Research Article

Oxygen Barrier Properties and Melt Crystallization Behavior of Poly(ethylene terephthalate)/Graphene Oxide Nanocomposites

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Poly(ethylene terephthalate) nanocomposites with low loading (0.1–0.5 wt%) of graphene oxide (GO) have been prepared by using *in situ* polymerization method. TEM study of nanocomposites morphology has shown uniform distribution of highly exfoliated graphene oxide nanoplatelets in PET matrix. Investigations of oxygen permeability of amorphous films of nanocomposites showed that the nanocomposites had better oxygen barrier properties than the neat PET. The improvement of oxygen permeability for PET nanocomposite films over the neat PET is approximately factors of 2–3.3. DSC study on the nonisothermal crystallization behaviors proves that GO acts as a nucleating agent to accelerate the crystallization of PET matrix. The evolution of the lamellar nanostructure of nanocomposite and neat PET was monitored by SAXS during nonisothermal crystallization from the melt. It was found that unfilled PET and nanocomposite with the highest concentration of GO (0.5 wt%) showed almost similar values of the long period ($L = 11.4$ nm for neat PET and $L = 11.5$ nm for PET/0.5GO).

1. Introduction

Since the discovery in 2004 by Novoselov et al. [1], graphene has initiated a growing interest in using it as a filler to polymer materials. Graphene is a one-atom-thick, two-dimensional sheet composed of sp^2 carbon atoms arranged in a plane structure [2], owning high intrinsic mobility ($2 \cdot 10^5$ cm²/Vs) [3, 4], excellent thermal conductivity (2000–5000 W/m·K), extraordinary thermal stability [5–7], remarkable structural flexibility [8, 9] and large surface area [10], with mechanical strength (with Young modulus of 1 TPa and ultimate strength of 130 GPa [9]) approximately 100 times greater than steel, which makes graphene the strongest material ever measured. Because of such superior properties, graphene has attracted much attention for a wide range of applications, including nanocomposites [11–13], sensors [14, 15], field effect transistors [16], transparent conductive films [17], and many more. Graphene is not naturally abundant due to its instability and

tendency to form three-dimensional structures (agglomeration). It can be synthesized by a variety of methods, such as chemical vapor deposition (CVD) [18, 19] arc discharge [20], epitaxial growth on SiC [21–23], chemical conversion [24], reduction of CO [25], unzipping carbon nanotubes [26, 27], and separation/exfoliation of graphite or graphite derivatives (such as graphite oxide (GO) and graphite fluoride) [28]. In addition, fast and low cost production of graphene and few-layer graphene (FLG) with high yield, where the synthesis consisted of mechanical ablation of pencil lead on a harsh glass surface with simultaneous ultrasonication followed by a purification to remove the inorganic binder present in the pencil lead was demonstrated by Janowska et al. [29]. Among those methods, it has been proven that the reduction of exfoliated graphene oxide (GO) is a reliable strategy owing to its cost-effective and massive scalability. Generally, GO is obtained by oxidation of the natural flake graphite in the presence of strong oxidants such as potassium permanganate

mixed with concentrated sulfuric acid, followed by sonication [30, 31]. After oxidation, abundant functional groups (e.g., hydroxyl, carboxyl, epoxy, and ketone) were introduced onto the graphitic layers, and simultaneously part of sp^2 -carbons were converted into sp^3 ones [32]. It is generally considered that the epoxy and carbonyl groups are attached above and below basal planes, while the carboxyl groups are located at the edges [33, 34].

Incorporation of nanofillers into a polymer matrix gives rise to a new class of materials known as polymer nanocomposites, which have greater potential for many applications. Significant improvement in properties of the composites depends mainly on the size and shape of particles nanofiller [35], surface area, degree of surface development, surface energy, and the spatial distribution of the polymer matrix of nanoparticles. It is assumed that the degree of exfoliation plays the critical role in determining the nanocomposites properties. The more homogeneous dispersions of the layered nanofillers (expanded graphite or others graphene derivatives) are, the greater improvements in properties can be obtained. Properties of polymer nanocomposites depend significantly not only on the degree of granularity and uniform dispersion of nanoparticles, but also on the type of polymer matrix and the nature of the nanofiller. In the case of the thermoplastic matrix (such as poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT)), nanofiller may also affect the crystallization rate and degree of crystallinity and the nature of the crystalline phase [36]. Crystallinity is an important field of interest in polymer science and engineering as the crystallinity affects physical properties such as modulus, tensile strength, toughness, hardness, and gas permeability.

Poly(ethylene terephthalate) (PET) is widely used in a range of high barrier applications because of its good mechanical properties and low cost. PET bottles are widely used in fruit juices, drinks, medicines, and food packaging. However, PET material has the poor barrier properties compared with glass and metal containers. Recently, packing industry has been very interested in improvement of barrier properties of PET for additional applications, due to the observed trend to a progressive change towards the use of containers of plastic material. The improvement of PET permeability to oxygen and even carbon dioxide can broaden its application to packing materials which are more sensitive to them. Enhanced barrier properties of PET properties can be achieved with the graphene nanoplatelets (GNPs) due to their unique morphology and size. Also graphene oxide possesses an excellent gas barrier without any chemical reduction [37]. Previous studies reported that GO layers and poly(ethylenimine) (PEI) layers deposited on a PET film surface PET decreased the oxygen transmittance rate (OTR) and light transmittance, and the electric conductivity increased [38]. Kim et al. [37] reported that the oxygen permeability of the poly(vinyl alcohol) (PVA)/reduced graphene oxide (RGO) (0.3 wt%) composite coated film was 17 times lower than that of the pure poly(ethylene terephthalate) (PET) film. Both the diffusivity and the solubility are reduced by dispersing RGO into PVA.

Graphene and graphene oxide and their uses in barrier polymers are broadly discussed in literature [37–41]. The platelet size, stacking orientation, and degree of graphene exfoliation in the polymer matrix are governing factors in determining the gas transport [39].

In our earlier work it was established that by using *in situ* polymerization method it is possible to obtain nanocomposites with highly exfoliated graphene sheets in PET matrix with electrical percolation threshold at 0.05 wt% loading of expanded graphite [42].

In the present study, up to 0.5 wt% of GO was introduced in PET matrix. The effect of GO presence in PET matrix on oxygen barrier properties and nonisothermal crystallization behavior of the obtained PET nanocomposites were investigated. The last studies are of great practical importance because the production of PET the production of PET products, including fiber spinning, extrusion, and injection molding, is largely controlled through nonisothermal crystallization processes. In fact, the interaction between the polymer and the functionalized groups on the surface of graphene sheets can alter the thermal properties of the nanocomposites.

2. Experimental

2.1. Materials. Poly(ethylene terephthalate) (PET) has been synthesized by using the following chemicals: dimethyl terephthalate (DMT) (Sigma-Aldrich); ethanediol (ED) (Sigma-Aldrich), zinc acetate (ester exchange catalyst) $Zn(CH_3COO)_2$ (Sigma-Aldrich); antimony trioxide–polycondensation catalyst: Sb_2O_3 (Sigma-Aldrich); thermal stabilizer Irganox 1010 (Ciba-Geigy, Switzerland).

Graphene oxide (GO) with average particle size of $5\ \mu m$ was provided by Polymer Institute of Slovak Academy of Sciences, where the natural graphite was converted to expanded graphite through chemical oxidation in the presence of concentrated H_2SO_4 and HNO_3 acids reported in [43]. C1s XPS spectra of GO are as follows: sp^2 -C: 60.00%; sp^3 -C: 12.92%; C–O: 9.22%; C=O: 6.42%; COO: 2.95%; π – π : 8.49%. O1s XPS spectra of GO are as follows: C=O: 37.45%, C–O: 52.49%, Na–O: 5.86%, and SiO_2 : 4.20%. Before adding nanofillers to the reaction mixture, they were combined with ethanediol in order to split agglomerates and to improve further exfoliation.

2.2. Preparation of PET/GO Nanocomposite. PET/GO nanocomposites were prepared by *in situ* polymerization in the steel reactor (Autoclave Engineers, USA) with capacity of $1000\ cm^3$. The process was conducted in two stages and followed the same procedure as described in our previous publications [42, 44, 45]. Before polymerization, the desired amount of GO was dispersed in ca. 250–300 mL of ED by using for 15 min intensive mixing with high-speed stirrer (Ultra-Turax T25) and then through ultrasonication for 15 min using sonicator (Homogenizer HD 2200, Sonoplus, with frequency of 20 kHz and 75% of power 200 W). Additionally, to improve the dispersion/exfoliation of GO in ED an ultrapower lower sonic bath (BANDELIN, Sonorex digitec,

with frequency of 35 kHz and power 140 W) was applied for 20 hours.

2.3. Characterization Techniques. The inherent viscosity $[\eta]$ of the polymers was determined at 30°C using an Ubbelohde viscometer (with capillary I_c , $K = 0.03294$), as described elsewhere [42, 45–47]. The polymer solution had a concentration of 0.5 g/dL in mixture phenol/1,1,2,2-tetrachloroethane (60/40 by weight). The polymer nanocomposite solution was filtered through 0.2 μm pore size polytetrafluoroethylene (PTFE) filter (Whatman; membrane type TE 35) to ensure that the intrinsic viscosity is not affected by present GO. After filtration, the polymer was precipitated and redissolved. The values of average viscosity molar mass of PET homopolymer was calculated according to the Mark–Houwink equation $[\eta] = 3.72 \times 10^{-4} \cdot M^{0.73}$ [48].

The melt volume rate (MVR) was measured using a melt indexer (CEAST, Italy) as melt flow in cm^3 per 10 min, at temperature of 280°C and at orifice diameter 1.050 mm and under 2.160 kg load, according to ISO 1133 specification.

The structure of nanocomposites was observed by transmission electron microscopy (TEM) analysis, which was carried out by a JEOL JEM-1200 Electron Microscope using an acceleration voltage of 80 kV. The TEM samples were thinly sliced (~100 nm) using Reichert Ultracut R ultramicrotome. The thin slice obtained was collected onto a 300 mesh copper grid.

Oxygen permeability was measured using a Mocon-Ox-Tran 2/10 instrument. Oxygen permeability was performed using 5 cm^2 samples of investigated polymer films in accordance with ASTM D3985-05 and ISO 15105-2 Standards. All film samples were additionally conditioned for 3 h in the test chamber of OX-Tran apparatus in test parameters (23°C and 0% humidity rate RH). The measurement was automatically terminated when apparatus obtained stable subsequent results. Samples were dried in vacuum at 80°C for 24 h, compression-moulded, and quenched into amorphous films. The temperature of the press was 255°C and pressure of 15 bar. Films with comparable thinness (330 μm) were prepared.

XRD diffraction patterns were recorded using a PAN-alytical X'Pert PRO diffractometer powered by a Philips PW3040/60 X-ray generator and fitted with an X'Celerator detector. The X-ray source (CuK α radiation, wavelength $\lambda = 1.5418 \text{ \AA}$) was generated using an applied voltage of 40 kV and a filament current of 35 mA. The data were collected and recorded in the 2θ range 4–40 with a step of 0.02.

The nonisothermal crystallization behaviours of samples were investigated using a differential scanning calorimetry (DSC, TA Instruments Q-1000). The samples were heated from room temperature to 270°C at heating rate 10°C/min and maintained for 3 min in the DSC cell to destroy any nuclei that might act as seed crystals. The samples were then cooled to 20°C at constant rate of 3, 5, and 10°C/min, respectively. All the DSC measurements were carried out in nitrogen atmosphere, and the weight of each sample was about 10 mg. The enthalpy of crystallization (ΔH_c) was determined from

the areas of the crystallization peaks. The degree of crystallinity (x_c , mass fraction) of the samples was calculated using the equation

$$x_c = \frac{\Delta H_c}{\Delta H^0 (1 - w)}, \quad (1)$$

where ΔH^0 (140 J/g) [44] is the enthalpy of melting for 100% crystalline PET, ΔH_c is the enthalpy of crystallization of the sample, and w is the content of GO.

Small angle X-ray scattering (SAXS) measurements were performed at beam line A2 at HASYLAB (DESY, Hamburg). The wavelength of the X-ray beam was $\lambda = 0.15 \text{ nm}$. Scattering patterns were collected by a two-dimensional MAR-CCD-165 detector placed at a distance of 2443 mm from the sample. The scattering-vectors were calibrated using a dray rat-tail tendon protein. The specimens (~25 mg) were mounted in Mettler hot stage and encased between aluminium-foil windows and were heated and cooled at heating rates of 5°C/min over a temperature range of 25–275°C. During cooling from the melt, data was collected with time scanning 60 and accumulation time 20 s. For SAXS data analysis, a computer program SAXSDAT [49] was used. Subsequently the linear correlation function $CF(x)$ (2) Fourier-transformed from the corresponding one-dimensional SAXS data $I(s)$ measured is calculated in this work following procedures described in [49]:

$$CF(x) = \frac{1}{Q} \int_0^\infty I(s) s^2 \cos(2\pi s x) ds. \quad (2)$$

The parameter Q in (2) is a measure of the scattering power of the system:

$$Q = \int_0^\infty I(s) s^2 ds = K \alpha_s (\rho_c - \rho_a)^2 \varphi_L (1 - \varphi_L), \quad (3)$$

where ρ_c is the electron density of the lamellar crystals, ρ_a is the electron density of the amorphous material between adjacent lamellae, α_s is the volume fraction of the lamellar crystals in the irradiated sample volume, and K is the a constant depending on the experimental conditions. From the correlation function, we estimate long period L (the first maximum) and the linear crystallinity φ_L using the equation [49–51]

$$\varphi_L (1 - \varphi_L) = \frac{P}{L}, \quad (4)$$

where P is the position of the first intercept of the correlation function with the x -axis. The thickness of the crystalline (l_c) and amorphous (l_a) layers in the stacks was calculated according to

$$\begin{aligned} l_l &= \varphi_L L, \\ l_a &= (1 - \varphi_L) L. \end{aligned} \quad (5)$$

The relationship between volume fraction of crystallinity and linear crystallinity is expressed as $x_v = \alpha_s \varphi_L$, where α_s is the fraction of the total volume of the sample occupied by stacks of lamellae [51]. Using the densities of the crystalline ($d_c = 1.445 \text{ g/cm}^3$) and amorphous ($d_a = 1.331 \text{ g/cm}^3$) phases

TABLE 1: Physical properties of neat PET and PET/GO nanocomposites.

Sample	$[\eta]$ dL/g	$M_v \times 10^4$ g/mol	MVR cm ³ /10 min
PET	0.536	2.124	72.8 ± 1.9
PET/0.1GO	0.532	2.100	72.5 ± 1.8
PET/0.3GO	0.529	2.090	71.9 ± 2.5
PET/0.5GO	0.499	1.927	72.8 ± 1.4

$[\eta]$: intrinsic viscosity; M_v : average viscosity molecular weight; MVR: melt volume rate at 280°C.

for PET [52], the volume fraction crystallinity ($x_v = \phi_L$) was transformed into mass fraction of crystallinity $x_{c,m}$ according to Swam equation [53]:

$$x_{c,m} = \left[1 + \frac{d_a}{d_c} \left(\frac{1 - x_v}{x_v} \right) \right]^{-1}. \quad (6)$$

3. Results and Discussion

3.1. Characterization of the PET/GO Nanocomposites. PET nanocomposites with low loading of graphene oxide (GO) were synthesized by *in situ* polymerization of monomers in the presence of GO sheets. Ultrasonication graphite oxide in monomer (ED) before synthesis and then polymerization was found to be an effective way to obtain PET nanocomposites with highly exfoliated GO into while maintaining a very high aspect. Additionally, for comparison purposes, unmodified PET was synthesized and characterized in the same manner as the nanocomposite. The characteristics of the obtained nanocomposites are presented in Table 1. The intrinsic viscosity of neat PET was 0.536 dL/g.

The presence of the GO in the polymerization mixture affected the reaction, leading to the slightly decrease of intrinsic viscosity. As shown in Table 1, the intrinsic viscosity decreased with the addition of GO to 0.499. The PET matrix in synthesized nanocomposites have high molecular weight, which is ranged between 21 000 and 19 200 g/mol and is close to the value for neat PET. The comparable value of melt volume rate for neat PET and PET/GO nanocomposites was due to the polymer-functionalized graphene sheets interactions.

The dispersion and exfoliation of functionalized graphene sheets (GO) in PET matrix were investigated using TEM analysis and representative images for composite with loading of 0.3 and 0.5 wt% are shown in Figure 1.

TEM images of the PET/GO nanocomposites demonstrate that the highly exfoliated graphene oxide nanoplatelets were rather uniformly dispersed in PET matrix. The presence of more or less transparent and graphene nanoplatelets conforms with high degree of exfoliation, although predominance of folded multilayer graphene and some small aggregates on the nanoscopic scale was observed. This was due to the extremely high specific area of GO and the strong particle-matrix interactions that take place. The fact that the graphene oxide flakes remain well-exfoliated and highly dispersed within PET matrix suggests these composites to potentially display gas barrier property improvement.

TABLE 2: Oxygen permeability of PET/GO nanocomposite films.

Sample	GO wt %	Thickness μ m	O ₂ transmission rate ^a cm ³ /m ² 24 h
PET	—	320	48.6 ± 3.7
PET/0.1GO	0.1	326	23.7 ± 2.3
PET/0.3GO	0.3	322	18.6 ± 1.6
PET/0.5GO	0.5	320	14.6 ± 2.1

^a Measured at 23°C and 0% relative humidity.

3.2. Oxygen Permeability of PET/GO Nanocomposites. Graphene nanoplatelets are believed to increase gas barrier properties in nanocomposites. The tortuous path being created by the graphene particles in PET nanocomposites can retards the diffusion of the gas molecules through the PET matrix region. The influence of functionalized graphene (GO) content on the barrier performance to oxygen was studied by investigating oxygen transmission rate of PET/GO nanocomposites.

Gas barrier properties of PET films can be influenced by sample crystallinity and thickness [54]. In order to avoid crystallinity effect on oxygen barrier properties of PET/GO nanocomposites the amorphous films with comparable thickness were prepared.

Figure 2 shows X-ray diffraction patterns of GO, neat PET, and PET/GO composite films. The X-ray patterns for PET and PET/GO nanocomposite films have a broad amorphous halo confirming that prepared films were amorphous. The X-ray diffraction patterns for GO give peaks at $2\theta = 12.5^\circ$ and $2\theta = 26.3^\circ$. The first peak corresponds to an interlayer spacing of 0.71 nm (002) indicating the presence of oxygen functional group. The second peak corresponds to (002) plane of graphite with interlayer spacing of 0.34 nm. The presence of any GO peaks in the XRD spectra of PET/GO nanocomposites can suggests that GO was well exfoliated and homogenous dispersed in the PET matrix. On the other hand, GO content in PET matrix can be too low to observe these peaks on X-ray diffraction spectra of PET/GO nanocomposite films.

The oxygen barrier properties through neat PET and PET/GO composite films with comparable thickness are listed in Table 2. The obtained results of oxygen transmission rate (OTR) for amorphous PET films are comparable with literature data [54]. As expected, the permeability of O₂ through the PET/GO nanocomposite films was found considerably reduced at low loading of GO. The improvement of O₂ permeability for PET nanocomposite films over the neat PET is approximately factors of 2–3.3.

Based on many studies of gas barrier properties of polymer-layered silicate nanocomposites, it was established that enhancements in gas barrier properties depend on factors such as the relative orientation of the nanofiller sheets in the polymer matrix and the state of aggregation and dispersion in polymer matrix, that is, intercalated, exfoliated, or mixed morphology [55]. For PET nanocomposites containing graphene nanoplatelets the mechanism of gas barrier properties enhancement can be influenced by many factors similar to polymer-layered silicate nanocomposites, for which the level of exfoliation of silicate layers is a critical

FIGURE 1: TEM images of PET/GO nanocomposite with 0.3 wt% (a-b) and 0.5 wt% (c-f) of GO. Image magnification: (a) 150 k, (b) 200 k, (c) 50 k, (d) 150 k, (e) 120 k, and (f) 100 k.

FIGURE 2: XRD diffractograms for GO, neat PET, and PET/GO nanocomposite films.

factor in determining the maximum performance of polymer silicate nanocomposites for barrier applications [56].

3.3. Effect of GO on Crystallization of PET Nanocomposites.

The effect of graphene oxide nanoplatelets on the non-isothermal crystallization of PET was investigated using DSC. Figure 3 shows the DSC cooling curves obtained at different cooling rates. Additionally, temperature-resolved SAXS studies of morphological changes in melt-crystallized PET and PET/GO composite with the highest concentration of GO (0.5 wt%) were carried out.

The values of the nonisothermal crystallization onset temperatures ($T_{c,on}$), crystallization peak temperatures (T_c), and the crystallization enthalpies of all the samples under different cooling rates (3, 5, and 10°C/min) are presented in Table 3. For all samples, the crystallization onset temperature and crystallization peak temperature decrease as the cooling rate increases. Compared with neat PET, it is observed that at given cooling rate, the onset and peak crystallization temperatures of the PET/GO nanocomposites was increased due to the presence of GO. It can be also seen that the width of crystallization peak for nanocomposites was less than for neat PET. The value of ($T_{c,on} - T_c$) reflects the overall crystallization rate of the sample; the lower value of the

FIGURE 3: DSC thermograms of neat PET (a) and PET/GO nanocomposites with 0.1 (b), 0.3 (c), and 0.5 (d) wt% of GO at different cooling rates.

TABLE 3: DSC data obtained from the cooling runs for PET/GO nanocomposites.

Sample	Scan rate °C/min	$T_{c,on}$ °C	T_c °C	$T_{c,on} - T_c$ °C	ΔH_c J/g	x_c
PET	3	222	215	7	52.9	0.378
	5	211	196	15	47.7	0.341
	10	200	180	20	42.7	0.305
PET/0.1GO	3	225	219	6	51.4	0.367
	5	219	212	7	47.8	0.342
	10	212	203	9	43.2	0.309
PET/0.3GO	3	231	225	6	63.2	0.453
	5	225	217	8	56.2	0.403
	10	218	208	10	51.5	0.369
PET/0.5GO	3	231	225	6	63.6	0.456
	5	225	218	7	57.9	0.416
	10	218	209	9	52.5	0.377

$T_{c,on}$, T_c : onset and peak crystallization temperature, ΔH_c : enthalpy of crystallization, and x_c : mass fraction of crystallinity.

FIGURE 4: The evolution of the Lorentz corrected SAXS patterns (after background correction) during crystallization of (a) neat PET and (b) PET/0.5GO nanocomposite.

FIGURE 5: One-dimensional correlation function for neat PET (a) and PET/0.5GO nanocomposite (b) during cooling at 5°C/min from the melt.

$(T_{c,on} - T_c)$ for nanocomposites especially at higher cooling rates (Table 3) indicates the higher overall crystallization rate. Moreover, the nonisothermally crystallized PET composites with 0.3 and 0.5 wt% of GO have higher degree of crystallinity than neat PET. These can indicate the efficiency of graphene oxide nanoplatelets at low loading as nucleation agents for crystallization of PET.

Effect of the presence of GO in PET matrix on the evolution of the lamellar nanostructure was monitored by SAXS during nonisothermal crystallization from the melt. The correlation function $\gamma(x)$ has been applied to follow the changes of the nanostructure of PET/GO composite and neat PET during crystallization from the melt. Figure 4 displays the evolution of SAXS patterns for neat PET and nanocomposite (PET/0.5GO) during cooling. According to procedure reported in [49–51] analysis of the $\gamma(x)$ (Figure 5) allows to determine: L , l_c , l_a , and crystallinity within the lamellar stacks (ϕ_L).

Figure 6 summarizes the results of the nanostructure studies during melt crystallization of neat PET and nanocomposite with loading of 0.5 wt% of GO. These data indicate that the average values of lamellar thickness accompanied by the decrease of the amorphous layer l_a decreases with decreasing temperature and consistent with previous data for other crystalline polymers and their nanocomposites [57–59]. The observed in the higher-temperature region sharp decrease of the average value of l_a could be connected with the sequential formation of either new crystal lamellae or lamellar stacks or both in the interlamellar amorphous regions [58, 59].

Finally, unfilled PET and nanocomposite showed almost the similar values of the long period ($L = 11.4$ nm for neat PET and $L = 11.5$ nm for PET/0.5GO, Table 4). Nanocomposite has comparable thickness of crystalline lamellae (Table 4) as neat PET. Slightly higher value of l_c for nanocomposite in comparison to unfilled PET was observed. The obtained volume and mass fraction crystallinity for

TABLE 4: Parameters of nanostructure determined from correlation function for neat PET and PET/0.5GO nanocomposite.

Sample	L [nm]	l_c [nm]	l_a [nm]	E [nm]	φ_L	$x_{c,m}$
PET	11.40	4.412	6.988	2.103	0.387	0.406
PET/0.5GO	11.51	4.627	6.883	1.969	0.402	0.422

L : long period; l_c : thickness of crystalline lamellae; l_a : thickness of amorphous layer; E : thickness of transition layer; φ_L : volume fraction of crystallinity; $x_{c,m}$: mass fraction of crystallinity determined from (6).

FIGURE 6: Changes of long period (L), thickness of crystalline, and amorphous layer (l_c , l_a) calculated from the one-dimensional correlation function for neat PET and PET/0.5GO nanocomposite during crystallization from the melt.

nanocomposite (0.402 and 0.422) are slightly higher than for neat PET (0.387 and 0.406).

The observed difference between values of mass fraction crystallinity determined by DSC (Table 3) and SAXS (Table 4) can be explained by different sample size, differences in thermal history, and the different selectivity of the method. Such differences can be excluded only by the simultaneous measurements with different techniques at the same sample volume, which reflect an identical thermophysical history.

4. Conclusions

The obtained PET nanocomposites with low loading of GO prepared by *in situ* polymerization show uniform dispersion of highly exfoliated graphene oxide nanosheets in PET matrix. Study of the oxygen transmission rate through nanocomposite and neat PET films has shown that the high aspect ratio and exfoliated structure of GO in PET matrix improved their oxygen barrier properties. The improvement of oxygen permeability for PET nanocomposite films at 0.3–0.5 wt% loading of GO over the neat PET is approximately factors of 2–3.3. These improvements of oxygen barrier properties of PET are important from the application point of view

in packing industry. For example oxygen sensitive materials can be stored in PET containers and their life time can be elongated. DSC study of nonisothermal crystallization of nanocomposites have shown that the graphene oxide nanosheets displayed a nucleating effect on the PET crystallization due to the increase in the onset and peak crystallization temperature of nanocomposites compared to neat PET. The degree of crystallinity of the nanocomposites containing of 0.3 and 0.5 wt% of GO are higher than for the neat PET. Analysis of nanostructure parameters obtained from SAXS measurements for PET/0.5GO composite and neat PET have shown that nonisothermally crystallized composite and neat PET have comparable values of long period.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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