

## INFLUENCE OF GRAPHENE DERIVATIVES ON THE SELECTED PROPERTIES OF POST-CONSUMER PETG FOIL

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### ABSTRACT

Herein, we present a comparative study on the influence of different types of graphene derivatives forms (GDFs) on the properties of glycol modified poly(ethylene terephthalate) (PETG), that constitutes the polymer matrix. Therefore, post-consumer foil of PETG has been glycosylated and subsequently condensed. Nanocomposites with 1wt % of GDFs have been prepared by so-called in situ polymerization. The structure of the prepared PETG/GDFs foils was characterized by optical microscopy in order to present distribution of nanoplatelets. It was indicated that none of the selected nanofiller affected the phase transition temperatures of prepared nanocomposites. Moreover, it was clearly found that the addition of GDFs at the concentration of 1wt% affect the barrier properties of PETG foils, which might give the opportunity in applying them in food packaging and beverages applications. This work is the continuation of our previously published [1] results on the PETG/GDFs nanocomposites.

### 1. INTRODUCTION

Poly(ethylene terephthalate) (PET), which is a semicrystalline thermoplastic polyester can be widely used in the manufacture of films, fibers, and beverage containers, due to its exceptional properties, like exceptional thermal and mechanical properties, high transparency and high dimensional stability [2-5]. 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. Nevertheless, in the last 20 years several strategies have been proposed in order 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<sub>2</sub> and CO<sub>2</sub> permeation [1]. One of the best approaches to improve PET properties even further is to prepare polymer nanocomposites. They are polymers based on thermoplastics, thermosets, or elastomers matrices, that can be reinforced with small addition of nanofillers (less than 5wt%). So far, different types of fillers, were applied, however, the discovery of graphene, due to its intriguing properties including high electron mobility at room temperature [6, 7], exceptional thermal conductivity [8], and superior mechanical properties [7] attracted much attention on nanocomposites with its content [9, 10]. Additionally, extremely high surface area and gas impermeability [11] prove great potential of graphene for improving electrical, mechanical, thermal, and gas barrier properties of polymers [1].

However, in contrast to semicrystalline PET, glycol-modified poly(ethylene terephthalate) (PETG), is an amorphous thermoplastic polyester that exhibits a glass transition temperature ( $T_g$ ) of about 80°C, similar to PET [12-14]. On account of its transparency and clarity, PETG is used in medical, pharmaceutical, and cosmetic packaging. Notwithstanding, among many investigations on PETG

based nanocomposites [15-21], none addresses the effect of GDFs on the processing properties and gas barrier permeability of the PETG-based nanocomposites, where the post-consumer foils has been applied as a polymer matrix.

## 2 MATERIALS AND METHODS

### 2.1. Preparation of PETG based nanocomposites

In order to obtain PETG based nanocomposites post-consumer foils were applied. PETG foils were granulated in the mill and then dried for 24h at the temperature of 60°C under vacuum. Nanocomposites were synthesised by glycolysis of granulated PETG foils and subsequently polycondensation accordingly to the procedure presented in the scheme (Fig.1) in a steel reactor (Autoclave Engineers Inc, USA) in the presence of the nanoplatelets under continuous mixing. For the poly(ethylene terephthalate glycol-modified) (PETG) and PETG based nanocomposites' synthesis the following chemicals were used: 1,2-ethanediol (ED) (Sigma - Aldrich) distilled before using, zinc acetate (glycolysis catalyst)  $Zn(CH_3COO)_2$  (Sigma - Aldrich) and antimony trioxide – polycondensation catalyst– $Sb_2O_3$  (Sigma - Aldrich); thermal stabilizer Irganox 1010 (Ciba – Geigy, Switzerland). Just before the introduction of nanofillers into the reactor, graphene derivatives (GNP-ANG, GNP-iGP2 and GNP-NH<sub>2</sub>) 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. As nanofillers were added at the content of 1.0 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-iGP2, purchased from Grafen Chemical Industries (Grafen Co., Ankara, Turkey) are industrial graphene nanoplatelets for general purposes with the diameter of ~10μm, oxygen content of ~1%, purity of 96-99%, surface area 13 or 15 m<sup>2</sup>/g and thickness of 50-100nm.
- GNP-NH<sub>2</sub>- was purchased from Nanoinnova Technologies SL (Madrid, Spain) in the form of reduced graphene oxide with NH<sub>2</sub> groups. 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<sub>2</sub>/g; the amount of NH<sub>2</sub> groups in rGO-NH<sub>2</sub> 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.

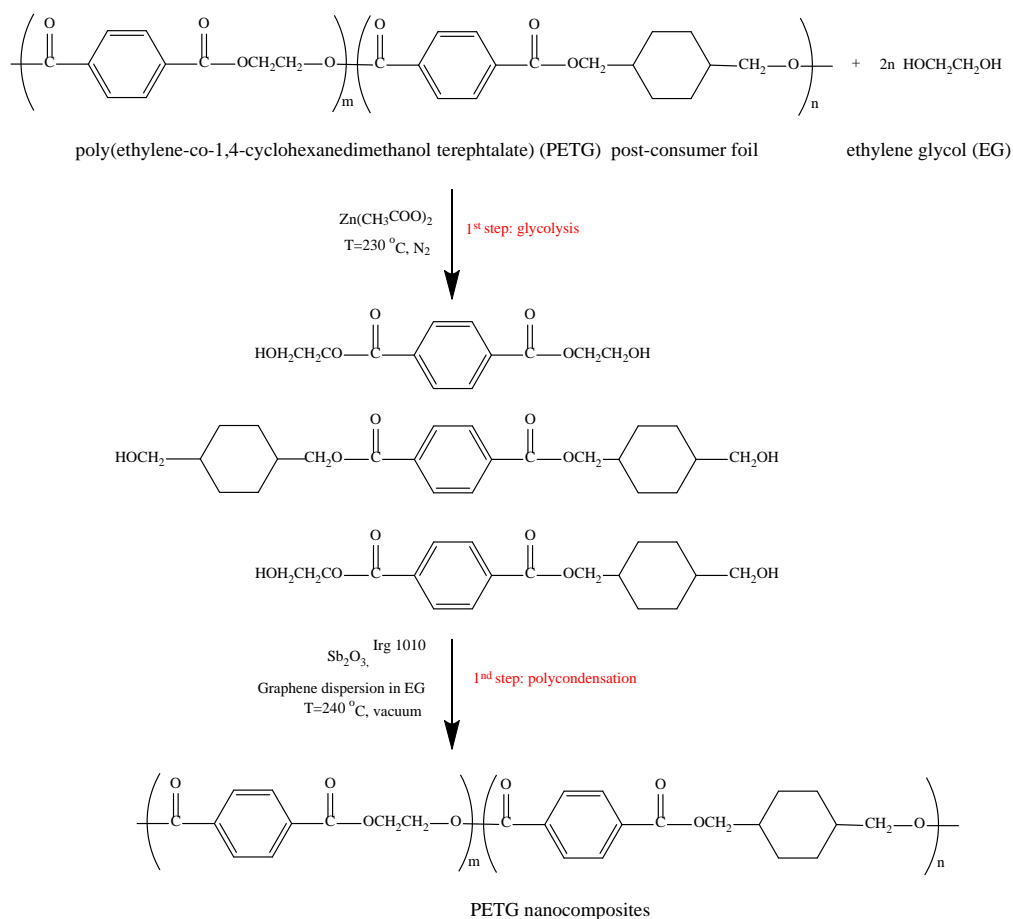


Figure 1: Scheme of the preparation process of PETG and PETG based nanocomposites

## 2.2. Characterization methods of PETG/GDFs nanocomposites

The distribution of all three types of graphene nanoplatelets in the PETG foils was analyzed with light microscopy that were performed using Nikon MM-40 microscope, operating at transmission light mode.

The basic physicochemical properties, i.e. average molecular mass, intrinsic viscosity, melt flow index and density, were determined. The average molecular mass was determined by using size exclusion chromatography (SEC) on a Waters GPC instrument, equipped with a Shimadzu LC-10AD pump, a WATERS 2414 differential refraction index detector (at 35 °C) and a MIDAS auto-injector (50mL injection volume) following the same procedure as described previously in [22]. The intrinsic viscosity  $[\eta]$  of PETG and PETG/GDFs 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 0.5 g/dl. 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. Melt flow index (MFI) was measured by using a melt indexer (CEAST, Italy) as weight of melt flow in grams per 10 min, at temperature of 195 °C, and at orifice diameter 2.095 mm and under 21.18 N load, according to ISO 1133 specification. Since all materials 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. Additionally, the glass transition temperature ( $T_g$ ) was determined from differential scanning calorimeter (DSC) measurements, that were carried out with a DSC1 (Mettler Toledo).

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<sup>2</sup> samples of examined polymer films accordingly to the procedure previously described in detail in [23]. All polymer samples were conditioned for 3h in the test chamber of OX-Tran apparatus in test parameters (23°C and 0% humidity rate RH).

### 3 RESULTS AND DISCUSSION

Fig. 2 shows the FTIR spectrum of the prepared PETG foil (reference sample), in which the peak at 1712 cm<sup>-1</sup> displays the C=O of ester groups, and the C-H out-of-plane deformation of two carbonyl substituents on the aromatic ring depicts at 730 cm<sup>-1</sup> [24, 25]. The two peaks at 1410 and 1240 cm<sup>-1</sup> are ascribed to -CH<sub>2</sub>- deformation band and C(O)-O stretching of ester groups, respectively [25].

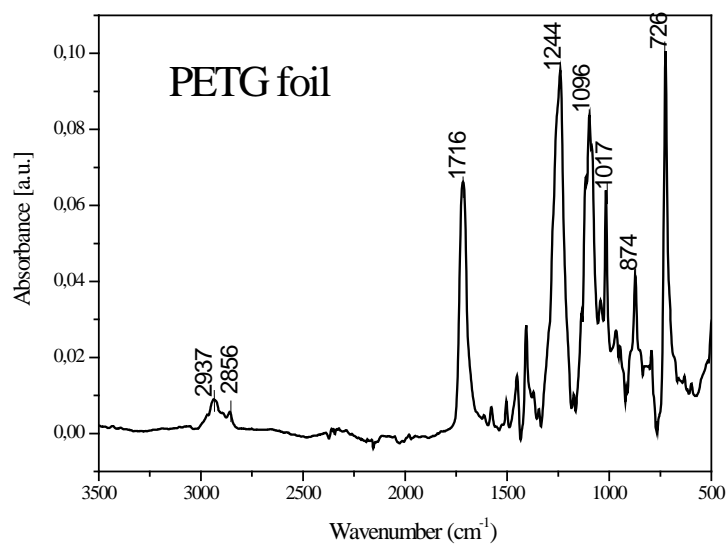


Figure 2: . FTIR spectrum of PETG foil.

PETG based nanocomposites with three different types of graphene derivatives forms, synthesized via *in situ* polymerization, were well dispersed throughout the polymer matrix, as determined by optical micrographs shown in Fig.3. Previous observations on the series of nanocomposites, also based on PETG but with 0.5wt% of GDFs [1] has shown that in situ polymerization is an effective process to obtain nanocomposites with degree of homogeneity of nanofillers' distribution.

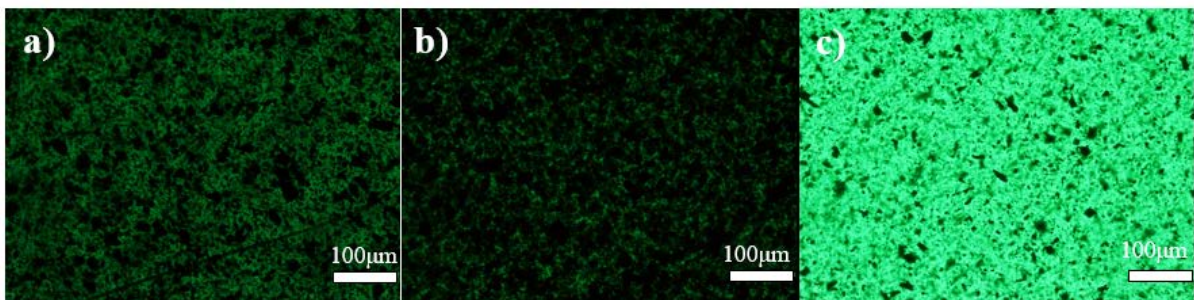


Figure 3: a-c optical microscopy images of nanocomposites thin foils used for permeability measurements: PETG/1.0GNP-ANG (a), PETG/1.0GNP-iGP2 (b), PETG/1.0GNP-NH<sub>2</sub> (c) at the magnification of 10 K).

In Table 1 the physico-chemical properties along with O<sub>2</sub> transmission rates are summarized.

Values of number average molecular masses for nanocomposites with GNP-ANG and iGP2 varied between 29 100 and 29 800 g/mol (Table 1) and they are close to the value obtained for the neat PETG (29 200 g/mol). Only GNP-NH<sub>2</sub> provided a slight decrease in *Mn*, which may result from the strong interactions between functional groups on the surface of GNP-NH<sub>2</sub> and PETG that caused an increase in the viscosity of the melt (decrease of MFI value). Similar observations were obtained for the values of intrinsic viscosity. Moreover, all three types of nanocomposites, in comparison to the neat PETG matrix exhibited comparable values of density. However, slightly higher values of density, obtained for the samples with GNP-NH<sub>2</sub>, might be due to better compatibility of carbon nanoparticles with the polymer matrix through chemical bonding between amine groups on the surface of GNP-NH<sub>2</sub>. Furthermore, for all nanocomposites the increase of softening temperature (around 13°C) estimated accordingly to the Boethius method, was observed. However, the addition of GDFs into PETG post-consumer foils didn't affect the glass transition temperature. A slight increase in T<sub>g</sub> (3oC) might be due to the existence of interfacial interactions exhibit between polymers matrix and functional groups on the surface of GNP-NH<sub>2</sub> [27].

Considering OTR (O<sub>2</sub> transmission rate), only the GNP-NH<sub>2</sub> improve the barrier properties of nanocomposite – the permeability was lower for about 24% that that observed for the neat PETG (Table 1). However, a decrease in OTR was observed for other (non-functionalized) graphene nanoplatelets, i.e. GNP-ANG and GNP-iGP2. One can clearly observe that the *in situ* polymerization allowed uniform distribution of all types of graphene nanoplatelets, however an improvement in the barrier properties against oxygen was obtained only for the modified nanoplatelets .

Sample	<i>Mn</i> ·10 <sup>4</sup> [g/mol]	[ $\eta$ ] [dl/g]	<i>d</i> [g/cm <sup>3</sup> ]	MFI [g/10min]	Soft. temp. <sup>B</sup> [°C]	T <sub>g</sub> [°C]	OTR [cm <sup>3</sup> /m <sup>2</sup> ·24h]	<i>t<sub>n</sub></i> [ $\mu$ m]
PETG	2.92	0.57	1.2356	4.12	123±3	69	38.2± 1.1	234
PETG/1.0GNP-ANG	2.91	0.55	1.2462	3.85	134±3	70	45.4±2.4	245
PETG/1.0GNP-iGP2	2.98	0.56	1.2581	3.70	135±3	70	46.5±0.8	266
PETG/1.0GNP-NH <sub>2</sub>	3.22	0.61	1.2725	2.75	136±5	72	29.2± 0.4	279

*Mn* – number average molar mass; [ $\eta$ ] – intrinsic viscosity; *d* – density measured at 23°C; MFI- melt flow index; B- softening temperature according to Boethius method; T<sub>g</sub> – glass transition temperature; OTR-oxygen transmission rate, *t<sub>n</sub>* - thickness of the polymer foil

Table 1: Physico-chemical and gas barrier properties for the obtained nanocomposites based on PETG

#### 4 CONCLUSIONS

Graphene nanoplatelets are multifunctional nanofillers that can play a key role in increasing the gas barrier properties of polymer foils at a very low concentration. Preliminary study of barrier properties of PETG films revealed that GDFs have the potential to improve the permeability toward gases, like oxygen molecules, while, on the other hand, the barrier efficiency of GDFs is strongly affected 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, and, at the same time, polar groups, like –NH<sub>2</sub>, might affect the solubility and permeability of O<sub>2</sub> molecules. However, the increase in OTR was observed for PETG/GNP-LTR and PETG/GNP-ANG nanocomposites. Thermal analysis indicated that the presence of GDFs at the loading of 1.0 wt % in PETG post-consumer foils has no effect on T<sub>g</sub> but causes an increase of the softening point of the material probably due to the decrease of molecular mobility of PETG chains.

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