

Poly(butylene terephthalate)/oxytetramethylene + oxidized single wall carbon nanotubes hybrids: mechanical and tribological behavior

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ABSTRACT

We have created functionalized single wall carbon nanotubes (fSWCNTs) before placing them in PBT/PTMO, a block copolymer of semicrystalline poly(butylene terephthalate) (PBT) with amorphous poly(oxytetramethylene) (PTMO). Together with the neat copolymer, nanohybrids containing 0.1, 0.2, 0.3 and 0.5 wt. % fSWCNTs were investigated. Scanning electron microscopy (SEM) shows significant agglomeration of CNTs at 0.2 % CNTs concentration. Tensile Young modulus as a function of concentration diagram has a maximum at 0.2 % CNTs. Tensile elongation at break is the highest at 0.3 % CNTs. Repetitive tensile tests were also performed; each loading cycle results in lowering the tensile modulus.

Keywords: nanohybrids, tensile testing, scratch resistance, sliding wear, brittleness

1 INTRODUCTION

Poly(ether-*b*-ester) copolymers have numerous applications as engineering materials due to their attractive combination of strength, high elasticity, melt stability and high crystallization rates [1]. Generally, properties of polymers can be modified and improved by addition of fillers with sizes in the nm range [2 - 17] - including carbon nanotubes (CNTs) [18 - 29]. Therefore, in this work we have applied single wall CNTs (SWCNTs) subjecting them to a functionalization process. Moreover, we have developed a method of making nanohybrids from oxidized single wall carbon nanotubes (fSWCNTs) in copolymer matrices by using an *in situ* polycondensation process. Such a process was first introduced for multiblock copoly(ether-*b*-ester)s based on semicrystalline poly(butylene terephthalate) (PBT) blocks with amorphous poly(oxytetra-methylene) (PTMO) blocks [25].

2 EXPERIMENTAL PART

2.1 Synthesis of carbon nanotubes

We have used chemical vapor deposition (CVD) - a simple and economic technique in which CNTs are synthesized at a low temperature under normal pressure [24]. The method lends itself to large scale production of CNTs. We have obtained high-purity and high-quality SWCNTs.

2.2 Functionalization of carbon nanotubes

There is a diversity of chemical reactions that can modify the surfaces of CNTs [27]. To achieve a good dispersion of CNT in the polymeric matrix and strong interface adhesion, the surfaces of CNTs should be chemically functionalized [26]. Kopczyńska and Ehrenstein discuss the importance of interfaces for properties of multiphase composites [30]. Chemical modification of a filler can even produce lowering of viscosity of the melt as compared to the neat molten polymer without a filler [31].

The process of functionalization of CNTs consists of the following three steps (Figure 1). The first step is oxidation. In our case, 4.1 g of CNTs were put into 200 ml distilled water and the suspension introduced into a three-necked flask placed in an oil bath. Thereafter, 200 ml of 65 % aq. nitric acid were added, thus in the 1:1 proportion. The mixture was slowly heated up to 100°C under ambient pressure and constant mixing to render a homogeneous dispersion. Helium gas was used to entrain gases formed during the reaction. The reaction took 20 hours.

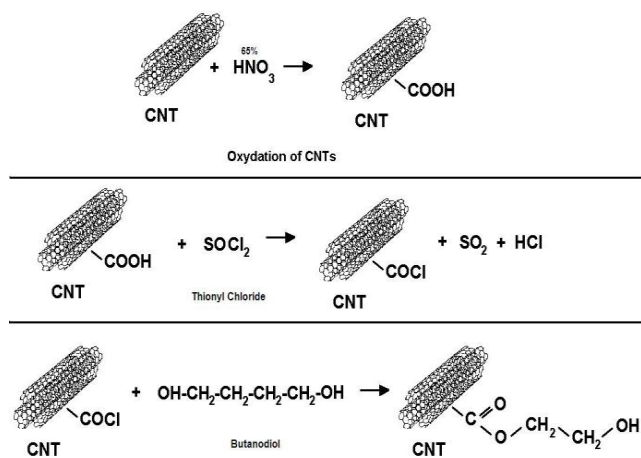


Figure 1: Reactions of functionalization of CNT

In the second stage we first turned off the heating. 300 ml of dimethyl sulfoxide and 10 ml thionyl chloride were added very slowly to the reaction mixture. The second step took 20 additional hours. Afterwards, 20 ml of N,N-dimethylformamide and 8 ml of butylene glycol were mixed together in a beaker and this composition added to

the flask (step 3). The temperature was maintained around 80°C and then our mixture was left for 24 hours. After functionalization we have washed carbon nanotubes in a suction flask with N,N-dimethylformamide until pH ≈ 7 was reached. The expected result was butanediol grafted on the surfaces of the CNTs.

2.3 Reaction of functionalized CNTs with PBT/PTMO copolymers

As described in [1], one can create block copoly(ether-b-ester)s based on hard segments of poly(butylene terephthalate) (PBT) and soft segments of poly(tetramethylene oxide) (PTMO). Such block copolymers were treated with varying amounts of functionalized single walls carbon nanotubes (SWCNTs-OH) in a two-stage process: transesterification and polycondensation. Transesterification: DMT, BD, SWCNTs-OH (were dispersed in BD) and catalyst were poured into reactor and mixed (90 rpm) at 175°C under normal pressure. The second step was polycondensation when liquid oxytetramethylene and a stabilizer were added (250°C, 40 rpm). Then the pressure was reduced to 50 Pa. These processes result in formation of two by-products: methanol (transesterification) and butylene glycol (polycondensation).

2.4 Characterization techniques

Tensile tests were conducted on a Zwick universal testing machine. Applied rate was 25 mm/min while the starting clamp distance was 32 mm. Young's module were calculated for the elongation range between 0.05 - 0.25 % at a constant crosshead rate of 25 mm/min. Three tests have been made for each kind of samples; we report averages here.

DMA testing was performed using a PerkinElmer DMA7 machine. Specimens were analyzed in rectangular form using a three point bending fixture in the temperature T scan mode from 25°C to 100°C at the heating rate of 5 K/minute. The frequency applied was 1.0 Hz. We have recorded the storage (solid-like) modulus E', the loss (liquid like) modulus E'' and $\tan \delta = E''/E'$.

Scratch tests were carried out on tensile test specimens using a CSM micro-scratch tester with a conical diamond indenter (200 mm diameter and 120° cone angle) following the procedure described in review articles [32, 33]. Both single scratches and sliding wear testing (= 15 scratches along the same groove) were performed under the following conditions: normal load 5.0, 10.0, 15.0 and 20.0 N; scratch length 5.0 mm, 5.0 mm/minute scratch speed at room temperature (25°C). For each test, the instantaneous penetration depth R_p and the residual depth R_r after healing were recorded.

3 TENSILE AND CYCLIC STRESSING RESULTS

Results of mechanical testing for pure PBT/PTMO and for nanohybrids with varying amounts of fSWCNTs are presented in Table 1. We found for pure copolymer E = 83

MPa, for 0.1 % CNTs we have E = 96.4 MPa, for 0.2 % CNTs is E = 97.5 MPa. For this last composition there is a maximum, at higher CNTs concentrations the modulus decreases – but it is still higher than for the neat copolymer. Among nanohybrids the lowest E = 87 MPa is seen for 0.5 wt. % CNTs, only 4 MPa higher than for pure copolymer. The highest stress at break σ_b is for the neat copolymer, ≈ 35 MPa. It is about 16 % higher than for our nanocomposites. By contrast, the strain at break ϵ_s is larger for nanohybrids than for the neat copolymer. The elongation at break is the highest for PBT/PTMO with 0.3 % fSWCNTs and has the value of 768 % that is more than 170 % higher than for the neat copolymer. Thus, functionalized CNTs in nanohybrids provide a plasticization effect.

We have also performed repetitive or cyclic tensile stressing tests. In general, multiple loading provides results similar to and confirming those from one time tensile testing.

Material	Young's Modulus E[MPa]	Stress at break σ_b [MPa]	Strain at break ϵ_b [%]
PBT/PTMO	83.0	34.8	596
PBT/PTMO + 0.1 wt. % fSWCNTs	96.4	30.1	697
PBT/PTMO + 0.2 wt. % fSWCNTs	97.5	31.0	719
PBT/PTMO + 0.3 wt. % fSWCNTs	86.8	30.6	768
PBT/PTMO + 0.5 wt. % fSWCNTs	87.0	29.6	683

Table 1: Tensile properties of PBT/PTMO block copolymers

However, we see that each loading cycle results in lowering the tensile modulus. Brittleness B of materials is defined [35] as:

$$B = \frac{1}{E' \cdot \epsilon_b} \quad (1)$$

Thus, B takes into account repetitive loading (fatigue in service) as well as one-time large deformation. We present B values for our materials in Table 2. We see that brittleness of PBT/PTMO decreased after addition of 0.1 wt. % fSWCNTs. We have B = 1.34 E-05 for the former and 1.10 E-05 for the latter. Clearly addition of fSWCNTs particles to the PBT/PTMO matrix decreases the brittleness. Overall, lowest brittleness was found for the simple containing 0.3 wt. % filler.

Material	Viscoelastic recovery at 20N load f[%]	Storage Modulus at 25°C E'[Pa]	Brittleness B
PBT/PTMO	90	90	1.34 E-05
PBT/PTMO + 0.1 wt. % fSWCNTs	94.9	130.7	1.10 E-05
PBT/PTMO + 0.2 wt. % fSWCNTs	95.4	139.9	0.99 E-05
PBT/PTMO + 0.3 wt. % fSWCNTs	95.2	142.7	0.91 E-05
PBT/PTMO + 0.5 wt. % fSWCNTs	96	142.2	1.03 E-05

Table 2: Brittleness and viscoelastic recovery results

4 SCRATCH TESTING AND SLIDING WEAR RESULTS

We show in Figure 2 sliding wear as a penetration depth R_p and residual (healing) depth R_h results for the load of 20 N. Results for other loads are omitted for brevity.

All the composites show the low penetration and residual depths compared to neat polymers. Furthermore, we see in Figure 1 that strain hardening in sliding wear discovered before [34] takes place in these materials also. Most polymers and polymer-based composites investigated so far exhibit this phenomenon. Polystyrene does not, a fact that has led to the definition of brittleness of materials [35].

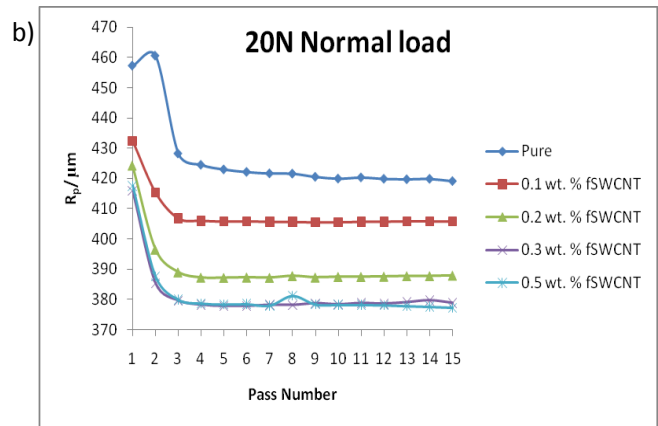
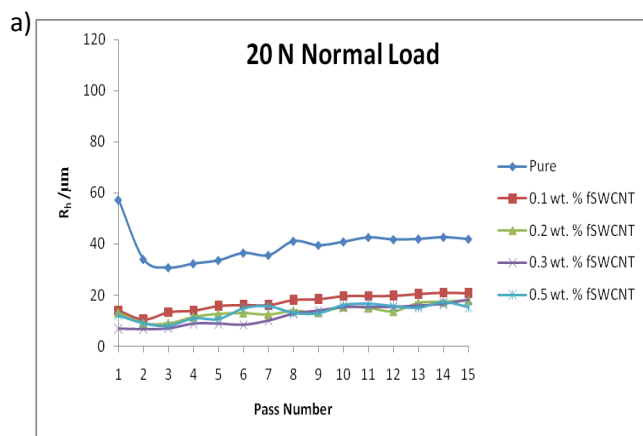


Figure 2: Sliding wear as (a) penetration depths (R_p) and (b) residual (healing) depths (R_h)

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