Synthesis and characterization of polyethylene terephthalate-reduced graphene oxide composites

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Abstract. By means of \textit{in situ} melt polycondensation of polyethylene terephthalate accompanied with simultaneous reduction of introduced graphene oxide, the composite of polyethylene terephthalate filled with reduced graphene oxide was prepared. Melting and crystallization of the reduced graphene oxide – polyethylene terephthalate composite was studied by the differential scanning calorimetry method, and the rheological test was carried out by rotational rheometry and compared to the pristine polyethylene terephthalate. The morphology of the reduced graphene oxide – polyethylene terephthalate composite was studied using optical microscopy. The reduced graphene oxide was isolated from the reduced graphene oxide – polyethylene terephthalate composite and characterized by thermogravimetry, X-ray photoelectron spectroscopy and X-Ray diffraction methods. Since a part of polymer could not be removed from reduced graphene oxide particles by trifluoroacetic acid, the hypothesis about probable grafting of polyethylene terephthalate on reduced graphene oxide sheets was suggested. Rheological behaviour of the reduced graphene oxide – polyethylene terephthalate composite melt confirms this suggestion. According to the calculations based on thermogravimetry, the reduced graphene oxide, isolated from the reduced graphene oxide – polyethylene terephthalate composite, consists of about 80% polyethylene terephthalate.

1. Introduction

Graphene is a two-dimensional material composed from sp\textsuperscript{2}-carbon honeycombs with unique mechanical and electrical properties attracting a lot of attention last year as a filler for polymer composites. However, graphene tends to aggregate due to strong π-π stacking interactions \cite{1}. As a result, dispersibility of graphene is very poor. It is a great challenge because the mechanical and electrical properties of composites strongly depend on the particles size, and qualitative distribution of graphene plates in polymer matrix is required to achieve outstanding properties of polymer-graphene composites. The most commonly used method of producing graphene is the reduction of exfoliated graphene oxide (GO). GO is typically produced by Hummers method \cite{2} and its modifications from graphite by strong oxidative reagents such as a mixture of K\textsubscript{2}MnO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4} and NaNO\textsubscript{3}. During oxidation, a lot of oxygen containing functional groups are attached to basal planes and edges of graphene sheets. The interplanar space between graphene sheets in GO increases in comparison with graphite. GO is hydrophilic and can be dispersed easily in water and polar organic solvents on few layers or even single layer structure by simple sonication \cite{3}. The reduction of GO produces a material which is called...
“reduced graphene oxide” (RGO). The chemical, thermal, solvothermal, electrochemical reduction methods were commonly used to produce RGO. Hydrazine, ascorbic acid, sodium borohydride are often used as chemical reducers of GO [3]. The reduction of GO dispersion in appropriate solvent at elevated temperatures is a solvothermal process [4].

Non-functionalized RGO possesses poor dispersibility in polymer matrix because of loss of the most of the oxygen containing functional groups which provide interaction of graphene nanosheets and solvent or polymer matrix. This drawback was overcome by various \textit{in situ} reduction approaches. Chemical reduction of GO in polymer solution or dispersion is widely used to prepare RGO-polymer composites [1,5]. The reduction of GO in polymer-GO composites by chemical [3] or thermal [6,7] post-treatment was also described. The process of polymerization in presence of GO dispersion accompanied with \textit{in situ} GO reduction is a promising approach for large-scale production. These methods were successfully used to prepare polyimide [8,9], polyamide-6 [10], polyethylene terephthalate (PET) [11] composites during polycondensation. Melt processing to prepare composites is more economically preferable and ecologically friendly in comparison with solution-based process, because no solvent recovery is required.

Herein, RGO-polyethylene terephthalate (RGO-PET) composites prepared via \textit{in situ} polycondensation with simultaneous reduction of GO are studied. RGO was isolated from polymer matrix and analyzed by thermogravimetry (TGA), X-Ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) methods. In addition, thermal properties of the RGO-PET composite and rheological properties of the RGO-PET melts were tested.

2. Experimental part

2.1. Materials
Sulfuric acid, hydrochloric acid, trifluoroacetic acid (“Sigma-Aldrich”), sodium permanganate (“Reachem”, Russia), dimethylformamide (DMF), potassium hydroxide, sodium, hydrogen peroxide, stibium oxide (III) (“Reachem”, Russia) and ethanol of reagent grade purity were used without additional purification. All solvents, acids and alkalis were purchased from “Ekos-1” company (Russia) if other is not specified. Thionyl chloride (reagent grade) purchased from “Chimmed” (Russia) was distilled before application. Toluene (reagent grade) was refluxed for 3 h with Dean-Stark apparatus, for 2 h over sodium and distilled. Pyridine (reagent grade) was refluxed for 6 h with KOH and distilled. The purified graphite for GO preparation (Zaval’e deposit, Ukraine) was ground by a mill and sifted through standard 0.08 mm mesh sieves. Deionized water (DI) with specific electro conductivity less than 1 μSm/cm was used. Dichloroacetic acid (DCA) purchased from “BRI LLC” company (Russia) for intrinsic and specific viscosity measurements has analytical grade purity. Terephthalic acid (TA), ethylene glycol (EG) and industrial polyethylene terephthalate containing 0.2 % isophthalic acid were kindly provided by ZAO “New Polymers Plant [Zavod Novikh Polymerov]” (Russia, Moscow region, Solnechnogorsk). TA and EG were “commercial grade purity”. Ethylene glycol for synthesis of bis-(2-hydroxyethyl) terephthalate was distilled over sodium.

2.2. Synthesis and exfoliation of GO
Oxidation of graphite was carried out according to modified Hummer’s method, using a mixture of KMnO\textsubscript{4}/H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{3}PO\textsubscript{4}[12]. Detailed synthesis and characterization of graphite oxide were described in our previous work [13]. GO aqueous dispersion was prepared by mixing of 0.199 g GO in 25 ml DI water with IKA T10 Basic Ultra-Turrax disperser for 30 min. The viscous dark-brown dispersion was filtered through 0.45 μm PTFE filter.

2.3. Synthesis of terephthaloyl dichloride
TA (0.352 mol), SOCl\textsubscript{2} (1.52 mol) were refluxed in presence of few drops of DMF during 8 h. Excess of SOCl\textsubscript{2} was distilled out, and a residue was recrystallized from anhydrous toluene (m.p. 82-83 °C).
2.4. **Synthesis of bis(2-hydroxyethyl) terephthalate (BHET)**

A flask with a magnetic stirrer, containing EG (110 g) was cooled by ice bath for 30 min, and 0.235 mol of terephthaloyl dichloride was charged into the flask. Anhydrous pyridine (0.47 mol) was then added dropwise to the reaction mixture for 10 min. The ice bath was removed, the reaction mixture was heated and kept for 2 h at 40 °C. White precipitate was filtered on Büchner funnel, repeatedly washed with water and dried.

2.5. **Polycondensation of RGO-PET**

BHET (39.5 g), Sb2O3 catalyst (10 mg) were charged into a 250 ml three-neck round bottom flask equipped with a mechanical glass paddle stirrer, an argon inlet and a vacuum outlet. Aqueous GO dispersion (25 ml) containing 0.199 g of GO was mixed with EG (25 ml) and poured into the flask. The flask was immersed into the wood bath preheated to 130-150 °C and kept there for about 30-40 min until most of the water was distilled out. In order to remove the excess of EG, the wood bath was heated to 230 °C for about 40 min in slow flow argon. Then, the temperature of the wood bath was raised to 270-280 °C and the vacuum was applied (~1 Torr). After about 11 h of polycondensation, the RGO-PET was evacuated from the flask under the stream of argon and cooled on air. The intrinsic viscosity of the RGO-PET was 1.0 dl/g in DCA at 25 °C.

2.6. **Isolation of RGO from RGO-PET**

The RGO-PET (1.00 g) was dissolved in about 20 ml of TFA, filtered through a 0.22 μm polypropylene membrane filter and dried. The filtrate was thoroughly washed with fresh TFA and air dried. The yield was 25 mg (2.5%).

2.7. **Thermal reduction of GO (RGO-300)**

The sample of GO (100 mg) was placed in a round bottom flask. The flask was immersed into the wood bath and kept for 1 h at 300 °C under slow flow of argon.

2.8. **Characterization**

Intrinsic and specific viscosity were measured in DCA at 25 °C using Ubbelode viscometer.

X-ray diffraction patterns were obtained with Rigaku Rotaflex RU-200 X-ray source with a rotating copper anode (Cu Kα – radiation with characteristic wavelength λ =1.542 Å, a secondary curved graphite monochromator was used) at apparatus operating conditions 50 kV – 160 mA. The unit was equipped with a horizontal wide-angle goniometer Rigaku D/MAX-RC using Bragg-Brentano scheme in θ-2θ geometry. Scanning was carried out in the 3-40 angle range at 2°/min with a speed of 0.04° increment. A scintillation counter was used as a detector of diffracted X-ray emission. XRD studies were carried out at room temperature.

XPS of the samples surface was carried out with the electron-ion spectroscopy module based on Nanofab 25 (NT-MDT) platform in ultrahigh oil-free vacuum (10⁻⁶ Pa). The X-ray source SPECS XR 50 without a monochromator with Mg anode as the X-ray source (1253.6 eV photon energy) was used. The spectra were registered with an electrostatic hemispherical energy analyzer SPECS Phoibos 225. The energy resolution based on the full width at half maximum (FWHM) of the spectrometer at the Ag3d5/2 line (peak) was 0.78 eV for non-monochromatic X-radiation Mg Kα. The energy positions of the spectra were calibrated with reference to the Cu2p3/2 (binding energy 932.62 eV), Ag3d5/2 (368.21 eV) and Au4f7/2 (83.95 eV) peaks. All survey spectra scans were recorded at the pass energy of 80 eV.

The TGA measurements were carried out using TGA / DSC 1 combined thermal analysis instrument, Mettler Toledo (Switzerland), in 70 μl alumina crucible at the heating rate of 10 °C / min from 30 to 1000 °C under 10 cm³/min flow rate of argon.

The differential scanning calorimetry (DCS) measurement was performed by DSC 823e Mettler Toledo (Switzerland) in 40 μl aluminum crucibles without perforation at the heating/cooling rate of 10 °C/min (30-300 °C) under 70 ml/min flow rate of argon. The crystallization was studied at first cooling from 300 °C to 30 °C. The melting point and enthalpy were determined at second heating.
The degree of crystallinity $X_c$ of PET and RGO-PET was measured using the following equation:

$$X_c = \frac{\Delta H_f (\text{PET})}{(\Delta H_f (\text{PET}) \times W(\text{PET}))^{\frac{1}{2}}} \times 100\%,$$  \hspace{1cm} (1)

where $\Delta H_f (\text{PET}) = 140 \text{ J/g}$ and $W(\text{PET})$ is weight fraction of PET [13].

The graphene concentration $X_g$ (TGA) in RGO was calculated from TGA using the following equation:

$$X_g(\text{TGA}) = \frac{R_{\text{RGO}} - R_{\text{PET}}}{R_{\text{GO}} - R_{\text{PET}}} \times 100\%$$  \hspace{1cm} (2)

where $R_{\text{RGO}}$, $R_{\text{GO}}$, $R_{\text{PET}}$ are the ratio of weight at 500 °C to weight at 300 °C for RGO, GO, and PET, respectively.

The graphene concentration $X_g$ (XPS) in RGO was calculated from XPS measurements using the following equation:

$$X_g(\text{XPS}) = \frac{\omega(C)_G - \omega(C)_{\text{RGO}}}{\omega(C)_G - \omega(C)_{\text{PET}}} \times 100\%$$  \hspace{1cm} (3)

where $\omega(C)_{\text{RGO}}$, $\omega(C)_G = 78\%$, $\omega(C)_{\text{PET}} = 65.2\%$ are weight fractions of carbon in RGO, graphene, and PET, respectively.

The rheological properties of melts at steady state shear flow were studied on a RS600 rotational rheometer (Thermo Haake, Germany) using a plate–plate operation unit at 270 °C in the shear rate range of $10^1$-$10^3$ s$^{-1}$.

Morphological study of the RGO-PET thin film (about 10 μm) was performed using a Biomed 6 PO polarization optical microscope (Russia). The thin film was prepared by drying of the RGO-PET solution in TFA on air.

3. Results and discussion

As was mentioned above, GO forms stable dispersion in a variety of polar solvents. Nevertheless, the preparation of the GO dispersions in water-miscible solvents were often proceeded via solvent-exchange technique [1] because of the exceptional dispersibility of GO in water. We also used the solvent-exchange method in situ in a polycondensation flask. A mixture containing exfoliated GO, water, excess of EG and BHET was employed as a starting material for polycondensation. The concentration of GO was 0.5% w/w regarding the weight of the monomer (BHET). The synthesis of RGO-PET represents a several stage process. Firstly, the water was removed from the polycondensation flask by distillation. Secondly, the excess of EG was distilled out with a slow stream of argon at higher temperature. The EG boiling point (197 °C) is significantly higher than the water boiling point, and the water was easily removed by distillation at 100 °C. During the second step, the reaction media became black because of the GO reducing. After removing most of EG, the mixture was heated to 270-280 °C, under reduced pressure and continuous stirring to remove volatile by-product of polycondensation. The polycondensation was stopped when the reaction media became too viscous to stir.

In order to study RGO from the RGO-PET composite, the weighted RGO-PET sample was dissolved in TFA and filtered through 0.22 μm membrane filter. The isolated RGO (2.5% w/w) was studied by TGA, XRD, and XPS methods. In addition, thermally reduced GO at 300 °C (RGO-300) was prepared and studied by XPS for chemical composition.

TGA data of GO, PET, RGO-PET, and RGO are presented in figure 1 and Table 1. GO is thermally unstable and demonstrates weight loss even below 100 °C (3%). The main weight loss of GO was observed at the range of 160-225 °C (43%). These values are different from the values described in [14,15]. Zhou et al. reported about 10% weight loss at 100 °C and 20% – at 200 °C. Evidently, GO thermal behaviour depends on the graphite oxidation method and post-treatment such as drying. RGO-PET and neat PET did not demonstrate mass loss below 300 °C, while GO and RGO showed 49.5% and 11.4% mass loss, respectively. The observed weight loss of GO takes place due to the removal of some oxygen-containing functional groups, and the weight loss of RGO is attributed to the removal of the
absorbed TFA, which was used for isolation of RGO. However, TFA was not detected in RGO by the XPS method which was carried out in ultrahigh vacuum (10^{-6} \text{ Pa}). Hence, we concluded that TFA was bonded to RGO primarily by Van der Waals or hydrogen bonds and it was removed in vacuum. A drastic mass loss was observed at 400-500 °C for RGO, neat PET and RGO-PET. The unusual thermal behavior of RGO demonstrates the presence of PET in RGO in spite of the thorough purification. Hence, the RGO sheets were functionalized by PET during the polycondensation. In order to calculate the weight fraction of grafted polymer in RGO, it was assumed that RGO is a mixture of PET and graphene. The second assumption is that the thermal behavior of graphene in RGO is the same as the thermal behavior of GO at temperatures above 300 °C. This assumption is reasonable because the polycondensation was carried out at 280 °C.

![Figure 1. TGA curves of GO, RGO, neat PET, RGO-PET.](image1)

![Figure 2. XRD pattern of GO and RGO.](image2)

| Temperature range, °C | Residual weight, % |
|-----------------------|--------------------|
|                       | GO  | RGO | RGO-PET | PET |
| 300-500               | 92.8| 35.8| 21.9    | 20.4|
| 300-1000              | 55.6| 26.3| 15.6    | 7.2 |

The XRD pattern of RGO and GO is shown in figure 2. The main reflex of GO appears at 10.3° corresponding to the interplanar distance between the graphene sheets equal to 0.858 nm. The diffraction peak of RGO is located at 26.4°. The presence of PET in RGO was revealed as a wide diffraction peak at about 20°, which was previously reported in [16].

The elemental analysis of GO, RGO, and RGO-300 was performed by the XPS method as it was described in [17]. The results are presented in Table 2.

| Elements | GO, % | RGO, % | RGO-300 |
|----------|-------|--------|---------|
| C        | 67.9  | 76.4   | 82.2    |
| O        | 27.4  | 23.6   | 17.8    |
| S        | 2.2   | –      | –       |
| N        | 2.5   | –      | –       |
According to the PET formula, C/O ratio in PET is 2.5. Thermally reduced GO (RGO-300) contains 82.2% of carbon. Assuming that RGO sheets should consist of 82.2% carbon, the calculated by equation (3) weight fraction of PET in RGO is 55%, which is lower compared to the results based on TGA (80%). The reduction of GO in polycondensation melt is different from thermal reduction of GO due to the presence of a reducing reagent such as EG and acetaldehyde. We suppose RGO is more reduced than RGO-300 and that the XPS method underestimates PET content in RGO. As mentioned above, the weight concentration of RGO in RGO-PET is 2.5%. Relying on the TGA results, the true concentration of graphene in RGO-PET is about 0.5%.

Grafting of RGO with PET also was proved by swelling in two different solvents. There was swelling of RGO in TFA which is a solvent of PET and no swelling in CHCl3 (figure 3).

DSC thermograms are presented in figure 4 and summarized in Table 3. The degree of crystallinity $X_c$ and crystallization temperature $T_c$ of RGO-PET are higher than $X_c$ and $T_c$ of neat PET. The increasing of $X_c$ and $T_c$ was also observed for PET/RGO composites prepared by mixing PET and RGO [16,18]. Glass transition temperature $T_g$ and melting temperature $T_m$ of RGO-PET are lower than that of PET.

Table 3. DSC results for RGO-PET and PET.

| Sample   | $T_g$, °C | $T_c$, °C | $T_m$, °C | $\Delta H_f$, J/g | $X_c$, % |
|----------|-----------|-----------|-----------|-------------------|----------|
| PET      | 81.2      | 174.9     | 253.5     | 41.15             | 29.5     |
| RGO-PET  | 77.4      | 205.6     | 250.8     | 42.78             | 30.7     |

The morphological features of the polymer composite were studied by optical microscopy (figure 5). Thanks to the obtained photographs, we observe a fairly uniform distribution of particles over the volume of the polymer. The sizes of agglomerates do not exceed 50 μm.
Traditionally, PET is a fiber forming polymer. That is why, to test the spinnability of melt filled with RGO, its rheological properties were measured. The flow curves of the neat PET melt and melt filled with RGO are shown in figure 6.

As is seen, the PET melt has almost Newtonian behavior, and only at high shear stresses, its flow becomes unstable. The rheological properties of PET in the presence of 0.5% change drastically. The viscosity of RGO-PET is significantly higher than that of native PET at low stresses. Increasing the shear stress resulted in decreasing of viscosity after the short branch of constancy. Presumably, the mobility of PET macromolecules is restricted due to the presence of RGO particles. The most probable explanation is the connection of macromolecules with the RGO surface by contact forces of chemical nature due to grafting PET macromolecules on RGO sheets. In addition, partial physical contacts between solid particles may occur, though percolation threshold at 0.5% of filler content hardly could be achieved.

4. Conclusion
The RGO-PET composite was successfully synthesized from the monomer and GO dispersion by in situ melt polycondensation and simultaneous reduction of GO. The thermal behavior of RGO-PET is almost the same as that of the previously described RGO-PET composites prepared by mixing PET and graphene. The addition of RGO increases the degree of crystallinity and crystallization temperature and decreases melt temperature. The glass transition temperature of RGO-PET is lower as that of pristine PET. RGO isolated from the RGO-PET composite by filtration represents the graphene sheets with strongly bonded macromolecules of PET, which is proved by TGA, XPS, and XRD methods. The rheological behavior of RGO-PET was studied. The viscosity of RGO-PET is significantly higher than neat PET at low stresses and decreases with increase shear stress.

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