Improvement of barrier properties of glycol modified poly(ethylene terephthalate) based nanocomposites containing graphene derivatives forms

Sandra Paszkiewicz1), *), Anna Szymczyk2), Daria Pawlikowska1), Izabela Irska1), Elżbieta Piesowicz1), Marek Jotko3), Sławomir Lisiecki3), Artur Bartkowiak3), Marta Sieradzka4), Ryszard Fryczkowski4), Agnieszka Kochmańska1), Paweł Kochmański1), Zbigniew Rosłaniec1)

DOI: dx.doi.org/10.14314/polimery.2017.868

Abstract: The development and further studies on several types of graphene nanoplatelets (GNP) have enabled manufacture of electrically conductive and reinforced polymer nanocomposites with enhanced gas barrier performance at extremely low loading. Herein, we present the synthesis process, morphology and gas barrier properties of the glycol modified poly(ethylene terephthalate) (PETG) based nanocomposites. For the first time, we compared how different types of GNPs, at the same nanofiller's content of 0.5 wt %, affect the properties of polymer matrix obtained by *in situ* polymerization.

Keywords: graphene derivatives forms, glycol-modified poly(ethylene terephthalate), *in situ* polymerization, barrier properties.

Poprawa właściwości barierowych nanokompozytów polimerowych opartych na modyfikowanym poli(tereftalanie etylenu) z dodatkiem pochodnych grafenu

Streszczenie: Opracowano nanokompozyty polimerowe (PETG) na bazie poli(tereftalanu etylenu) (PET) modyfikowanego glikolem cykloalifatycznym z niewielkim dodatkiem wybranych typów płytek grafenowych (GNP). Zbadano morfologię PETG oraz ich właściwości barierowe. Oceniono wpływ dodatku różnego typu nanopłytek grafenowych na właściwości osnowy polimerowej w nanokompozytach otrzymanych metodą polimeryzacji *in situ*. Stwierdzono, że otrzymane, wzmocnione nanocząstkami grafenu i elektrycznie przewodzące kompozyty PETG odznaczały się zwiększoną barierowością w stosunku do par i gazów.

Słowa kluczowe: pochodne grafenu, poli(tereftalan etylenu) modyfikowany glikolem cykloalifatycznym, polimeryzacja *in situ*, właściwości barierowe.

Poly(ethylene terephthalate) (PET), a semicrystalline thermoplastic polyester is widely used in the manufacture of fibers, films, and beverage containers, due to its exceptional properties, like high transparency, high dimensional stability, and good thermal and mechanical properties [1–4]. In numerous applications, PET can directly compete with polyethylene (PE), polypropylene (PP) and polystyrene (PS) on food and beverage packaging markets. One can use PET to make containers for soft drinks, juices, alcoholic drinks, water, edible oils, house-hold cleaners, and other food and non-food applications [5]. In the case of the barrier and packaging industry, one of the main fields of PET applications is the plastic bottles market for carbonated soft drinks on account of its inherent properties including good resistance to gas permeation (particularly oxygen and carbon dioxide). Along with an increasing demand for high performance PET based materials for sensitive beverages applications, such as beer, wine, juices, *etc*., recent studies have been focused to produce products at minimal changes in equipment, processes and cost of inputs, with enhanced barrier properties for food packaging and beverages applications [5].

---

1) West Pomeranian University of Technology, Institute of Material Science and Engineering, Al. Piastow 19, 70-310 Szczecin, Poland.

2) West Pomeranian University of Technology, Institute of Physics, Al. Piastow 48, 70-311 Szczecin, Poland.

3) West Pomeranian University of Technology, Faculty of Food Sciences and Fisheries, Center of Bioimmobilisation and Innovative Packaging Materials, Klemensa Janickiego 35, 71-270 Szczecin, Poland.

4) University of Bielsko-Biala, Institute of Textile Engineering and Polymer Materials, Willowa 2, 43–309 Bielsko-Biala, Poland.

*) Author for correspondence; e-mail: spaszkiewicz@zut.edu.pl

In the last 20 years several strategies have been proposed in order to achieve these objectives, *i.e.*, to increase barrier properties of PET to gases (in particular oxygen and carbon dioxide). For instance, some companies such as DuPont, Sidel, and PPG have developed bottle coating systems for the reduction of both O_2 and CO_2 permeation. Another approach consists in blending PET with high barrier constituents that can be dispersed as domains oriented perpendicular to the direction of gas flow thus increasing tortuosity of the diffusion pathway [6]. However, this approach is limited due to the non-perfect compatibility between PET and polyamides, which results in yellow color and haziness, in oriented blend films and in bottle walls [7]. Notwithstanding, preparation of polymer nanocomposites may be the best approach. They are polymers (thermoplastics, thermosets, or elastomers) that one can reinforce with small quantities (less than 5 % by weight) of very high aspect ratio ($l/d > 300$) fillers. So far, among different types of fillers, those based on clays and natural silicates were very widely used in packing applications due to their abundance and easy availability. Uniformly dispersed nanoclays of very high aspect ratios have proved to provide a wide variety of added benefits by the combination of mechanical, thermal, optical and fore mostly, barrier properties to the material [8–11]. However, the discovery of graphene, due to its intriguing properties including high electron mobility at room temperature [12, 13], exceptional thermal conductivity [14], and superior mechanical properties [13] attracted much attention on nanocomposites with its content [15, 16]. Additionally, extremely high surface area and gas impermeability [17] prove great potential of graphene for improving electrical, mechanical, thermal, and gas barrier properties of polymers.

In contrast to semicrystalline PET, glycol modified poly(ethylene terephthalate) (PETG) copolyester is an amorphous thermoplastic polyester that exhibits a glass transition temperature (T_g) of about 80 °C, similar to PET [18–20]. On account of its transparency and clarity, PETG is used in medical, pharmaceutical and cosmetic packaging. Recently, several studies of PETG/layered silicate nanocomposites have been published. Kalgaonkar *et al.* [21–24] investigated how the intercalant affected the viscoelastic properties of the PETG/layered silicate nanocomposites, which were prepared by melt blending PETG with organically modified montmorillonites. The melt blending method was also used to prepare PETG/montmorillonite nanocomposites and studied the effects of surfactant concentrations on the dispersion of montmorillonite in PETG matrix by Ranade *et al.* [25]. In turn, Couderc *et al.* [26] studied the relaxation of PETG/montmorillonite nanocomposites by dielectric methods. Additionally, Tsai *et al.* [27] studied how the layered silicate affects the gas barrier, optical transparency, physical, and thermal properties of PETG based nanocomposites *via in situ* intercalation polymerization. The optical transmittances of nanocomposites that contained 0.5, 1.0 and 3.0 wt % of organoclay were 86.8 %, 84.4 % and 77.4 %, respectively. The oxygen transmission rate of the nanocomposite that contained 3 wt % of organoclay decreased of about 50 % of this value for PETG based polymer.

Among these investigations, none addresses the effect of different types of graphene nanoplatelets on both the gas barrier and processing properties of the PETG based nanocomposites, without sacrificing their optical properties.

EXPERIMENTAL PART

Materials

For the glycol modified poly(ethylene terephthalate) (PETG) and PETG based nanocomposites' synthesis the following chemicals were used: dimethyl terephthalate (DMT) (Sigma-Aldrich), ethane-1,2-diol (ED) (Sigma-Aldrich) distilled before using, 1,4-cyclohexanedimethanol (CHDM) (Sigma-Aldrich), zinc acetate (ester exchange catalyst) $Zn(CH_3COO)_2$ (Sigma-Aldrich), germanium dioxide – polycondensation catalyst – GeO_2 (PPM Pure Metals GmbH), thermal stabilizer Irganox 1010 (Ciba-Geigy, Switzerland).

As nanofillers, three types of graphene nanoplatelets (GNPs) were added at the content of 0.5 wt %, *i.e.*:

– GNP-ANG, was purchased from Angstron Materials (Dayton, Ohio, USA) in the form of a powder with the thickness of less than three graphene layers, average platelets size of up to 10 μm, carbon content of ~ 97.0 % and the oxygen content of ~ 2.10 %.

– GNP-LTR, which was provided by the group of Professor R. Fryczkowski and obtained *via* low temperature reduction of graphene oxide below 240 °C (wherein graphene oxide was obtained following the procedure published in [28, 29]), exhibited an average number of 7 layers as determined by XRD studies, the average size that did not exceed 20 μm, while the C and O content was 85.42 % and 14.58 %, respectively, based on the XPS.

– GNP-NH_2 was purchased from NanoInnova Technologies SL (Madrid, Spain) in the form of reduced graphene oxide with NH_2 groups (rGO-NH_2). According to producer data sheet: average nanosheets size of up to 10 μm, the oxygen to carbon ratio of 0.006 and nitrogen to carbon ratio of 0.162; the number of free amino groups measured with a quantitative Kaiser test of 0.1 mmol NH_2/g; to estimate the amount of NH_2 groups in rGO-NH_2 a reaction with tetrabromophthalic anhydride performed and the Br amount was quantified by X-ray fluorescence spectroscopy and by the Schöniger flask test and corresponds to 0.23 mmol/g and 0.21 mmol/g, respectively.

In situ synthesis of PET/carbon nanofiller composites

Nanocomposites based on PETG and three types of graphene derivatives were prepared by *in situ* polymerization following the same procedure as already published in [30, 31]. Graphene derivatives (GNP-ANG, GNP-LTR and GNP-NH_2) were dispersed by high-speed stirring

(Ultra-Turax T25) and sonicator (Homogenizer HD 2200, Sonoplus) in ED for 30 min each and subsequently dispersed using a low-power sonic bath for 8 hours. This additional step of dispersing graphene nanosheets in liquid monomer led to much better exfoliation, which has been previously confirmed for PET based nanocomposites containing expanded graphite [32]. The *in situ* polycondensation was carried out in a steel reactor (Autoclave Engineers Inc, USA) in the presence of the nanoplatelets under continuous mixing. At the end of the synthesis the nanocomposite or the polymer was extruded from the reactor using compressed nitrogen into water bath. This method allows to obtain samples with GNP-ANG, GNP-LTR and GNP-NH_2 at the weight concentration of 0.5 wt % in PETG matrix.

Sample preparation

In order to prepare the test samples, the obtained materials were granulated and injection molded into dumbbell shape samples (type 3) with a total length of 60 mm, a rectangular cross section of 2 x 4 [mm^2] and a gage length of 20 mm. Thin polymer foils with a thickness of ~ 220 μm were prepared for optical microscopy and barrier studies by press molding (Collin P 200E) at 250 °C, and the pressure of 0.5 MPa for 2 min and 1.0 MPa for another 1 min and subsequently quenched in ice water. The thickness of thin films was measured with a Micrometer mod. 293-521 from Mitutoyo. The thickness is an average value.

Methods of testing

– The intrinsic viscosity [η] of the polymer and the series of nanocomposites was determined at 30 °C in the mixture of phenol/1,1,2,2-tetrachloroethane (60/40 by weight). The concentration of the polymer solution was of 5 g/dm^3. The measurement was carried using a capillary Ubbelohde viscometer (type Ic, $K = 0.03294$). The density of the dumbbell shape samples was measured at 23 °C on hydrostatic scales (Radwag WPE 600C, Poland), calibrated according to standards with known density.

– The amorphous structure of the samples was confirmed by differential scanning calorimeter (DSC), measurements were carried out with a DSC1 (Mettler Toledo) which was calibrated for temperature and melting enthalpy by using indium and *n*-octane as standards under a N_2 atmosphere with a heating rate of 10 deg/min in the temperature range of 25–300 °C. Then, from the second heating the glass transition T_g was determined. Since all samples were found to be amorphous, the softening temperatures of the samples were determined using Boethius apparatus. The method's principle was to observe the moment, when the edges of the samples start to melt as a result of constantly increasing temperature.

– The quality of the dispersion of three types of graphene nanoplatelets used in this study was analyzed with scanning electron microscopy using FE-SEM Hitachi SU–70 microscope. The nanocomposite samples were cryofractured in liquid nitrogen and then coated with palladium-gold alloy thin film using thermal evaporation PVD (physical vapor deposition) method to provide electric conductivity. SEM analyses were performed at accelerating voltage of 5 kV and secondary electron images were acquired. Moreover, light microscopy observations were performed using Nikon MM-40 microscope, operating at transmission light mode.

– Oxygen permeability was measured using a Mocon--OX-Tran 2/10 instrument (23 °C and 0 % humidity rate *RH*) in accordance with ISO 15105-2 standard, while water vapor permeability was measured using a moisture analyzer (MAC 50, RADWAG, Poland) equipped with Sampler 2000, both using 5 cm^2 samples of examined polymer films accordingly to the procedure previously described in detail in [33]. All polymer samples were conditioned for 3 h in the test chamber of OX-Tran apparatus in test parameters (23 °C and 0 % humidity rate *RH*).

RESULTS AND DISCUSSION

PETG and PETG based nanocomposites containing 0.5 wt % of three types of graphene nanoplatelets were obtained by *in situ* polymerization. The chemical structure of the PETG [with 30 mol % of poly(ethylene-*co*-cyclohexanedimethanol)terephthalate] was already confirmed using ^1H NMR and gas chromatography in [31]. In Table 1 the physicochemical properties by means of intrinsic viscosity, density and softening temperature along with H_2O and O_2 transmission rates are summarized.

The average viscosity molecular masses for the prepared materials were not estimated, since the values of

T a b l e 1. Physicochemical and gas barrier properties for the obtained nanocomposites based on PETG

Sample	[η] dl/g	*d* g/cm^3	Softening temperature^B °C	Thickness of the polymer foil μm	H_2O transmission rate $cm^3/(m^2 \cdot 24\ h)$	O_2 transmission rate $cm^3/(m^2 \cdot 24\ h)$
PETG	0.696	1.2426	123 ± 3	206 ± 5	7.1 ± 0.4	63.8 ± 1.1
PETG/0.5GNP-ANG	0.553	1.2459	130 ± 3	205 ± 3	9.1 ± 0.8	51.4 ± 4.7
PETG/0.5GNP-LTR	0.559	1.2769	131 ± 3	208 ± 7	6.2 ± 0.2	56.3 ± 4.2
PETG/0.5GNP-NH_2	0.543	1.2630	130 ± 5	205 ± 4	10.7 ± 2.1	61.6 ± 0.5

[η] – Intrinsic viscosity, *d* – density measured at 23 °C, ^{B} – softening temperature according to Boethius method.

the adequate coefficients in the Mark-Houwink equation (from which one can calculate the average viscosity molecular mass) have not been designated so far. The decrease of intrinsic viscosity [η] values were observed when graphene nanoplatelets were added into PETG matrix. In general, the addition of carbon nanofillers, and in particular GNPs, cause the decrease in intrinsic viscosity and thus molecular masses of polymer nanocomposites prepared by *in situ* polymerization [31–35]. It results from the influence of nanoparticles on the polymerization process, causing an increase of the melt viscosity of the polymer, which is due to polymer-nanofiller and nanofiller-nanofiller interactions. Moreover, all three types of GNPs brought about the increase of the hydrostatic density. The density of the PETG, similarly like amorphous PET [4], is lower than the density of GNPs. Since the incorporation of GNPs didn't affect the crystallization of PETG (no peaks of melting and crystallization in Fig. 1), one can conclude that this increase is only caused by the direct influence of the addition of the component with higher density.

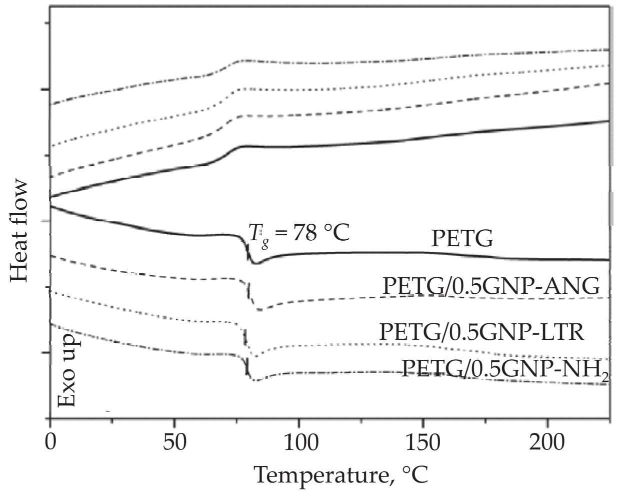

Fig. 1. DSC thermograms during 2nd heating and cooling for PETG based nanocomposites containing GNPs

Furthermore, for all nanocomposites the increase of softening temperature estimated accordingly to the Boethius method, was observed. However, the addition of GNPs into PETG matrix didn't affect the glass transition temperature. This is in the agreement with our previous studies on the nanocomposites based on thermoplastic polyesters matrices [31, 35]. However, the extensive studies made by the group of Macosko [36, 37] showed that the T_g of polymer nanocomposites containing GNPs can be increased only if strong interfacial interactions exhibit between polymers matrix and nanofillers. It was noted, that blending processes (like solvent and melt blending) that did not involve covalent bonding to the graphene surface, were generally incapable of providing enough restriction by interactions between the polymer matrices and fillers. However, the blending processes involving chemical reactions, such as chemically modified graphene or *in situ* polymerization of monomers in the presence of thermally or chemically reduced graphene (TRG or CRG), or graphene oxide (GO), were capable of providing strong confinement by covalent bonds between matrix polymers and fillers. One exception was *in situ* polymerized monomers in the presence of pristine graphene, which showed no T_g change of the resulting nanocomposites [38]. This was because no oxidized functional groups or reactive C=C exist on pristine graphene surface for the monomer to chemically react with. Since, in this case no effect on the T_g was observed, even for PETG/0.5GNP-NH$_2$, one can conclude that no strong interfacial interactions exhibit between polymers matrix and nanofillers which might restrict the polymer chains movements. However, some weak interactions exhibited between both phases, since the improvement in gas barrier properties was observed (Table 1), but they were not strong enough to affect the T_g. Indeed, several studies [39–41] confirmed a significant change in T_g even at the very low loading of GNPs but all of these nanocomposites were prepared by solvent blending. However, since the chemical blending processes such as *in situ* polymerization or chemically modified fillers yielded significant T_g increases in polymer/GNPs nanocomposites [37], our research will be extended upon different types of GNPs or different concentrations in PETG.

Due to its unique structure, GNPs exhibited excellent thermal, mechanical and electrical properties [42–45]. However, one of the most promising applications of graphene is its incorporation into polymer nanocomposites. However, one can find this application of graphene to be hampered by the poor solubility of pristine graphene in the most commonly used solvents. Furthermore, the large surface area of graphene results in significant aggregation in a polymer matrix due to van der Waals interactions [44]. A challenge is to achieve good dispersion of the atomically thin sheets of graphene in the whole volume of the polymer matrix. One approach to fabricate well dispersed graphene based nanocomposites, is an appropriate surface modification in order to obtain graphene oxide (GO) nanosheets [46–49]. The functional groups on the surface of graphene, such as hydroxyl, epoxide, carbonyl, and carboxyl, are effective in improving interfacial bonding between the GO nanosheets and the polymer matrix. While the second approach is to use the appropriate method of fabrication of polymer/GNPs nanocomposites. Therefore, in this study we compared how several types of graphene nanoplatelets, including chemically modified GNP containing NH$_2$ groups, affect the water vapor and oxygen barrier properties of PETG nanocomposites prepared by *in situ* polymerization, which enabled to obtain well-dispersed nanoparticles (Figs. 2, 3).

In the case of water vapor barrier properties, the improvement was observed only when GNP-LTR was used a nanofiller. It was probably due to the size of nanoplatelets (~ 20 μm) [28, 29] at the relatively good distribution of these nanoplatelets in polymer matrix (Fig. 2b). In other cases, especially in the case of PETG that contained

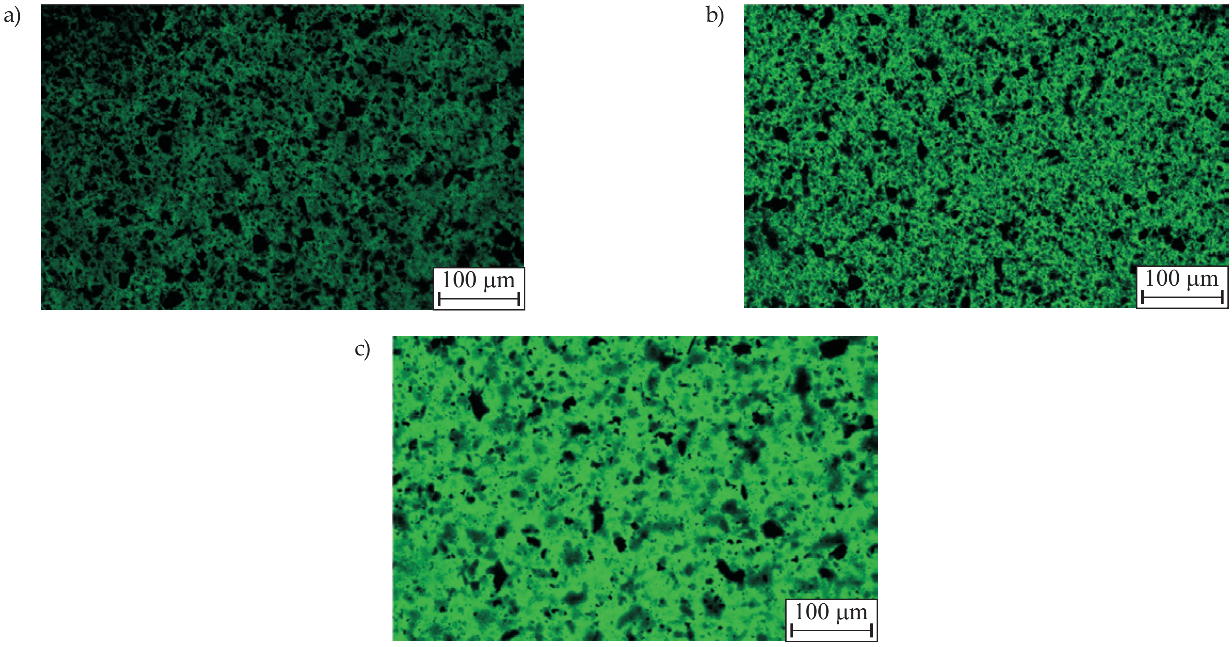

Fig. 2. Optical microscopy images of nanocomposites thin foils used for permeability measurements: a) PETG/0.5GNP-ANG, b) PETG/0.5GNP-LTR, c) PETG/0.5GNP-NH$_2$

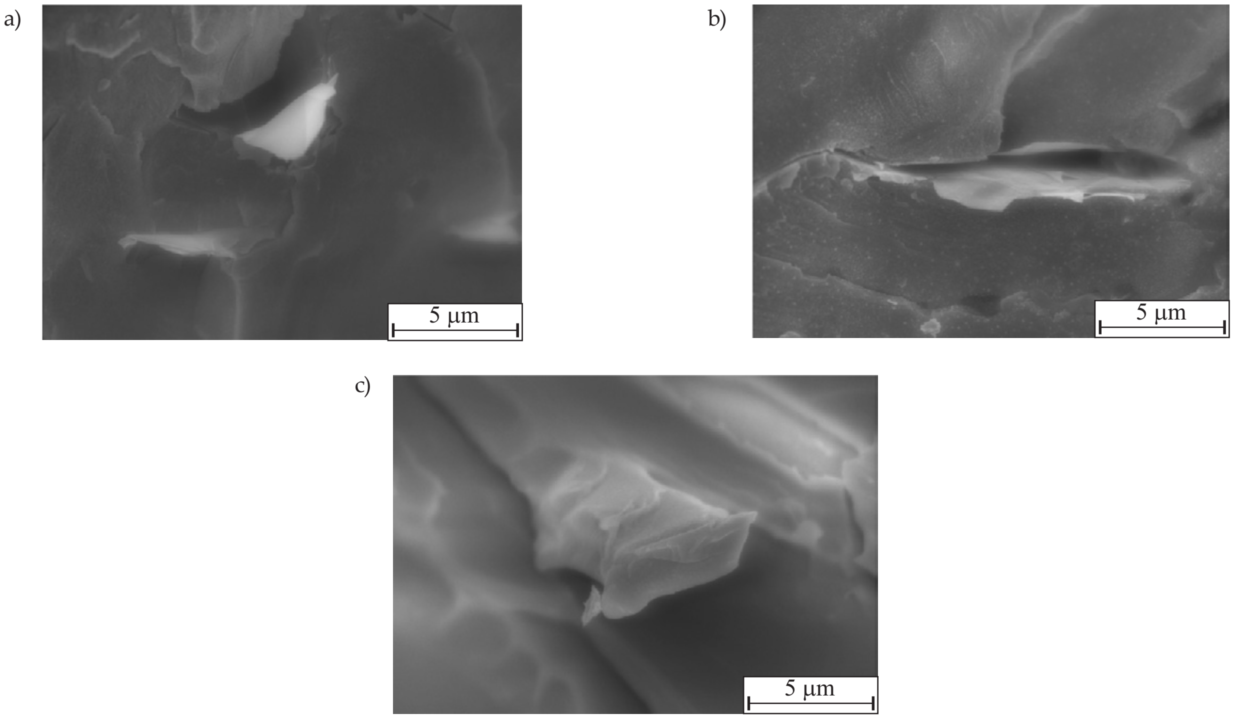

Fig. 3. Scanning electron micrographs of nanocomposites thin foils used for permeability measurements: a) PETG/0.5GNP-ANG, b) PETG/0.5GNP-LTR, c) PETG/0.5GNP-NH$_2$

0.5 wt % of GNP-NH$_2$ a marked increase in water vapor transmission rate was noted (*ca.* 35 %). It is probably due to interactions between hydrogen (from NH$_2$ group) and the carbonyl groups in PETG matrix (hydrogen bonds are formed) [50, 51]. The functionalization of graphene surface with NH$_2$ groups improved the dispersion of nanoplatelets (Fig. 2c) and simultaneously improved "anchoring" of the nanofiller within the polymer matrix (Fig. 3c – GNP-NH$_2$ seemed to be covered with the polymer matrix). Unfortunately, the barrier properties towards water vapor of PETG/GNP-NH$_2$ were impaired, since the NH$_2$ group is clearly hydrophilic. Considering *OTR* (oxygen transmission rate), here again the GNP-NH$_2$ didn't improve the barrier properties of nanocomposite – the permeability was at similar level as for the neat PETG (Table 1). However, the decrease in *OTR* was observed for other (non-functionalized) graphene nanoplatelets, *i.e.*, GNP-LTR and GNP-ANG. One can clearly observe that the *in situ* polymerization allowed uniform distribution of both smaller (GNP-ANG, platelets' size of *ca.* 10 μm) (Figs. 2a and 3a) and bigger (GNP-LTR, platelets' size of *ca.* 20 μm) (Figs. 2b and 3b) graphene nanoplatelets, thus improving the barrier properties against oxygen.

Of special importance is to underline the remark that the *in situ* polymerization method enabled good distribution of nanofillers, both functionalized and non-functionalized (Figs. 2, 3), since in polymer nanocomposites, aggregated nanofillers have been shown to give rise to new pathways for water diffusion at the nanofiller-polymer interfacial zones, and therefore increase water or other gases permeation [52, 53]. Regardless of the fact, if the nanoplatelets stick out from the matrix (Figs. 3a, 3b) or are covered with the polymer (Fig. 3c), their distribution was homogeneous in the whole volume even at the "microscopic" level (Figs. 2a–c). Although one can often observe agglomeration effects in polymer nanocomposites, it is obvious that for graphene nanocomposites, the critical filler concentration above which these effects are found might occur at very low concentrations, for instance: 0.1 wt % graphene [54], 0.06 wt % graphene oxide [55], 0.8 wt % graphene oxide [56], 1 wt % graphite [57], *etc.* Thereby it seems that polymer/graphene nanocomposites are particularly susceptible to agglomeration/aggregation effects at low filler concentrations, which could impair the utilization of gas-impermeable nature of GNPs. Therefore, achieving very high degree of distribution (proper dispersion) of graphene nanoplatelets allows us to expand this study upon different GNPs at lower or higher concentrations in order to obtain greater improvement in barrier properties, and thus to contribute to the expansion of knowledge about polymer nanocomposites based on PETG at the packaging market.

CONCLUSIONS

Graphene derivatives forms are multifunctional nanofillers that can play a significant role in increasing the gas barrier properties of polymer films at very low loading. Preliminary study of barrier properties of PETG films revealed that graphene nanoplatelets have the potential to retard the diffusion of permeating molecules (O_2, H_2O) while, on the other hand, barrier efficiency of graphene derivatives is balanced by the degree of exfoliation of graphene nanoplatelets in polymer matrix, their size and presence of functional group on their surface. Some functional groups can improve the dispersion of GNP, however, at the same time, polar groups, like NH_2, might affect the solubility and permeability of O_2 and H_2O molecules. This has been observed in PETG/GNP-NH_2 nanocomposite, where the *OTR* was at similar level as for the neat PETG. In turn, the decrease in *OTR* was observed for PETG/GNP-LTR and PETG/GNP--ANG nanocomposites. Thermal analysis indicates that the presence of different types of GNPs at the loading of 0.5 wt % in PETG matrix has no effect on T_g but causes an increase of the softening point of the material probably due to the decrease of molecular mobility of PETG chains.

This work is the result of the research project GEKON2/O5/266860/24/2016 funded by the National Centre for Research and Development and National Fund for Environmental Protection and Water Management, Poland.

REFERENCES

[1] Awaja F., Dumitru P.: *European Polymer Journal* **2005**, *41*, 1453. http://dx.doi.org/10.1016/j.eurpolymj.2005.02.005
[2] Jabarin S.A.: *Polymeric Materials Encyclopedia* **1996**, *8*, 6078.
[3] Jabarin S.A.: *Polymer Enigeering & Science* **1984**, *24*, 376. http://dx.doi.org/10.1002/pen.760240513
[4] Scheirs J., Long T.E.: "Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters" (Eds. Scheirs J., Long T.E.), John Wiley & Sons, Ltd 2003. http://dx.doi.org/10.1002/0470090685
[5] Wang Y.: "PET and MXD6 montmorillonite nanocomposites", Theses and Dissertations, The University of Toledo 2012, p. 462.
[6] Subramanian P.M., Mehra V.: *Polymer Engineering & Science* **1987**, *27*, 663. http://dx.doi.org/10.1002/pen.760270910
[7] Maruhashi Y., Iida S.: *Polymer Engineering & Science* **2001**, *41*, 1987. http://dx.doi.org/10.1002/pen.10895
[8] Maiti P., Nam P.H., Okamoto M. *et al.*: *Macromolecules* **2002**, *35*, 2042. http://dx.doi.org/10.1021/ma010852z
[9] Picard E., Vermogen A., Gérard J.F. *et al.*: *Journal of Membrane Science* **2007**, *292*, 133. http://dx.doi.org/10.1016/j.memsci.2007.01.030
[10] Yano K., Usuki A., Okada A. *et al.*: *Journal of Polymer Science Part A: Polymer Chemistry* **1997**, *35*, 2289. http://dx.doi.org/10.1002/(SICI)1099-0518(199708)35:11<2289::AID-POLA20>3.0.CO;2-9
[11] Bharadwaj R.K., Mehrabi A.R., Hamilton C. *et al.*: *Polymer* **2002**, *43*, 3699. http://dx.doi.org/10.1016/S0032-3861(02)00187-8
[12] Geim A.K., Novoselov K.S.: *Nature Materials* **2007**, *6*, 183. http://dx.doi.org/10.1038/nmat1849
[13] Lee C., Wei X., Kysar J.W. *et al.*: *Science* **2008**, *321*, 385. http://dx.doi.org/10.1126/science.1157996
[14] Balandin A.A., Ghosh S., Bao W. *et al.*: *Nano Letters* **2008**, *8*, 902. http://dx.doi.org/10.1021/nl0731872
[15] Singh V., Joung D., Zhai L. *et al.*: *Progress in Materials Science* **2011**, *56*, 1178. http://dx.doi.org/10.1016/j.pmatsci.2011.03.003
[16] Bunch J.S., Verbridge S.S., Alden J.S. *et al.*: *Nano Letters* **2008**, *8*, 2458. http://dx.doi.org/10.1021/nl801457b
[17] Shah R., Datashvili T., Cai T. *et al.*: *Material Research Innovations* **2015**, *19*, 97. http://dx.doi.org/10.1179/1433075X14Y.0000000220
[18] Turner S.R.: *Journal of Polymer Science Part A: Polymer Chemistry* **2004**, *42*, 5847.

http://dx.doi.org/10.1002/pola.20460
[19] Tsai Y., Fan C.H., Hung C.Y. *et al.*: *Journal of Applied Polymer Science* **2007**, *104*, 279. http://dx.doi.org/10.1002/app.25592
[20] Tsai Y., Fan C.H., Hung C.Y. *et al.*: *Journal of Applied Polymer Science* **2008**, *109*, 2598. http://dx.doi.org/10.1002/app.28385
[21] Kalgaonkar R.A., Jog J.P.: *Journal of Polymer Science Part B: Polymer Physics* **2003**, *41*, 3102. http://dx.doi.org/10.1002/polb.10616
[22] Kalgaonkar R.A., Jog J.P.: *Journal of Macromolecular Science, Part B: Physics* **2004**, *43*, 421.
[23] Kalgaonkar R.A., Nandi S., Tambe S.S. *et al.*: *Journal of Polymer Science Part B: Polymer Physics* **2004**, *42*, 2657. http://dx.doi.org/10.1002/polb.20128
[24] Kalgaonkar R.A., Jog J.P.: *Journal of Polymer Science Part B: Polymer Physics* **2008**, *46*, 2539. http://dx.doi.org/10.1002/polb.21603
[25] Ranade A., D'Souza N., Thellen C. *et al.*: *Polymer International* **2005**, *54*, 875. http://dx.doi.org/10.1002/pi.1777
[26] Couderc H., Delbreilh L., Saiter A. *et al.*: *Journal of Non-Crystalline Solids* **2007**, *353*, 4334. http://dx.doi.org/10.1016/j.jnoncrysol.2007.03.046
[27] Tsai Y., Fan C.H., Hung C.Y. *et al.*: *Polymer Composites* **2011**, *32*, 89. http://dx.doi.org/10.1002/pc.21021
[28] Fryczkowski R., Gorczowska M., Ślusarczyk C. *et al.*: *Composite Science and Technology* **2013**, *80*, 87. http://dx.doi.org/10.1016/j.compscitech.2013.03.012
[29] Fryczkowska B., Sieradzka M., Sarna E. *et al.*: *Journal of Applied Polymer Science* **2015**, *132*. http://dx.doi.org/10.1002/APP.42789
[30] Paszkiewicz S., Pawelec I., Szymczyk A. *et al.*: *International Journal of Materials Engineering and Technology* **2014**, *11*, 139.
[31] Paszkiewicz S., Szymczyk A., Spitalsky Z. *et al.*: *Polimery* **2013**, *58*, 893. http://dx.doi.org/10.14314/polimery.2013.893
[32] Paszkiewicz S., Szymczyk A., Špitalský Z. *et al.*: *Journal of Polymer Science Part B: Polymer Physics* **2012**, *50*, 1645. http://dx.doi.org/10.1002/polb.23176
[33] Szymczyk A., Paszkiewicz S., Pawelec I. *et al.*: *Journal of Nanomaterials* **2015**, ID 382610. http://dx.doi.org/10.1155/2015/382610
[34] Paszkiewicz S., Szymczyk A., Špitalský Z. *et al.*: *European Polymer Journal* **2014**, *50*, 69. http://dx.doi.org/10.1016/j.eurpolymj.2013.10.031
[35] Paszkiewicz S., Pawelec I., Szymczyk A. *et al.*: *Polymer Engineering and Science* **2015**, *55*, 2222. http://dx.doi.org/10.1002/pen.24107
[36] Macosko C.: "Does graphene increase T_g of polymer nanocomposites?", 6th International Conference on Carbon Nano Particle Based Composites, Dresden, Germany, September 22–25, 2013.
[37] Liao K.H., Aoyama S., Abdala A.A. *et al.*: *Macromolecules* **2014**, *47*, 8311. http://dx.doi.org/10.1021/ma501799z
[38] Wang X.W., Zhang C.A., Wang P.L. *et al.*: *Langmuir* **2012**, *28*, 7091. http://dx.doi.org/10.1021/la204894h
[39] Keddie J.L., Jones R.A.L., Cory R.A.: *Faraday Discuss* **1994**, *98*, 219. http://dx.doi.org/10.1039/FD9949800219
[40] Ellison C.J., Torkelson J.M.: *Nature Materials* **2003**, *2*, 695. http://dx.doi.org/10.1038/nmat980
[41] Grohens Y., Hamon L., Reiter G. *et al.*: *The European Physical Journal E* **2002**, *8*, 217. http://dx.doi.org/10.1140/epje/i2001-10088-4
[42] Potts J.R., Dreyer D.R., Bielawski C.W. *et al.*: *Polymer* **2011**, *52*, 5. http://dx.doi.org/10.1016/j.polymer.2010.11.042
[43] Verdejo R., Bernal M.M., Romasanta L.J. *et al.*: *Journal of Materials Chemistry* **2011**, *21*, 3301. http://dx.doi.org/10.1039/C0JM02708A
[44] Kuilla T., Bhadra S., Yao D. *et al.*: *Progress in Polymer Science* **2010**, *35*, 1350. http://dx.doi.org/10.1016/j.progpolymsci.2010.07.005
[45] Wang J., Xu C., Hu H. *et al.*: *Journal of Nanoparticle Research* **2011**, *13*, 869. http://dx.doi.org/10.1007/s11051-010-0088-y
[46] Compton O.C., Nguyen S.T. *et al.*: *Small* **2010**, *6*, 711. http://dx.doi.org/10.1002/smll.200901934
[47] Loryuenyong V., Totepvimarn K., Eimburanapravat P. *et al.*: *Advances in Materials Science and Engineering* **2013**, ID 923403. http://dx.doi.org/10.1155/2013/923403
[48] Kuila T., Bose S., Mishra A.K. *et al.*: *Progress in Materials Science* **2012**, *57*, 1061. http://dx.doi.org/10.1016/j.pmatsci.2012.03.002
[49] Spitalsky Z., Danko M., Mosnacek J.: *Current Organic Chemistry* **2011**, *15*, 1133. http://dx.doi.org/10.2174/138527211795202988
[50] Lu X., Wang Y., Wu X.: *Polymer* **1994**, *35*, 2315. http://dx.doi.org/10.1016/0032-3861(94)90767-6
[51] Mattia J., Painter P.A.: *Macromolecules* **2007**, *40*, 1546. http://dx.doi.org/10.1021/ma0626362
[52] Alexandre B., Langevin D., Médéric P. *et al.*: *Journal of Membrane Science* **2009**, *328*, 186. http://dx.doi.org/10.1016/j.memsci.2008.12.004
[53] Tan B., Thomas N.L.: *Journal of Membrane Science Volume* **2016**, *514*, 595. http://dx.doi.org/10.1016/j.memsci.2016.05.026
[54] Jin J., Rafiq R., Gill Y.Q. *et al.*: *European Polymer Journal* **2013**, *49*, 2617. http://dx.doi.org/10.1016/j.eurpolymj.2013.06.004
[55] Lai C.L., Fu Y.J., Chen J.T. *et al.*: *Carbon* **2015**, *90*, 85. http://dx.doi.org/10.1016/j.carbon.2015.04.006
[56] Kabiri R., Namazi H.: *Cellulose* **2014**, *21*, 3527. http://dx.doi.org/10.1007/s10570-014-0366-4
[57] Kwon H., Kim D. *et al.*: *Macromolecular Research* **2013**, *21*, 987. http://dx.doi.org/10.1007/s13233-013-1124-4

Received 3 I 2017.