

## Nanocomposites Based on Polybutylene Terephthalate Synthesized from Cyclic Oligomers of Butylene Terephthalate and Multiwalled Carbon Nanotubes

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The paper describes the structure and electric properties of nanocomposites based on polybutylene terephthalate (PBT) filled by multiwalled carbon nanotubes (MWCNTs). Cyclic butylene terephthalate oligomers with low melt viscosity were used for PBT/MWCNTs nanocomposites synthesis to reach better dispersion of MWCNTs. The dependence of electrical conductivity of nanocomposites on processing methods was established as well as electrical percolation threshold for PBT/MWCNTs was determined as 0.22 wt. % of MWCNTs.

**Keywords:** Polymer nanocomposites, Carbon nanotubes, Cyclic oligomers, Percolation threshold, SEM, TEM.

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### 1. INTRODUCTION

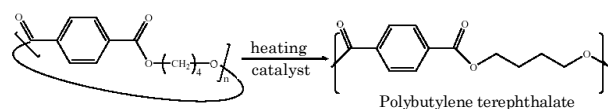
Carbon nanotubes (CNTs) are widely used as filler of polymers due to the possibility to achieve such properties as high thermal stability and mechanical indices, electrical and thermal conduction that is associated, first of all, with the CNTs structural features [1, 2].

The basic methods of formation of polymer CNTs-containing nanocomposites are the following: dispersion of the solvent; dispersion of CNTs in the monomer solution with further polymerization of the latter, i.e. the in situ polymerization method. Both methods usually require expensive and toxic solvents as well as complex technological equipment.

However, the third method consisting in the use of the polymer melt can be applied for thermoplastics. It is obvious that the use of the polymer melt is more reasonable in industrial environments, but this method is less efficient on the stage of the CNTs dispersion. An alternative technique for obtaining thermoplastics/CNTs nanocomposites of the composition is the synthesis of the polymer component of the nanocomposite from low-viscosity oligomers, for example, recently synthesized alkyl phthalate cyclic oligomers, such as oligomers of cyclic ethylene terephthalate (CET) and cyclic butylene terephthalate (CBT) [2-6] which are technologically easily converted to high-molecular linear thermoplastic polymers – polyethylene terephthalate (cPET) or polybutylene terephthalate (cPBT). Such macrocyclic oligomers have several important advantages, in particular, low viscosity (similar to water), ability to fast polymerization with the formation of high-molecular polymers (Fig. 1) and ability to process as thermosetting resins.

A special attention is devoted to PBT which (among the known thermoplastic polyester resins) is most often used as the raw material for injection molding of the products such as parts of cars, electrical and electronic devices that is conditioned by easiness of the formation

process as well as excellent mechanical properties, thermal and chemical stability and other physical and chemical properties of PBT [4].



**Fig. 1** – Scheme of polymerization of cyclic butylene terephthalate (CBT) oligomers and formation of polybutylene terephthalate (cPBT) [2]

Several works [7-11] have been published up to now on synthesis and characterization of cPBT/CNTs nanocomposites, where PBT was synthesized from CBT; and few works are devoted to obtaining PBT/CNTs based on industrial PBT [12-19]. The authors of the specified papers have studied some electrical, thermal and physical-chemical properties of the obtained nanocomposites.

Since data on the study of electrical properties of nanocomposites based on CBT as well as their dependences on the structure of polymer nanocomposites obtained by different techniques is currently absent, the aim of the present work was to establish the structure-electrical properties relationships.

### 2. EXPERIMENTAL

CBT oligomers with the degree of oligomerization of  $n = 2-5$ , which were granted by the Cyclics Corp. (USA) (trade mark CBT 160), were used as the initial oligomers for the synthesis of cPBT. CBT is white crystal granules with the CBT melting temperature ( $T_m$ ) of  $\sim 413$  K and viscosity ( $\eta$ ) of  $\sim 20$  mPa·s (at  $T_m$ ). According to the information of the manufacturer, CBT granules contained of 0.5 wt. % of tin dihydroxy butyl chloride catalyst (trade mark Fascat 4101) which catalyzes the cPBT synthesis process by the coordination and ligand exchange mechanism. Multiwalled carbon nanotubes (MWCNTs) of the trade mark C100 granted by the Arkema Comp. (France)

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are obtained by the chemical deposition method from the gaseous phase. MWCNTs were applied in this work as nano-filler and represented a crumbly black powder. All the above specified chemical substances were used without additional purification. Before synthesis CBT was vacuumized during 12 hours at  $T \approx 353$  K for the moisture removal. Nanocomposites were obtained by the reactive extrusion method, namely, in situ cPBT synthesis from CBT oligomers in the presence of MWCNTs. Dispersion of MWCNTs and in situ synthesis of the nanocomposites samples were directly carried out in the laboratory twin screw extruder DSM 15 (DSM Research Comp., Netherlands) at the following conditions: temperature was equal to  $T \approx 503$  K, screw rotation speed – 100 rpm, dispersion time of MWCNTs in CBT and cPBT synthesis time –  $10 \div 15$  min. After synthesis nanocomposite samples were formed by several methods for further investigations: 1) were obtained in the form of the strands from extruder; 2) films and plates were formed using, respectively, hot pressing of extrusion strand or injection molding.

cPBT/MWCNTs nanocomposites with the content of MWCNTs (wt. %) of 0.01; 0.05; 0.10; 0.30; 0.50; 1.00, and 2.00 were synthesized.

### 3. RESULTS AND DISCUSSION

It is known that electron microscopy is one of the main methods for nanomaterials research, since it allows to directly see the nano-objects studied. For example, discovery of CNTs became possible due to application of the transmission electron microscopy (TEM) method [20]. We have studied by TEM the MWCNTs used in the work and established that the external diameter of MWCNTs was  $D \approx 10 \div 17$  nm, internal diameter –  $D_i \approx 4 \div 7$  nm and nanotubes length –  $L \approx 0.1 \div 10$   $\mu\text{m}$  and so  $L/D \sim 6 \div 1000$  (see Fig. 2).

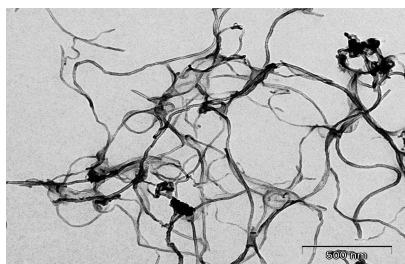


Fig. 2 – TEM micrograph of the MWCNTs used

Surface morphology and structure of the obtained cPBT/MWCNTs nanocomposites with different content of nanotubes were studied by scanning and transmission electron microscopy methods (SEM and TEM, respectively). It is seen from the micrographs (Fig. 3, 4) that MWCNTs are effectively dispersed and CNTs are located over the whole sample surface (SEM method, Fig. 3) in all the nanocomposites obtained. At that, it is possible to see both the separate nanotubes (light filamentous inclusions) and the CNTs ends (light round dots) wrapped in a polymer layer.

This is confirmed by the investigations of the external diameter of the nanotubes in the samples of the given nanocomposites using the Image J program. It is established that the nanotubes diameter in the nanocomposites samples is  $\sim 5 \div 25$  nm larger than the diameter of

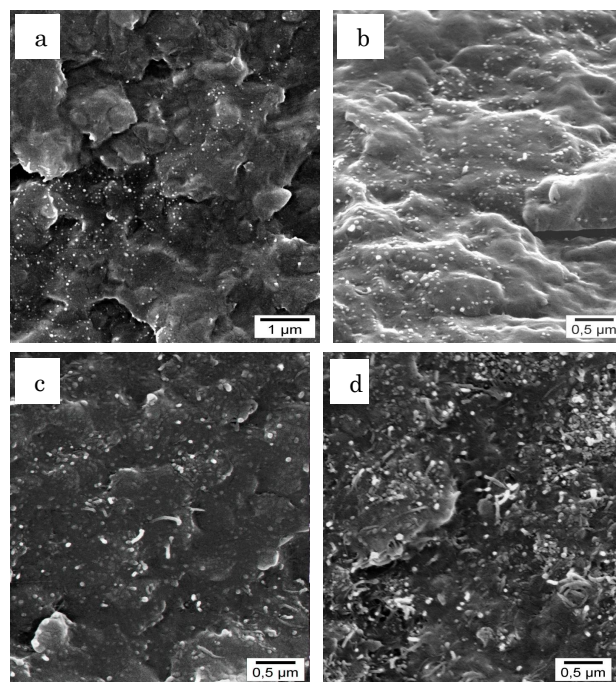


Fig. 3 – SEM micrographs of cPBT/MWCNTs nanocomposites (the samples are obtained by the extrusion strand hot pressing) with different MWCNTs content, wt. %: a – 0.1; b – 0.3; c – 1.0, and d – 2.0

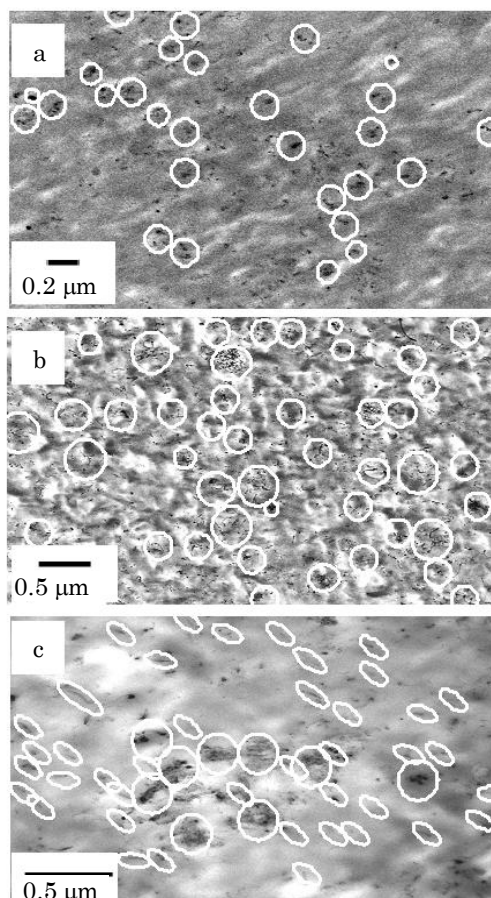


Fig. 4 – TEM micrographs of cPBT/MWCNTs nanocomposites (2 wt. % of MWCNTs) obtained by different methods: a – extrusion strand; b – hot pressing of extrusion strand; c – injection molding; aggregates of CNTs are denoted by open circles (a, b), oriented CNTs – by open ellipses (c)

the initial MWCNTs. This is the known phenomenon of polymer “wrapping” of CNTs that only takes place in the systems with high adhesion between polymer matrix and CNTs [21].

In Fig. 4 we illustrate the TEM micrographs for the cPBT/MWCNTs nanocomposite samples with the filler content of 2 wt. % formed by different methods. Individual nanotubes and their aggregates are present on the micrograph of the extrusion strand sample of cPBT/MWCNTs nanocomposite. For the sample obtained by the strand hot pressing method one observes the maximum amount of MWCNTs aggregates in comparison with the sample obtained by injection molding or extrusion strand sample. This indicates re-aggregation of nanotubes during pressing as a result of the action of Van-der-Waals forces between nanotubes, increased temperature and pressure. The same phenomenon has been also fixed using the microscopy method by Alig et al. [22] for the polycarbonate/nanotubes systems during their aging at temperatures higher than the polymer matrix melting temperature (i.e., in fact, during their annealing) resulting in the processes of reverse aggregation. Orientation of individual MWCNTs or their aggregates (open ellipses), obviously, in the direction of cPBT/MWCNTs melt flow is observed in the samples formed by the injection molding method. Thus, one can conclude that by choosing the samples formation technique, it is possible to controllably adjust their morphology.

Until recently, it was considered that to achieve maximum benefits using CNTs as an effective nanofiller for high-technology nanocomposites, nanotubes should be well dispersed without aggregation [23]. Certainly, this works in the case when it is necessary to enhance mechanical properties of CNTs-containing nanocomposites. However, as noted above, it is established in recent works [22, 24] that secondary aggregation (re-aggregation) of CNTs dispersed in the polymer, which appears as a result of the action on the sample of high temperatures during synthesis or formation of polymer materials, leads to enhancement of the electrical conductivity of the composite.

For cPBT/MWCNTs nanocomposites obtained by different methods of formation we have determined their electrical conductivity, and the corresponding data are presented in Table 1. It is established that the samples formed by the hot pressing method have the highest electrical conductivity ( $\sigma \sim 6.97 \cdot 10^{-3}$ ) that is explained by the formation of three-dimensional percolation conductive network on account of re-aggregation of CNTs during the hot pressing process under the action of high temperatures and pressure.

**Table 1** – Effect of the MWCNTs on the electrical conductivity of the cPBT/MWCNTs nanocomposites (2 wt. % of CNTs) obtained by different methods

Method of sample formation	$\sigma$ , S/cm
Hot pressing	$6.97 \cdot 10^{-3}$
Extrusion strand	$3.02 \cdot 10^{-4}$
Injection molding	$2.04 \cdot 10^{-8}$

As seen from the data of Table 1, the samples formed by the injection molding method do not conduct electricity at all ( $\sigma \sim 2.04 \cdot 10^{-8}$ ) that is very unusual for nanocomposites with such a high content of CNTs (2 wt. %).

This fact can be explained by the orientation of CNTs during casting in the direction of cPBT/MWCNTs melt flow that is confirmed by the TEM data (Fig. 4c). Obviously, orientation of nanotubes prevents the formation of three-dimensional percolation conductive network that is why the given samples cannot conduct electricity.

Electrical properties of a series of samples obtained by the hot pressing method were analyzed according to the percolation theory [25] on which at a low content of the filler electrical conductivity of the material is determined by the polymer matrix [26], at a certain critical volume fraction of the electrically conductive filler percolation threshold ( $p_c$ ) is achieved, and, as a result, the value of conductivity suddenly and rapidly increases by many orders of magnitude even at a very insignificant increase in the filler content. At a nanofiller content lower than the value of  $p_c$ , there is no so-called conducting channels in the system (i.e. space percolation cluster is not formed), however, when filler content is larger than  $p_c$ , a large number of continuous conducting channels is formed resulting in the formation of the space percolation cluster and composite acquires conducting properties. Classical percolation theory predicts that conductivity ( $\sigma$ ) should be described by the exponential law in the range of concentrations higher than  $p_c$  [25]

$$\sigma = \sigma_0 (p - p_c)^t, \tag{1}$$

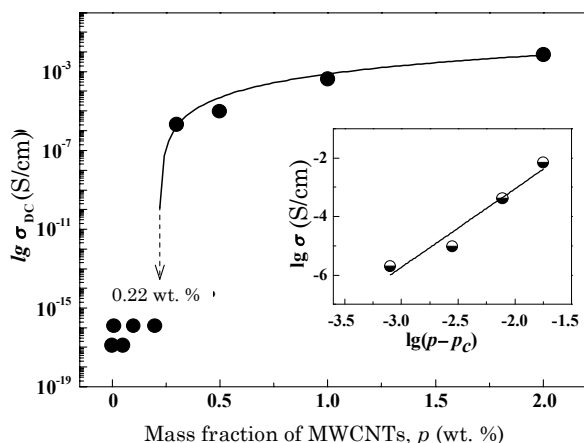
where  $\sigma_0$  is the scale factor;  $p_c$  is the percolation threshold;  $t$  is the universal exponent depending only on the system dimension and topology ( $t = 1.33$  for two-dimensional and  $t = 2.0$  for three-dimensional systems [27]).

It is known [27] that the experimental values of  $t$  described for CNTs-filled polymer nanocomposites are in the range of  $t = 0.7 \div 7.5$ . We should note that since the density of CNTs can be determined only approximately ( $\rho(\text{CNTs}) \approx 1.4\text{-}1.9 \text{ g/cm}^3$  by the data of [28] and  $\rho(\text{CNTs}) \approx 2.045 \text{ g/cm}^3$  in [29]), then it is reasonable to use in the calculations the mass fraction (instead of the volume one) of MWCNTs in the composite.

It is seen from Fig. 5, where the dependences of the conductivity  $\sigma$  (direct current) of cPBT/MWCNTs nanocomposites on the content of MWCNTs are represented, that electrical conductivity  $\sigma$  exhibits the percolation behavior, namely, in the range of low concentrations of MWCNTs, from 0 to  $\sim 0.2$  wt. %, the value of  $\sigma$  is not almost changed and equal to  $\sigma \sim 10^{-16}$  S/cm. With the increase in the MWCNTs concentration in the composites, electrical conductivity  $\sigma$  abruptly increases by 10 decimal orders of magnitude in a narrow concentration range of  $\sim 0.2 \div 0.3$  wt. %. Further increase in the MWCNTs concentration conditions a slow growth in the value of  $\sigma$  by  $\sim 3$  decimal orders of magnitude in the range of concentrations of  $\sim 0.3 \div 2.0$  wt. %.

Experimental dependences  $\sigma = f(\text{MWCNTs})$  (Fig. 5) were theoretically approximated using equation (1). To this end, the dependences  $\lg \sigma = f \lg(p - p_c)$  were plotted, and varying the value of  $p_c$  we have found the best linear approximation of the mentioned experimental data. As seen (Fig. 5), theoretical and experimental data of the electrical conductivity agree well with each other; the value of the calculated percolation threshold  $p_c$  and the value of the critical exponent  $t$  are given in Table 2.





**Fig. 5** – Dependence of the electrical conductivity  $\sigma$  (direct current) of cPBT/MWCNTs nanocomposites on the content of MWCNTs; dots are the experimental data; lines are the theoretical data (according to equation (1)); on the inset we show the dependence  $\lg \sigma = f(p - p_c)$  for  $p > p_c$ ; samples are formed by the hot pressing method

**Table 2** – Percolation threshold  $p_c$  and critical exponent  $t$  for composites of the cPBT/MWCNTs and cPBT/CF

Percolation parameters	cPBT/MWCNTs	cPBT/CF
$p_c$	0.0022	0.0254
$t$	2.68	2.51

Thus, it is possible to separate the percolation areas for cPBT/MWCNTs systems in the range of MWCNTs concentrations of 0.2÷0.3 wt. % and, so, the percolation behavior of the given system can be characterized by two values of the critical concentration:  $p_c \approx 0.22$  wt. %, when conducting cluster begins to form and  $p_c^* \approx 0.3$  wt. % that corresponds to the completion of cluster formation.

The values of the critical exponent  $t$  are slightly larger than the theoretically predicted ones ( $t = 2.00$ ) and, apparently, this is connected with the fact that the statistical percolation theory describes ideal systems containing homogeneously dispersed identical conducting particles. Because of the spread of the CNTs characteristics (different sizes, chirality, complication, aggregation, defects, etc.), real nanocomposites cannot be considered the systems with an ideal filler (the values of  $t$  in the range of 0.7÷7.5 are given in the literature [27]).

Thus, a new approach to the synthesis of CNTs-containing nanocomposites from low-viscosity cyclic oligomers of butylene terephthalate allows to obtain nanocomposites with low percolation threshold ( $p_c \sim 0.22$  or

0.0022 wt. %) and, thus, improved electrical properties. Such low values of the percolation threshold in the given nanocomposites are provided by specific characteristics of CNTs (developed active surface of the external walls) and by formation of the three-dimensional conducting percolation network.

In Table 2 we present the percolation parameters of the investigated composites based on cPBT. We have synthesized earlier [30] composites based on cPBT and carbon fiber (CF) with the diameter of  $\sim 7 \mu\text{m}$  and ratio  $L/D \sim 900$ . If compare the percolation thresholds for the cPBT/MWCNTs nanocomposites and cPBT/CF composites (Table 2), one can conclude that percolation threshold in nanocomposites is more than 10 times lower compared with the composite where a usual conducting filler, CF, was used. Indisputably, in the production of polymer materials for special purposes, for example, with the properties of the electric current conductor, the use of CNTs as the conducting filler is more promising and cost-effective in comparison with the traditional conducting fillers (for example, CF).

#### 4. CONCLUSIONS

Thus, it is established in this work that the choice of the method of formation of cPBT/MWCNTs nanocomposites has a significant impact on their structure and electrical conductivity. It is determined that orientation of CNTs prevents formation of the conducting cluster when producing samples by the injection molding method. Secondary aggregation of CNTs, which considerably improves the ability to conduct electrical current, takes places in the polymer matrix when producing samples by the hot pressing method. Electrical percolation threshold for nanocomposites obtained by the hot pressing method is equal to  $p_c \sim 0.22$  wt. % (MWCNTs) that evidences the formation of the three-dimensional percolation conducting network based on MWCNTs. Thus, eventually, in this work we have optimized the methods of dispersing CNTs, synthesis of cPBT from CBT oligomers in the presence of MWCNTs and formation of polymer cPBT/MWCNTs nanomaterials, and discussed in detail the electrical properties of the obtained nanocomposites.

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