STUDIES ON MORPHOLOGY AND INTERPHASE OF POLY(BUTYLENE TEREPHTHALATE)/CARBON NANOTUBES NANOCOMPOSITES

L. A. S. de A. Prado¹, M. Kwiatkowska², S. S. Funari³, Z. Roslaniec², G. Broza¹ and K. Schulte¹

¹ *Institute of Polymers and Composites – Technische Universität Hamburg-Harburg, Denickestrasse
15 (Geb. K, M-11), 21073 Hamburg, Germany*

² *Szczecin University of Technology – Institute of Materials Science and Engineering, Plastow Av. 19,
71310 Szczecin, Poland*

³ *HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg, Germany*

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ABSTRACT

The microstructure of poly(butylene terephthalate) (PBT) nanocomposites was investigated by simultaneous small angle X-ray scattering/wide angle X-ray scattering (SAXS/WAXS) measurements at room temperature. The PBT crystallized in the α -phase. The dispersion of single-wall carbon nanotubes (SWCNTs) in PBT, using the in situ polymerization method, produced materials having higher crystallinity degree than neat PBT. SAXS results indicated that the SWCNT may be preferentially distributed in the amorphous phase of PBT, although WAXS results suggested a nucleation ability of SWCNT, which was supported by the DSC results. Much more complex changes were induced by the dispersion of multi-wall carbon nanotubes (MWCNTs) in the PBT matrix. Evidences for the formation of interphase with restricted chain mobility were found by dynamical mechanical thermal analysis (DMTA). Differential scanning calorimetry (DSC) and WAXS indicated an increase of the crystallinity of the nanocomposites in comparison to neat PBT.

Key-words: polymer nanocomposites; polyesters; in situ polymerization; carbon nanotubes; small angle X-ray scattering, wide angle X-ray scattering

INTRODUCTION

Thermoplastic polyesters are important materials due to their good mechanical properties in combination with processability, compatibility with organic dyes, and good thermal stability. In this context, the polyesters derived from aromatic dicarboxylic acids (e.g. poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalene-dicarboxylate), among others) gained importance due to their supreme thermal stability[1,2], good barrier properties[3-5]. Poly(butylene terephthalate), PBT, is particularly important for the automobile industry as components for bumpers[6], and fenders[7]. Thermoplastic elastomers, having PBT as hard segment and poly(tetramethylene oxide) as soft segment, combines the processability of the thermoplastic materials with the flexibility of rubbers[8], are another example of PBT-based material with technological relevance.

The application spectrum of PBT and thermoplastic elastomers therefrom may be expanded through the manufacturing of polymer nanocomposites. In this regard, Carbon Nanotubes (CNTs) are interesting fillers due to their unique combination of properties such as high elongation strength, outstanding Young's Modulus, as well as high electrical- and thermal conductivities [9-11]. Although these properties can be strongly influenced by the type of carbon nanotube (single-walled, double-walled or multi-walled), and presence of defects; stemmed from the production process of these materials, or their functionalisation, a lot of work has been done in order to imprint the stiffness and electrical and thermal conductivity of CNTs into different polymeric matrices. For instance, the electrical conductivity of epoxy resins at extremely low CNT loadings has been reported[12]. The dispersion of functionalized and as-received CNTs in polyesters like poly(butylene terephthalate) (PBT) leads to improvement of the stiffness of the PBT matrix and changes of crystallinity and improvement of electrical conductivity due to the presence of these nanoparticles [13-16]. Very significant

improvements of mechanical properties and electrical conductivity could be also realized through the dispersion of CNTs in PBT-based thermoplastic elastomers[17].

In order to understand the obtained results, investigations on polymer microstructure should be carried out. In this communication, we summarize the first results on the analysis of the microstructure of different PBT /CNT nanocomposites.

EXPERIMENTAL

Materials

Poly(butylene terephthalate), PBT, was obtained from 1,4-butanediol (BASF) and dimethyl terephthalate (DuPont, USA) using tetrabutyl ortotitanate (Aldrich GmbH, Germany), as catalyst [15]. These chemicals were used as received. Single-wall carbon nanotubes (SWCNT) were used as received from Carbon Nanotechnologies Inc. (CNI), USA. Pristine multi-wall carbon nanotubes (MWCNTs) were kindly provided by Nanocyl, Belgium. This material contains more than 90% MWCNT without any functional group.

Nanocomposite preparation [13,15]

All the polyesters nanocomposites reported here were produced through *in situ* polymerization starting from dimethyl terephthalate and butanediol, for the PBT synthesis. The nanotubes were dispersed in the polymer matrix during the polymerisation process. This method yields for an outstanding dispersion of the filler in the polymer matrix.

Processing of nanocomposites via *in situ* polycondensation of PBT is explained in the following example, which clarifies the preparation of a nanocomposite containing 0.1 wt-% of CNTs. 245 g of 1,4-butanediol and 0.3 g of CNTs were stirred for 5 min at 20.000 rpm, followed by degassing in a vacuum oven at 50 °C. Secondly, the dispersion was sonicated for 5 min at room temperature. The first step and the second step were repeated six times. Finally, the system has been degassed again for 30 min at 50 °C in the vacuum oven. In a steel reactor,

270 g of dimethyl terephthalate (DMT) (1.4 mol) and 60 mg (21mmol) of tetrabutyl ortotitane (TiBu) were mixed. CNT-BD was slowly added to this mixture and mechanically stirred in order to obtain a homogeneous dispersion. The resulting mixture was slowly heated for 1 h up to 180 °C under a steady stream of N₂ gas. Next, the temperature was further increased up to 225 °C and hold for 2 h. During this period, continuous generation of distilled BD and methanol, in the relation of the theoretical amount, was observed. Finally, the system was heated for 2 h at 260°C under reduced pressure.

The resulting polymer was extruded from the reactor by compressed nitrogen and cooled to room temperature, washed copiously with water, and dried in vacuum at 60 °C for 1 day, and granulated. The materials were pressed at temperatures above the melting point of PBT for at least one hour in order to remove any orientation effect due to the polymerisation process.

Measurements

Information concerning the crystallinity of the samples was obtained with a Seiko DSC SSC 5200 differential scanning calorimeter. The measurements were made under a nitrogen atmosphere, from -50°C to 280°C, at a heating rate of 10°C/min.

Dynamical mechanical thermal analysis (DMTA) was performed in an Eplexor 500 N instrument by Gabo Qualimeter, operated in tensile mode. The temperature range analyzed was -50°C to 150°C, at a constant frequency of 1 Hz. The samples were analyzed as of stripes 4x2 the cross-section and 40mm in length.

Transmission small and wide-angle X-ray scattering (SAXS/WAXS) experiments were performed at beamline A2 of HASYLAB/DESY, with 8 keV X-rays and two linear detectors. The raw data were background and detector response corrected. The SAXS scattering-vectors were calibrated using a rat-tail tendon protein. The WAXS data were calibrated using reflections of poly(ethylene terephthalate) (PET) film.

The scattering intensity $I(s)$ was plotted against the scattering vector s , which is defined by the equation (1).

$$s = \frac{2}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (1)$$

where θ and λ correspond to the scattering angle and to the wave-length of the incident X-rays, respectively.

RESULTS AND DISCUSSION

PBT/SWCNT Nanocomposites

Fig. 1 displays the SAXS curves of PBT/SWCNT nanocomposites (SWCNT represents single-walled carbon nanotubes). All the curves had a peak, which can be associated with the correlation distance between the crystalline lamellae, also referred as long period (L_B)[18]. L_B can be estimated using the equation (2), which correlates with the s -value corresponding to the maximum intensity (s_{MAX}).

$$L_B = \frac{1}{s_{MAX}} \quad (2)$$

Although the correlation peak could be observed for all the samples, the scattering power of the nanocomposites was poorer than for the neat PBT. This can be explained by the formation of an amorphous interphase, which is denser than the amorphous phase of the neat PBT matrix. DMTA studies on PBT/oxidized SWCNT did indicate that the SWCNTs might be also on the amorphous phase of PBT matrix[15]. This result supported the conclusion drawn from the analysis of the DMTA curves, as discussed in the next paragraphs.

Using the equation (2) it is possible to propose that the crystalline lamellae are separated by a distance of 11 nm for all the nanocomposites investigated. However, the interlamellar distance measured for neat PBT is 9.9 nm.

(Insert Fig. 1 here)

More information about the structure of the crystalline phases of PBT and PBT/SWCNTs prepared in this work could be extracted from WAXS curves (Fig. 2). All the curves have the reflections associated with the (hkl) (0 -1 1); (0 1 0); (-1 1 0); (1 0 0) and (1 -1 1) planes of α -PBT [19-21]. All the WAXS curves of the PBT/SWCNT have reflections much sharper than the neat PBT, suggesting a higher crystallinity degree for the nanocomposites and better quality of the crystals as well. Although, preliminary results on PBT/oxidized SWCNT did suggest a nucleating effect of these fillers[15], the DMTA results on similar nanocomposites reported in the present investigation indicated a very tiny nucleating effect.

(Insert Fig. 2 here)

Further information concerning the capability of SWCNT to act as nuclei for the crystallization could be extracted from the DSC curves of the PBT/SWCNT nanocomposites

(see data displayed in Table 2). The second heating cycle evidences the effect of SWCNT on the melting enthalpy, onset of melting point and the melting temperature of the PBT crystallites in neat PBT and PBT/SWCNT nanocomposites. It can be seen that the crystals of neat PBT melted at temperatures lower than all the nanocomposites, thus indicating another distribution of crystalline lamellae thickness for the neat polymer in comparison to the SWCNT-containing nanocomposites. The melting double-peak can be associated with the melting-recrystallization process, i.e., the thinner lamellae melted away giving rise to more thick lamellae which have higher melting points. This effect became less and less evident as the SWCNT loading increased. This fact suggests that the SWCNT also affected this re-crystallization process.

The cooling cycles of the DSC curves confirmed these statements, since the crystallization peak temperature and the onset temperatures of the crystallization process were shifted to higher values for the SWCNT-containing nanocomposites. This fact can be explained in terms of facilitated crystallization of PBT chains at the surface of the CNTs.

DMTA has been often utilized to complement SAXS studies on the microstructure of polymeric materials [22-25]. The mobility of the amorphous phase of PBT could be evaluated by DMTA curves of the neat PBT and the PBT/SWCNT nanocomposites. The glass-transition temperature (T_g) of PBT prepared in this work is 56-60°C, as determined by DMTA (see Fig. 4). As the SWCNT load increases, the T_g slightly decreases to values close to 55°C, which is within the experimental error. The intensity of the β -relaxation peak changed as the load increased, which can be explained in terms of restricted mobility of the polymeric chains- due to favorable interactions between the polymer matrix and the SWCNTs.

The formation of an interphase has been often mentioned as an explanation for the outstanding mechanical properties of polymer composites reinforced by nanoparticles[26-29]. The interphase might be regarded as the polymer chains which are in direct contact with the

nanoparticle surface and therefore is influenced by the Van der Waals forces between these particles and the matrix. When dealing with aromatic polymers like PBT, a special effect might rise from the interactions between the grapheme rings of the SWCNTs and the benzene rings of the terephthalate moiety. DMTA has been systematically used as tool for the indirect identification of the interphase. As stated by Brinson and co-workers, the changes in the shape and intensity of Tg peak can be better evaluated by normalizing the loss modulus by the loss modulus value at Tg and by subtracting the Tg from the measured temperature. The normalized Tg peak of PBT / SWCNT nanocomposites was narrower than for neat PBT, which can be indicative of changes in the molecular dynamics for the polymer nanocomposites. A noticeable decrease of the β -relaxation peak was observed for the nanocomposites having higher SWCNT loadings. Since this peak is mostly associated with the motions of the short chain-segments of PBT and it is cooperatively related to the glass transition, the decrease of the peak associated with this transition might be regarded as evidence for the partial immobilization of PBT chains by the SWCNTs. This immobilization effect might cause the change in the shape of the glass-transition peak.

In other words, the system PBT/SWCNT might be regarded as four-phase systems constituted by the bulk amorphous PBT, the crystalline PBT, the interphase and the SWCNTs. Therefore, the DSC and DMTA results supported both SAXS and WAXS results concerning the PBT/SWCNT nanocomposites.

PBT/MWCNT Nanocomposites

The SAXS and WAXS curves of PBT/MWCNT (MWCNT: multi-walled carbon nanotubes) nanocomposites are displayed in the Fig. 4 and Fig 5, respectively. SAXS curve of the PBT/MWCNT nanocomposites has a correlation peak at low angles, which is associated with

the crystalline layers separated by the amorphous polymer chains. An enormous increase of the intensity of this peak is observed for the nanocomposite containing 0.01% MWCNT. This effect cannot be explained solely in terms of the densification of the amorphous phase, as observed for the PBT/SWCNT nanocomposites. The peak was shifted to lower angles, corresponds to the long-period (distances between the crystalline PBT lamellae) of 11 nm (for neat PBT this value was 9.9nm).

WAXS curves of PBT/MWCNT are depicted in Fig. 5. Here, the PBT chains crystallized also in the α -phase. As the filler loading increased, the intensity of the peak associated with the (0 1 0) reflection became sharper and more intense than for neat PBT. The relatively high shear forces could contribute to a partial alignment of the MWCNTs in the polymerization reactor, used for the production of the PBT nanocomposites reported in the present paper. In order to confirm this possibility, the SAXS/WAXS experiments will be repeated using a 2-dimensional detector, which are able to identify any anisotropy in the microstructure of the nanocomposites. Although the nanocomposite films have been pressed above the melting point in order to eliminate any anisotropy, this treatment might not be sufficient for eliminating the orientation effect. It must be acknowledged that no convincing evidence for an orientation effect was found in this stage of the investigation.

Furthermore, the peaks associated with the crystalline phase of PBT became more defined for the nanocomposites, suggesting; again, a higher crystallinity degree and/or a better quality of the crystallites for the nanocomposites (larger crystals).

(Insert Fig. 5 and Fig. 6 here)

The increased crystallinity of the PBT/MWCNT nanocomposites was confirmed by DSC results, which also confirms that the capability of MWCNT to act as nucleating agents for the

crystallization of PBT (see Table 2 for details). This effect has been also reported in previous publication from our group [15].

DMTA results demonstrated that the MWCNT have a less pronounced effect on the formation of an interphase than SWCNTs. That might be also explained in terms of lower specific surface area of MWCNTs in comparison to SWCNTs. The β -relaxation peak of the PBT/MWCNT (see Fig. 6) was slightly changed in comparison to neat PBT polymer.

CONCLUSION

SAXS/WAXS studies on PBT/SWCNT nanocomposites indicated that the SWCNT have a nucleation effect on the crystalline phase, although this filler is distributed mostly in the amorphous phase. On the other hand, MWCNT changed dramatically the microstructure of the PBT matrix, as evidenced by SAXS. WAXS and DSC measurements indicated that MWCNT had a strong effect on the crystalline phase of PBT nanocomposites, since these materials exhibit higher crystallization degree values than neat PBT. Crystallization kinetic experiments will be carried out for a more detailed evaluation of the ability of SWCNT and MWCNT to act as nucleating agents for PBT.

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Table 1. Melting temperature (T_m), crystallinity degree (X_c) and crystallization temperature (T_c) of PBT; PBT/SWCNT and PBT/MWCNT nanocomposites obtained by in-situ polycondensation .

Sample	T_m (°C)	X_c (%)	T_c (°C)
Neat PBT	222	35.3	186
PBT/SWCNT 0.01 wt.-%	223	40.6	197
PBT/SWCNT 0.05 wt.-%	223	41.1	199
PBT/SWCNT 0.20 wt.-%	223	35.2	200
PBT/MWCNT 0.01 wt.-%	226	38.0	200
PBT/MWCNT 0.10 wt.-%	226	44.1	201
PBT/MWCNT 0.30 wt.-%	227	45.2	202

Fig. 1. SAXS patterns of PBT/SWCNT nanocomposites (the curves have been shifted vertically for the sake of clarity).

Fig. 2. WAXS patterns of PBT/SWCNT nanocomposites (the curves have been shifted vertically for the sake of clarity).

Fig. 3. Loss modulus as a function of temperature for PBT/SWCNT showing the changes in the β -relaxation and glass-transition peaks: (a) raw DMTA curves; (b) normalized DMTA curves.

Fig. 4. SAXS patterns of PBT/MWCNT nanocomposites (the curves have been shifted vertically for the sake of clarity).

Fig. 5. WAXS patterns of PBT/MWCNT nanocomposites (the curves have been shifted vertically for the sake of clarity).

Fig. 6. Normalized Loss modulus as a function of temperature for PBT/MWCNT showing the changes in the β -relaxation and glass-transition peaks using the normalized DMTA curve (see text for details).