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Compatibilization of polyolefins waste based blends by reactive modifiers with anhydride or oxazoline functional groups

RAPID COMMUNICATION

Summary — The effects of reactive modifiers with anhydride or oxazoline functional groups on the morphology and the mechanical properties of polyolefins waste based blends prepared by melt blending have been studied. The materials were first subjected to morphological analyses by scanning electron microscopy (SEM). The modifiers act as compatibilizers in the structurally heterogeneous blends. Tensile tests showed that the blends had significantly improved elongation and impact strength over their unmodified analogues. Improvements in tensile and impact properties depend on the blend composition and the modifier used.

Key words: recycling, polyolefins, blends, reactive modifiers, reactive extrusion.

KOMPATYBILIZACJA MIESZANIN OTRZYMANYCH Z ODPADÓW POLIOLEFIN ZA POMOCĄ MODYFIKATORÓW ZAWIERAJĄCYCH BEZWODNIKOWE LUB OKSAZOLINOWE GRUPY FUNKCYJNE

Określono wpływ reaktywnych modyfikatorów posiadających bezwodnikowe lub oksazolinowe grupy funkcyjne na strukturę i właściwości mechaniczne mieszanin otrzymanych metodą wytłaczania na podstawie odpadów poliolefin (tabela 1). Za pomocą skaningowej mikroskopii elektronowej (SEM) wykonano badania morfologii otrzymanych próbek (rys. 1—3). Stwierdzono, że modyfikowane próbki charakteryzują się kompatybilną strukturą heterogeniczną powstającą podczas wytłaczania na skutek reakcji z udziałem bezwodnikowych i oksazolinowych grup funkcyjnych. Wykazano, że zastosowanie modyfikatorów powoduje obniżenie masowego wskaźnika szybkości płynięcia (*MFR*) i modułu sprężystości, natomiast wydłużenie przy zerwaniu oraz udarność badanych mieszanin wzrasta (tabela 2). Poprawę tych właściwości można osiągnąć zmieniając skład mieszaniny odpadowych poliolefin oraz rodzaj i ilość użytego modyfikatora.

Słowa kluczowe: recykling, poliolefiny, mieszaniny, reaktywne modyfikatory, wytłaczanie reaktywne.

The recent growth of plastics recycling presents an opportunity for developing new value-added blend products from post-consumer recycled polymers. In general, high performance in properties of polymer blend such as high impact strength, ductility and solvent resistance are highly desirable to enhance its value and application potential. However, in the majority of the cases, attaining of these requirements with recycled materials is very difficult because of several reprocessing problems, in which degradation plays a significant role. Another important problem in recycling is that most polymer are incompatible, and therefore the blends have poor mechanical properties [1—4].

Polymer processing involving chemical reactions that couple dissimilar polymer chains create more stable and useful blends. The formation of chemical bonds between polymer molecules from different phases may be instrumental in preventing molecular slippage at polymer–polymer interphase [5—7]. Moreover, such co-crosslinked materials which are formed at the interlayer of two polymers may play similar role to that of block or grafted, copolymers by acting as potential solid phase dispersants.

In this work, the effects of reactive modifiers with anhydride or oxazoline functional groups, on the morphology and the mechanical properties of polyolefins waste based blends prepared by extrusion have been investigated.

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EXPERIMENTAL

Materials

Low-density polyethylene (PE-LD), high-density polyethylene (PE-HD), polypropylene (PP), polystyrene (PS), polyamide 6 (PA), polycarbonate compact disc grade (PC) and poly(ethylene terephthalate) (PET) waste, were used in this work. Before using, all the polymers were disintegrated and accurately dried under vacuum for 8 h at 85 °C (for polyolefins and PS) or 110 °C (for PET, PC and PA). Reactive modifiers low-density polyethylene grafted with maleic anhydride (PE-LD-*g*-MAH) and poly(ethylene terephthalate) modified with 2,2′-(1,3-phenylene)-bis(2-oxazoline) (PET-OX) were elaborated in the Industrial Chemistry Research Institute, according to procedure described in detail elsewhere [4—6].

Extrusion of blends

Reactive extrusion experiments were carried out using a Berstoff 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 ratio equal 33. A flat temperature profile of 245 °C was employed across the extrusion barrel with the exception of the feed zone, which was maintained at 240 °C. Screw speed remained constant 100 rpm and output was controlled at a throughput of 90 g/min with a calibrated anger feeder. Under these conditions, the mean residence time experienced by the polymer blends was approximately 2.0 min.

Table 1. Samples compositions and their denotations

Symbol of blend sample	Composition, %						
	PE-LD	PE-HD	PP	PS	PA	PET	PC
A	10	20	20	20	20	10	—
B	15	30	25	20	10	—	—
C	20	20	—	30	—	—	30

Example samples compositions and their denotations are presented in Table 1.

Methods of characterizations

The fractures of surfaces of the sample cooled with liquid nitrogen and coated with gold were observed by scanning electron microscopy (SEM) using Joel JSM-6100 microscope.

The tensile data were collected according to standard ISO 527. 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 using Zwick testing system at room temperature according to ISO 179 standard.

Melt mass-flow rate (*MFR*) was examined by Plastometer type II RT (Russia), according to ISO 1133 standard.

RESULTS AND DISCUSSION

The microstructures of the fracture surfaces of various modified blends are analyzed by SEM. First, the blends with no modifier were investigated and relevant micrographs are shown in Fig. 1. These blends display the morphology with a poor dispersion and no interfacial adhesion. Next the blends modified with PET-OX and PE-LD-*g*-MAH were analyzed. The micrographs presented in Figs. 2 and 3 show heterogeneous compatible structures with good interfacial adhesion between the phases. In fact, the phases of the blend become practically indistinguishable already after addition of 25 wt. % of PET-OX (Fig. 2). It is more reasonable to assume that a considerable number of modifier molecules react with the end groups of blend components to produce

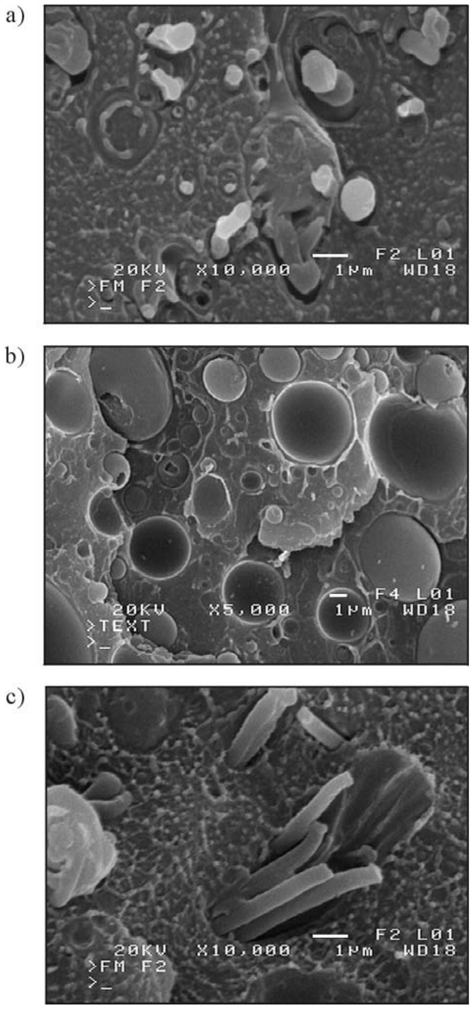

Fig. 1. SEM micrographs of the blends: a) A, b) B, c) C

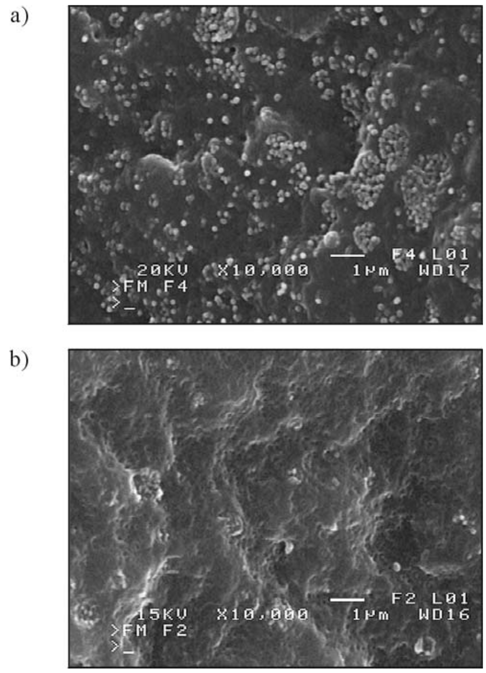

Fig. 2. SEM micrographs of the blends: a) A/PET-OX, b) B/PET-OX; in both cases components' ratio by weight was equal 75/25

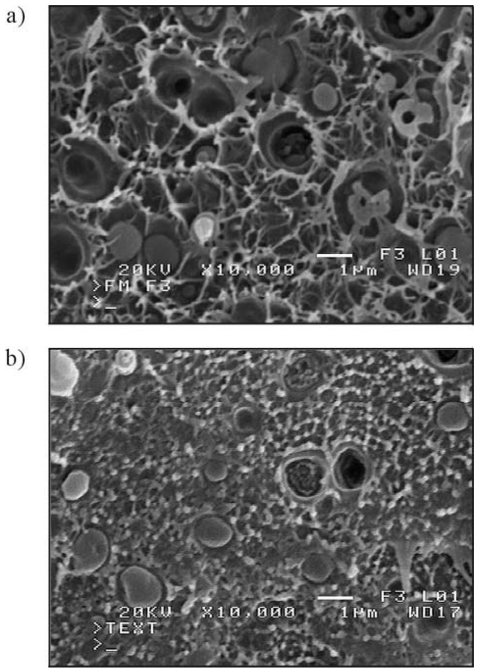

Fig. 3. SEM micrographs of C/PE-LD-g-MAH blends with components' ratios by weight: a) 85/15, b) 65/35

T a b l e 2. Melt mass-flow rate (*MFR*) and mechanical properties of blends modified with PET-OX or PE-LD-*g*-MAH

Sample composition	Modifier content wt. %	*MFR* g/10 min	Tensile modulus MPa	Tensile strength at break, MPa	Elongation at break, %	Charpy notched impact strength kJ/m^2
A/PET-OX	0	8.2[a)]	1290	19	2	3
	25	6.4[a)]	1200	26	8	9
B/PET-OX	0	7.6[a)]	920	16	7	5
	25	5.2[a)]	810	20	15	10
C/PE-LD-*g*-MAH	0	10.1[b)]	1275	17	2	2
	15	7.9[b)]	1020	16	4	5
	25	6.7[b)]	900	15	6	6

[a)] 250 °C, 2,16 kg; [b)] 270 °C, 1,2 kg.

block copolymers located in the interface. The block copolymers formed during reactive processing, because of interchain exchange reactions, play a role of compatibilizer.

The occurrence and the extent of the chemical interactions taking place in a molten state between polyolefins, PS, PET, PA, PC and reactive modifiers were qualitatively assessed by *MFR* measurements. Reactions between these polymers and the modifiers will result in an increase in the molecular weight and viscosity on the one hand in a decrease in *MFR* on the other one. Table 2 illustrates an effect of addition of two types of modifiers on mechanical properties of the blends investigated. From the data shown in Table 2 we can see, that *MFR* values of the samples containing the modifier are smaller than unmodified samples. Example of C/PE-LD-*g*-MAH sample shows that increasing modifier content causes decrease in *MFR*. This behavior is typical for compatibilized blends and suggests a substantial role of interfacial reactions and molecular weight increase.

The data of tensile properties of unmodified and modified blends are also listed in Table 2. Modified blends show significantly improved elongation in comparison with their unmodified counterparts. Moreover, as it was also found for *MFR*, an increase in PE-LD-*g*-MAH concentration from 15 to 35 wt. % enhanced the elongation further. With respect to the unmodified sample A, the modulus of the modified blend is about 8 % lower, the tensile strength is increased by 50 % and elongation at break by 300 %. The results of the mechanical characterization are in good agreement with all other experimental evidences indicating that the modifiers do actually help the *in situ* formation of graft copolymer compatibilizers.

The effectiveness of the compatibilizing system studied in this work was confirmed by an investigation of the impact properties of unmodified and modified blends (Table 2). Addition of the modifier significantly improves the impact strength, confirming that these modifiers do actually behave as compatibilizer precursors. This finding provides the most convincing proof of the effectiveness of the compatibilizing procedure studied in this work.

CONCLUSIONS

Polyolefins waste based blends can be prepared by a reactive melt mixing process. These blends have fine morphology and significantly improved elongation and impact strength in comparison with their unmodified analogues. *MFR* characterization, the tensile behavior and, more clearly, the impact tests showed that coupling reactions between the modifier and blend components were effective in the compatibilization of the blends investigated. Improvement in tensile and impact properties depends on the blend composition, the type and concentration of modifier used. The maximum increase was obtained for A blend modified with 25 wt. % of PET-OX. About 4-fold increase in elongation at break and 3-fold increase in impact strength were achieved. However, the maximum values of these properties were obtained for B/PET-OX with 25 wt. % content of modifier.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

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- — Wpływ wodoru lub metanu na polimeryzację styrenu katalizowaną układem $CpTiCl_2(OC_6H_4Cl\text{-}p)$/MAO (*j. ang.*)
- — Kationomery poliuretanowe syntetyzowane z 4,4′-diizocyjanianu difenylenometanu, glikolu poli(oksypropylenowego) i *N*-alkilodietanoloamin — budowa chemiczna oraz swobodna energia powierzchniowa i jej składowe
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