Influence of thermally exfoliated graphite on physicochemical, thermal and mechanical properties of copolyester nanocomposites

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Abstract: New materials which were composites filled with thermally exfoliated graphite (tEG) were prepared. In these composites segmented multi-block thermoplastic elastomer containing 60 wt % of hard segments as in poly(ethylene terephthalate) (PET) and 40 wt % of soft segments comprising amorphous sequences of ethylene ester of dilinoleic acid (DLA) was used as a polymer matrix. The filler, *i.e.* tEG, which is graphene-like material, was introduced into the polymer matrix in various content (0.1, 0.2, 0.3 and 0.5 wt %) during *in situ* polycondensation. Scanning electron microscope images of the nanocomposites showed very good nanofiller dispersion in the polymer matrix with few agglomerates. The addition of nanofiller affected the degree of polymer crystallinity as well as the mechanical properties of PET-DLA nanocomposites. Importantly, thermally exfoliated graphite reduced the water contact angle of nanocomposites thus making their surface more hydrophilic and potentially more attractive in medical applications.

Keywords: thermoplastic elastomers, poly(ethylene terephthalate), graphene, dilinoleic acid, thermal analysis.

Wpływ termicznie eksfoliowanego grafitu na właściwości fizykochemiczne, termiczne i mechaniczne nanokompozytów kopoliesterowych

Streszczenie: Otrzymano nowe kompozyty kopoliestrowe napełnione termicznie zredukowanym grafitem (tEG). Jako matrycę polimerową zastosowano segmentowy elastomer termoplastyczny, zawierający 60 % mas. segmentów sztywnych [poli(tereftalan etylenu)] oraz 40 % mas. segmentów giętkich, będących sekwencjami pochodzącymi od dimeru kwasu linolowego (DLA). Napełniacz – tEG, o strukturze podobnej do grafenu, wprowadzono do matrycy polimerowej w różnych ilościach (0,1, 0,2, 0,3 lub 0,5 % mas.) podczas polikondensacji *in situ*. Obrazy nanokompozytów otrzymane za pomocą skaningowego mikroskopu elektronowego pokazały bardzo dobre rozproszenie nanonapełniacza w matrycy polimerowej z występującymi nielicznie aglomeratami. Stwierdzono, że dodatek nanonapełniacza powodował zmniejszenie stopnia krystaliczności nanokompozytów PET-DLA oraz zwiększenie granicy plastyczności praktycznie nie wpływając na moduł Younga. Ponadto obecność tEG w kompozycie zmniejszała kąt zwilżania, dzięki czemu uzyskana powierzchnia stawała się bardziej hydrofilowa. Zmiana właściwości nanokompozytów na skutek wprowadzenia tEG wpływa korzystnie na możliwości ich zastosowania do celów medycznych.

Słowa kluczowe: elastomery termoplastyczne, poli(tereftalan etylenu), grafen, kwas dilinoleinowy, analiza termiczna.

Polymeric nanocomposites are widely used and actively developed materials for a broad range of applications, including electronics, automotive, and various biomedical fields [1–7]. By reducing the size of the reinforcing phase from micrometers down to nanometers, new and unique features can be obtained within resulting materials. An excellent example of improved biofunctionality due to nanosized features is increased osteoblast (bone forming cells) adhesion on aluminum, titanium, and hydroxyapatite with nanometer grain sizes, as compared to conventional (micrometer scale) grain sizes [8]. It has been also demonstrated that nanoscale surface roughness is responsible for increased protein adsorption and greater tissue growth on carbon nanotube based polymer composites [9].

In recent years, graphene has been attracting considerable attention as a revolutionary breakthrough in modern chemistry, physics, and materials science and engineering [10, 11]. Graphene is under the spotlight in the

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nanomaterials science due to its many unique attributes. Graphene sheets, nanoscale platelets composed of one or more graphenes (0.34–100 nm in thickness) [12], exhibit outstanding physical, mechanical and optical properties [13]. Graphene-reinforced polymer matrix composites with increased elastic modulus and ultimate tensile strength have been explored by Ramanathan *et al.* [14] and Lee *et al.* [15]. Further, significant changes in thermal properties of nanocomposites filled with graphene have also been observed, demonstrating increment in crystallization temperatures and glass transition temperatures [16, 17].

Beyond the applications and properties already mentioned, the biomedical application of graphene is a relatively new area with substantial potential. Applications such as drug delivery systems, antibacterial materials, biosensors or biocompatible scaffolds for tissue engineering could make a great impact in medical practice [18]. There are some reports on using graphene as a filler in polymeric materials for bioapplications [19–21], but these polymeric matrices are made of biodegradable poly(ε-caprolactone), poly(lactic-glycolic acid) or chitosan, raising questions regarding the biological fate of the nanofiller after degradation of a material. Promisingly, graphene-based nanocomposites based on poly(*N*--vinylcarbazole) (PVK) revealed both low mammalian cell toxicity and efficient antimicrobial characteristics [22]. However, the use of graphene for biomaterial applications still remains a challenge [23]. In particular, the issues of biocompatibility, toxicity and cellular-uptake mechanisms require further investigation.

Thermoplastic elastomers (TPEs), such as the well known segmented poly(urethane/ester/ether/carbonate)s, are widely used for blood contacting devices, including catheters, peacemaker or elements of artificial heart [24], due to their excellent biocompatibility, good solvent resistance, elasticity, tear strength, *etc*. The resulting properties are a consequence of microphase separation being a result of thermodynamic incompatibility of discrete (nanoscale) building block, so called hard and soft segments [25]. Polyester type multi-block TPEs, containing terephthalate and dilinoleate (ester of dimer of linoleic acid) units (abbreviated as PED) are also microphase separated segmented polyesters which have also demonstrated excellent biocompatibility *in vitro* and *in vivo* and are being investigated systematically for biomedical applications [26]. Importantly, PED copolymers are obtained without thermal stabilizers, due to excellent thermal stability of soft segments [27]. The further modification of PEDs via nanofillers may improve performance and functionality in the field of medical devices and artificial biomaterials [28]. We have already demonstrated that poly(butylene terephthalate)-dilinoleic acid (PBT-DLA) copolymers possess excellent fatigue resistance [29], and their nanocomposites with nanometer carbon black [30] or silica oxide [31] showed good mechanical properties under static and dynamic test conditions.

In this work, we attempt to modify the structural analogues of PBT-DLA, namely PET-DLA copolymers, with thermally exfoliated graphite considering all the advantages assigned to the graphene. PET-DLA copolymers containing 60 wt % of hard segments were selected for this work as a matrix for nanocomposites, due to their hardness of 53 Shore D, similar to hardness of biomedical polyurethane copolymer, Bionate used for blood contacting devices [32]. Bionate is a biostable and biocompatible thermoplastic polycarbonate polyurethane used in long-term implants like vascular implants, artificial heart, hip and knee joints or cardiac assist and diagnostic devices [33]. The obtained composite materials were subjected to structural, morphological, thermal and mechanical studies. The favorable improvement of PET-DLA materials by using graphene may provide better performance and functionality in the field of medical devices and artificial biomaterials.

EXPERIMENTAL PART

Materials

In this study the following materials were used:

– graphite delivered by NGS Naturgraphite GmbH (Germany);

– dimethyl terephthalate (DMT) provided by Elana (Poland);

– dilinoleic acid (DLA) of trade name Pripol 1009 supplied by Croda (The Netherlands);

– *N*-methyl-2-pyrrolidone (NMP) and ethylene glycol (EG), both delivered by Sigma-Aldrich (Germany).

Preparation of thermally exfoliated graphite

Graphite is almost completely exfoliated to multilayer structures comprising less than 5 layers when dissolved in *N*-methyl-2-pyrrolidone (NMP), gamma-butyrolactone (GBL) or 1,3-dimethyl-2-imidazolidinone (DMEU), yielding significant quantities of individual monolayers in the dispersion [34]. This can occur when the net ener-

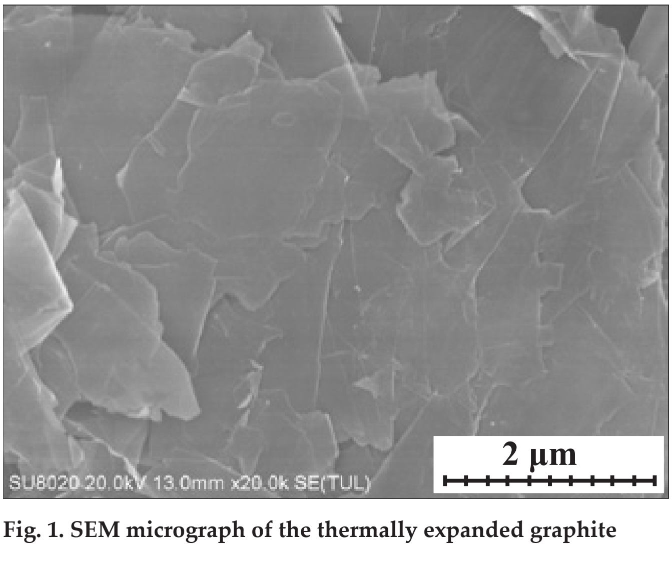
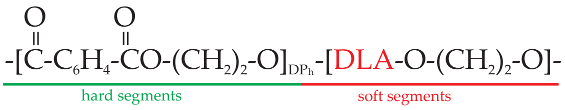


Fig. 1. SEM micrograph of the thermally expanded graphite

getic cost is very small. The enthalpy of mixing for the exfoliated graphite dispersed in appropriate solvents is very close to zero and the solvent-graphene interaction is of van der Waals type rather than covalent. Here, the thermally exfoliated graphite (tEG) was prepared by dispersing graphite in NMP. Briefly, after ultra-sonication for 10 h, the suspensions were centrifuged at 4000 rpm for 30 min. Then, the obtained materials (platelets, 1–2 μm large as it was shown in Fig. 1) were placed into an oven preheated to 800 °C for 180 s. Subsequently, tEG was dispersed in EG for 10 h by using ultra-sonication.

Preparation of PET-DLA-tEG composites

Nanocomposites of tEG nanoplatelets and PET-DLA matrix were prepared *in situ* during polymerization. The synthesis was a standard two stage melt polymerization. Briefly, the first step was transesterification of DMT and EG with dispersed tEG and was carried out at normal pressure and at the temperature of about 200 °C in the presence of zinc acetate (manufactured) as a catalyst. After the removal of methanol (95 % from stoichiometry), DLA along with tEG was added. The polycondensation step was carried out under reduced pressure at the temperature of about 265 °C, until the power consumption of stirrer motor reached its peak value. The catalyst for the polycondensation step was germanium dioxide. The obtained materials were extruded from the reactor at a pressure of nitrogen in the form of polymer wire. The hard (ethylene terephthalate as in PET) to soft (ethylene dilinoleate, here abbreviated as DLA) the segment ratio was 60 : 40, and 0.1, 0.2, 0.3 or 0.5 wt % of tEG was used. The hard segments content was 60 wt %, corresponding to the degree of polycondensation of hard segments, DP_h = 4.65. Chemical structure of synthesized PET-DLA copolymer is given by formula (I).



$$\underbrace{-[\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}O-(CH_2)_2-O]_{DP_h}}_{\text{hard segments}}\underbrace{-[DLA-O-(CH_2)_2-O]-}_{\text{soft segments}}$$

(I)

Methods of testing

To characterize chemical structure of new materials, attenuated total reflection IR spectroscopy (FT-IR ATR) was performed with spectrophotometer (Nexus, Thermo Nicolet) in the range between 400 and 4000 cm^{-1}. Thin films were obtained by compression molding on hot press.

The contact angle was measured using KRUSS DSA100 digital goniometer. Contact angle measurements were performed by placing a droplet of deionized water on the surface of the obtained, degreased materials. Water droplets with volume about 1 μL were generated using the automatic dispenser of the goniometer.

To determine thermal properties, differential scanning calorimetry (DSC) was performed using Q100, TA Instruments apparatus. The samples were dried in vacuum at 70 °C for 24 h. The DSC process was carried out in a triple cycle, „heating-cooling-heating", in the temperature range between -100 and 300 °C. The heating/cooling rate was 10 deg/min. The glass transition temperature (T_g) was determined from the second run, in order to eliminate the thermal history from the sample as the temperature corresponding to the upper inflection point or the maximum of the curve. The melting temperature (T_m) and crystallization temperature (T_c) were determined as the values corresponding to the maximum of endothermic curve and the minimum of exothermic curve, respectively.

The mechanical properties of the PET-DLA-tEG nanocomposites were evaluated using Instron 3366 Testing Machine with a 500 N load cell and speed of 100 mm/min. The test samples ("dog bone" shaped, 0.5 mm thick) were prepared using hot press and injection molding (Boy 35A) for fracture surface examination.

The scanning electron microscopy (SEM) of samples fractured in liquid nitrogen was carried out with Hitachi 10 SU8020 apparatus and a beam intensity of 15–20 kV.

RESULTS AND DISCUSSION

New nanocomposites containing different concentration of tEG were synthesized *in situ* during polycondensation. This preparation method of nanocomposites provides material with nanostructures embedded in a polymer matrix. If the nanofiller is chemically functionalized, it should provide chemical interaction with a polymer matrix. In order to understand the interaction of tEG prepared for this work with PET-DLA matrix, the FT-IR spectra of the obtained nanocomposites were examined. All obtained FT-IR spectra were practically identical; thus, for clarity, only the neat polymer and the nanocomposite containing 0.5 wt % of tEG are presented in Fig. 2. Absorption spectrum in the region 2800–3300 cm^{-1} corresponds to the stretching vibration of the aliphatic and aromatic -C-H. The ester carbonyl bonds can be observed at the wavelength of 1700–1740 cm^{-1}. Two peaks at 1245 cm^{-1} and 1100 cm^{-1} correspond to the oscillations of the C-O bond stretching in the ester aromatic and aliphatic groups, respectively. As expected, because the tEG nanofiller was not functionalized, PET nanocomposites exhibited similar absorption bands to those of neat PET-DLA copolymer. An absence of significant changes in band positions indicate that synthesized nanocomposites and the reference material have the same structural properties and no new chemical bonds were formed [35]. The minor changes in peak intensities may be caused by slightly different hard to soft segment ratios of the polymers, since materials were synthesized *in situ* during polymerization with slightly different polymerization degree.

The fracture surfaces of injection molded nanocomposite samples were examined with scanning electron microscopy (SEM) to evaluate the quality of distribution of exfoliated graphite in the polymer matrix. SEM micrographs of samples with different nanofiller concentra-

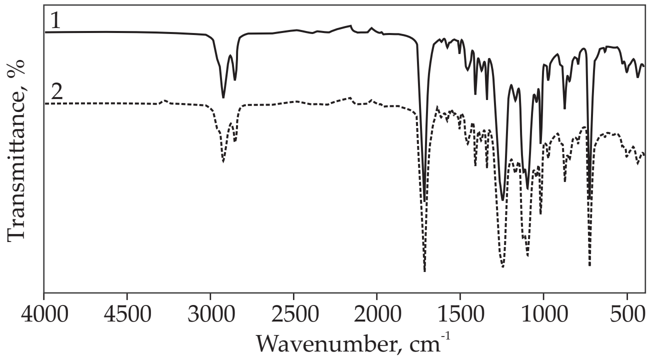


Fig. 2. FT-IR ATR spectra of: 1 – neat PET-DLA, 2 – PET-DLA-tEG with 0.5 wt % of tEG

tions are presented in Fig. 3. In general, good dispersion of tEG (seen as white spots) in a polymer matrix was observed, however some agglomerations can also be seen.

In order to determine thermal properties of synthesized nanocomposites DSC measurements were performed. The heating and cooling thermograms of obtained materials are shown in Fig. 4. From presented curves the values of T_g, T_m and T_c of the composites together with change of the heat capacity (ΔC_p), melting and crystallization enthalpy of the hard segments (ΔH_m and ΔH_c, respectively) were determined. The crystalline phase content in the polymer (W_c) was calculated using the equation:

$$W_c = \frac{\Delta H_m}{\Delta H_f} \cdot 100\% \qquad (1)$$

where: ΔH_m – the melting enthalpy of the hard segments of the polymer (J/g of polymer), $\Delta H_f = 140$ J/g · °C – the melting enthalpy of the crystalline PET phase [36].

Next the crystalline phase content in the hard phase ($W_{c,h}$) was calculated using the equation:

$$W_{c,h} = \frac{W_c}{W_h} \cdot 100\ \% \qquad (2)$$

where: W_h – the content of hard segments.

All determined parameters are collected in Table 1.

In general, all synthesized materials show low T_g and high T_m values (determined during the second heating, Fig. 4a) thus indicating formation of microphase separated structure of soft and hard segments independently of the amount of used nanofiller. For all of the nanocomposites, T_c values were shifted towards higher temperatures with increasing tEG content and were higher as compared to neat material (Fig. 4b). This can be explained by the heterogeneous nucleation effect of the tEG, result-

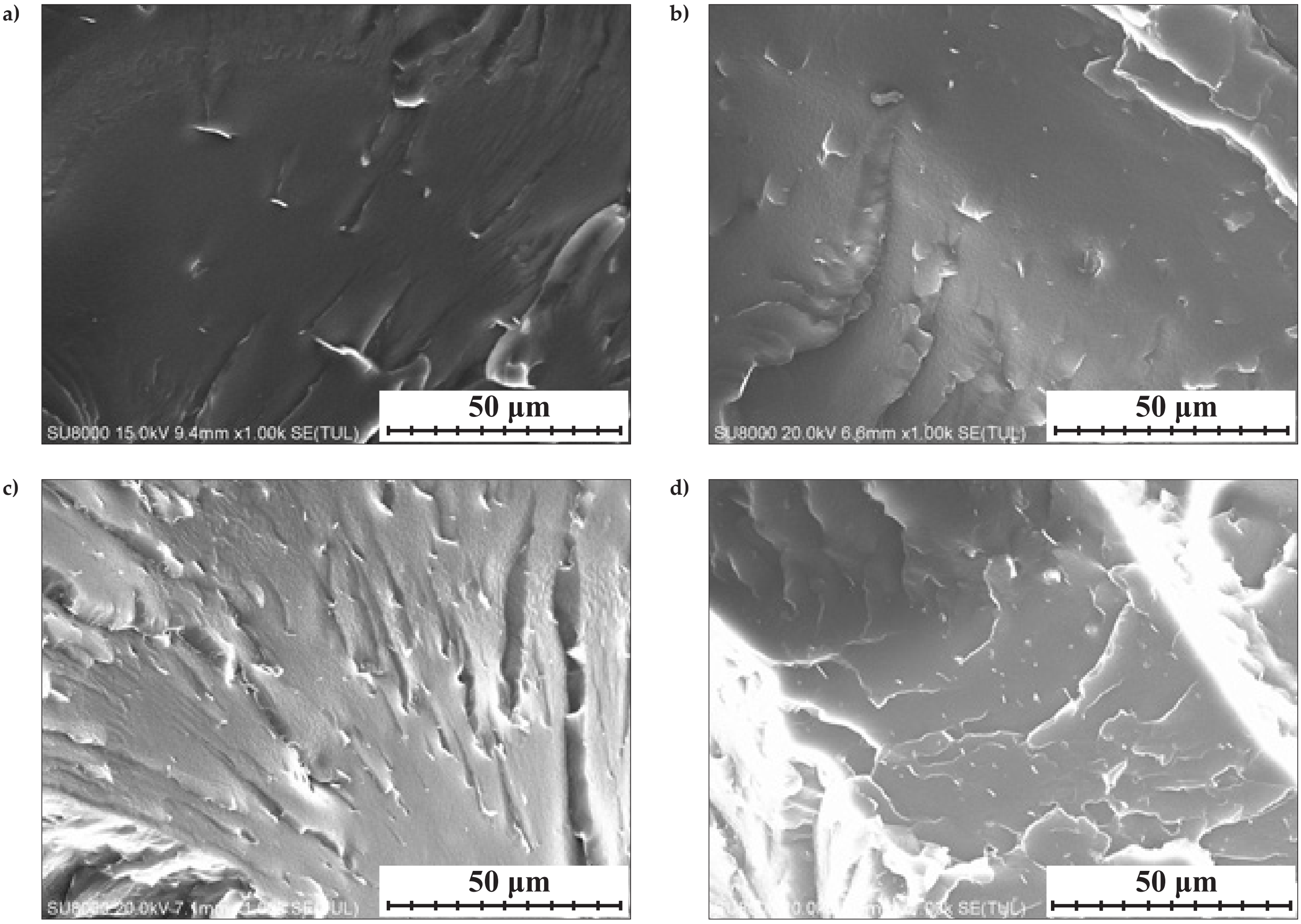


Fig. 3. SEM micrographs with tEG content of: a) 0.1 wt %, b) 0.2 wt %, c) 0.3 wt %, d) 0.5 wt %

T a b l e 1. Thermal properties of synthesized composites

tEG content wt %	ΔC_p J/g · °C	T_g °C	T_m °C	ΔH_m J/g	T_c °C	ΔH_c J/g	W_c %	$W_{c,h}$ %
0	0.42	-6.0	210	22.8	120	21.4	16	27
0.1	0.37	-8.9	211	21.6	148	25.6	15	26
0.2	0.42	-6.5	210	20.6	152	23.3	15	25
0.3	0.44	-8.9	210	20.9	157	23.8	15	25
0.5	0.42	-4.6	210	19.0	156	22.9	14	23

ing in crystallization of polymer at higher temperatures. A similar effect has been previously observed for various polyesters and polyolefin nanocomposites [37, 38]. Moreover, a significant difference in the shape of crystallization exotherms can be noticed – this means that nanocomposites (showing higher enthalpy values) were more easily crystallized than the neat material. Additionally, the presence of nanoplatelets affected W_c and $W_{c,h}$, which decreased with the increasing amount of the nanofiller from 16.2 % (for neat polymer) to 13.5 % (for 0.5 wt % of tEG) (Table 1). This can be explained by the restriction of the mobility of polymer chains during crystallization by the presence of nanofiller. Acting as a heterogeneous nucleation agent, tEG causes less crystalline phase formation – thus W_c and $W_{c,h}$ of all obtained nanocomposites have lower values than the neat material. Further, the tEG may constrain polymer chains, limiting rearrangement and formation of the crystalline phase similar to stated for polyamide 12 with graphene [39]. It was also observed that the addition of tEG shifts T_g of materials containing 0.1, 0.2 and 0.3 wt % of tEG towards lower temperatures, thus increasing microphase separation. A similar tendency when introducing functionalized graphene sheets into polyurethane matrix was observed in [40]. The observed effect is very favorable, since high crystallinity within a polymer can make the processing more difficult. Materials with higher W_c may require higher temperatures for melt processing, what eventually can lead to thermal degradation.

The wetting properties of polymeric nanocomposite are very important in term of cell-material interactions in the case of final application of the material in biomedical devices or implants [41]. It is already known that hydrophilic surfaces have improved protein adsorption capacity and also significantly affect proliferation and cell attachment [42]. To study the surface hydrophobic or hydrophilic character of the obtained materials, contact angle measurements were performed. To calculate the contact angle from the shape of the water drop, automated image analysis was used. All measurements were repeated five times, in different regions of the sample surface. The effect of tEG content on the water contact angles of synthesized materials is shown in Fig. 5. Neat PET-DLA is a hydrophobic copolymer as indicated by the contact angle of 94°. Upon modification, materials showed lower values of the contact angle of about 65° for materials containing 0.1 and 0.2 wt % tEG and about 75° for materials containing 0.3 and 0.5 wt % tEG, indicating that obtained nanocomposites have a slightly more hydrophilic surface than the neat material. A surface of neat PET-DLA that has long alkane chains is more hydrophobic since the hydrogen atoms reduce the surface energy. Slightly lower contact angle for nanocomposites may be a result of the presence of oxygen-containing functional

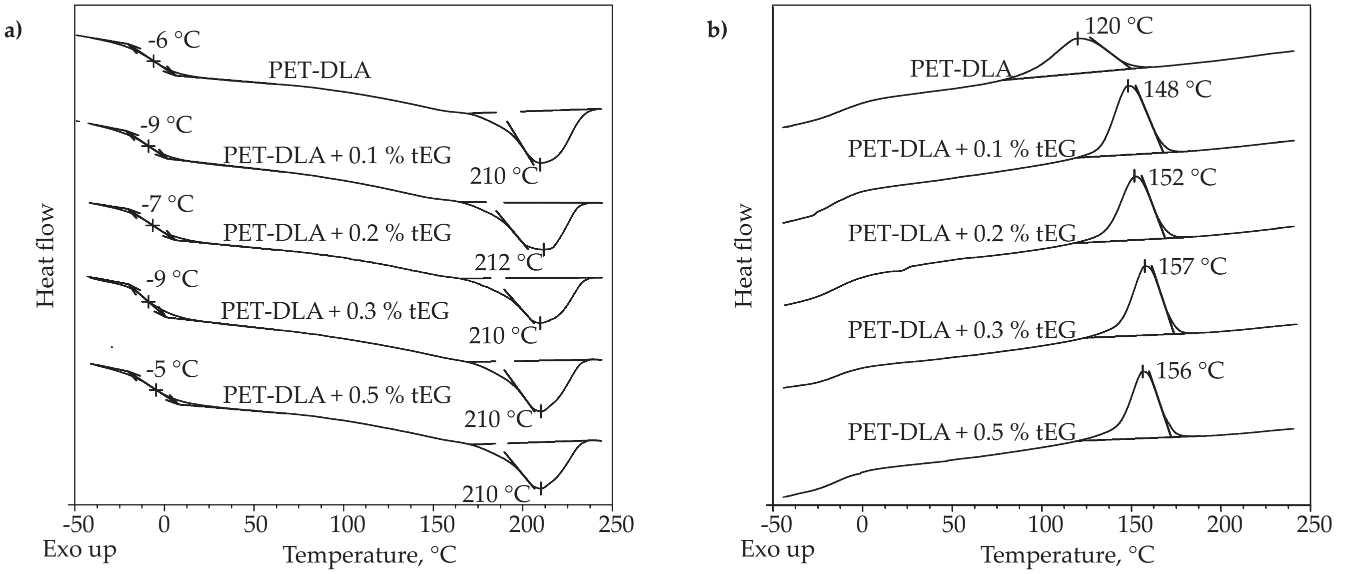


Fig. 4. Thermal properties of PET-DLA expanded graphite nanocomposites: a) second heating thermograms, b) cooling thermograms

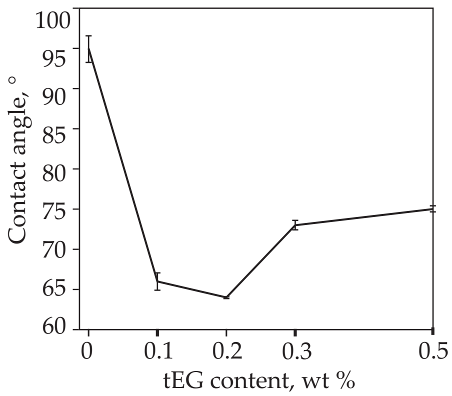


Fig. 5. Contact angle values of synthesized composites

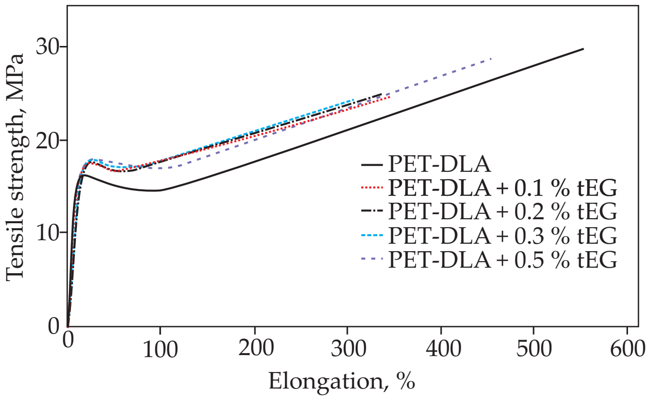


Fig. 6. Stress-strain curves of obtained materials

groups, since carboxyl and hydroxyl groups raise the surface energy. Moreover, it is well known that the contact angle decreases with increase in surface energy and smoothness [43]. Since graphene sheets have high surface area with high surface energy, the addition of graphene nanofillers increases the surface area of obtained nanocomposites. The obtained results may suggest their favorable behavior in a direct contact with cells, however further studies are necessary.

The mechanical properties of synthesized materials are listed in Table 2 and presented in Fig. 6. Tensile tests were performed on thin films (0.5 mm) cut into "dog bone" shape. The elongation at break values of the composites decrease with increasing tEG content, and these values are lower as compared to the value of the neat copolymer. However, no significant changes in tensile strength were noticed for materials containing 0.1, 0.2 and 0.3 wt % of nanofiller. The Young's modulus values dropped with the increasing amount of tEG in these materials. However, the material with the highest amount of nanofiller showed similar properties to the neat one. Interestingly, all nanocomposites show similar, but higher then observed for neat copolymer, values of yield strength, thus indicating that there might be an improvement in adhesion between filler and polymer matrix due to the high surface area of the filler [44]. In general, mechanical properties of polymers are strictly connected with the degree of crystallinity. In case of multi-block thermoplastic elastomers, mechanical properties increase with crystallization degree and the type and morphology of crystals is very important for fracture toughness of composites [45]. Here, for all obtained nanocomposites, W_c values are lower than that for the neat material (Table 1). Therefore, we did not notice any improvement in mechanical properties of obtained nanocomposites. Since NMP was used as a solvent for preparation of dispersion, it is also possible that used nanofiller might decrease catalytic activity of polycondensation due to polar groups on the surface of graphene [46]. Finally, as the FT-IR spectra indicated, there is no significant chemical interaction between nanofiller and the polymer matrix; thus, we can expect only physical interaction between tEG and the polymer matrix, therefore improvement in tensile strength is not observed (Fig. 6).

CONCLUSIONS

In the present work, segmented PET-DLA nanocomposites containing tEG nanoplatelets as nanofiller were successfully synthesized *in situ* during polycondensation. The advantage of this method is relatively uniform distribution of tEG in the polymer matrix. It was observed that the addition of exfoliated graphite affected T_{cr}, T_m and T_g values of new materials. Favorably, the addition of nanofiller caused a reduction in W_c of the polymers what favors easier processing. Addition of tEG affected mechanical properties in term of increased yield strength thus enhancing material properties in the elastic deformation region. No significant changes in Young's modulus and tensile strength were noticed due to lack of chemical interaction between nanofiller and polymer matrix. This filler also decreases the water contact angle

Table 2. Mechanical properties of synthesized nanocomposites

tEG content wt %	Young's modulus MPa	Yield strength MPa	Tensile strength MPa	Elongation at break %
0	303 ± 8	15 ± 1.1	29 ± 4	550 ± 30
0.1	236 ± 20	18 ± 0.4	24 ± 3	350 ± 40
0.2	190 ± 27	18 ± 1.1	25 ± 2	340 ± 25
0.3	180 ± 7	18 ± 0.9	24 ± 1	311 ± 21
0.5	290 ± 21	18 ± 0.3	28 ± 2	450 ± 40

of nanocomposites thus making their surface more hydrophilic. Since graphene as a nanofiller may improve biocompatibility and hemocompatibility of composites, the obtained results suggest that the synthesized materials, especially material containing 0.5 wt % of nanofiller, are promising candidates for further biocompatibility research.

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