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Effect of oxazoline grafted polyethylene on the structure and properties of poly(butylene terephthalate)/polyamide 6 blends

RAPID COMMUNICATIONS

Summary — Structural phases and blends properties of poly(butylene terephthalate)/polyamide 6 blends were studied in a chemical modification involving reactive extrusion with a ricinol-2-oxazoline methylmaleate (ROM) grafted polyethylene. The interfacial reaction between blend components were studied by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The static tensile and flexural properties and impact resistance response of the blends were tested. According to DSC data, the reactive processing results in formation of heterogenous blends. Phase structure and mechanical behavior studies showed that interfacial reactions between PE-*g*-ROM, poly(butylene terephthalate) and polyamide 6 containing co-reactive groups were effective in the compatibilization of blends investigated. Phase morphology of the blends was of interpenetrating polymer network (IPN) type according to SEM results which was in accordance with learnings from DTA spectra. FT-IR, DSC and DTA investigations suggest evidence for the chemical reaction. The graft polymer formed during the reactive extrusion results in an alloy with good interfacial adhesion and high impact resistance.

Key words: PBT/PA 6 blends, compatibilization, oxazoline functionalized low density polyethylene, ricinol-2-oxazoline methylmaleate, reactive extrusion, morphology, mechanical properties.

Reactive processing is today an important field of industrial and scientific activities. The modification of thermoplastics in twin screw extruders to produce new materials is an inexpensive and rapid way to obtain new commercially valuable polymers. The functionalization reaction has a great potential for making new products with higher commercial value from general-purpose polymers. Functionalization of polyolefins (PO) by melt grafting of unsaturated polar groups onto the polymer backbone chain by using organic peroxides as free radical initiators has received considerable attention recently [1—3]. For instance, maleic anhydride, acrylic acid and glycidyl methacrylate have been grafted onto polyolefins especially in order to improve their compatibility with polar thermoplastics (*e.g.* polyamides and polyesters) and to promote their adhesion to glass fibres in polymer composites. Also, polyethylene grafted with vinyl silanes can be crosslinked in the presence of moisture *via* hydrolysis and further condensation [4]. As a result, its creep, abrasion, heat deformation and chemical resistances are enhanced.

Functionalized polymers are widely used as *in situ* compatibilizers in polymer blends [5—9]. Because only a few polymers are miscible, an effective compatibilizer is required to reduce the interfacial tension and increase the interfacial adhesion.

The overall objective of this work was to evaluate the effectiveness of ricinol-2-oxazoline methylmaleate (ROM) grafted polyethylene (PE-*g*-ROM) on the morphology, phase behavior and properties of poly(butylene terephthalate)/polyamide 6 blends.

EXPERIMENTAL

Materials

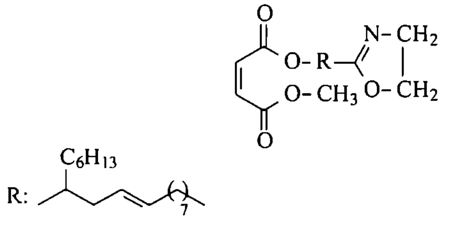
Polyethylene (PE) used in this study was low density polyethylene (Polish Petroleum Concern Orlen SA, Poland) showing melt flow rate (*MFR*) of 2.1 g/10 min [PN-EN ISO 1133:2002 (U), 190 °C, 2.16 kg]. PE was dried at 80 °C for 2 h before using.

Functionalized polyethylene was prepared by melt grafting of ricinol-2-oxazoline methylmaleate onto PE homopolymer (*MFR* = 1.7 g/10 min).

Poly(butylene terephthalate) (PBT) was obtained from Jelchem SA, Poland [*MFR* = 5.4 g/10 min according to PN-EN ISO 1133:2002 (U), 270 °C, 1.2 kg, die I]. PBT was dried at 110 °C for 4 h under vacuum.

Polyamide 6 (PA 6) was supplied by Nitrogen Works Tarnów SA, Poland [*MFR* = 2.6 g/10 min according to PN-EN ISO 1133:2002 (U), 230 °C, 0.32 kg]. PA 6 was dried at 85 °C for 8 h.

Ricinol-2-oxazoline methylmaleate [Formula (I)] (Loxamid VEP 8515) was obtained from Henkel, Germany.

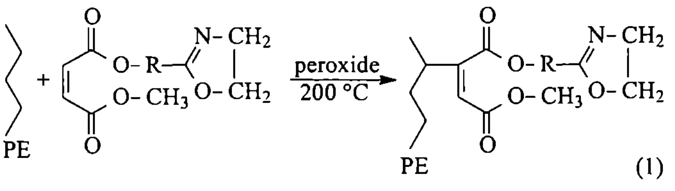


(I)

As peroxide initiator di-*tert*-butyl peroxide (DTBP of Riedel-de-Haen, Germany) was selected.

Melt grafting of ricinol-2-oxazoline methylmaleate onto polyethylene

Melt grafting of ROM onto PE-LD [equation (I)] was carried out at 180—200 °C in a pilot plant twin-screw co-rotating extruder Berstorff ZE-25—33*D* (*D* = 25 mm, *L*/*D* = 33, feeding rate 3—4 kg/h, 80 rpm.), according to the procedure published elsewhere [10—13].



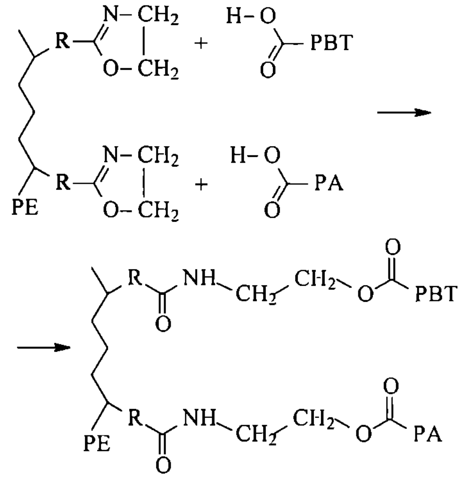
(I)

In a typical grafting process, the peroxide initiator was mixed with ROM in the ribbon mixer and the mixture was added to solid PE. The wet mixture was then fed into the mentioned above twin-screw co-rotating extruder and allowed to react for 3 min. The reaction product (PE-*g*-ROM) was cooled in water, pelletized and dried for 4 h in a vacuum oven at 80 °C.

For purification, PE-*g*-ROM was dissolved in refluxing toluene or xylene at a concentration of 4 % (wt./vol.). The solution was precipitated into seven volumes of methanol and the product was filtered, washed, and dried under vacuum at 75 °C for 48 h. The purified product was characterized using FT-IR spectroscopy.

Preparation of poly(butylene terephthalate)/polyamide 6 blends by means of PE-*g*-ROM

Poly(butylene terephthalate)/polyamide 6 blends (PBT/PA 6) were prepared using the same Berstorff extruder as used for the grafting process. PE-*g*-ROM was coupled together with PBT and PA 6 and allowed to react for 3 min at 210—230 °C [equation (2)]. This way produced PBT/PE-*g*-ROM/PA 6 blends of different compositions (see Table 1) were then ground to small pellets for injection molding. Injection molding process was performed with the injection molder (Arburg) at temperature 3—5 °C higher than melting point determined at Boetius apparatus.



(2)

Structure and physicochemical methods

Thin films (50 μm in thickness) of the purified grafted polyethylene was compression molded at 210 °C under a pressure of 13.8 MPa for 1 min. FT-IR spectra of these thin films were recorded by Spectrum 1000 Perkin-Elmer FT-IR spectrometer at room temperature using a resolution of 4 cm^{-1}.

The morphologies of the fracture surfaces of the specimens were studied by scanning electron microscope JSM 6100, Jeol. Samples were fractured under liquid nitrogen after 3 min and then vacuum coated with gold.

Differential scanning calorimetry (DSC) was performed with Perkin-Elmer (DSC-2) apparatus. The process was carried out in a triple cycle heating—cooling—heating in the temperature ranges from -100 °C to 300 °C with the rate of heating or cooling 10 °C/min. Glass transition temperature (T_g) was determined from the temperature diagrams as the temperature corresponding to the upper inflection point or maximum of the curve. Melting point (T_m) and crystallization temperature (T_c) were determined as corresponding to the maximum of the endothermic curve and the minimum of the exothermic curve, respectively.

Dynamic mechanical thermal analysis (DMTA) was preformed with RDS-II-Rheometrics apparatus within temperature range from 0 °C to 300 °C at 1 Hz with heating rate 3 °C/min. The complex modulus (G^*), dynamic viscosity (η^*) and loss tangent (tg δ) were determined by this method.

Solubility tests of the samples were carried out with Soxhlet apparatus in 85 wt. % formic acid.

Mechanical properties

Flexural strength and modulus were measured according to PN-EN ISO 178:1998, and the tests were carried out at Instron 4505 apparatus at room temperature.

The tests concerning tensile data (according to PN-EN ISO 527-2:1998) were carried out at room temperature using Instron 4505 tensile tester at a crosshead speed of 5 mm/min.

Charpy impact notched and unnotched tests were performed according to PN-EN ISO 179-1:2002 (U).

Deflection temperature was measured according to PN-EN ISO 75-2:1998.

Hardness was estimated according to PN-EN ISO 2039-1:2002 (U).

Melt flow rate (*MFR*) was examined using plastometer type II RT according to PN-EN ISO 1133:2002 (U) (270 °C, 1.2 kg, die I).

RESULTS AND DISCUSSION

Chemical structure

FT-IR spectra of purified ROM-grafted PE showed a new peak at 1644 cm^{-1} characteristic for oxazoline ring, confirming that the grafting process was successful [12, 13].

Blends components miscibility

The effect of PE-*g*-ROM in compatibilizing of PBT/PA 6 blends was first observed in SEM images (Fig. 1). The micrographs of the fractured surfaces of the blends samples presented in Fig. 1 demonstrate a compatible heterophasic character of interpenetrating polymer network (IPN) type, which was in accordance with learnings from DMTA spectra (Fig. 2). This is due to the very good adhesion and confirms the formation of block copolymers located in the interface.

Phase structure studies showed that interfacial reactions between functionalized PE-*g*-ROM, PBT and PA 6 containing co-reactive groups are effective in the compatibilization of investigated blends. The graft copolymers formed during reactive processing, because of interchain exchange reactions, play a role of compatibilizers.

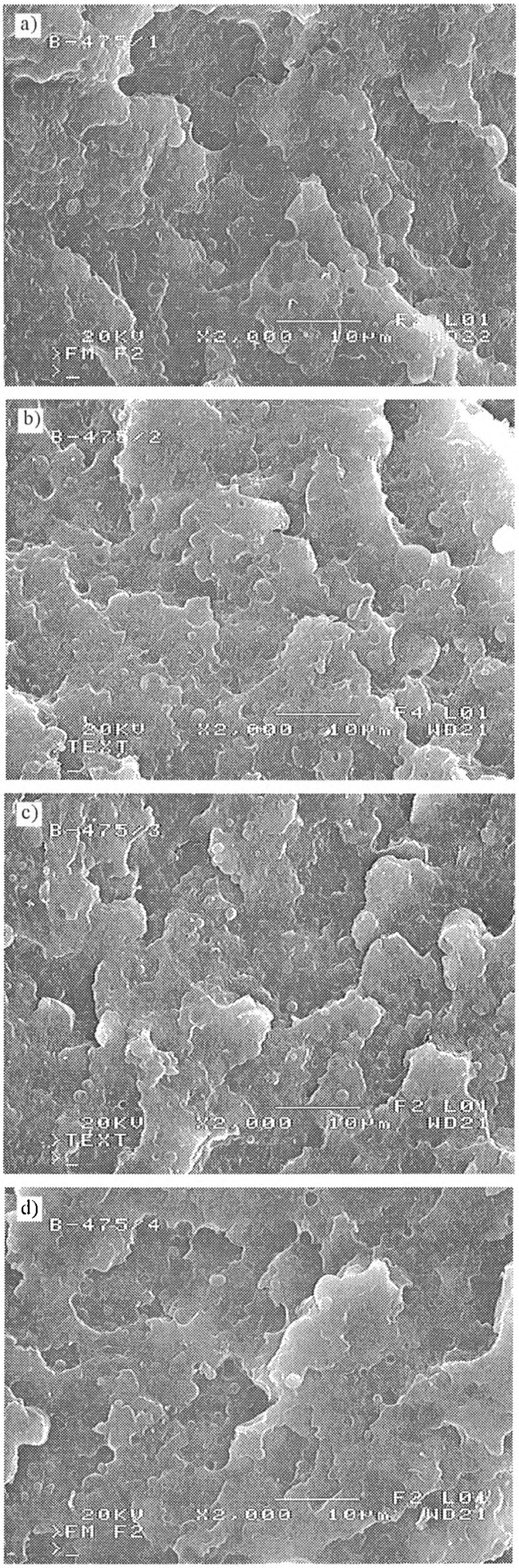


Fig. 1. SEM micrographs of fracture sections of PBT/PE-g-ROM/PA 6 blends: a) 30/20/50, b) 25/25/50, c) 40/20/40, d) 40/25/35

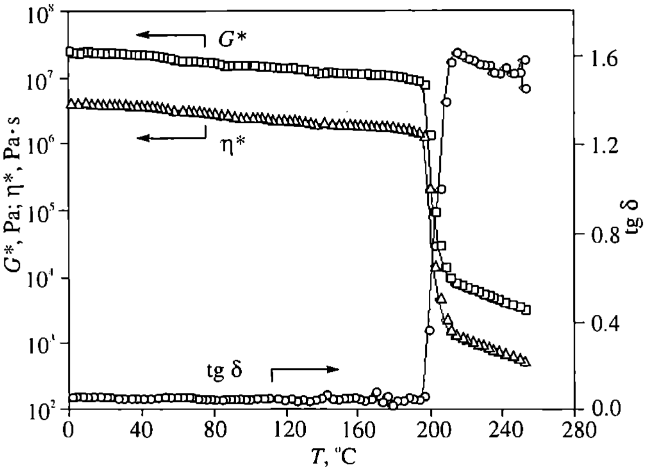


Fig. 2. DMTA data of PBT/PE-g-ROM/PA 6 (30/20/50) blend; for symbols see text

Phase transitions of the blends

According to DSC data of PBT/PE-*g*-ROM/PA 6 blends presented in Table 1 and in Figures 3 and 4, the two-stage process results in heterophasic blends with two marked melting peaks (T_m) and two crystallization regions (T_c) corresponding to the blends components. Melting point of PE fraction is found the same as that of the neat PE (111—113 °C), while the enthalpy is growing up. Maxima of curves presenting the effects of endothermic or egzothermic processes observed in melting and crystallization regions are the results of an overlapping of the thermographs of blend components (PBT and PA 6) due to their close attitude or microphase dispersion and compatibilization.

This, together with the disappearance of glass transition temperatures associated with PBT and PA 6 indicates, indirectly, that interfacial reactions have occurred between the oxazoline groups in PE with the functional groups in PBT and PA 6 phases during reactive extrusion.

Table 1. DSC results of PBT/PE-*g*-ROM/PA 6 blends*)

PBT/PE-*g*--ROM/PA %	T_g, °C (ΔC_p, J/g · K)	T_{m1}, °C (ΔH_{m1}, J/g)	T_{c1}, °C (ΔH_{c1}, J/g)	T_{m2}, °C (ΔH_{m2}, J/g)	T_{c2}, °C (ΔH_{c2}, J/g)
100/0/0	44 (0.13)	—	—	121, **226** (49.7)	190 (58.0)
0/0/100	40 (0.32)	—	—	221 (62.4)	171 (63.5)
40/20/40	—	111 (169.5)	**101**, 60 (129.1)	224 (55.7)	192, **185** (68.6)
35/25/40	—	112 (139.4)	**101**, 59 (122.3)	225 (55.0)	192, **186** (66.8)
30/20/50	—	112 (163.3)	**101**, 60 (126.5)	224 (57.7)	193, **187** (68.5)
25/25/50	—	113 (154.2)	**101**, 60 (126.1)	224 (61.0)	188 (71.5)
0/100/0	—	113 (130.9)	**101**, 64 (131.8)	—	—

*) ΔH_{m1}, ΔH_{m2}, (J/g of the blend component) — melting enthalpy; ΔH_{c1}, ΔH_{c2}, (J/g of the blend component) — crystallization heat; ΔC_p — heat capacity difference at T_g; bolding values — main effect; index 1 concerns PE-*g*-ROM, while index 2 — PBT + PA 6.

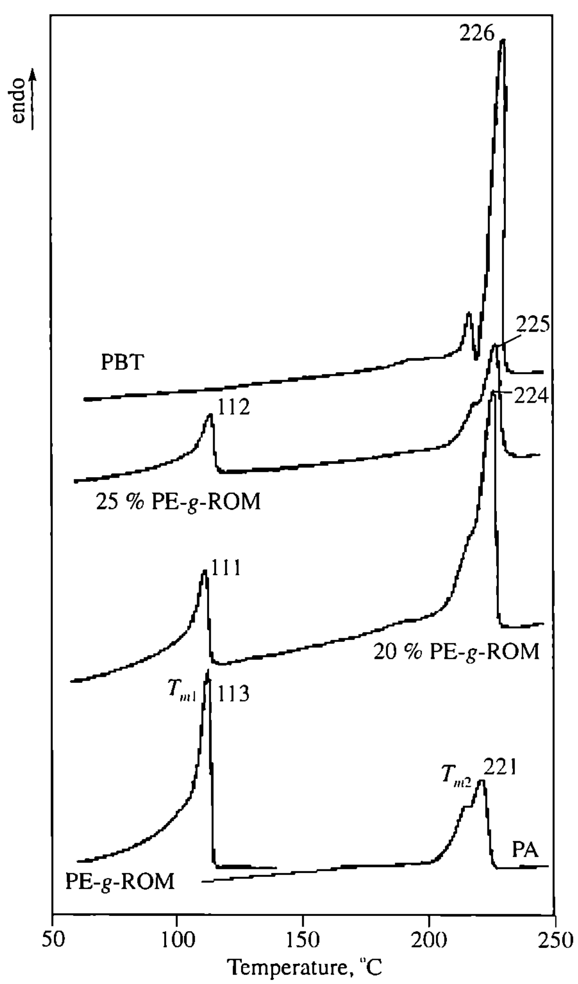


Fig. 3. DSC thermograms of PBT/PE-g-ROM/PA 6 blends, and of blend components over 0—250 °C; second heat run

Solubility data

Data of the resulting blends solubilities in a formic acid can be used for qualitative evaluation of the final polymer compositions. Solubility of the product obtained by reactive processing of polyester/polyamide 6 blends in the presence of oxazoline functionality decreases significantly, which confirms the formation of graft copolymers and better chemical resistance. As can be seen from Table 2 the solubility changes with blend composition. The resulting polymer systems can be considered as PBT/PE-*g*-ROM/PA 6 block copolymers with

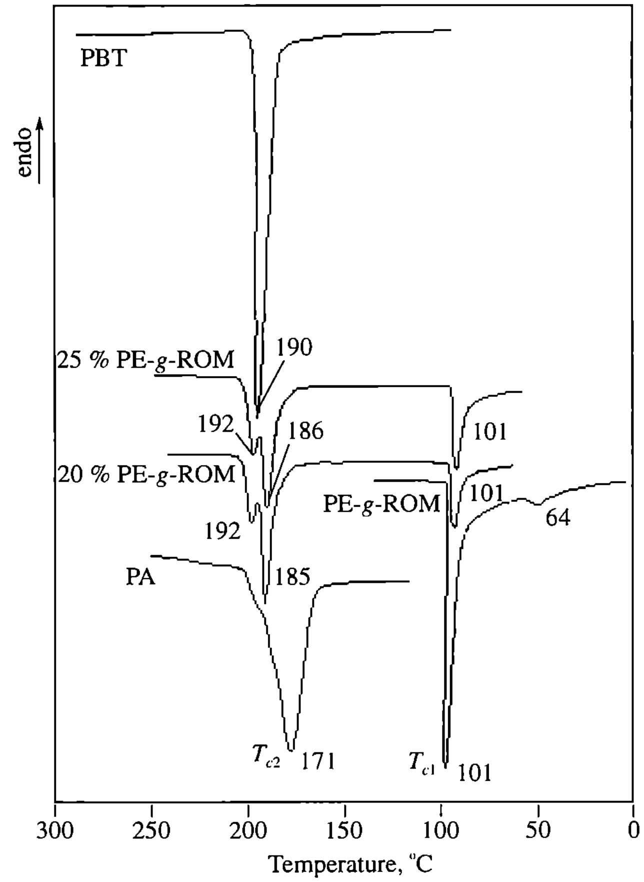


Fig. 4. DSC thermograms of PBT/PE-g-ROM/PA 6 blends and of blend components in a crystallization region; second heat run

some contents of starting homopolymers. It should be noted that the data of the solubility tests do not provide the possibility to calculate exactly the polymer composition of the resulting product.

Table 2. Solubility of PBT/PE-*g*-ROM/PA 6 blends in a formic acid (85 wt. %)

PBT/PE-*g*-ROM/PA 6	Solubility, wt. %
100/0/0	0
40/20/40	19
35/25/40	17
30/20/50	27
25/25/50	25
0/0/100	100

Impact properties

PBT/PA 6 blends were investigated mainly in order to develop new engineering polymers showing high impact strength. The results proved that this aim could be achieved. Table 3 shows the effect of the functionalized PE on the impact strength of the investigated blends. There was impact strength improvement in the blends, in comparison with PBT and PA 6, respectively. This phenomenon may be due to mentioned earlier reaction with participation of functional groups of three components of a blend. The improvement in impact strength enhanced slightly with increasing concentration of the functionalized PE.

Table 3. Mechanical properties of PBT, PA 6 and reactive PBT/PE-*g*-ROM/PA 6 blends

Property	PBT	PBT/PE-*g*-ROM/PA 6				PA 6
		40/20 /40	35/25 /40	30/20 /50	25/25 /50	
Yield point, MPa	52	55	52	58	53	78
Elongation at yield point, %	3.8	6.2	7.3	5.6	5.8	4.0
Strength at break, MPa	46	50	50	55	50	50
Elongation at break, %	16	22	20	18	22	50
Flexural strength, MPa	72	60	54	60	57	82
Flexural modulus, MPa	2544	2000	1800	2000	1870	2800
Charpy unnotched impact strength, kJ/m^{2} *)	nb	nb	nb	nb	nb	nb
Charpy notched impact strength, kJ/m^{2}	10	10	12	12	14	7
Deflection temperature (1.8 MPa), °C	53	59	60	60	59	60
Ball hardness, N/mm^{2}	79	82	75	83	78	79
MFR, g/10 min	5.4	0.8	0.6	0.7	0.6	2.6 **)

*) nb — no break.

**) 230 °C, 0.32 kg die II.

Other mechanical properties

The investigated blends retain properties of engineering polymers. As evident from Table 3, an increase in PE-*g*-ROM amount in the blends results in lower strength and modulus on one hand, and higher elongation at yield point on the other. However, the blends show higher tensile strength, elongation at break, and deflection temperature in comparison with PBT. *MFR* of the blends dramatically decreased. This fact indicates substantial amounts of interfacial reaction and molecular weight increase.

CONCLUSIONS

It has been shown that the interfacial reactions between polyethylene, reactively functionalized with an oxazoline group, and PBT and PA 6 containing co-reactive groups are effective in the compatibilization of the polymer blends. The graft copolymer formed during the reactive extrusion results in an alloy with good interfacial adhesion. The presented method of reactive extrusion by two-stage process provides a possibility to produce a variety of new high-impact and good chemical resistance (better than PA 6) polymeric materials by varying the concentration of PE-*g*-ROM and initial polymer composition.

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