

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.

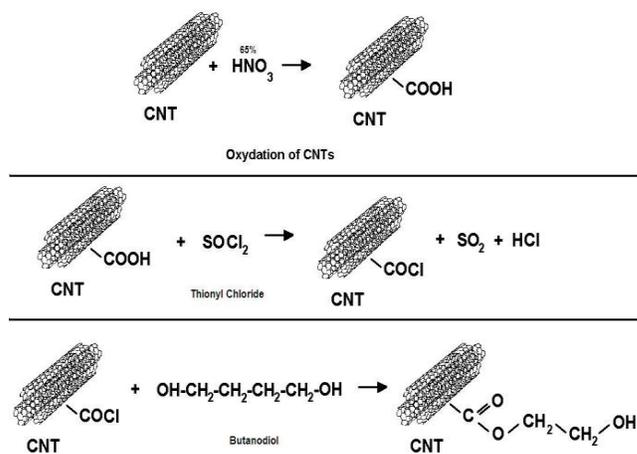


Figure 1: Reactions of functionalization of CNT

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 $B = 1.34 \text{ E-}05$ for the former and $1.10 \text{ E-}05$ 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].

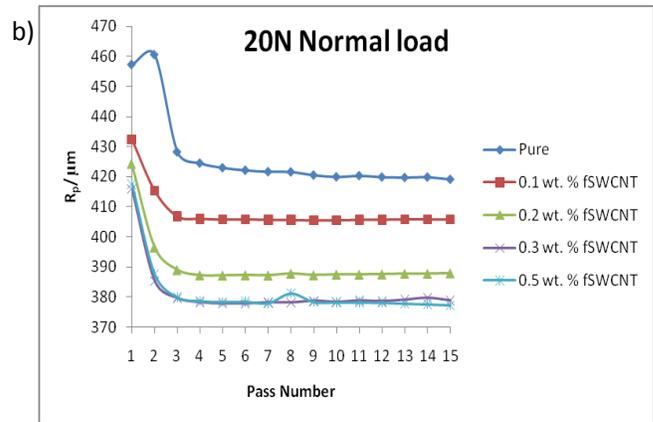
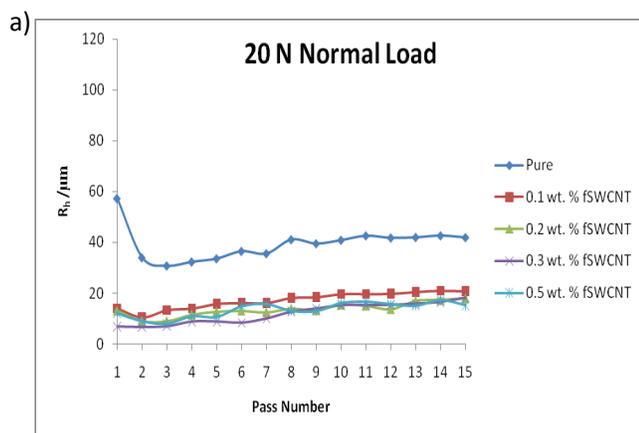


Figure 2: Sliding wear as (a) penetration depths (R_p) and (b) residual (healing) depths (R_h)

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REFERENCES

- [1] G. Broza, K. Schulte "Orientation Behavior in Axial Tension of Half-Melt Poly(ether-b-ester) Copolymers" in Block Copolymers, editors F. J. Baltá Calleja & Z. Roslaniec, Chapter 15: 407-434 (2000).
- [2] Rabello, M.: Aditivacão de Polimeros, Artliber, São Paulo (2000).
- [3] S. Varghese, J. Karger-Kocsis & K.G. Gatos, "Melt compounded epoxidized natural rubber/layered silicate nanocomposites: structure-properties relationships", Polymer 2003, 44, 3977-3983.
- [4] K.G. Gatos, R. Thomann, J. Karger-Kocsis "Characteristics of ethylene propylene diene monomer rubber/organoclay nanocomposites resulting from different processing conditions and formulations", Polymer Internat. 53, 1191-1197 (2004).
- [5] D.S. dos Santos Jr., P.J.G. Goulet, N.P.W. Pieczonka, O.N. Oliveira Jr. and J.R. Aroca, "Gold Nanoparticle Embedded, Self-Sustained Chitosan Films as Substrates for Surface-Enhanced Raman Scattering", Langmuir 20, 10273-10277 (2004).
- [6] W. Brostow, M. Keselman, I. Mironi-Harpaz, M. Narkis & R. Peirce, "Effects of carbon black on tribology of blends of poly(vinylidene fluoride) with irradiated and non-irradiated ultrahigh molecular weight polyethylene", Polymer, 46, 5058 (2005)
- [7] W.S. Chow, Z.A. Mohd Ishar, J. Karger-Kocsis, "An Atomic Force Microscopy Study On The Blend Morphology And Clay Dispersion In Polyamide-6 Polypropylene/Organoclay System", J. Polymer Sci. B 43, 1198-1204 (2005).

- [8] W. Brostow, B.P.Gorman, O. Olea-Mejia, "Focused ion beam milling and scanning electron microscopy characterization of polymer + metal hybrids", *Materials Letters* 61, 1333–1336 (2007)
- [9] K.G. Gatos, K. Kameo, J. Karger-Kocsis, "On the friction and sliding wear of rubber/layered silicate nanocomposites", *Express Polymer Letters* 1, 27-31 (2007). DOI: 10.1016/j.matlet.2006.07.026
- [10] W. Brostow, A. Buchman, E. Buchman, O. Olea-Mejia, "Microhybrids of metal powder incorporated in polymeric matrices: Friction, mechanical behavior, and microstructure", *Polymer Engineering and Science*, 48, 1977–1981 (2008). DOI: 10.1002/pen.21119
- [11] J. Karger-Kocsis, P.P. Shang, Z.A. Mohd Ishak, M. Rösch, "Melting and crystallization of in-situ polymerized cyclic butylene terephthalates with and without organoclay: a modulated DSC study", *Express Polymer Letters* 1, 60-68 (2007).
- [12] A. Pegoretti, A. Dorigato, A. Penati, "Tensile mechanical response of polyethylene-clay nanocomposites", *Express Polymer Letters* 1, 123-131 (2007).
- [13] W. Brostow, T. Datashvili & K.P. Hackenberg, "Synthesis and characterization of poly(methyl acrylate) + SiO₂ hybrids", *e-Polymers* 2008, no. 054.
- [14] F. J. Carrión, A. Arribas, M.-D. Bermúdez, A. Guillaumon, "Physical and tribological properties of a new polycarbonate-organoclay nanocomposites" *European Polymer Journal*, 44, 968–977 (2008). DOI: 10.1016/j.eurpolymj.2008.01.038
- [15] L.D. Perez, L.F. Giraldo, W. Brostow & B.L. Lopez, "Poly(methyl acrylate) + mesoporous silica nanohybrids: Mechanical and thermophysical properties", *e-Polymers*, no. 029 (2007).
- [16] A. Arribas, M.-D. Bermúdez, W. Brostow, F.-J. Carrión-Vilches & O. Olea-Mejia, "Scratch resistance of a polycarbonate + organoclay nanohybrid", *Express Polymer Letters* 2009, 3, 621.
- [17] W. Brostow, W. Chonkaew, T. Datashvili, K.P. Menard, "Tribological properties of epoxy + silica hybrid materials" *Journal of Nanoscience and Nanotechnology*, 9, 1916–1922 (2009). DOI: 10.1166/jnn.2009.368
- [18] O. Lourie and H.D. Wagner, "Evaluation of Young's modulus of carbon nanotubes by micro-Raman spectroscopy", *Journal of Materials Research* 13, 2418–2422 (1998)
- [19] H.D. Wagner, O. Lourie, Y. Feldman and R. Tenne, "Stress-induced fragmentation of multiwall carbon nanotubes in a polymer matrix", *Applied Physics Letters* 73, 3527–3529 (1998).
- [20] J. Sandler, M.S.P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte and A.H. Windle, "Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties" *Polymer* 40 (1999), pp. 5967–5971
- [21] Ming Su, Bo Zheng and Jie Liu "A scalable CVD method for the synthesis of single-walled carbon nanotubes with high catalyst productivity" *Chemical Physics Letters*: 322(5):321-326 (2000)
- [22] Z. Roslaniec, G. Broza, K. Schulte, "Nanocomposites based on multiblock polyester elastomers (PEE) and carbon nanotubes (CNT)", *Composite Interfaces* 10, 95-102 (2003).
- [23] A. Assouline, A. Lustiger, A.H. Barber, C.A Cooper, E. Klein, E. Wachtel, H.D Wagner, "Nucleation ability of multiwall carbon nanotubes in polypropylene composites" *Journal of Polymer Science Physics* 41, 520-527 (2003).
- [24] Y. Ando, X. Zhao, T. Sugai, M. Kumar, "Growing carbon nanotubes", *Materials Today* 7: 22-29 (2004)
- [25] G. Broza, M. Kwiatkowska, Z. Roslaniec, K. Schulte, "Processing and assessment of poly(butylene terephthalate) nanocomposites reinforced with oxidized single wall carbon nanotubes", *Polymer*:46(16):5860-5867 (2005)
- [26] X. -L. Xie, Y. -W. Mai, X.-P. Zhou, "Dispersion and alignment of carbon nanotubes in polymer matrix", *Materials Science and Engineering Reports* 49: 89-112 (2005).
- [27] F. H. Gojny "Evaluation of the potential of carbon nanotubes as nano-structured modification of (glass-fibre reinforced) epoxy – based composites", *Dissertation, Technische Universität Hamburg*, Chapter 3: 17-51 (2006)
- [28] L.F. Giraldo, W. Brostow, E. Devaux, B.L. López, L.D. Pérez, D. León, "Scratch and wear resistance of Polyamide 6 reinforced with multiwall carbon nanotubes", *Journal of Nanoscience and Nanotechnology*, 8, 3176–3183 (2008). DOI: 10.1166/jnn.2008.092
- [29] L.F. Giraldo, B.L. López, W. Brostow, "Effects of the type of carbon nanotubes on tribological properties of Polyamide 6", *Polymer Engineering and Science*, 49, 896–902 (2009). DOI: 10.1002/pen.21386
- [30] A. Kopczyńska and G.W. Ehrenstein, "Polymeric surfaces and their true surface tension in solids and melts" *J. Mater. Ed.*, 29, 325-340 (2007)
- [31] P. Blaszczyk, W. Brostow, T. Datashvili & H.E. Hagg Lobland, "Rheology of low-density polyethylene + Boehmite composites", *Polymer Composites*, 31, 1909 (2010).
- [32] W. Brostow, J.-L. Deborde, M. Jaklewicz, and P. Olszynski, "Tribology with emphasis on polymers: Friction, scratch resistance and wear", *J. Mater. Ed.* 25, 119 (2003).
- [33] W. Brostow, V. Kovacevic, D. Vrsaljko & J. Whitworth, "Tribology of polymers and polymer-based composites", *J. Mater. Ed.*, 32, 273 (2010).
- [34] W. Brostow, G. Damarla, J. Howe & D. Pietkiewicz, "Determination of wear of surfaces by scratch testing", *e-Polymers*, no. 025(2004)
- [35] W. Brostow, H.E. Hagg Lobland & M. Narkis, "Sliding wear, viscoelasticity and brittleness of polymers", *J. Mater. Res.* 21, 2422 (2006).