

Development of nanocomposites with carbon nanotubes in a thermoplastic elastomer matrix

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ABSTRACT

We have developed a polycondensation process, which allows the manufacturing of thermoplastic elastomers with carbon nanotubes (CNTs). The nanocomposites are obtained by introducing the CNTs into the reaction mixture whilst the synthesis of polybutylene terephthalate/polyoxytetramethylene (PBT/PTMO) blockcopolymers. In the first step the CNTs were dispersed in dimethyl terephthalate (DMT) and 1,4-butanediol (BD) by ultrasonication and ultrahigh speed stirring. The nanocomposites were characterized by transmission, scanning electron microscopy, atomic force microscopy, tensile testing and dynamic-mechanical analysis. Only a small amount of CNTs was needed to improve the mechanical and dynamical properties, reversibility and energy absorption of the nanocomposites.

Keywords: carbon nanotubes, thermoplastic elastomers, nanocomposites

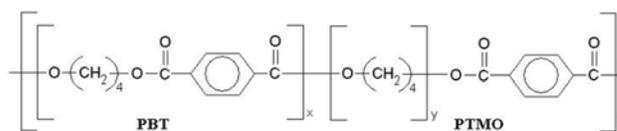
1 INTRODUCTION

Carbon nanotubes (CNTs) are a promising new class of material with exceptional mechanical, electrical and thermal properties [1-3]. Their presence in polymer at very low concentrations may improve mechanical properties and electrical conductivity [4-7]. However strong interfacial bonding between filler and polymer matrix as well as good wetting of the filler surface by the polymer and its homogenous dispersion in the polymer system have to be ensured in order to obtain a maximum effect of reinforcement in composites [8].

We have obtained polymer matrix + CNT nanocomposites by introducing CNTs into a reaction mixture during the synthesis of poly(ether-ester) block copolymers (PBT/PTMO). The polymers without and with carbon nanotubes were synthesised using an in situ polycondensation reaction process [9-10]. After polycondensation the nanocomposites were extruded and then injection moulded. The Young's modulus, tensile strength, and also strain to failure go all up with increasing amounts of CNTs in the PBT/PTMO matrix. However, an addition of only a small amounts of CNTs to the matrix is sufficient to improve the mechanical and dynamical mechanical (DMA) properties.

2 EXPERIMENTAL

2.1 Materials



Polybutylene terephthalate/polyoxytetramethylene (PBT/PTMO) was used and synthesised in a two-stage process: transesterification followed by polycondensation in the melt as described in [11,12], with a content PTMO of 55 wt%.

2.1.1 Characterization of carbon nanotubes (CNTs)

The multi walled nanotubes (MWCNT) used for the experiments were purchased from Nanocyl S.A. (Belgium) and used without further purification process. For the experiments very thin multi-wall carbon nanotubes (MWCNT) were used. Typically, their outer diameter range is 3-15 nm, length up to 50 μ m. The CNTs were produced by catalytic chemical vapour deposition method (CCVD) [13]. The structure of the bundles of the multi wall nanotubes was investigated using TEM (Fig. 1).

The single walled carbon nanotubes (SWCNT) were ready supplied by CNI Technology Co., TX, USA, synthesised by the HIPCO method [14]. The diameter of the SWCNT was 0.7-1.2 nm with a length of a few μ m. A TEM image of the SWCNT is shown in Fig. 2.



Figure 1: TEM image of the multi walled nanotubes

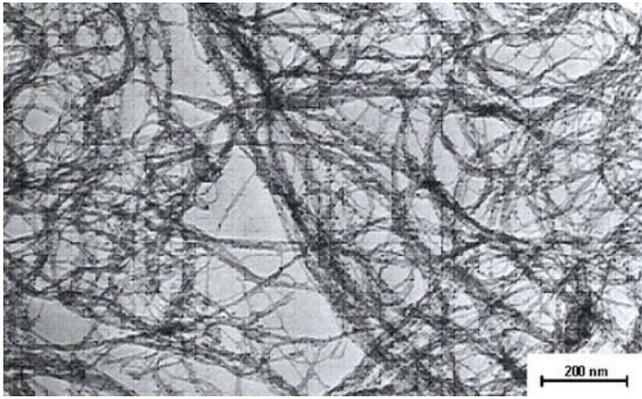


Figure 2: TEM image of the single walled nanotubes, SWCNTs

2.2 Processing of PBT/PTMO with CNTs

2.2.1 Dispersion of CNTs in DMT

Dimethyl terephthalate (DMT) was melt in butanediol (BD), at 140°C. The CNTs were dispersed in this mixture. The mixture was ultrahigh speed stirred for 5 min. at 20,000 rpm and sonicated for 5 min. at room temperature, applying a SONOPLUS-Homogenisator HD 2200 with a titanium sonotrode made by BANDELIN ELECTRONIK GmbH, Berlin, Germany. The first step and the second step were repeated six times. The bundles of nanotubes are suspended in DMT+BD.

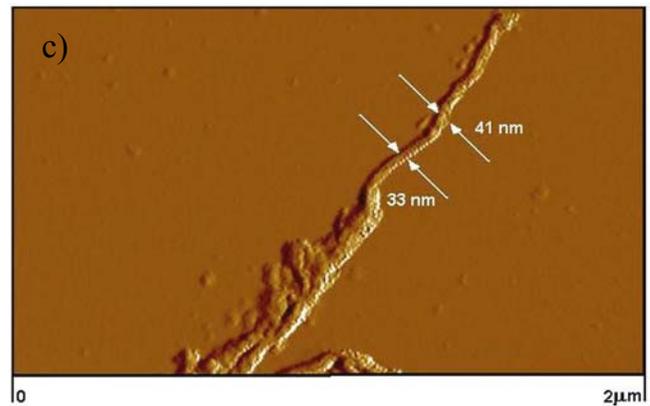
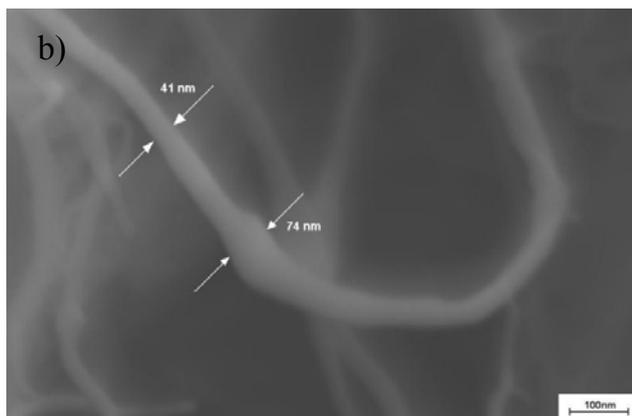
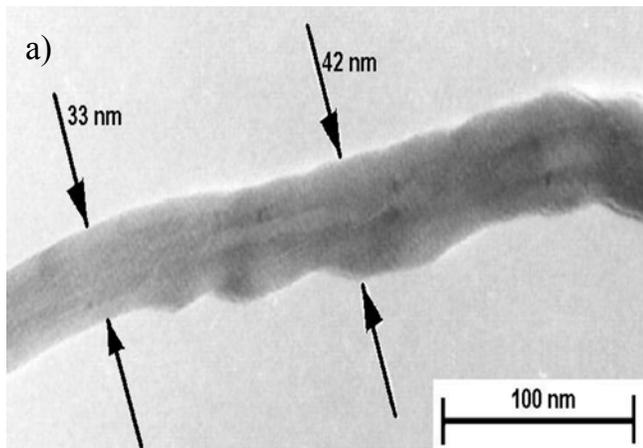


Figure 3: (a) TEM image, (b) SEM image, (c) AFM image showing the dispersion of MWCNTs in DMT+BD. The different diameters of MWCNT are due to the surrounding of the surface of nanotubes with DMT+BD layer.

The molten dispersion was casted onto a plate, and after cooling down to room temperature the material crystallized. It was then crushed and added to the reactor. The TEM micrograph confirms the covering of nanotubes by a layer of DMT+BD.

Fig. 3 shows a) the TEM micrographs b) SEM micrograph and c) AFM micrograph of the crystallized powder of DMT+BD containing MWCNTs.

The TEM characterization in Fig. 3(a) provides a clearer view of the nanotube surface covering due to the DMT+BD in crystallized powder. In this figure changes in diameter of the nanotubes are in the range of 33 to 42 nm, which is comparable to the diameter range taken from AFM showed in Fig. 3(c). Only SEM image in Fig. 3(b) shows the different diameters of the nanotubes, which change in the range from 33 to 74 nm.

2.2.2 Schematic illustration of the PBT/PTMO+CNT nanocomposites processing

In a steel reactor (Autoclave Eng. Inc., USA) dimethyl terephthalate (DMT) and catalyst were mixed; CNT+BD system was slowly added to this mixture and was mechanically stirred to obtain a homogeneous dispersed system. The nanocomposite formed were extruded from the reactor by compressed nitrogen and cooled down to room temperature. All nanocomposites were granulated and dried before processing. In the present investigation the nanocomposites containing 0.1 wt% of SWCNT, and 0.5 wt% of MWCNT were included. The samples of neat PBT/PTMO were synthesized as a reference.

The process is schematically shown in Fig. 4

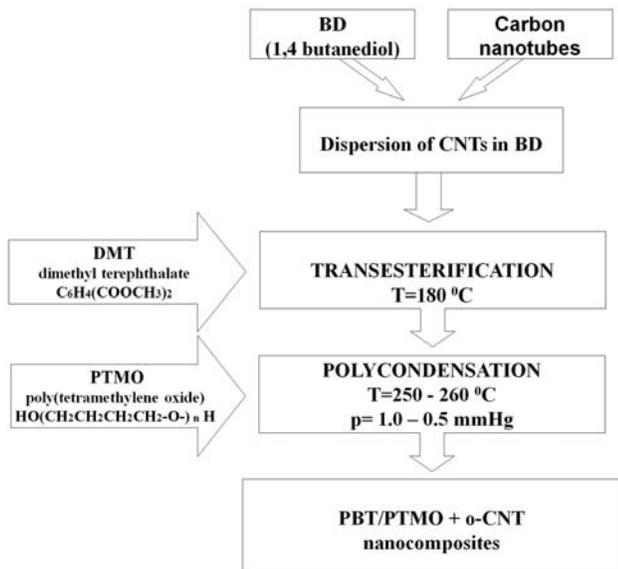


Figure 4: Schematic illustration of the PBT/PTMO+CNT composites processing

3 RESULTS AND DISCUSSION

3.1 Morphology

A LEO 1530 SEM FEG (Field Scanning Electron Microscope) was used to characterize the morphology of the failure surfaces of the PBT/PTMO+CNT nanocomposites. As shown in Fig. 5, the nanotubes which protrude from the fracture surface appear to be coated by a thin layer of the PBT/PTMO matrix. The coating layer was found to have a thickness of 80 to 200 nm.

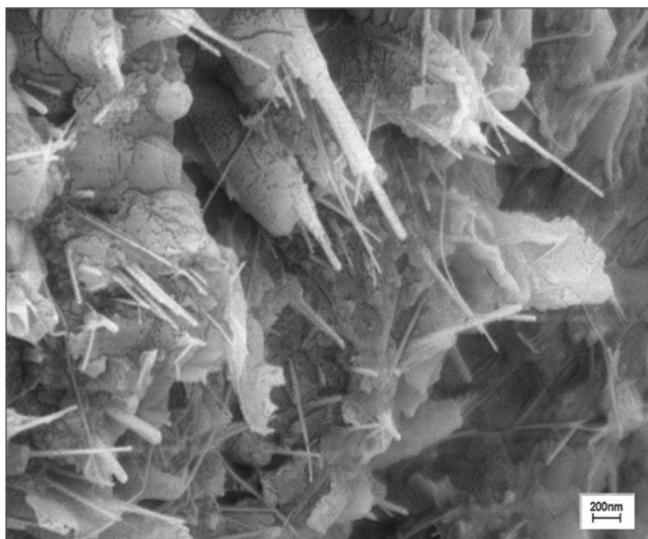
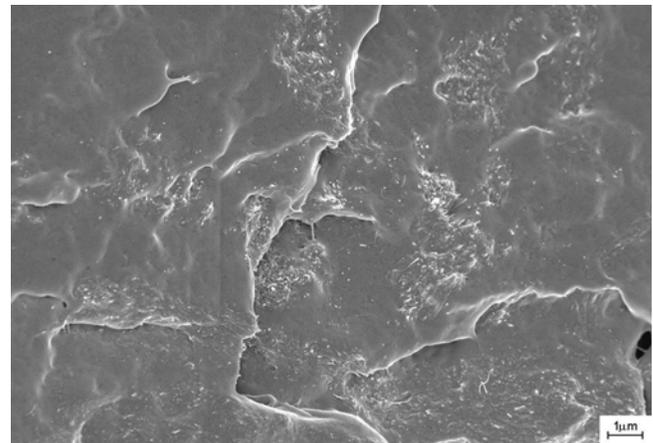


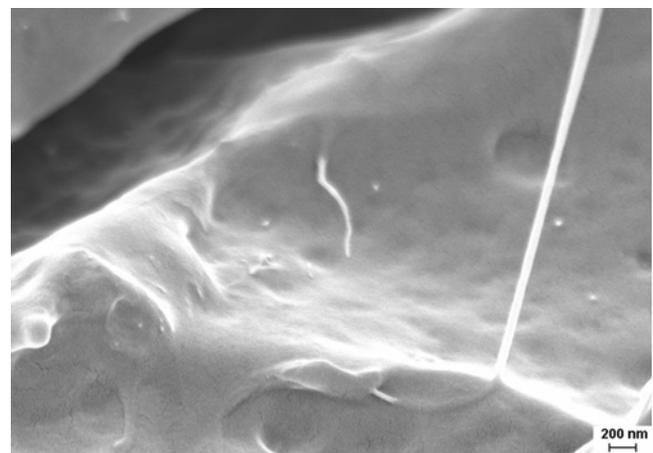
Figure 5: SEM micrograph of the fracture surface of the granulated PBT/PTMO nanocomposite with MWCNTs dispersed in DMT+BD before injection moulding

Fig.6 a,b shows the distribution of carbon nanotubes after injection molding. It is quite clear that the CNTs are uniformly distributed in the PBT/PTMO phase, even

though the nanocomposite was prepared via in situ polykondensation reaction.



a)



b)

Figure 6 a,b: SEM micrographs of the fracture surface of the granulated PBT/PTMO nanocomposite with MWCNTs dispersed in DMT+BD after injection moulding

3.2 Mechanical and dynamical properties

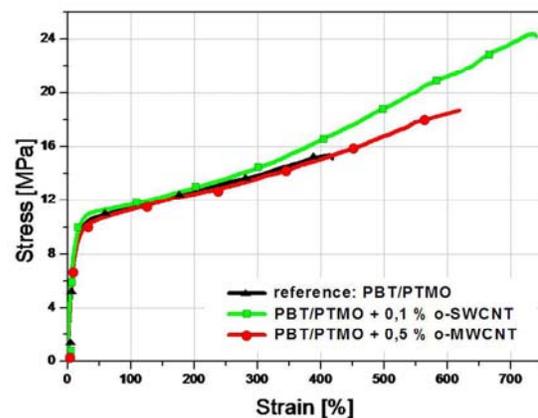


Figure 7: Stress-strain curves of pure PBT/PTMO and PBT/PTMO nanocomposites with different weight fraction and type of carbon nanotubes.

Table 1 lists the average values for Young's modulus, tensile strength, and fracture strain for SWCNT and MWCNT content in the PBT/PTMO matrix. In comparison to the neat PBT/PTMO tensile tests results show that nanotubes dispersed via in situ polycondensation in PBT/PTMO have an improved tensile strength and the tensile strain (Fig.7).

| Sample | E [MPa] | σ [MPa] | ε [%] | E' at temp. 50°C [MPa] |
|--------------------------------------------|---------|----------------|-------------------|------------------------|
| Reference: PBT/PTMO (45% of hard segments) | 88,1 | 15,4 | 433,61 | 77,44 |
| PBT/PTMO +0,1wt% SWCNT | 109,9 | 24,4 | 735,69 | 88,58 |
| PBT/PTMO +0,5wt% MWCNT | 93,5 | 18,7 | 620,13 | 84,11 |

Table 1: The mechanical and dynamical-mechanical properties of PBT/PTMO+CNT nanocomposites

The dynamic mechanical properties of the neat matrix and the nanocomposites were studied by DMTA. Fig.8 shows the temperature dependent storage modulus E' of PBT/PTMO and the nanocomposites.

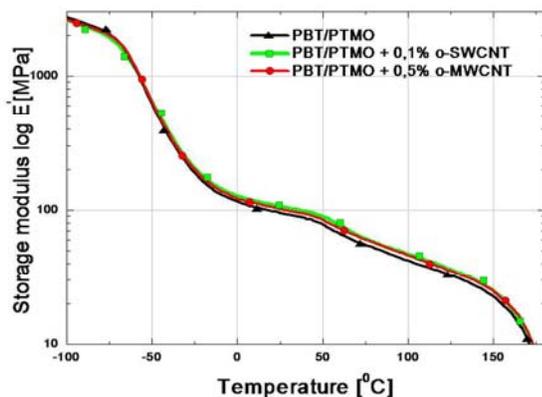


Figure 8: Storage modulus – temperature curves of pure PBT/PTMO and PBT/PTMO nanocomposites with different weight fraction and type of carbon nanotubes

In the nanocomposites the incorporation of CNTs causes a measurable increase in stiffness. The storage modulus E' of PBT/PTMO is increased by the stiffening effect of the nanotubes, which is particularly significant at temperatures between T= -50 and + 150 °C. This is a hint that the reinforcement effect of CNTs is mainly active not only in the soft segments (PTMO) but also in the amorphous phase of PBT, which leads to the suggestion that the nanotubes are only present in the amorphous phases.

The two-stage polycondensation method in molten state was successfully applied to obtain block ether-ester elastomers with carbon nanotubes dispersed in dimethyl terephthalate (DMT) and 1,4-butanediol (BD) and added to the reaction mixture. The essential element of obtaining the nanocomposites in such a way the total dispersion of nanotubes in BD just before starting the synthesis. The CNTs were relatively uniformly dispersed with a minor trend for agglomeration, and incorporated in thermoplastic elastomers in order to assess the effectiveness of the polycondensations process. Tensile test results showed that nanotubes dispersed via in situ polycondensation in PBT/PTMO could improve the tensile strength and the tensile strain concomitantly. The E-modulus of the nanocomposite with SWCNTs reached slightly higher values as MWCNT.

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4 CONCLUSIONS