# Poly(butylene terephthalate/carbon nanotubes nanocomposites
# Part II. Structure and properties

**Elżbieta Piesowicz[1], Izabela Irska[1], *), Katarzyna Bryll[2], Katarzyna Gawdzińska[2], Michael Bratychak[3]**

**Abstract**: The properties of poly(butylene terephthalate) (PBT) based nanocomposites filled with MWCNTs (multiwall carbon nanotubes) and epoxy peroxide functionalized MWCNTs (EpMWCNTs) have been studied. The analysis was focused on the influence of EpMWCNTs on the phase structure, thermal, mechanical and electrical properties of synthesized materials. Functionalized MWCNTs were observed to be highly dispersed and well integrated in the PBT matrix. Obtained results demonstrate that the incorporation of EpMWCNTs into the PBT matrix yields materials of enhanced thermo-oxidative stability. It was found that the crystallization temperature for all the obtained nanocomposites is slightly higher than that for the neat polymer. Increasing the concentration of nanofiller in both MWCNT and EpMWCNT systems improved the mechanical properties Young's modulus, tensile strength and fracture strain. The electrical conductivity of nanocomposites decreased due to the functionalization of MWCNTs with epoxy peroxide.

**Keywords**: nanocomposites, poly(butylene terephthalate), carbon nanotubes, properties.

### Nanokompozyty poli(tereftalan butylenu)/nanorurki węglowe. Cz. II. Struktura i właściwości

**Streszczenie**: Scharakteryzowano, otrzymane w Cz. I., nanokompozyty na osnowie poli(tereftalanu butylenu) (PBT) napełnionej wielościennymi nanorurkami węglowymi, niemodyfikowanymi (MWCNT) lub funkcjonalizowanymi epoksynadtlenkiem (EpMWCNT). Zbadano wpływ EpMWCNT na strukturę fazową, właściwości termiczne, mechaniczne i elektryczne otrzymanych materiałów. Potwierdzono dobrą dyspersję i integrację EpMWCNT w matrycy PBT. Otrzymane wyniki świadczą o korzystnym wpływie funkcjonalizowanych nanorurek węglowych na stabilność termooksydacyjną materiału. Temperatura krystalizacji każdego z wytworzonych nanokompozytów jest wyższa niż nienapełnionego polimeru. Zaobserwowano poprawę właściwości mechanicznych nanokompozytów zarówno z MWCNT, jak i z EpMWCNT ze zwiększeniem zawartości nanonapełniacza. Nanokompozyty z udziałem nanorurek sfunkcjonalizowanych epoksynadtlenkiem wykazały gorsze przewodnictwo elektryczne niż nanokompozyty z udziałem nanorurek niemodyfikowanych.

**Słowa kluczowe**: nanokompozyty, poli(tereftalan butylenu), nanorurki węglowe, właściwości.

Poly(butylene terephthalate) (PBT) is a semicrystalline thermoplastic polyester with high stiffness, hardness, dimensional stability, good resistance to chemicals and excellent processability. PBT applications include electronic and communication equipment [1—3]. PBT can be tailored to suit numerous applications by blending it with other polymers or by using different nanofillers.

In recent years many experiments were devoted to obtain enhanced thermal and mechanical properties of PBT.

For instance, Xiao *et al*. [4] found that the incorporation of organic-modified montmorillonite (cethyl pyridium chloride modified) increase the melting temperature, crystallinity and crystallization rate in PBT nanocomposites, but the thermal stability does not remarkably increase. Rejisha *et al*. in their recent studies [1] showed improved thermal and mechanical properties of PBT/PC (PC — polycarbonate) blends due to the incorporation of MWCTNs (multi-walled carbon nanotubes). Kim *et al*. [2] in their work presented improved mechanical properties, heat distortion temperature and the thermal stability of PBT/CNTs (CNTs — carbon nanotubes) nanocomposites prepared by simple melt blending.

[1] West Pomeranian University of Technology, Institute of Materials Science and Engineering, Al. Piastów 19, 70-310 Szczecin, Poland.
[2] Maritime University of Szczecin, Institute of Basic Technical Sciences, Podgórna 51/53, 70-205 Szczecin, Poland.
[3] Lviv Polytechnic National University, Department of Petroleum Chemistry and Technology, 12 Bandera Street, 79013 Lviv, Ukraine.
*) Author for correspondence; e-mail: Izabela.Irska@zut.edu.pl

Avoiding agglomeration of CNTs in the polymer matrix and forming a strong interactions between the nanotube and the polymer matrix are a key issues in maximizing the advantage of CNTs reinforcements [5–9]. Many efforts have been made to obtain homogenous dispersion of CNT in polymer matrix, including the introduction of functional groups onto CNT surface [9–12]. Tseng *et al.* [13] presented improved compatibility between CNTs and polymer matrix due to CNT functionalization. In addition it has been proved that *in situ* polymerization is a very effective method to achieve a homogenous distribution of a nanofiller in the polymer matrix [6, 7, 14, 15].

The epoxy peroxide was successfully grafted onto to the MWCNTs, forming functionalized carbon nanotubes — EpMWCNTs. MWCNT and EpMWCNTs were incorporated into PBT matrix, with the aim of improving the thermal stability of PBT. The CNT functionalization procedure and the *in situ* synthesis of PBT/CNT nanocomposites are reported in a companion paper [16].

The purpose of this paper is to show the effects of unmodified and modified (epoxy peroxide) multiwall carbon nanotubes on the morphology, thermal, mechanical, and electrical properties of PBT.

<div align="center">EXPERIMENTAL PART</div>

**Synthesis of polymers and polymer composites**

The *in situ* polymerization method was applied to obtain PBT nanocomposites with MWCNTs/EpMWCNTs weight concentration from 0.1 % to 0.3 %. Materials used for the preparation of a polymer nanocomposites and procedure of the synthesis are described in more detail in Part I. CNTs functionalization and *in situ* synthesis [16].

**Sample preparation**

The dumbbell shape samples used in DMTA analysis, tensile tests and SEM investigations were obtained by using an injection molding machine (Dr. Boy GmbH & Co., Germany). The injection pressure was around 50 MPa and the temperatures were 15 °C higher than the melting point of the polymer determined by differential scanning calorimetry (DSC). The round shaped films (0.6 mm thick and 50 mm in diameter) used in electrical conductivity studies were prepared by compression molding at 245 °C for 5 min and cooled down in a mix of ethylene glycol and water (60:40).

**Methods of testing**

— The morphology and phase structure of the PBT and its nanocomposites were characterized by scanning electron microscopy (SEM, JEOL JSM 6100) at acceleration voltage 5 kV. All samples were cryo-fractured in liquid nitrogen and coated with a thin homogenous gold layer by ion-sputtering to facilitate the measurements.

— Thermal behavior of all samples was examined using differential scanning calorimetry (DSC). Measurements were carried out on the TA Q 100 (TA Instruments), at a heating rate of 10 °C/min, from 0 °C to 250 °C. Each DSC testing cycle consisted of heating, cooling and repeating the scans. Samples weighing approximately 10 mg were used. The crystallization and melting temperatures ($T_c$ and $T_m$) were determined from the maximum of the exothermic and endothermic peaks, respectively. The heat of fusion ($\Delta H_m$) and crystallization ($\Delta H_c$) were determined from the areas under melting and crystallization peaks. The degree of crystallinity ($x_c$) was calculated as the ratio $x_c = (\Delta H_m/\Delta H_m^0)\cdot100$ %, where $\Delta H_m$ and $\Delta H_m^0$ denote, respectively, heat fusion of a sample estimated from the second heating scan and the theoretical value of enthalpy for 100 % crystalline PBT $\Delta H_m^0 = 140$ J/g [18].

— Thermal properties of obtained nanocomposites were measured by dynamic mechanical thermal analysis (DMTA) with a Polymer Laboratories MK II dynamic mechanical thermal analyzer working in a bending mode. The tensile storage modulus ($E'$) and loss modulus ($E''$) were measured with a frequency of 1 Hz and a heating rate of 3 °C/min. The temperature dependence of storage modulus and loss modulus was measured from -20 °C to 230 °C.

— Thermogravimetric analysis (TGA) was conducted to determine the decomposition temperature of the functionalized MWCNTs and nanocomposites. TGA was carried out using an SETARAM TGA 92-16 thermal analyzer under an atmosphere of argon and air (the flow rate was 20 cm$^3$/min), with a hating rate of 10 °C/min.

— Electrical resistance of samples was measured at 100 V according to IEC 93:1980, using a high resistance meter (Model 6519A) connected to an 8009 resistivity test fixture (Keithley Instruments, Inc.). Each reported value is an average of six test specimens.

— The tensile properties of the samples were measured with an Instron testing machine (model 4206-006) at a constant crosshead speed of 5 mm/min. Measurements were performed at room temperature. Each reported value is an average of seven measurements.

— Shore D hardness was measured using a Zwick 3100 Shore D tester (Zwick GmbH, Germany).

<div align="center">RESULTS AND DISCUSSION</div>

The poly(butylene terephthalate) based nanocomposites filled with MWCNTs and epoxy peroxide functionalized MWCNTs have been prepared by a two-step melt polycondensation method (*in situ* synthesis). The prepared nanocomposites of PBT/MWCNT and PBT/EpMWCNT contain 0.1, 0.2, 0.3 wt % of nanotubes. The unreinforced PBT polymer was synthesized as reference. The obtained materials have a relatively high molar mass, confirming the correct selection of synthesis parameters [16].

## Morphology and phase behavior of PBT/MWCNT nanocomposites

The morphology of the polymer matrix in obtained materials was studied by SEM (Fig. 1). PBT matrix exhibits a relatively smooth fracture surface (Fig. 1a). SEM studies were focused on the 0.3 % loading samples for PBT/MWCNT and PBT/EpMWCNT nanocomposites. The SEM images of the composite fracture surface, show that MWCNTs are well dispersed in the PBT matrix (Fig.

1b). Good CNT distribution was also achieved for the functionalized MWCNTs. The fracture surface of PBT/MWCNTs (Figs. 1c and 1d) shows considerably different features than PBT/EpMWCNT (Figs. 1e and 1f). On the PBT/MWCNT nanocomposite fracture surface a number of pull-outs of the CNTs from the surrounding matrix can be observed (Figs. 1c and 1d). The presence of pull out nanotubes on the fracture surface of PBT/EpMWCNT nanocomposites was not observed, additionally CNTs seem to be wrapped by the PET matrix,
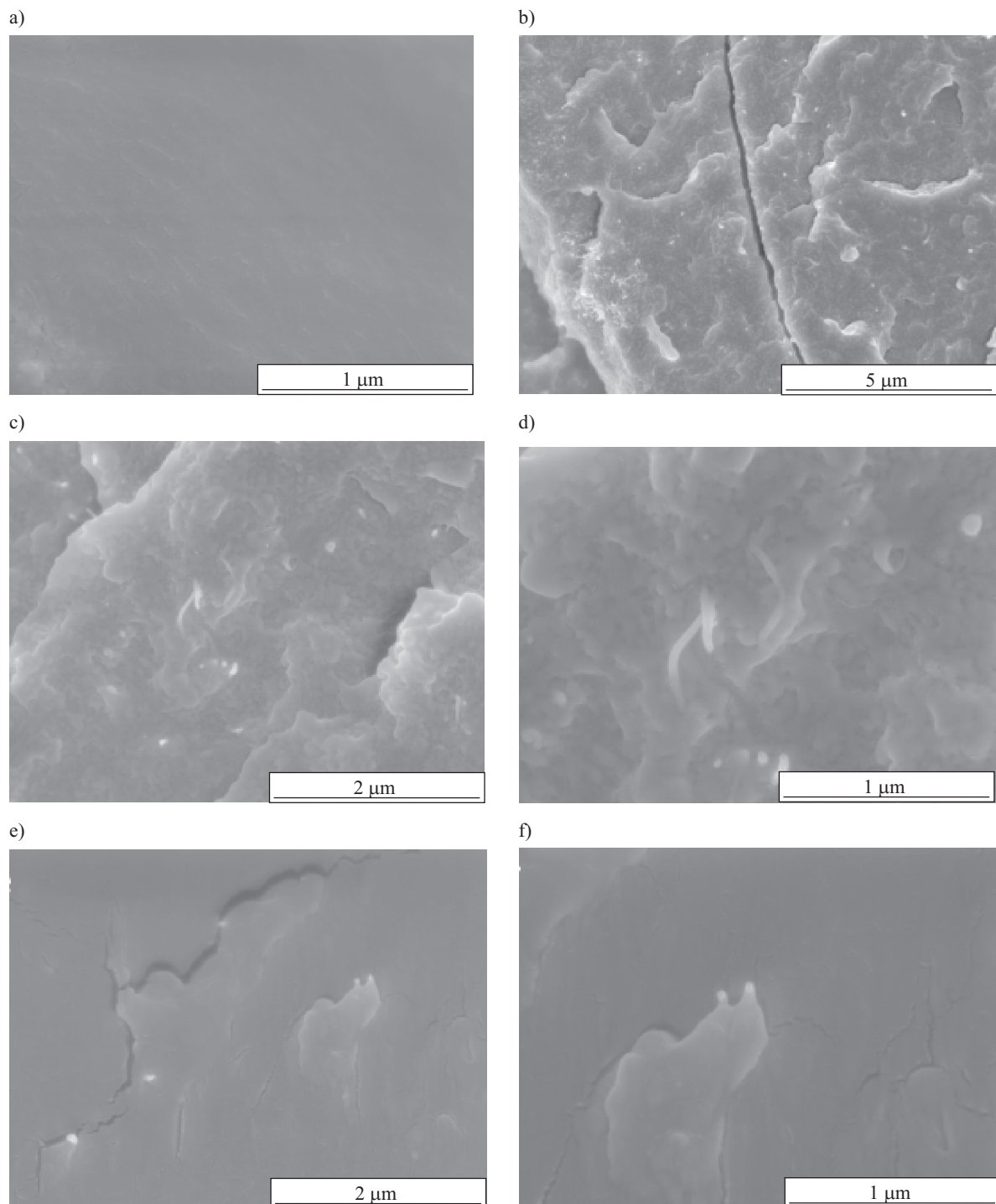
a)

b)

1 µm

5 µm

c)

d)

2 µm

1 µm

e)

f)

2 µm

1 µm

**Fig. 1. SEM micrographs of: a) the neat PBT, b, c, d) PBT/MWCNTs, e, f) PBT/EpMWCNT at different magnifications**

T a b l e 1.  **Thermal properties and crystallinity of PBT, PBT/MWCNTs and PBT/EpMWCNTs nanocomposites**

| Sample | $T_g$, °C | $T_g$ ($E''$), °C | $T_m$, °C | $\Delta H_m$, J/g | $T_c$, °C | $\Delta H_c$, J/g | $x_c$, % |
|---|---|---|---|---|---|---|---|
| PBT | 52.9 | 55.55 | 223.1 | 46.8 | 185.3 | 52.7 | 33.4 |
| PBT/0.1 MWCNT | 53.1 | 54.63 | 222.9 | 46.9 | 202.4 | 45.9 | 36.9 |
| PBT/0.2 MWCNT | 53.0 | 54.74 | 223.3 | 46.9 | 203.7 | 45.9 | 36.2 |
| PBT/0.3 MWCNT | 52.6 | 54.79 | 223.7 | 48.6 | 205.3 | 48.0 | 38.3 |
| PBT/0.1 EpMWCNT | 52.4 | 54.21 | 222.5 | 48.0 | 202.3 | 47.9 | 36.4 |
| PBT/0.2 EpMWCNT | 52.9 | 56.11 | 223.0 | 46.7 | 204.0 | 45.5 | 32.5 |
| PBT/0.3 EpMWCNT | 53.9 | 55.01 | 222.7 | 48.0 | 204.4 | 46.4 | 36.6 |

$T_g$ — glass transition temperature (determined from 1st heating of PBT and PBT/CNT nanocomposites); $T_g$ ($E''$) — temperature of β-relaxation corresponding to the glass transition temperature determined from maximum of loss modulus ($E''$), $T_m$, $\Delta H_m$ — temperature and enthalpy of melting of polymer, respectively; $T_c$, $\Delta H_c$ — temperature and enthalpy of crystallisation of polymer, respectively; $x_c$ — degree of crystallinity.



a)

b)
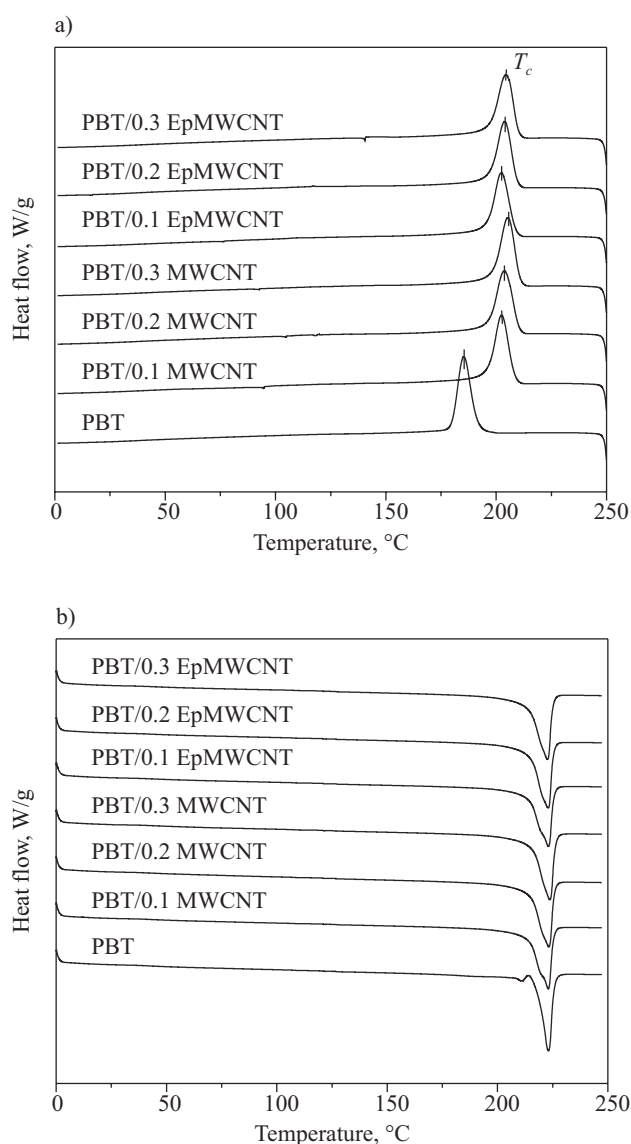
**Fig. 2. DSC thermograms of the PBT, PBT/MWCNTs and PBT/EpMWCNTs nanocomposites: a) cooling scans, b) heating scans**

suggesting that a strong interaction exist between the PBT matrix and functionalized MWCNTs (Figs. 1e and

1f). The presence of a modified epoxy resin seems to stabilize the MWCNTs dispersion by interaction with the PBT matrix.

The effect of the presence of functionalized MWCNTs on the phase structure of PBT/MWCNT nanocomposites was studied using DSC and DMTA analysis. The results of the second DSC heating and cooling scans for PBT, PBT/MWCNT and PBT/EpMWCNT nanocomposites are shown in Fig. 2. The thermal parameters of melting temperature ($T_m$), crystallization temperature ($T_c$), melting enthalpy ($\Delta H_m$), crystallization enthalpy ($\Delta H_c$) and the degree of crystallinity ($x_c$) determined from DSC thermograms are given in Table 1.

It was found that the presence of nanoadditives in the polymer phase has a significant influence on its ability to form the crystalline phase [5, 6]. It was also reported that CNTs distributed in the PBT matrix assist the nucleation and growth of crystallites [6]. The crystallization peaks of DSC curves shift to about 7–10 °C higher temperature with comparison to neat PBT. The crystallization temperature of the nanocomposites also increased with the concentration of CNTs, indicating their efficiency as the nucleating agent for PBT crystallization. The degrees of crystallinity of the prepared nanocomposites increased (3–4 %) in comparison to neat PBT. The temperature of melting (Fig. 2b) of the obtained materials seem not to be affected by the presence of the nanofillers. However, relevant differences can be observed in the widths of thermal effects connected with melting of nanocomposites crystalline phase in comparison with neat PBT. The multiple melting peak of neat PBT appeared, possibly due to the presence of more than one crystal modification [19]. The occurrence of small peaks at a slightly lower temperatures may be also attributed to the changes in crystalline size or perfection, or the variation of crystal thickness [20]. Only one melting endothermic peak was recorded during second heating for both PBT/MWCNT and PBT/EpMWCNT nanocomposites. Moreover, with an increase in content of both MWCNT and EpMWCNT the endothermic peak shape became more regular, suggesting overlapping the two possible structures. The thermal
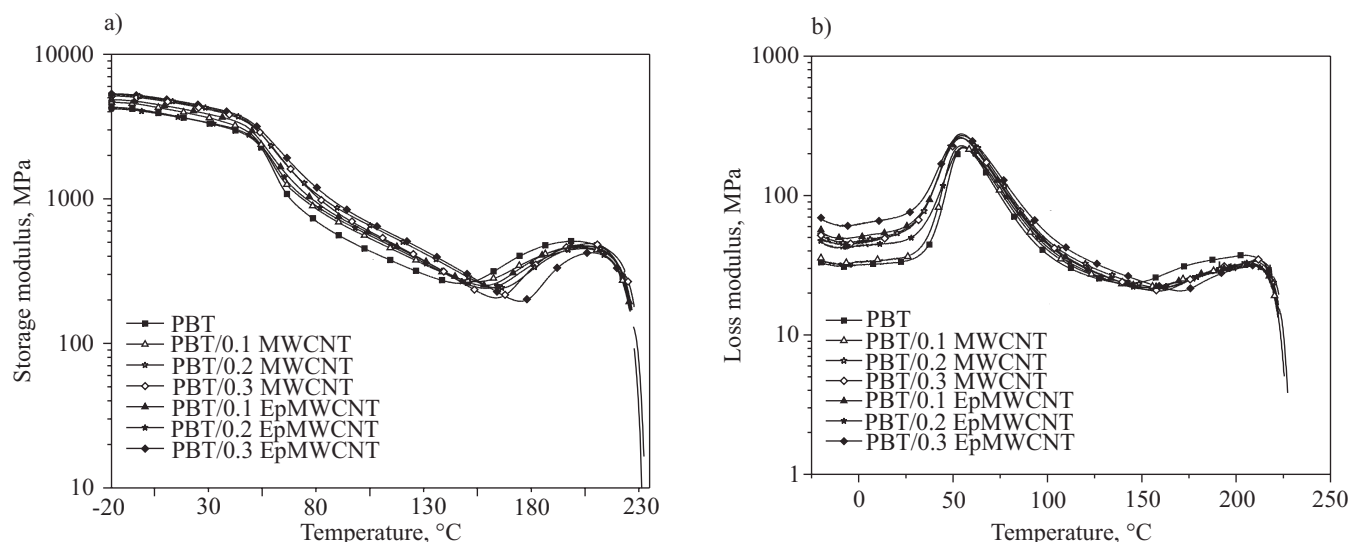
Fig. 3. a) The storage modulus, b) loss modulus as a function of temperature for PBT and nanocomposites with different weight concentration of MWCNT or EpMWCNT

parameters determined for PBT/MWCNT are comparable to those determined for PBT/EpMWCNT nanocomposites.

Figure 3 shows the results of DMTA analysis: a storage modulus ($E'$), loss modulus ($E''$), for neat PBT, PBT/MWCNTs and PBT/EpMWCNT nanocomposites as a function of temperature.

Figure 3a shows the DMTA plots of storage modulus versus temperature as a function of CNTs loading for MWCNT and EpMWCNT based nanocomposites. It can be observed that the storage modulus of nanocomposites is higher than that of neat PBT. The variation of storage modulus is similar for both types of MWCNTs — based composites. The storage modulus of PBT/CNT nanocomposites is increased by the stiffening effect of the CNTs.

Figure 3b shows the dependence of loss modulus ($E''$) on temperature for PBT, PBT/MWCNTs and PBT/EpMWCNTs nanocomposites. The loss modulus peaks of PBT nanocomposites were not significantly affected in the presence of CNTs. The maximum of loss modulus peak was commonly taken as glass transition temperature ($T_g$) and it is similar for all the tested samples ~55 °C (determined at the maximum of β-relaxation peak). No significant change in $T_g$ was also confirmed by DSC studies (Table 1).

## Thermal stability of PBT/MWCNT nanocomposites

To analyze the influence of the MWCNTs and the compatibilizer on the thermal stability of PBT/MWCNT nanocomposites, TGA was carried out in oxidative and inert atmospheres. The mass loss (TG) and DTG curves under oxidative and inert atmosphere are shown in Fig. 4.

In Table 3 temperatures corresponding to the 10 %, 50 % and 80 % mass loss under oxidative and inert atmosphere are presented. PBT polymer decomposes in a single step beginning at approximately 350 °C. For both types of MWCNT — based composites the $T_{10 \%}$, $T_{50 \%}$, $T_{80 \%}$ and the temperature at the maximum of mass loss rate (DTG peak) are shifted to higher temperatures, especially in air atmosphere. For MWCNT/PBT nanocomposites the total mass loss was 98 %, while for EpMWCNT/PBT nanocomposties it was 91 %. Obtained results suggest that the modification of CNTs with epoxy peroxide enhanced the thermo-oxidative stability of PBT/CNT nanocomposites.

T a b l e 2. Thermal properties of PBT, PBT/MWCNTs and PBT/EpMWCNTs nanocomposites

| Sample | $T_{10 \%}$, °C | | $T_{50 \%}$, °C | | $T_{80 \%}$, °C | |
|---|---|---|---|---|---|---|
| | air | Ar | air | Ar | air | Ar |
| PBT | 380 | 384 | 403 | 405 | 420 | 421 |
| PBT/0.3 MWCNT | 384 | 386 | 407 | 408 | 421 | 423 |
| PBT/0.3 EpMWCNT | 391 | 384 | 413 | 407 | 427 | 419 |

$T_{10 \%}$, $T_{50 \%}$, $T_{80 \%}$ — decomposition temperatures at 10 %, 50 % and 80 % mass loss under air and argon atmosphere.

T a b l e 3. The tensile properties of PBT, PBT/MWCNT and PBT/EpMWCNT nanocomposites

| Sample | $E$, MPa | $R_m$, MPa | ε, % | Sh D |
|---|---|---|---|---|
| PBT | 2268 | 41 | 3.8 | 87 |
| PBT/0.1 MWCNT | 2492 | 47 | 10.2 | 83 |
| PBT/0.2 MWCNT | 2515 | 48 | 12.0 | 82 |
| PBT/0.3 MWCNT | 2565 | 49 | 15.4 | 85 |
| PBT/0.1 EpMWCNT | 2469 | 45 | 9.0 | 83 |
| PBT/0.2 EpMWCNT | 2500 | 47 | 10.0 | 84 |
| PBT/0.3 EpMWCNT | 2568 | 49 | 11.8 | 86 |

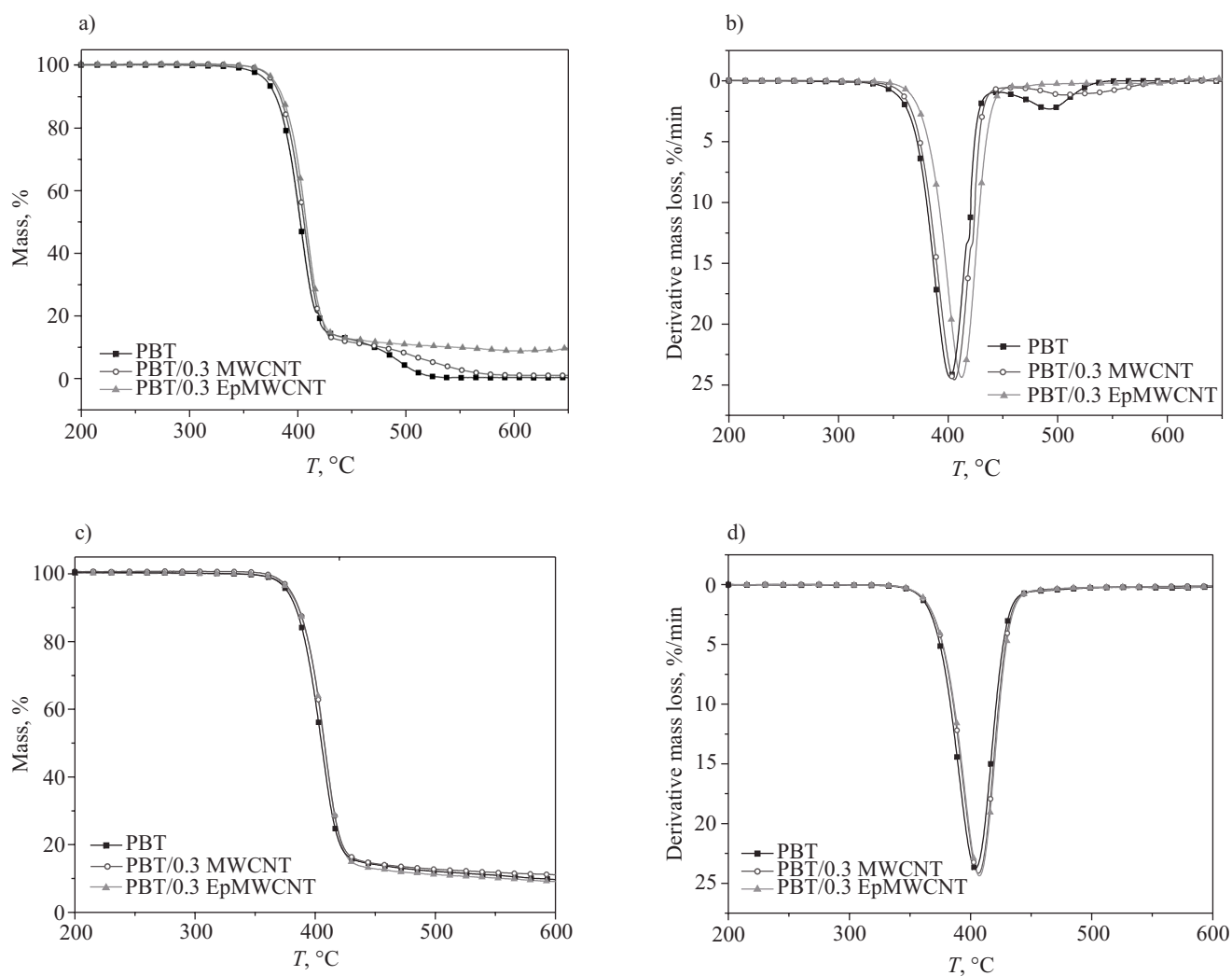$E$ — Young's modulus; $R_m$ — tensile strength; ε — fracture strain; Sh D — Shore hardness.

**Fig. 4. a, c) TG, b, d) DTG curves for PBT/MWCNTs and PBT/EpMWCNTs in air (a, b) and argon (c, d) atmosphere**

## Electrical properties

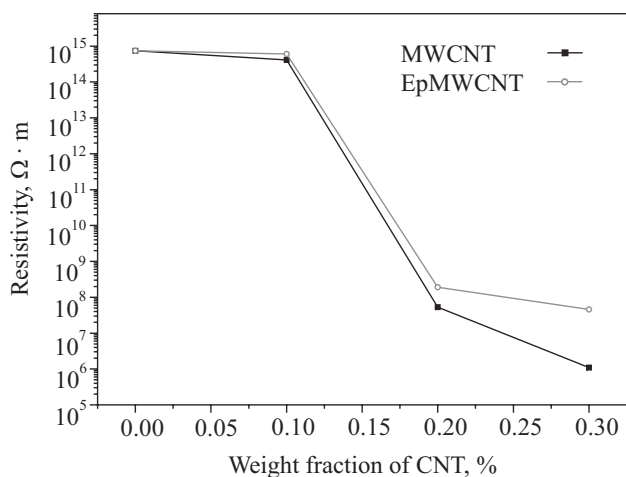The round shaped films (0.6 mm thick and 50 mm in diameter) manufactured by compression moulding at 245 °C were used in electrical conductivity studies. The volume resistivity is plotted as a function of weight concentration of MWCNT or EpMWCNT in Fig. 5. As expected, the electrical resistivity of PBT/MWCNT and PBT/EpMWCNT nanocomposites decreased in comparison to neat PBT. Nanocomposites with 0.2 wt % and 0.3 wt % of MWCNTs exhibited volume resistivity values at $10^7$ Ω·m and $10^6$ Ω·m, respectively. For the same filler content, the resistivity of nanocomposites containing EpMWCNTs increased by one order of magnitude in each case. The higher electrical resistivity of PBT/EpMWCNT compared to the untreated MWCNT was expected. The electrical conductivity of nanocomposites containing EpMWCNT decreased due to the wrapping of nonconductive epoxyperoxide. The wrapped polymer perturbs the π electron system of the CNT walls. Similar phenomena occur for other nanocomposites containing functionalized CNT [21].

## Tensile properties of nanocomposites

Tensile testing was performed to evaluate the effect of MWCNT and functionalized MWCNT on the mechanical



**Fig. 5. Effect of MWCNT and EpMWCNT weight concentration on volume resistivity of PBT nanocomposites**

properties of PBT. Table 3 demonstrates a summary of the obtained mechanical properties: Young modulus, tensile strength, fracture strain and Shore D hardness. The tensile test results showed that obtained nanocomposites have improved mechanical properties in comparison to the neat PBT. After adding MWCNTs the Young modulus increased by approximately 10 % (based on averages) in both systems PBT/MWCNTs and PBT/EpMWCNTs. With respect to the neat PBT, the obtained nanocomposites showed also an increase in the strength and fracture strain. It is observed that Young modulus, tensile strength and fracture stress was improved with CNT reinforcement in both PBT/MWCNT and PBT/EpMWCNT systems. The obtained mechanical properties are similar for PBT/MWCNT composites in which MWCNTs were used as received to those in which functionalized MWCNTs were applied. In none of the studied nanocomposites a significant increase in Shore D hardness can be observed.

In general, the tensile strength and modulus of semi-crystalline polymer increase with the degree of crystallinity [5]. The DSC measurements indicate that the addition of both MWCNTs and functionalized MWCNTs resulting in a slight increase in the degree of crystallinity, but the difference between neat PBT and obtained nanocomposites is lower than 4 % (Table 1). Due to a slight increase of crystallinity, improvement in tensile strength and modulus can be attributed to the presence of CNTs.

## CONCLUSIONS

Nanocomposites consisting of poly(butylene terephthalate) and multi-walled carbon nanotubes or epoxy peroxide functionalized multi-walled carbon nanotubes were prepared by *in situ* polymerization method. SEM micrographs confirmed that this method leads to the uniform dispersion of CNTs in the PBT matrix. There was no significant change in the melting point and the glass transition temperature due to MWCNT or EpMWCNT incorporation. The degree of crystallinity for all obtained nanocomposites was slightly higher than that of neat PBT. The incorporation of low concentration MWCNTs/EpMWCNTs enhances the nucleation process in PBT crystallization. The presence of EpMWCNTs improves the thermal stability of PBT under air, but has little effect on the thermal degradation behavior of PBT under nitrogen atmosphere. The results seem to indicate that the addition of MWCNTs/EpMWCNTs enhances the mechanical properties of PBT (Young modulus, tensile strength and fracture stress) but fails to significantly increase Shore D hardness. The electrical conductivity of nanocomposites containing EpMWCNT decreased in comparison to pristine MWCNT due to the wrapping of nonconductive epoxy peroxide.

## REFERENCES

[1] Rejisha C.P., Soundararajan S., Sivapatham N., Palanivelu K.: *Journal of Polymers* **2014**, *2014*, 1. https://dx.doi.org/10.1155/2014/157137

[2] Kim J.Y.: *Journal of Applied Polymer Science* **2009**, *112*, 2589. https://dx.doi.org/10.1002/app.29560

[3] Chrissafis K., Bikiaris D.: *Thermochimica Acta* **2011**, *523*, 1. https://dx.doi.org/10.1016/j.tca.2011.06.010

[4] Xiao J., Hu Y., Wang Z. *et al.*: *European Polymer Journal* **2005**, *41*, 1030. https://dx.doi.org/10.1016/j.eurpolymj.2004.11.025

[5] Anna S.: *Journal of Applied Polymer Science* **2012**, *126*, 796. https://dx.doi.org/10.1002/app.36961

[6] Broza G., Kwiatkowska M., Rosłaniec Z., Schulte K.: *Polymer* **2005**, *46*, 5860. https://dx.doi.org/10.1016/j.polymer.2005.05.073

[7] Hernández J.J., García-Gutiérrez M.C., Nogales A. *et al.*: *Composites Science and Technology* **2009**, *69*, 1867. https://dx.doi.org/10.1016/j.compscitech.2009.04.002

[8] Liao S.-H., Yen C.-Y., Hung C.-H. *et al.*: *Journal of Materials Chemistry* **2008**, *18*, 33. https://dx.doi.org/10.1039/b806054a

[9] Park S.J., Cho M.S., Lim S.T. *et al.*: *Macromolecular Rapid Communications* **2003**, *24*, 1070. https://dx.doi.org/10.1002/marc.200300089

[10] Yang S.-Y., Ma C.-C.M., Teng C.-C. *et al.*: *Carbon* **2010**, *48*, 592. https://dx.doi.org/10.1016/j.carbon.2009.08.047

[11] Sydlik S.A., Lee J.-H., Walish J.J. *et al.*: *Carbon* **2013**, *59*, 109. https://dx.doi.org/10.1016/j.carbon.2013.02.061

[12] Datsyuk V., Kalyva M., Papagelis K. *et al.*: *Carbon* **2008**, *46*, 833. https://dx.doi.org/10.1016/j.carbon.2008.02.012

[13] Tseng C.-H., Wang C.-C., Chen C.-Y.: *Chemistry of Materials* **2007**, *19*, 308. https://dx.doi.org/10.1021/cm062277p

[14] Pilawka R., Paszkiewicz S., Rosłaniec Z.: *Journal of Thermal Analysis and Calorimetry* **2014**, *115*, 451. https://dx.doi.org/10.1007/s10973-013-3239-4

[15] Roslaniec Z., Broza G., Schulte K.: *Composite Interfaces* **2003**, *10*, 95. https://dx.doi.org/10.1163/156855403763586819

[16] Piesowicz E., Irska I., Bratychak M., Rosłaniec Z.: *Polimery* **2015**, *60*, nr 11-12.

[17] http://www.nanocyl.com/de/Products-Solutions/Products/Nanocyl-NC-7000-Thin-Multiwall-Carbon-Nanotubes, (data dostępu 19.12.2014).

[18] Shyang C.W.: *Malaysian Polymer Journal* **2008**, *3* (*1*), 1.

[19] Kim H.G., Robertson R.E.: *Journal of Polymer Science Part B: Polymer Physics* **1998**, *36*, 1757. https://dx.doi.org/10.1002/(SICI)1099-0488(19980730)36:10<1757::AID-POLB17>3.0.CO;2-8

[20] Sharma R., Jain P., Sadhu Susmita D., Kaur B.: *Journal of Polymer Engineering* **2013**, *33*, 489. http://dx.doi.org/10.1515/polyeng-2012-0163

[21] Ma P.C., Kim J.-K., Tang B.Z.: *Composites Science and Technology* **2007**, *67*, 2965. https://dx.doi.org/10.1016/j.compscitech.2007.05.006