

***In situ*-polymerization route for the preparation of PET/MWCNT polymer nanocomposites**

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1. Abstract

Polymer nanocomposites of polyethylene terephthalate (PET) and multi-walled carbon nanotubes were prepared by *in-situ* polymerization and characterized by physicochemical methods. Raw (MWCNT) and –OH functionalized (MWCNT-OH) carbon nanotubes were used, with 0, 1, and 2 wt/wt % loadings. It was determined that the molecular weight of PET is significantly low when 2 wt/wt% loadings were used. The interface interaction was enhanced when MWCNT-OH were used improving the nanotubes dispersion as confirmed by SEM. SAXS analysis suggests all samples have a lamellar structure. Finally, the electrical conductivity of nanocomposites increases 14 orders of magnitude compared to the PET homopolymer.

Keywords: *In-situ* polymerization, PET, MWCNT, Nanocomposites, Morphology.

2. Introduction

High performance thermoplastic polymers such as PET, PBT and Polyamide-6, [1-4] have been compounded with carbon nanofibers and nanotubes in order to enhance among others mechanical, and electrical properties. Homogeneous dispersion and interface adhesion are two key elements to attain the desire properties in polymer nanocomposites. Furthermore, *in-situ* polymerization of monomers in the presence of functionalized carbon nanotubes can lead to the formation of a hybrid nanocomposite. In this case, the final properties of the nanocomposite are enhanced significantly [3]. In this report, we incorporated MWCNT and MWCNT-OH during *in situ* polymerization of PET in order to study their effect on molecular weight, dispersion, crystalline structure and electrical properties.

3. Experimental

3.1 Materials

MWCNTs were purchased to NanoLab, Inc., having an outer average diameter of 30 nm, 1-5

μm in length and a purity $>95\%$. MWCNT-OH was obtained by surface modification with ethylene glycol plasma in order to promote dispersion and adhesion with polymer matrix; the experimental procedure was reported previously [4]. Dimethyl terephthalate (DMT) was gently donated by PetroTemex SA de CV and was reactive grade. Anhydrous Ethylene glycol 99.8% purity was purchased to Sigma-Aldrich. Both chemicals were used as received.

3.2 Sample preparation

In situ polymerization of PET was carried out in a Parr Reactor model 4561. In a typical example 29 g of dimethyl terephthalate (DMT), 19 mL of ethylene glycol, 1 or 2-wt % of MWCNT and MWCNT-OH respectively were poured into the reactor, and Sb_2O_3 was used as catalyst. PET synthesis was carried out following the procedure reported by Lee [1].

3.2 Methods

Molecular weight determinations were carried out in a GPC Waters Alliance model 2900, using chloroform as solvent. SEM analysis was performed in a FE-SEM JEOL JSM 7401F with a voltage of 5 kV and 25 000 magnifications; samples were cryogenically fractured and spray coated with Au/Pd. Two points electrical resistance measurements were recorded with a Keithley SourceMeter model 2400; average value is reported for three samples. SAXS patterns were collected at Beamline X27C at National Synchrotron Light Source-Brookhaven National Laboratory; the sample detector distance was 80.5 cm, and silver behenate was used as standard.

4. Results and discussions

Average molecular weight for PET and nanocomposites are showed in Table 1. PET homopolymer showed a value of $M_w = 25,241$ g/g-mol, which can be considered as a low molecular weight polymer. Nanocomposites with 1 wt/wt% of MWCNT and MWCNT-OH have molecular weight similar to that determined for the pure polymer. Several reports suggested that carbon nanotubes do not affect polymerization reaction for loading up to 1 wt/wt % [1-3]. The molecular weight of samples containing 2 wt/wt% of MWCNT and MWCNT-OH is considerable lower respect to the homopolymer. This can be attributed to the low diffusion of the monomer due to the presence of well-dispersed carbon nanotubes.

Electrical conductivity for PET and nanocomposites is presented in Table 1. Samples with 1

and 2 wt/wt% MWCNT show an increase of 14 orders of magnitude compared to pure PET,

Table 1. Physicochemical properties for PET and nanocomposites.

Sample	M _w (g/g-mol)	σ _v (S/cm)	L (nm)
PET-0% MWCNT	25,241	5.55 x 10 ⁻¹⁹	11.77
PET-1% MWCNT	21,543	1.19 x 10 ⁻⁵	12.36
PET-2% MWCNT	11,174	3.93 x 10 ⁻⁵	12.36
PET-1% MWCNT-OH	25,143	6.16 x 10 ⁻⁶	11.58
PET-2% MWCNT-OH	14,602	N/A	N/A

M_w, average molecular weight

σ_v, electrical conductivity. Electrical conductivity of PET was obtained from E. L. Lawton and E. L. Ringwald, in: Polymer Handbook,

Vol. 4, Eds. J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe and D. R. Bloch, (John Wiley & Sons, USA, 1999) p. V/103.

L, long period

meanwhile the sample containing 1 wt/wt% MWCNT-OH exhibit a lower value of conductivity compared to the non-functionalized sample. These results can give an idea of dispersion level of MWCNT and MWCNT-OH inside the matrix and are similar to the others reports [1-3]. It was not possible to determine the electrical conductivity for the sample containing 2 wt/wt% MWCNT-OH, suggesting a non-homogeneous dispersion of carbon nanotubes. This may be due to the high population of functional –OH groups that can hold together MWCNT-OH by intermolecular hydrogen bond instead van der Waals forces.

SEM micrographs for samples having 2 wt/wt% of MWCNT (A) and MWCNT-OH (B) in PET matrix are shown in Figure 1. The absence of agglomerates and the observation of individual MWCNT in Figure 1(A) suggest the formation of a conductive network (indicated by black arrow). On the other hand, Figure 1(B) shows a more dense population of MWCNT-OH. Here we observe that some carbon nanotube tips are coated by polymer (indicated by red arrow). Furthermore a good adhesion was observed between both phases (not shown).

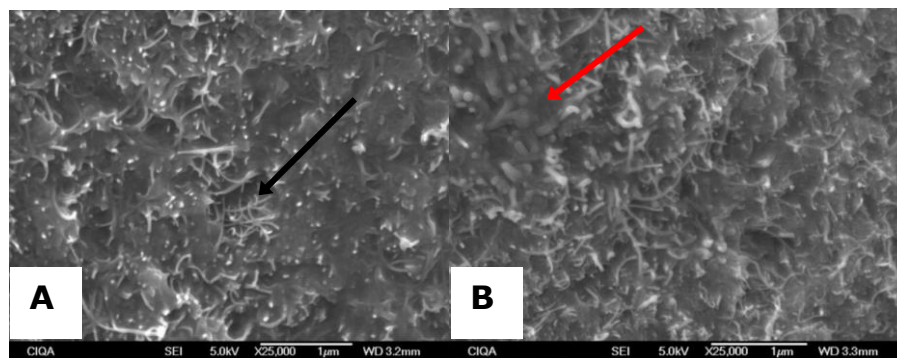


Figure 1. SEM micrographs for PET/MWCNT (98/2 wt/wt%) (A), and PET/MWCNT-OH (98/2 wt/wt%) (B).

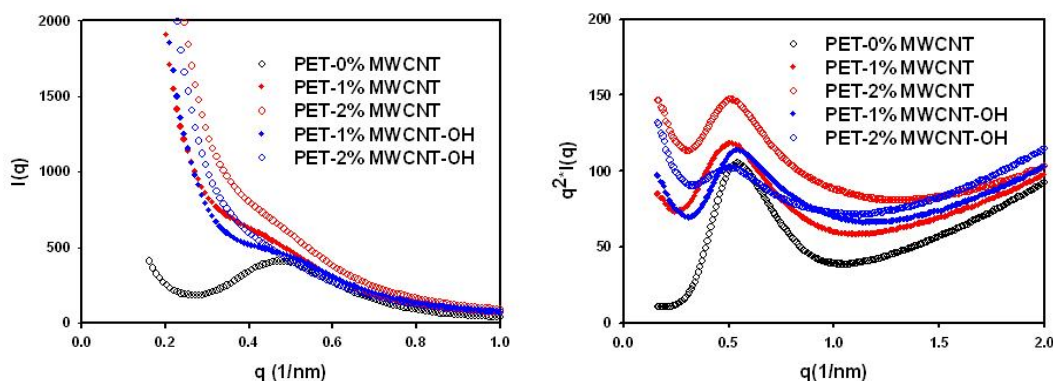


Figure 2. SAXS profiles for PET and nanocomposites, Intensity (A) and Lorentz-corrected (B).

Lamellar structure for PET and nanocomposites was determined by small-angle X-ray scattering (SAXS). Intensity and Lorentz-corrected curves are shown in Figure 2. The stacking of crystal and amorphous lamella forms a lamellar structure, where distance from one phase to another one of the same type gives the periodicity of the lamellar structure. The periodicity is also known as long period, L . The long period can be obtained from q_{\max} using the following relation $L=2\pi/q_{\max}$ [5], where q_{\max} is the maximum in a Lorentz-corrected curve. Figure 2(B) shows that all samples have a maximum, q_{\max} , although the peak tends to disappear for the sample with 2 wt/wt% MWCNT-OH. This indicates that all samples have a lamellar structure. The long periods obtained using this method are shown in Table 1.

5. Conclusions

In-situ polymerization of PET with MWCNT and MWCNT-OH results in low molecular weights due to the low diffusion of the monomer. SEM micrographs showed that carbon nanotubes are homogeneously dispersed in the PET matrix. Electrical conductivity increases up to 14 orders of

magnitude with the use of MWCNT compared to the pure PET. PET and nanocomposites have a lamellar structure, although it tends to disappear with the use of MWCNT-OH.

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7. References

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