Mica as a Filler for PET Scrap/Oxazoline Functionalized Polyethylene Blends

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Summary: A series of mica filled PET scrap/PE-*g*-ROM blends was studied in a chemical modification involving reactive extrusion with a ricinoloxazoline maleinate. Studies were conducted concerning mechanical properties (flexural and impact strength), thermal properties (DSC and Vicat softening temperature) and flame retardancy. The phase morphology of the blends was of interpenetrating network (IPN) type according to SEM results. Mica filled blends offer good mechanical properties, reduced flammability and increased Vicat point. The composition with 30% of mica gives the best properties and efficiency in reducing the rate of burning.

Introduction

Mica has an advantage over the fibers because it provides reinforcements in a plane instead of along a single axis, and may be used as a cheaper substitute of fiberglass, with double the modulus, and the benefit of being abundant throughout the world. In general, mica reinforced thermoplastics offer: high rigidity, excellent chemical resistance, good dielectric properties, low thermal expansion, reduced flammability and increased heat distortion temperature, among other properties[1)].

Based on the above-mentioned reasons, this study tries to meet the development requirements for PET scrap/oxazoline functionalized PE (PETs/PE-*g*-ROM) blends filled with mica, and get a composite with better thermal properties, flammability characteristics, and low-cost. Studies were conducted concerning mechanical properties (flexural and impact strength), thermal properties (DSC and Vicat softening temperature), flame retardancy, and morphology (SEM).

Experimental

Low-density polyethylene (PE) was commercial product supplied by Polski Koncern Naftowy SA, Poland. PET waste flakes (intrinsic viscosity 0.66 dlg^{-1} in dichlorobenzene/phenol, 50/50 wt/wt, at 25^0C) was supplied by Customer, Poland (Tab. 1). Ricinoloxazoline maleinate was

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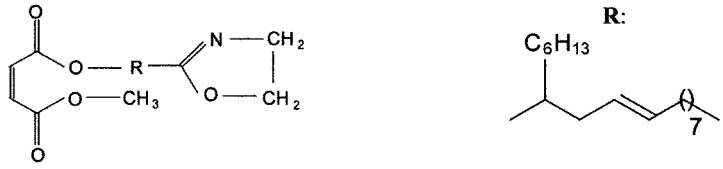
obtained from Henkel, Germany (Formula 1). Mica (density 2.75 g/cm^3, particle size < 60 μm) was purchased from Aspanger, Austria. Before using, PE and PET flakes were dried under vacuum at 85^{0}C.

Table 1. PET scrap characteristic

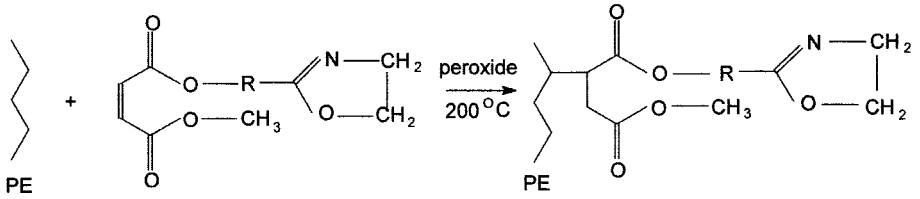
Property	Value
Dimension	
> 8 mm, < 0.6 mm	< 1 %, < 0.5 %
Metal content	< 3 ppm
Paper content	< 10 ppm
PVC content	< 25 ppm
Polyolefins content	< 25 ppm
Sugar content	< 10 ppm
Humidity	< 0.02 %



Formula 1

Procedure

Recycling of PET scrap was performed in a pilot-plant twin-screw extruder "Berstorff ZE-25-33D" according to the procedure published elsewhere [2-5]. At stage I, ricinoloxazoline maleinate (ROM) was melt grafted onto a low density polyethylene homopolymer (PE) at 180 – 200^{0}C using a peroxide initiator (Reaction 1); at stage II, PE reactively functionalized with an oxazoline group (PE-*g*-ROM) was extruded together with waste PET flakes at 245 – 260^{0}C (Reaction 2). Mica was added to the reaction mix at 15D length down the barrel. The residence time of the reactants was 3 minutes, respectively.



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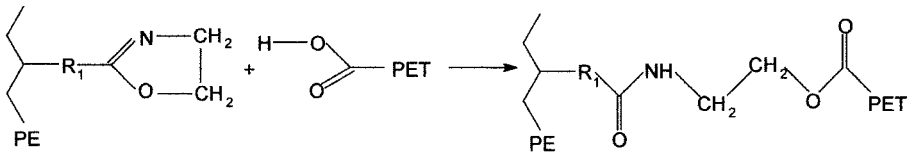

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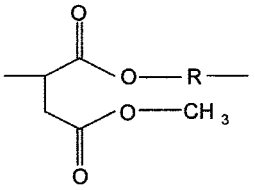

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Testing methods

The intrinsic viscosity was calculated from viscosity measurements of diluted solutions in dichlorobenzene/phenol (50/50 wt/wt) at 25^{0}C using Ubbelohde viscometers.

Carboxylic end-group concentrations were determined by dissolving the samples in hot aniline, diluting with chloroform, and titrating with methylalcoholic sodium hydroxide[6].

The morphology of the fracture surface of the specimens was studied *via* scanning electron microscope JSM 6100, Jeol. Samples were fractured under liquid nitrogen after 3 min and then vacuum coated with gold.

Flexural strength and modulus were obtained acording to PN-EN ISO 179, and the tests were carried out with a Zwick apparatus at room temperature.

Charpy impact test was performed according to PN-81/C-89029. The tests were carried out at room temperature, on notched specimens.

The Vicat Softening Temperature was obtained according to PN-93/C-89024, Rate A (120^0/h).

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-2 apparatus. The process was carried out in a triple cycle „heating-cooling-heating" from 0 to 250^{0}C at a heating and cooling rate of 10^{0}C min^{-1}. The data obtained in this analysis were the glass transition temperature, T_g, and T_g width, ΔT_g.

Flammability tests were carried out according to ASTM D2863-87, and the data obtained was oxygen index.

Results and discussion

As is seen in Fig. 1 oxazoline increased intrinsic viscosity and decreased amount of PET carboxyl end groups in PETs/PE-g-ROM blends as an effect of interchain exchange reactions, leading to higher molecular weight and better impact strength[5]. Effect of oxazoline functionalized PE addition on the impact strength of the PETs/PE-*g*-ROM blends is shown in Fig. 2.

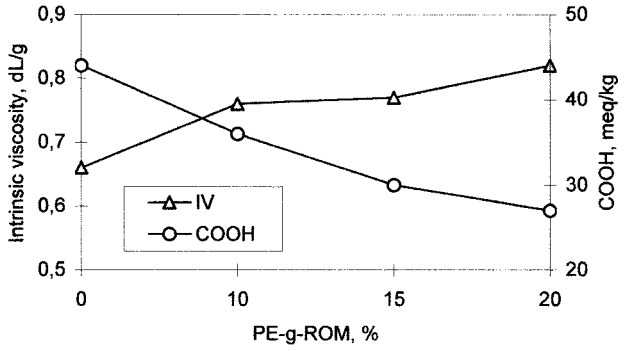

Fig. 1: Effect of oxazoline functionalized PE addition on the intrinsic viscosity and COOH group content of the PETs/PE-*g*-ROM blend.

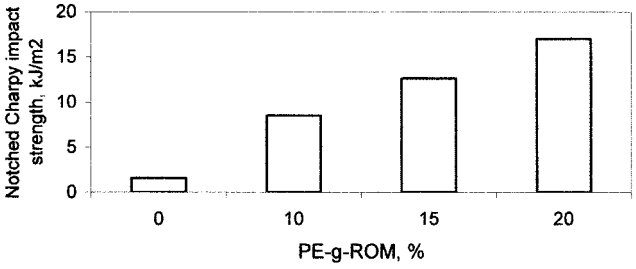

Fig. 2: Effect of oxazoline functionalized PE addition on the impact strength of the PETs/PE-*g*-ROM blends.

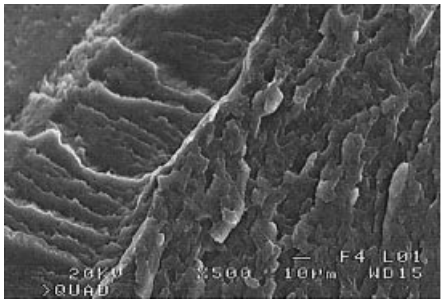

Fig. 3: SEM image of PETs/PE-*g*-ROM (85/15) blend.

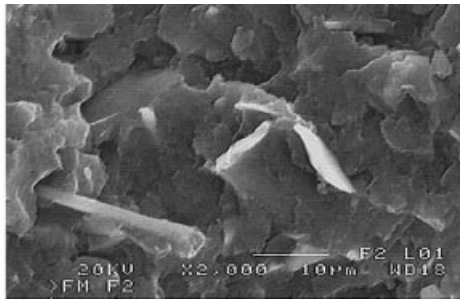

Fig. 4: SEM image of PETs/PE-*g*-ROM blend filled with 20% of mica.

As an example Figures 3 and 4 show micrographs of PETs/PE-*g*-ROM blends with and without mica. SEM results demonstrate a compatible structure with continuous and interpenetrated phases of PE-*g*-ROM and waste PET (Fig. 3) and strong adhesion between mica and the polymer matrix (Fig. 4) as a result of intermolecular reactions.

Table 2 indicates the properties of PETs/PE-*g*-ROM (80/20) blends as a function of mica load. As would be expected, flexural strength decrease with the addition of mica. This could be attributed to a reduction in the polymer matrix mobility due to presence of the filler particles. An opposite behavior was noted for blends modulus that raised with increasing concentration levels of filler. It was also expected that with the addition of a higher modulus material, like mica (1.72 x 10^5MPa), the polymer would exhibit a modulus increase[7]. The impact strength shows a sharp decrease with the addition of the inorganic filler (Fig. 5).

Table 2. The PETs/PE-*g*-ROM blends properties as a function of mica load

Properties	Unit	Mica, %			
		0	10	20	30
Flexural strength	MPa	63	57	58	60
Flexural modulus	MPa	2100	3000	3600	4000
Notched impact strength (Charpy)	kJ/m^2	17	8.0	6.0	7.0
Heat distortion temperature (load 1.8 MPa)	^0C	79	84	88	90
Softening point, Vicat (load 10 N)	^0C	180	> 210	> 210	> 210
Glass transition temperature/ $\Delta T_{gPET\ phase}$	$^0C/^0C$	81	75/6	78/3	79/2
Oxygen index	%	22	24	25	26

The most important effect of mica addition process was a significant enhancement of the Vicat point.

Values for PETs/PE-*g*-ROM blends calorimetric parameters as a function of the mica load are shown in Table 2. It is possible to observe from Table 2 that the first addition of mica leads to

a decrease in the PET phase transition value (T_{gPET}) but, higher levels of mica do not have significant effects on the PET phase transition temperature.

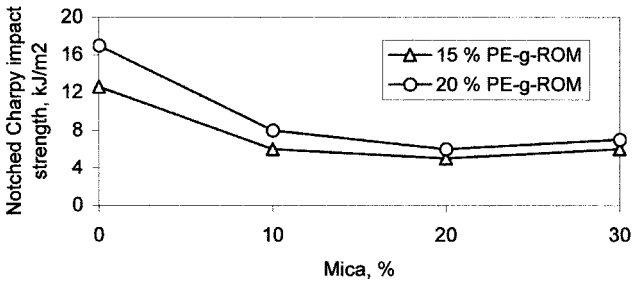

Fig. 5: The PETs/PE-*g*-ROM blend impact strength as a function of mica and PE-*g*-ROM load.

Data of the T_g width are also reported in Table 2. This parameter could be employed to study the homogeneity of blends[7]. It could be noted, that for the samples 20 and 30 phr of mica, T_g values were lower than for other sample, which indicates a higher homogeneity and corroborates with the better properties obtained for this filler amount (Fig. 6).

The composition with 30 phr of mica gives the best properties and efficiency in reducing the rate of burning.

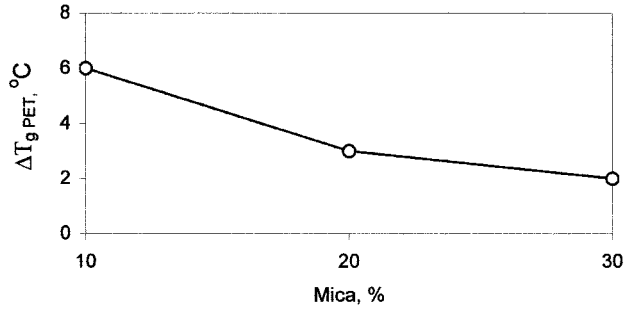

Fig. 6: Effect of mica addition on the ΔT_g of the PET phase of the PETs/PE-*g*-ROM blend.

Conclusion

It has been shown that the interfacial reactions between polyethylene reactively functionalized with an oxazoline group and PET having co-reactive groups are effective in the compatibilization of the polymer blends. The graft copolymer formed on the reactive extrusion results in an alloy with good interfacial adhesion. Mica filled blends offer good mechanical properties, reduced flammability and increased Vicat point. The process of recycling PET scrap on reactive extrusion combined with mica reinforcing provides a possibility to produce a variety of new polymeric materials by varying the concentration of PE-*g*-ROM and mica. Cost reduction opportunities of the recipes by using PET waste have also been explored.

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