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Polycarbonate/maleic anhydride grafted polyethylene/graphite composites

RAPID COMMUNICATION

Summary — Mechanical behavior of graphite-filled recycled polycarbonate/maleic anhydride grafted polyethylene [PC/PE-*g*-MAH (80/20)] composites prepared by melt blending was investigated. The materials were first subjected to morphological analyses using wide-angle X-ray scattering (WAXS) and scanning electron microscopy (SEM). The modifier acts as a reactive compatibilizer in the structurally heterogeneous PC/PE blends. Tensile tests showed that stiffness, strength, and ductility were markedly modified by the presence of graphite in the composites. Furthermore, an enhancement of thermal stability was observed, without any significant deterioration of the mechanical properties. The relationships among these effects and microstructural characteristics of the products obtained were also analyzed.

Key words: polycarbonate, recycling, composites, reactive processing, graphite.

KOMPOZYTY POLIWĘGLAN/POLIETYLEN SZCZEPIONY BEZWODNIKIEM MALEINOWYM/GRAFIT

Streszczenie — Przeprowadzono badania właściwości mechanicznych mieszanin poliwęglanu (PC, 80 % mas.) i polietylenu szczepionego bezwodnikiem maleinowym (PE-*g*-MAH, 20 % mas.) napełnionych grafitem, które otrzymano metodą wytłaczania. Przedstawiono wyniki badań struktury za pomocą szerokokątowego rozpraszania promieni rentgenowskich (WAXS) (rys. 1 i 2) i skaningowej mikroskopii elektronowej (SEM) (rys. 3). Wykazano, że zastosowanie grafitu jako napełniacza powoduje znaczne zmiany sztywności, wytrzymałości i ciągliwości badanych kompozytów. Zaobserwowano także polepszenie właściwości cieplnych. Przeprowadzono analizę wpływu mikrostruktury na właściwości mechaniczne otrzymanych produktów.

Słowa kluczowe: poliwęglan, recykling, kompozyty, reaktywne wytłaczanie, grafit.

Polymer composites attract a great attention and have been the focus of study for a large number of research groups. In particular, polymer/layered-inorganic and polymer/clay nanocomposites have been studied extensively due to their wide potential applications [1—9]. Graphite is a layered material, showing a structure where carbon atoms are linked by covalent bonds to other carbons in the same plane however, between successive layers only van der Waals's forces are active. Since the van der Waals's forces are relatively weak, it is possible for a wide range of atoms, molecules, and ions to intercalate between graphite sheets [10, 11]. In contrast to the clays, there is no net charge on graphite; thus, ion exchange processes like those used to organically modified clays, are not possible for graphite. However, graphite intercalation may provide a possible way for nanocomposite formation with polymers, as it was described for polyamide 6 in [12]. It will be interesting to investigate also other polymers.

Polycarbonate (PC) is an amorphous thermoplastic polymer with high value of glass transition temperature (T_g = 145 °C), characterized by high impact strength and stiffness, good dimensional stability in a broad temperature range, low flammability, high creep resistance, and low water absorption. Its sensitivity to hydrolysis strongly influences the mechanical and specially impact properties [13]. It is one of the highest value thermoplastics available on the market today. Therefore recycling of PC is worth considering from an economic point of view.

In this study, we attempt a comprehensive study on the structure, thermal and mechanical properties of recycled PC and its composites with polyethylene grafted maleic anhydride and composites with graphite prepared by melt blending.

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EXPERIMENTAL

Materials

Polycarbonate (PC) as post industrial waste was used in this work. The melt flow rate, measured at 270 °C and 1.2 kg, was 7.8 g/10 min. Low-density polyethylene with 0.5 % of grafted MAH (PE-*g*-MAH) were prepared by extrusion in the Industrial Chemistry Research Institute according to the procedure publish elsewhere [14].

Virgin graphite (G) (flakes: length 75 μm, width 1—2 μm) was obtained from Aldrich and used as received.

Preparation of composites

Series of PC and PE-*g*-MAH waste composites with weight ratio 80/20 and different concentration of graphite (3, 5 or 8 wt. %) were prepared by melt blending at 250 °C for 2 min using a Berstorff ZE-25x33D modular intermeshing co-rotating twin-screw extruder equipped with a vacuum vent and having a screw diameter of 25 mm and L/D of 33, according to a procedure published elsewhere [15]. The screw speed was 250 rpm.

Methods of testing

A thermal stability was studied using thermogravimetry (TGA; Perkin-Elmer 7 Series; Perkin Elmer Cetus Instruments, Norwalk, CT) with a scan rate of 20 °C/min under nitrogen atmosphere.

The crystalline structure of composites was determined by means of wide angle X-ray scattering (WAXS). The examinations were performed with the CuK$_\alpha$ radiation at a wavelength 1.5418 Å and nickel filtering. Measurements at standard parameters (voltage 30 kV, anodic current 25 mA) were done within 2θ angle range 0.7—30°.

Scanning electron microscopy (SEM) observations of the surfaces, produced by fracturing of the samples cooled at liquid nitrogen and coated with gold, were made using Jeol JSM-6100 microscope.

The tensile data were collected according to ISO 527, and the tests were carried out at room temperature using an Instron 4505 tensile tester at a crosshead speed of 5 mm/min.

Charpy impact tests were performed according to ISO 179 at room temperature.

RESULTS AND DISCUSSION

Morphology

Graphite is layered material which is characterized by strong interlayer covalent bonds within the carbon layers and weak van der Waals's interactions between successive carbon layers. For virgin graphite, the d-spacing (the distance between successive carbon layers) is 3.35 Å, which corresponds average to 2θ =26.6° determined using WAXS method, as it is shown in Fig. 1. A variety of atoms and molecules can be placed between the carbon sheets, resulting in the formation of the intercalated graphite [7, 8].

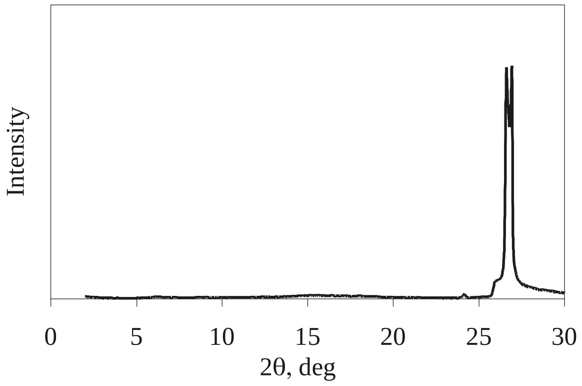

Fig. 1. WAXS pattern of graphite

X-ray patterns and typical SEM images of selected composites are shown in Figs. 2 and 3, respectively. WAXS analysis revealed that the presence of graphite in the composite induced modifications of the polymeric crystalline structure. The relations between the intensity of the peaks at 2θ (at 22° and 24°) and also changes in the shape of the diffraction patterns indicate the changes in the structure of PE phase for graphite-filled composites. Furthermore, it was observed that since PC/PE-*g*-MAH did not show a strong peak at 2θ =26.6°, the sharp diffraction peak at 2θ =26.6° in PC/PE-*g*-MAH/G composites should be attributed to the non-intercalated/exfoliated graphite. The appearance of this sharp peak suggests that the graphite galleries were not expanded and subsequently the packets composed of graphite layers were dispersed in PC/PE-*g*-MAH matrix. Thus, the WAXS results indicate that the PC/PE-*g*-MAH/G composites in this study include non-expanded graphite clusters. SEM images can provide us more direct information about these structures.

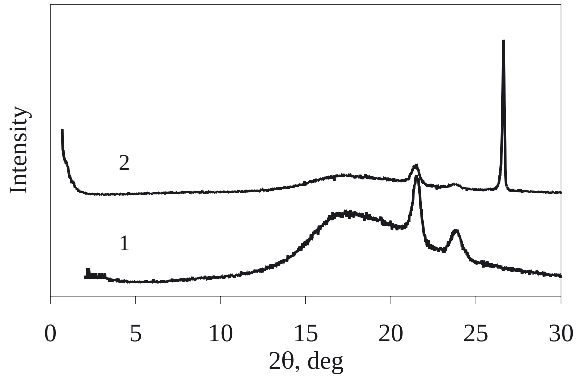

Fig. 2. WAXS patterns of the samples: 1 — PC/PE-g-MAH (80/20), 2 — PC/PE-g-MAH/G 80/20/5 (patterns shifted for clarity)

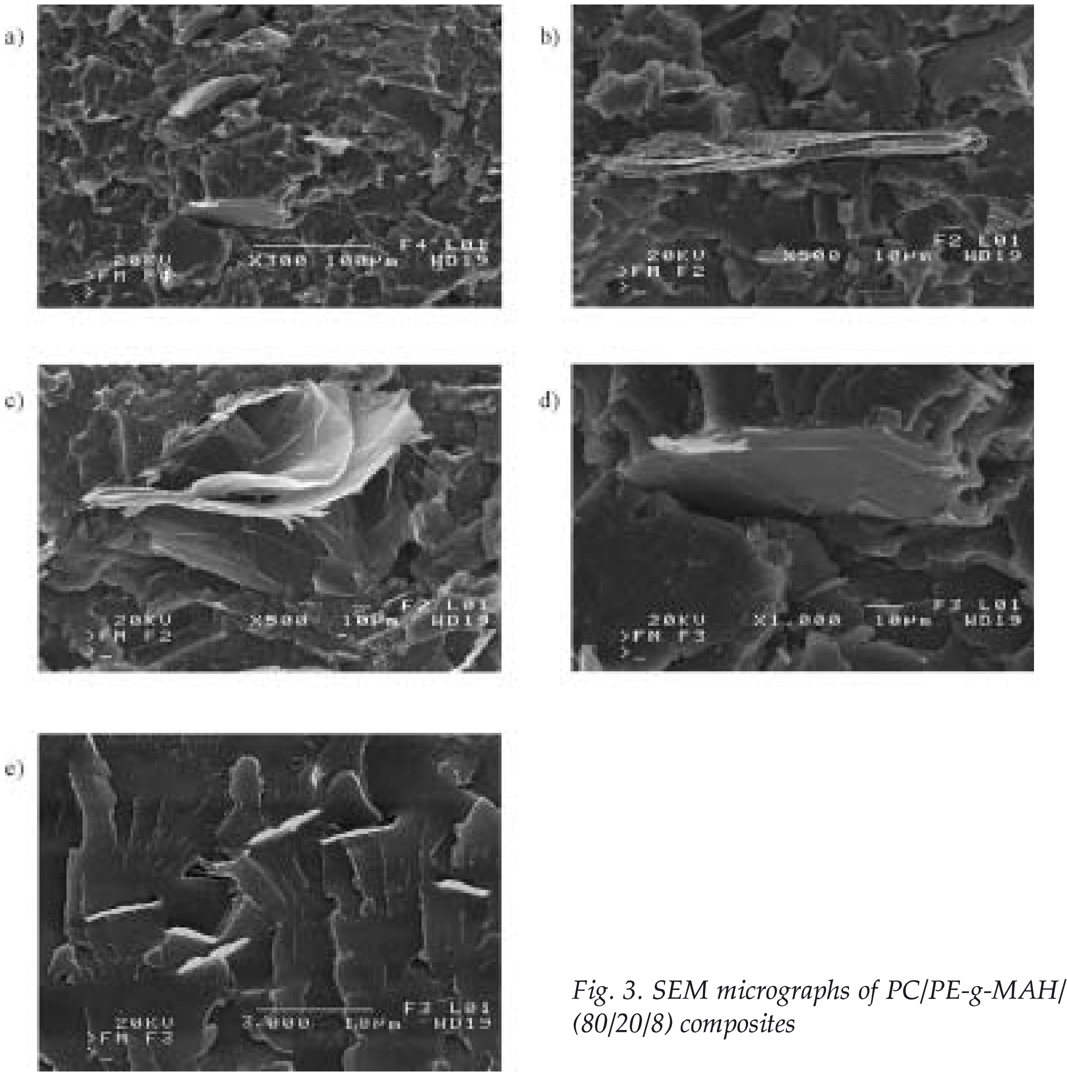

Fig. 3. SEM micrographs of PC/PE-g-MAH/G (80/20/8) composites

The SEM micrographs of PC/PE-*g*-MAH/G composite are shown in Fig. 3. In particular, for PC/PE-*g*-MAH/G (80/20/8) composites, well-dispersed graphite clusters are observed in all high magnification images. Moreover, there is a coexistence of single fragments of dispersed graphite layers and of "tactoids" consisting of several layers. These results could be indicative of the particulate PC/PE-*g*-MAH/G composite, which does not resemble the *in situ* polyamide-6/clay nanocomposites [16, 17], wherein almost all silicate layers are exfoliated/disordered throughout the polymer matrix, they do not resemble the melt-mixed polymer/montmorillonite nanocomposites [18], where a coexistence of fully exfoliated and partially miscible (*e.g.* intercalated) layers is the norm. Similar results were obtained for graphite/polyamide-6 nanocomposites [12]. The observed structure will be further investigated by transmission electron microscopy (TEM).

Thermogravimetric analysis (TGA)

To explore the thermal decomposition of composites, thermogravimetric analyses were undertaken. The temperature of 10 % weight loss ($T_{10\ \%}$), maximum weight loss (T_{max}) and char residue were investigated. The TGA data for PC/PE-*g*-MAH/G composites (Table 1) show that there is no significant difference in onset temperature of degradation. However, a significant increase in the maximum temperature of degradation (11—16 deg) is observed, which suggests that thermal stability of these composites is enhanced by the presence of graphite. Enhanced char formation is of paramount importance for flame retardance and the observed effect will be further investigated.

Table 1. Thermogravimetric analysis data for PC/PE-*g*-MAH/G composites

Sample	Graphite wt. %	$T_{10\%}$, °C	T_{max}, °C	Char, %
PC/PE-*g*-MAH 80/20/0.1	0	459	532	11.4
	3	459	543	13.4
	5	460	545	13.7
	8	459	548	14.8

Stress-strain behavior

Typical stress-strain curves of various materials investigated, shown in Figure 4, indicate that for all three G concentrations, the mechanical behavior of G-filled composites was considerably different from that of recycled PC and PC/PE-*g*-MAH sample. Melt flow rate (*MFR*) data and static tensile properties in comparison with those of recycled PC and PC-based composites are summarized in Table 2.

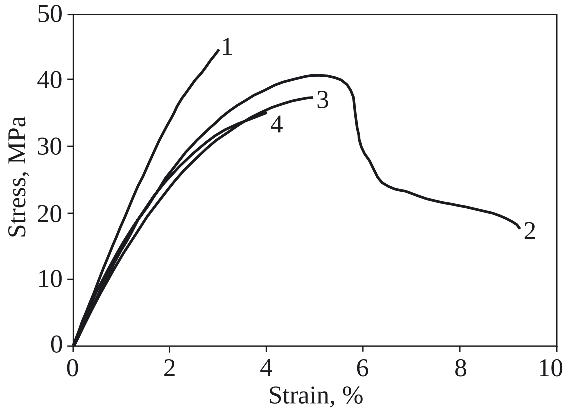

Fig. 4. Stress-strain curves for the samples: 1 — PC, 2 — PC/PE-g-MAH (80/20), 3 — PC/PE-g-MAH/G (80/20/5), 4 — PC/PE-g-MAH/G (80/20/8)

Table 2. Melt flow rate (*MFR*, 270 °C, 1.2 kg) and static mechanical properties of PC/PE-*g*-MAH/G composites

Sample	Graphite content wt. %	*MFR* g/10 min	Tensile modulus MPa	Tensile strength MPa	Elongation at break %	Charpy notched impact strength kJ/m^2
recycled PC	0	7.8	2200	43	3	1
PC/PE-*g*-MAH 80/20/0.1	0	2.8	1820	41	9	50
	3	2.4	1900	37	5	25
	5	2.5	2000	37	5	20
	8	2.6	2100	35	4	20

First, a significant decrease in a melt flow rate (*MFR*) of PC containing PE-*g*-MAH can be observed. This fact suggests a substantial amount of interfacial reactions and molecular weight increase. Further, the PC/PE-*g*-MAH system shows a significant increase in impact strength and ductility in comparison to recycled PC, indicating that the modifier acts as a reactive compatibilizer in the structurally heterogeneous PC/PE system. Moreover, it can be pointed out that the values of tensile strength of recycled PC and PC/PE-*g*-MAH are quite similar.

As for the results obtained for tensile modulus, it can be observed that the presence of graphite within PC/PE-*g*-MAH resulted in increased stiffness. Furthermore, stiffness was improved with increasing content of G. However, for the G-filled composites, the values of tensile modulus are lower in comparison with PC. When compared to PA-6/montmorillonite clay nanocomposites, the PC/PE-*g*-MAH/G composites are less beneficial to stiffness. This fact is herein attributed to the weak hydrogen bonding between PC, PE and G.

The yielding and post yielding behavior of the materials investigated showed that the presence of G in PC/PE-*g*-MAH system resulted in decreased strength and ductility, as shown by the decrease in elongation at break. Moreover, it was observed that impact strength decreased with increasing concentration of G in the system. However, the values of impact strength of the systems studied are remarkably higher than of PC.

CONCLUSIONS

Polycarbonate waste-based composites were prepared by melt blending using maleic anhydride grafted polyethylene as a compatibilizer. Good dispersion of graphite was achieved for composites investigated; based on WAXS analyses and SEM observations the PC/PE-*g*-MAH/G composites showed partially a particulate composite structure. Thermogravimetric analyses under nitrogen showed little change in a thermal stability. The tensile modulus of PC/PE-*g*-MAH composite was slightly improved by the graphite addition, although this improvement took place at the expense of elongation at break and tensile and impact strengths.

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