THE IN-SITU SYNTHESIS OF POLYBUTYLENE TEREPHTHALATE / CARBON NANOTUBES COMPOSITES

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Abstract Composites containing different kinds of carbon nanotubes (CNTs) in poly(butylene terephthalate) (PBT) thermoplastic matrix have been studied. For preparation of composite materials the *in situ* synthesis method was employed, i.e. CNTs were introduced into polymer matrix during its synthesis. The effectiveness of the method in providing nanofiller's homogenous distribution in composite system as well as the influence of different kinds of CNTs on polymer properties have been investigated. The microscopic analysis of nanocomposite samples fractures by SEM confirmed good dispersion of nanotubes, but the presence of agglomerates was also stated. Thermal analysis (DSC, DMTA) and mechanical testing of composite materials revealed changes in the structure and physical properties of PBT compared to unfilled polymer.

1. INTRODUCTION

In recent years polymer composites have become a great challenge for scientists to create new quality of polymer systems with novel and enhanced physical and chemical properties.

Carbon nanotubes (CNTs) constitute the promising group of materials for special applications due to their unique 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 filler surface by polymer and its homogenous dispersion in polymer system have to be ensured in order to obtain a maximum effect of reinforcement in composites [8]. In the case of CNT, strong Van der Waals' interections among individual nanotubes and their entangled forms being the result of synthesis process lead to formation of agglomerated structures and, in turn, make uniform dispersion difficult to produce. The modification of nanofiller surface by attaching reactive groups or short polymer chians capable of physical or chemical bonding with polymer matrix can be good way to facilitate the composite preparation [9-10].

Both thermoplastic and thermosetting polymers are applied as a matrix in preparation of CNT based nanocomposites, however, a rising importance of thermoplastics is observed (usually PMMA, PC, PP, PA, *etc*.) owing to an easy processability and good

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physical properties. Most composites with thermoplastic matrix are obtained in melt processing, where carbon nanotubes are mechanically dispersed in a polymer in molten state using high shear methods (e.g. twin screw extrusion) [5,11-13]. An alternative for these methods could be the preparation of composites by introducing CNT into polymer during its synthesis (the *in situ* method) [14,15]. Dispersing nanotubes in liquid substrate and subsequent continuous stirring of the system during the chemical reaction seems to be a good way for homogenous distribution of nanofiller in the whole polymer system.

In this paper the '*in situ*' polycondensation as a method of polymer nanocomposites preparation as well as the effect of carbon nanotubes on the properties of poly(butylene terephthalate) (PBT) thermoplastic matrix are presented. Previous results concerning the investigations of oSWCNT/PBT 'in situ' nanocomposites have been described in [16,17]. Here we have compiled the results of adding three various kinds of CNTs (oSWCNT, MWCNT, and MWCNT-NH$_2$) to compare the changes in PBT properties. Thermal characterization of nanocomposites was performed by means of DSC and DMTA analysis, the structure and state of CNT dispersion - by electron microscopy (SEM), and mechanical properties were investigated in tensile tests.

2. EXPERIMENTAL

Materials

The following kinds of CNTs were applied to prepare polymer nanocomposites :

1) multi-walled carbon nanotubes (MWCNT) supplied by Nanocyl S.A., Belgium with characteristic dimensions: diameter $d \approx 10$ nm, length l - 50 μm, purity > 95 wt.%.

2) multi-walled carbon nanotubes with amine groups (MWCNT-NH$_2$) with the same parameters.

3) oxidized single-walled carbon nanotubes (oSWCNT) supplied by CNI Technology Co., Texas, USA, with characteristic dimensions: diameter 0.7 ÷ 1.2 nm and length of few μm.

Commercially available reagents for polymer synthesis were purchased as follows: dimethyl terephthalate (DMT) from Elana S.A., Torun, Poland, 1,4 – butanediol (BD) from BASF, Germany, tetrabuty orthotitanate as a catalyst from Sigma-Aldrich, Poland and Irganox 1010 as a stabilizer from Ciba, Switzerland. Before the synthesis BD was distilled in 229 °C to eliminate present contaminants.

Nanocomposites preparation

Investigated nanocomposites were obtained by polycondensation in molten state. In the first step of the process, an appropriate amount of CNT was dispersed in BD using two mixing tools alternately: ultrasound (Homogenisator HD 2200, Sonoplus) and ultra-high speed (Ultra-Turrax T 25) stirrers. The complete time of dispersing amounted to 30 min. As-prepared CNT dispersion together with DMT and the catalyst was introduced into the steel polycondensation reactor (Autoclave Eng. Inc., USA) equipped with horseshoe stirrer, controlled heating system, stirrer torque measurement, and vacuum pomp. When the synthesis finished, the molten composite was extruded from reactor as filament directly into a cooling bath. All composites were granulated and dried before processing. In presented investigations the nanocomposites containing 0.2 wt.% of MWCNT, MWCNT-NH$_2$, and oSWCNT were included. The samples of neat PBT were synthesized as a reference.

Investigations

The samples for mechanical testing were injection moulded using Baby Plast Model 6/10 (Cronoplast S.L. Comp.) injection machine into test specimens according to EN ISO 294. Static tensile tests were conducted on tensile test machine Zwick 1474 (Zwick GmbH, Germany) with crosshead speed of 5 mm/min. The differential scanning calorimetry (DSC) (Seico Instruments, Japan) was employed for thermal analysis of composite materials. Non-isothermal crystallization analysis was performed according to standard procedure: temperature range from –50 to 260 °C for heating and cooling with a scan rate 10 °C/min. The percent of crystallinity X_c of investigated composites was determined basing on DSC measurements by Eq (1).

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} 100\% \, , \qquad (1)$$

where: ΔH_m – melting enthalpy of sample [J/g]; ΔH_m^0=141 [J/g] – theoretical value of enthalpy for 100% crystalline PBT homopolymer (31 kJ/mol) [18].

Dynamic mechanical properties of PBT/CNT composites were determined in tension mode using DMTA analyzer (Qualimeter EXPLEOR 500N, Gabo Comp., Germany). The measurements were performed at frequency of 10 Hz in the temperature range from -120 to +180 °C with a ramp of 3 °C/min.

Table 1. Characteristic physical properties of PBT/CNT nanocomposites.

Sample	T_g [^{0}C]	T_m [^{0}C]	T_c [^{0}C]	d [g/cm^3]	ΔH_m [J/g]	X_c [%]
neat PBT[*]	70	226	187	1.26	49	35
PBT/0.2wt.% MWCNT	70	227	204	1.31	56	40
PBT/0.2wt.% MWCNT-NH$_2$	69	227	202	1.30	62	44
PBT/0.2wt.% oSWCNT	66	223	200	1.31	49	35

Note: T_g – glass transition temperature (DMTA), T_m – melting point in 2nd heating, T_c – crystallization maximum peak, d – density, ΔH_m – melting enthalpy, X_c – percent of crystallinity.
[*] The values for homopolymer can differ from [16] due to using samples from new series.

The morphology of composites was characterized using scanning electron microscopy (SEM) (LEO 1530, Leo Electron Microscopy Ltd., UK) on cryogenic fractured surfaces of samples. A very thin layer of gold was sputtered the scanned surfaces in order to facilitate the microscopic observations.

3. RESULTS AND DISSCUSION

The *in situ* polycondensation seems to be a promising method to fabricate polymer/CNT composites in industrial scale. However, dispergation of CNT in a liquid substrate is the crucial issue in obtaining a homogenous distribution of nanotubes in the whole composite system. In the case of PBT/CNT, nanotubes were sonicated and mechanically mixed in 1,4– butanediol to break up existed agglomerates and suspend the CNT powder. The increase of mixture's temperature, induced by friction forces, facilitated mixing. The whole operation was performed just before the synthesis to prevent CNT sedimentation. The whole process of PBT nanocomposites synthesis was described in details in [16], all conditions and parameters were determined experimentally. The presence of carbon nanotubes in reactive mixture had a slight influence on the reaction of polymer chains growth, which proceeded slower compared to 'neat' polymer, what was affirmed by slower increase of reactive mixture viscosity (stirrer torque). However, no differences in the polycondensation course were observed depending on the kind of applied nanotubes.

The effect of different kinds of carbon nanotubes on the crystallization of PBT was analyzed by non-isothermal DSC measurements. As it was described in numerous papers [11,19], the presence of CNT in polymer system has a relevant influence on its ability to form a crystalline phase. Nanoparticles distributed in polymer matrix assist nucleation and growth of crystallites. Similar phenomena is observed in a case of PBT/CNT nanocomposites. Table 1 presents the values of characteristic parameters: glass transition temperature T_g, melting point T_m, crystallization temperature T_c, melting enthalpy ΔH_m and percent of composites crystallinity X_c, determined according to DSC and DMTA tests. Detailed DSC curves (Fig. 1) perform crystallization and melting courses of specimens containing MWCNT, MWCNT-NH$_2$, and oSWCNT during cooling and heating processes respectively. Analyzing the cooling thermograms of composites materials (Fig. 1a), a distinct shift of exothermic effects toward higher temperatures (in the range of 12 to 17 °C) is observed in comparison with neat PBT. This phenomena is characteristic for all investigated composite samples and it could suggest that the interactions between nanofiller and polymer matrix occur. The melting thermograms (Fig. 1b) show that there is no influence of nanotubes presence on melting points T_m of materials and the difference of 1 – 3 °C between peak's maximums are contained in the measuring effort range. Relevant differences, however, can be recognized in the widths of thermal effects connected with melting of nanocomposites crystalline phase
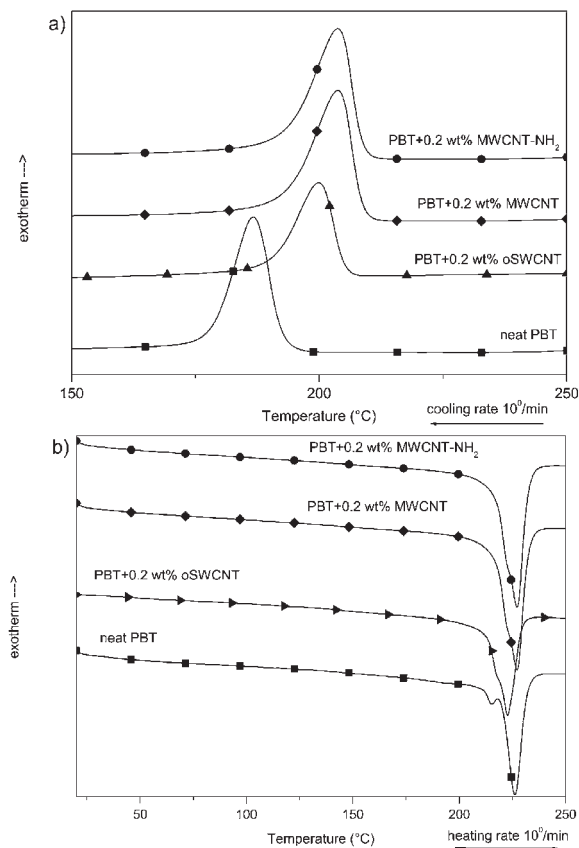
Fig. 1. DSC thermal analysis: a) crystallization process during cooling, b) polymer melting during heating.

Fig. 2. Dynamic mechanical properties of PBT and PBT/CNT composites: a) dynamic storage modulus E', b) tanδ.

in comparison with PBT homopolymer. It is particularly evident in the values of ΔH_m, which rise in the presence of MWCNT and the highest values were achieved for MWCNT-NH$_2$. Such phenomena happen if the amount of crystalline phase in composites increases. It is confirmed by the calculated percent of crystallinity values X_c (Table 1), however, the crystals are more defected or the distribution of their size is brother than that in unfilled PBT. Such dependence is not observed for the addition of oSWCNT. The sizes of individual nanotubes are probably under the critical size of crystal nucleuses; therefore, they can not act as active centers of crystals growth.

The addition of CNT affects the dynamic mechanical properties of polymer, what was proved by DMTA analysis (Fig. 2). The presence of both single- and multi-walled nanotubes induced an increase of
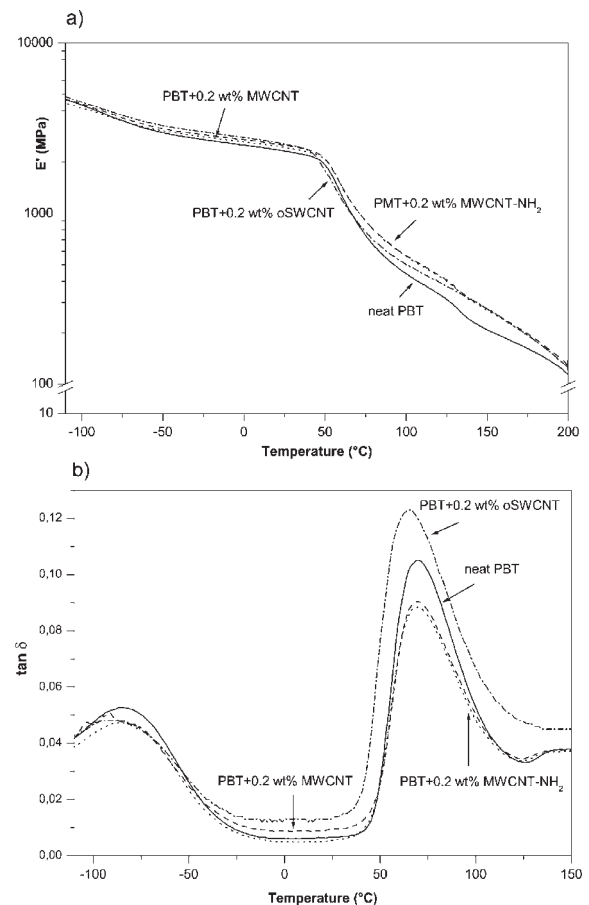
storage modulus E' slightly under T_g and visibly above. Probably, it results from the variations in molecular mobility of polymer chains connected with the addition of nanofiller as well as the stiffening effect of CNT. The thermograms of tanδ show that there is no significant influence of nanotubes on T_g values regardless of the kind, but the differences in tanδ peaks magnitude are visible. Composite containing oSWCNT reveals much higher peak than neat PBT, whilst tanδ maximum peaks of composites containing MWCNTs are inferior. The decrease of this value can be the result of restricted molecular mobility related to the presence of MWCNT. However, in the case of oSWCNT, which sizes are smaller and thermal conductivity high, the increase of peak magnitude could result from better ability of composite to heat distribution [20].
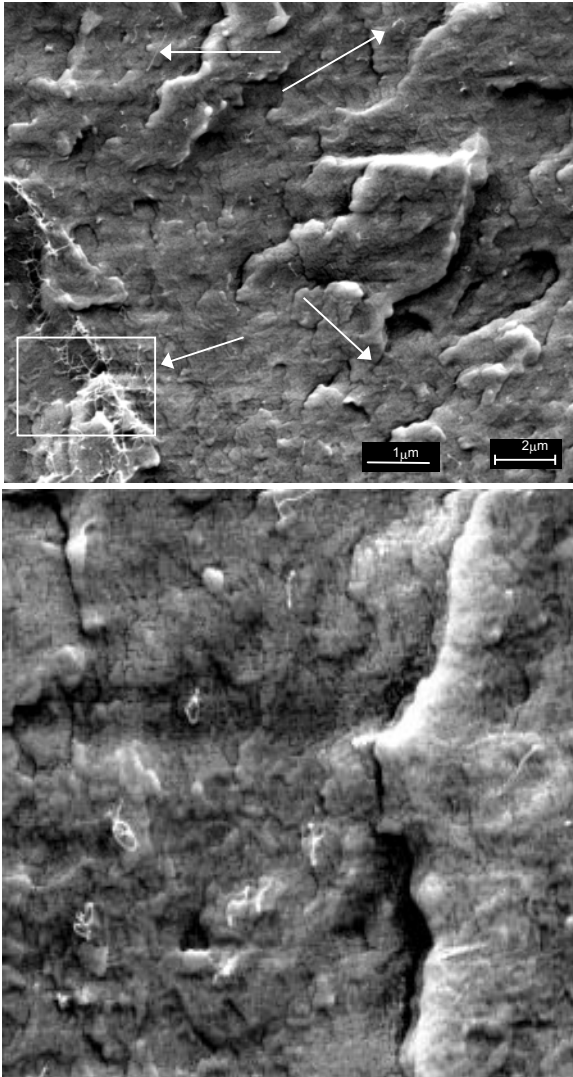
Fig. 4. PBT / CNT nanocomposites stress – strain curves.

Fig. 3. SEM micrographs of fracture surface of PBT / 0.2 wt.% of CNT.

Microscopic investigations of PBT/CNT nanocomposites confirm rather homogenous distribution of CNT in polymer matrix (Fig. 3). Some individual nanotubes, apparently pulled out from the matrix during fracturing, can be distinguished. However, the places with highly entangled nanotubes can be also observed. The presence of such agglomerated forms is of great importance in forming conducting paths, but, on the other hand, such cage–like nanotube structures, could close small amounts of glycol inside during dispergation of CNT
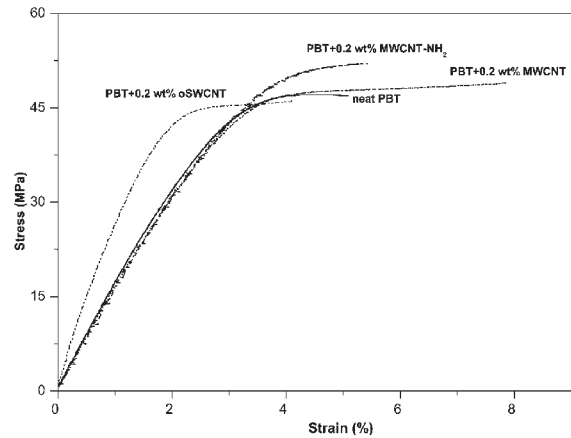
in BD; so it would not be able to react with other reagents. As a consequence, the presence of such places in the composite system could result in weakening of material and reducing its practical properties.

Mechanical properties of PBT/CNT nanocomposites characterized in static tensile tests are presented in Fig. 4. Analyzing the stress-strain curves, one can see that the elastic modulus is practically unchanged in the case of samples containing MWCNT and MWCNT-NH$_2$, while a distinct increase of this parameter with a decrease of tensile strength is observed in a presence of oSWCNT. In order to explain such phenomena, it is essential to add that the polycondensation reaction was carried out up to the definite viscosity of reactive mixture (in definite temperature) controlled by the stirrer torque. Single-walled carbon nanotubes, due to their size, reveal higher developed surface compared with multi-walled nanotubes. Therefore, the boundary surface between polymer matrix and nanofiller tubes is larger and that could be a reason of modulus increase. On the other side, the same phenomena causes the increase of polymer composite viscosity; thus, when the reaction was finished, the molecular weight of oSWCNT containing polymer might have been lower compared with PBT/MWCNT. This could be a reason why the tensile strength of composite falls compared with PBT homopolymer.

4. CONCLUSION

Poly(butylene terephthalate) based nanocomposites containing three kinds of carbon nanotubes: MWCNT, MWCNT-NH$_2$, and oSWCNT were investigated. All composites were obtained via *in situ* polycondesation method, i.e. introducing nanofiller into polymer during its synthesis. The study of composite structure confirm the effectiveness of the method as a good way to ensure the homogenous CNT distribution, nevertheless further work on the way of nanotubes dispergation in glycol is required in order to eliminate existing aggregates and agglomerates. Microscopic investigations reveal also some nanotubes pulled out from the matrix during making a fracture. It proves rather weak interfacial bonding, not sufficient to transfer the load from matrix to nanotubes and could be the reason of rather slight increase of mechanical properties.

Thermal analysis (DSC) reveals that the presence of all applied kinds of CNT in polymer enhances the nucleation process and MWCNTs affect the increase of amount of crystalline phase. The addition of CNT also gives rise to the increase of dynamic elastic modulus; while the glass transition temperature T_g remains similar to that for neat PBT. Mechanical tests reveal only slight increase of maximal tensile stress in the case of multi-walled nanotubes and practically negligible influence on elastic modulus, whilst the addition of oSWCNT significantly improves it.

Using two kinds of MWCNT (modified and unmodified) in this examination, we expect significant differences in nanocomposites properties resulting from the presence of reactive amine groups. However, the results for both kinds of CNT are similar. There is not an unequivocal information about the concentration of functional groups in supplied nanopowder. Thus, it is possible that the effect of CNT modification was not sufficient to improve the strength of interactions nanofiller – polymer matrix.

ACKNOWLEDGEMENTS

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