melt processing using a twin-screw extruder. Polyamide 12 (PA12), Poly(methylmetacrylate) (PMMA) and CNT were blended at 78:18:4 weight ratios, incorporating the ingredients at various positions along the barrel. The CNT remained in the PA12 phase independently of the order of admission in the extruder. To achieve electrical conductivity in CNT/polymer blend composites a double percolation has to be attained [1], the polymer phase bearing the CNT has to be continuous and the CNT dispersed inside that phase have to form a conductive network. Monofilaments were drawn, their morphology and electrical conductivity were studied. The monofilaments were electrically conductive, even at the higher drawing ratios.

Experimental

The polymers used for the production of carbon/polymer composite monofilament yarns were PMMA, Altuglas from Arkema and PA12, Rilsan AMNO TLD from Arkema. The CNT were NC 7000 from Nanocyl.

Polymer blending was performed on a Coperion ZSK 27 MegaCompounder modular co-rotating twin screw extruder (L/D = 40). The extrudate was cooled down in a water through, dried with blown air and cut into pellets by means of a rotary cutter. The composites prepared are described in Table 1.

Monofilaments were processed using a prototype extrusion line consisting of a Periplast (Portugal) single screw extruder (25 mm screw) and downstream equipment comprising cooling tank, first set of pulling rolls, oven, second set of pulling rolls and winder. The set temperature profile was adjusted to the characteristics of the material being processed. Identically, setting the temperature of the first oven was critical, as it determined the stretchability of the material. Whenever possible, the first set of rolls was adjusted to provide the same stretching ratio of all the emerging extrudates, while the second set of rolls was set at increasing speeds, in order to obtain monofilaments with greater molecular orientation.

The extruder/die temperature profiles and 1st oven temperature used for each composition are presented in Table 1. Monofilaments were produced with all the compositions prepared at the drawing ratios indicated in Table 1.

Table 1. Processing conditions for PMMA/PA12/CNT.

	Temp. Profile (ºC)	Oven Temp. (ºC)	Draw ratio
PA12 / PMMA (80:20)	160/185/195/ 195 (die)	150	1.2; 1.4; 2.9; 5; 7
PMMA / CNT / PA12 (18:4:78)		145	2; 3; 4; 5; 6
PA12 / CNT / PMMA (78:4:18)		145	1.4; 1.6; 2; 3; 4; 5; 6; 7

The volume resistivity of the filaments was estimated by measuring the characteristic I–V curves at room temperature with a Keithley 6487 picoammeter/voltage source. The voltage was varied from -10V to 10V, and the corresponding current was measured. The resistivity was calculated accounting for the geometrical factors of the filament. The filament length between contacts was approximately 65 mm. At least 5 samples were analyzed for each type of composite.

Filament cross-sections were observed by scanning electron microscopy on a NanoSEM-FEI Nova 200 (FEG/SEM), to assess the blend morphology and CNT distribution and dispersion.

Results and Discussion

SEM micrographs of the cross sections of filaments of PA12/PMMA, PA12/CNT/PMMA, and PMMA/CNT/PA12 obtained at the lower draw ratio are presented in Figure 1 and 2. Without nanotubes, the composition of 80% PA12 and 20% PMMA created a dispersed morphology (Figure 2 A). With the addition of 4% of nanotubes, a co-continuous structure of PMMA filaments inside a PA12 matrix seems to form. The nanotubes were always localized inside the PA12 phase irrespective of the polymer feeding sequence. This observation was confirmed by dissolution of the PMMA phase present on a cryo-fractured filament surface with dichloromethane, and observation of the cross section by SEM. Figure 1 shows the cavities produced by PMMA dissolution, and the continuous matrix phase of PA12 with CNT.

The volume electrical resistivity results obtained for the composite filaments are presented in Table 2. All the composite filaments studied presented resistivity values in the range of conductive behavior. The resistivity results did not present a clear variation with draw ratio for the range of DR studied.

Table 2. Volume electrical resistivity results obtained for the composite filaments.

Composition	D.R.	Diameter (mm)	Length (m)	Resistivity (ohm.m)
PA12/CNT/ PMMA (78:4:18)	1.6	0.98 ± 0.03	6,50E-02	$(2 \pm 0.3) \times 10^3$
	3	0.8 ± 0.2		$(3 \pm 1) \times 10^2$
	5	0.6 ± 0.1		$(3 \pm 4) \times 10^3$
	7	0.46 ± 0.01		$(1 \pm 1) \times 10^7$
PMMA/CNT/ PA12 (18:4:78)	3	0.93 ± 0.06		$(3 \pm 2) \times 10^2$
	5	0.9 ± 0.1		$(2 \pm 1) \times 10^4$
	6	0.93 ± 0.03		$(5.3 \pm 0.3) \times 10^3$

PMMA(18%) / CNT (4%)/ PA12 (78%)

PA12(78%) / CNT (4%) / PMMA (18%)

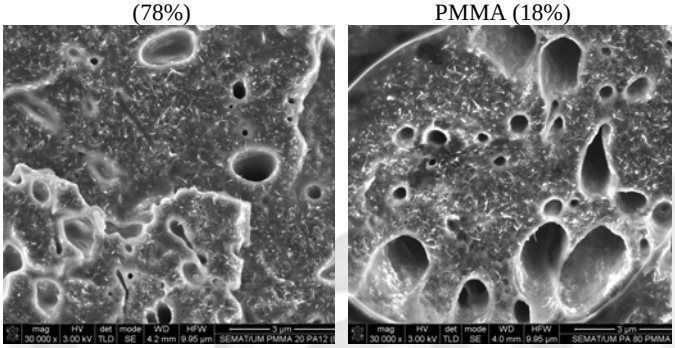

Fig. 1 SEM micrographs of the cryo-fractured cross sections of the filament composites after dissolution of PMMA phase.

Conclusions

Composites of PA12, PMMA and CNT were prepared by melt blending in a twin screw extruder. Monofilament composites were prepared at different draw ratios. The morphology of the composites of PA12, PMMA and CNT was studied by SEM, and the electrical resistivity was measured. It was observed that:

- The CNT were preferentially localized in the PA12 phase, irrespective of the polymer feeding sequence in the twin-screw extruder during composite mixing.
- The filaments produced presented resistivity values in the range of conductive behavior.

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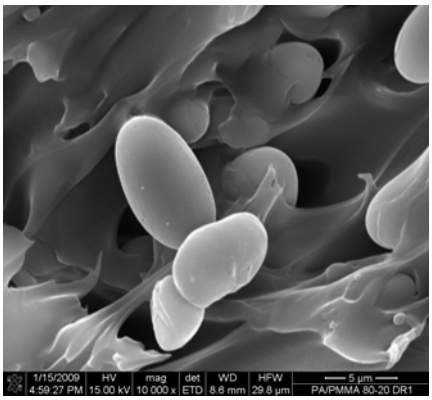
A



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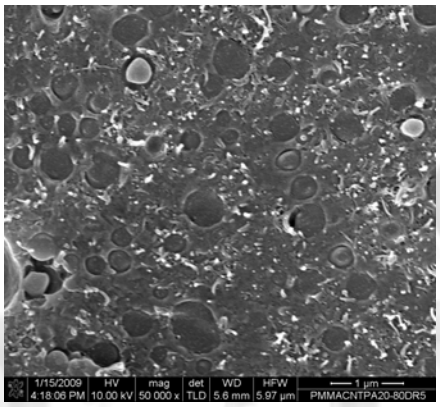

C

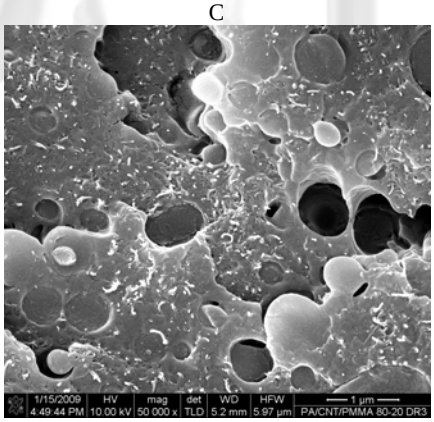

Fig. 2 SEM micrographs of the cross sections of PA12 / PMMA (A), PMMA(18%)/CNT (4%)/PA12 (78%) (B), and PA12(78%)/CNT (4%)/PMMA (18%) (C).

References

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