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Reactive compatibilization and properties of recycled poly(ethylene terephthalate)/polyethylene blends

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Summary

Blends of recycled poly(ethylene terephthalate) (R-PET) and high-density polyethylene (R-PE), obtained from post-consumer packaging materials, were prepared both by melt mixing and extrusion processes and compatibilized by addition of various copolymers containing functional reactive groups, such as maleic anhydride, acrylic acid and glycidyl methacrylate. The effect of the type and concentration of compatibilizer, as well as the mixing conditions, on the phase morphology, thermal behaviour, rheological and mechanical properties of the blends was investigated. The results indicated that addition (5÷10 pph) of ethylene-*co*-glycidyl methacrylate copolymer (E-GMA) allows for a marked improvement of processability and physical/mechanical performances of R-PET/R-PE blends.

Introduction

Poly(ethylene terephthalate) (PET) and polyolefins (HDPE, LDPE, PP, etc.) constitute the majority of thermoplastics currently used as packaging materials. As their use is continuously increasing, the problem of the post-consumer recycling of these materials has become a very important issue both for economical and environmental reasons. Blending of scrap polymers may provide an alternate route for the production of recycled materials with satisfactory cost/performance and wide application potential. This can be achieved if suitable compatibilization methods and processing technologies are used in order to enhance the phase dispersion and interfacial adhesion in the blends. Efforts to develop effective compatibilization of PET/polyolefin blends are mainly turned to reactive mixing processes through the addition of polyolefins bearing functional groups (anhydryde, carboxyl, epoxy, etc.) in the chains, capable of giving rise to chemical reactions with the carboxyl and/or hydroxyl end-groups of PET during melt blending (*in situ* compatibilization) [1-5]. This leads to the formation of graft copolymers between the two components, which are mostly located at the interface of the polymer phases and contribute to decrease the interfacial tension as well as to increase the adhesion between thephases [6].

So far the reactive compatibilization processes of blends of recycled or scrap materials and their effect on the upgrade of the properties have not yet been extensively investigated [7]. In a previous paper we reported on the functionalization of HDPE by melt radical grafting with glycidyl methacrylate (GMA) and the properties of blends with recycled PET [8]. In the present paper, a study of the compatibilization processes and physical-mechanical characterization of blends of PET and polyethylene, obtained from post-consumer packaging materials, is reported. The main aim was to analyse the effect of the addition of various functionalized polymers, with different type and content of reactive groups, on the morphology, phase interactions, mechanical and rheological properties of the blends, in order to determine the most effective compatibilization conditions of these systems. The research has been developed within the framework of a European Community INCO-Copernicus Project (Contract No. IC15 CT96 0731).

Experimental

The polymers examined were commercial products of high-density polyethylene (HDPE) (Eltex, Solvay), recycled PET (R-PET) (I.V.= 0.75 dL/g) and recycled polyethylene (R-PE) (98% PE, 2% PP) in the form of ground flakes or pellets from waste plastic bottles, supplied by Replastic (Italy) and GTX Hanex Co. (Poland). All materials, both as received and re-processed, were characterised by chemical and physical standard methods in order to determine molecular weight of the components, type and impurity content, thermal properties and oxidation stability [9, 10].

Blends R-PET/R-PE and R-PET/HDPE with composition ratios 75/25 and 25/75 (w/w %) were obtained by using a Brabender Plastograph internal mixer (T= 270°C, 70 rpm, 5 min) and a Mapre twin-screw extruder (D=30 mm, L/D=33, T=270°C, 500 rpm) under nitrogen flux. The blend compatibilization was carried out by using various types of compatibilizers at concentrations in the range 3÷15 pph (parts per hundred of blend). The compatibilizers used were HDPE grafted with 4 wt.% maleic anhydride (HDPE-*g*-MA) (Polybond 3009, Uniroyal), ethylene-propylene copolymer grafted with 1 wt.% maleic anhydride (EPR-*g*-MA) (Fusabond N, Du Pont), ethylene-*co*-acrylic acid copolymer (E-AA) containing 6.2 wt.% AA (Escor 5000, Exxon), ethylene-*co*-glycidyl methacrylate copolymer (E-GMA) containing 8 wt.% GMA (Lotader AX8840, Elf Atochem) and styrene-ethylene/butylene-styrene block copolymer grafted with 1.7 wt% maleic anhydride (SEBS-*g*-MA) (Kraton FG 1901X, Shell). Blending was performed by one or two-step procedures: all components were melt mixed together, or the compatibilizer was first mixed with the polyolefin and then PET was added. Binary mixtures of R-PET with various compatibilizers were also prepared by means of the internal mixer (T= 270°C, 70 rpm, 5 min).

The morphology of the polymer blends was examined by a Jeol T300 scanning electron microscope (SEM) on cryogenically fractured samples; the size distribution of the dispersed phase was measured by a NIH image analysis programme. Thermal behaviour was analysed with a Perkin-Elmer DSC-2C differential scanning calorimeter at a heating/ cooling rate of 10°C/min under N_2 flux. Samples were first heated to 290°C, then cooled to 30°C and re-heated up to complete melting (2nd run). FTIR analysis was carried out by a Perkin-Elmer 1600 spectrometer. Melt viscosities were measured by a CEAST capillary viscosimeter (L/D= 40) at 275°C in the shear rate range $10^1 \div 10^3$ sec^{-1}. Tensile mechanical analysis and impact tests were performed at 23°C by an Instron machine and a Ceast-Resil impact tester on injected molded samples, according to standards (ASTM D638).

Results and discussion

For all the compositions examined, binary blends of R-PET with R-PE, or HDPE, show the typical morphological features of incompatible systems with a poor dispersion of the components and no interfacial adhesion between matrix and dispersed phase. A wide distribution of the dispersed particle size, due to coalescence phenomena of the minor phase during the melt blending, was generally observed (Fig. 1a).

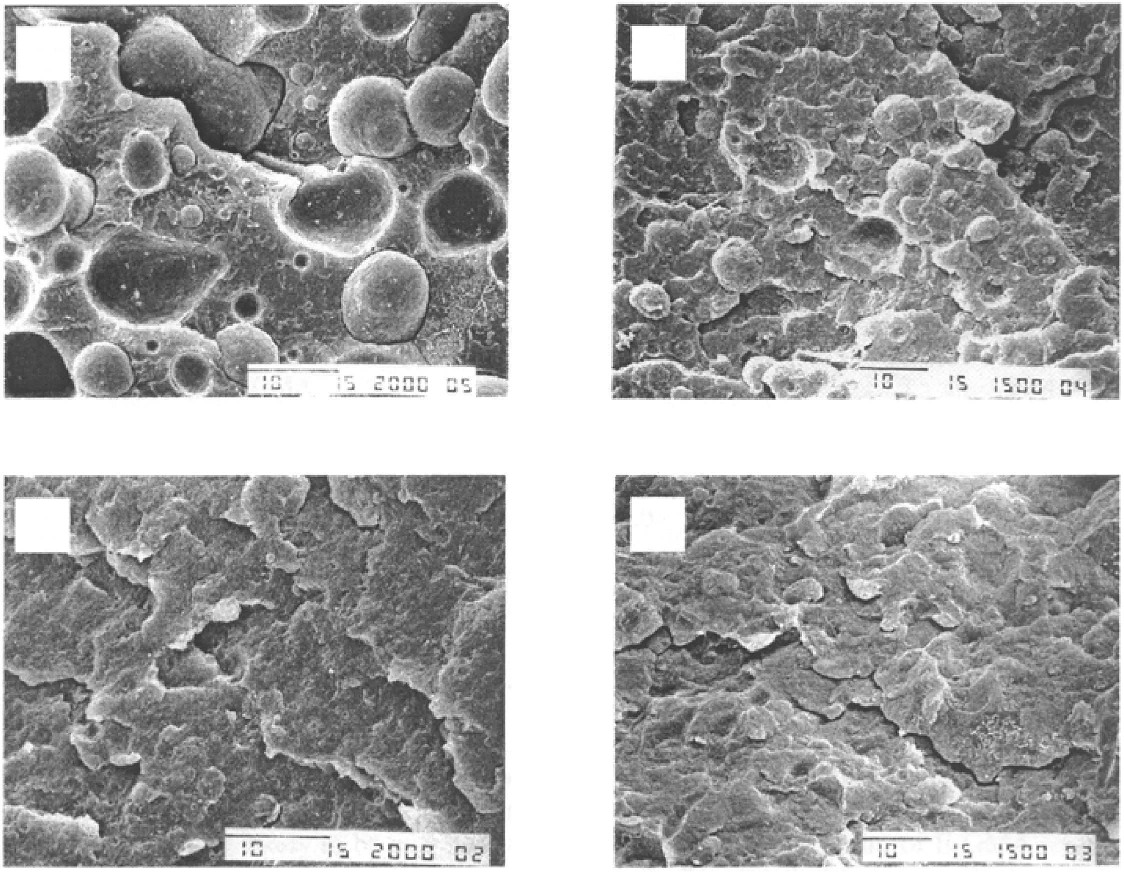

Fig.1 SEM micrographs of fracture surfaces of (a) R-PET/R-PE (75/25) blend and of the same blend compatibilized with (b) E-GMA (5 pph), (c) E-GMA (10 pph) and SEBS-*g*-MA (10 pph) (bar length: 10 μm).

The morphological characteristics of the compatibilized blends are markedly affected by the type and concentration of functionalized polyolefin, as well as by the mixing procedures. As shown in the SEM micrographs of Fig.s 1b-d for compatibilized R-PET/R-PE blends with PET matrix, a higher phase dispersion with small particle sizes and improved adhesion at the polymer-polymer interface is noticed, as compared with the non-compatibilized blend at the same composition. The number-average diameter of dispersed PE particles varies from about 5 μm for R-PET/R-PE (75/25) blend to 2.8 μm and 0.5 μm for the same blend compatibilized with 5 and 10 pph E-GMA, respectively. The effect of compatibilizer concentration on the size of dispersed PE phase was investigated for R-PET/HDPE (75/25) blends compatibilized with E-GMA. The average particle size decreases from 5 μm to 0.3 μm with increasing the amount of E-GMA until reaching a saturation value (less than 10 pph EGMA), corresponding to the decrease of interfacial energy in the blends [11].

The phase behaviour of the components in the compatibilized blends is clearly influenced by the type and amount of compatibilizer. In Table 1, the values of crystallization temperatures (*T*c) and heats of crystallization (Δ*H*c) and melting (Δ*H*m) of PE and PET phase are reported for binary and ternary blends compatibilized with E-GMA or SEBS-*g*-MA (5-10 pph).

Table 1. DSC data from cooling and 2nd heating run of R-PET/HDPE and R-PET/R-PE blends.

Blend Composition	PE			PET		
	Tc (°C)	ΔHc (J/g)	ΔHm (J/g)	Tc (°C)	ΔHc (J/g)	ΔHm (J/g)
R-PET/HDPE 75/25	114.3	-140.8	178.0	190.2	-33.9	30.8
R-PET/R-PE 75/25	115.7	-180.8	179.2	194.1	-35.2	40.3
R-PET/R-PE/E-GMA 75/25/5	115.8	-146.5	146.5	194.1	-34.7	37.4
R-PET/R-PE/E-GMA 75/25/10	115.1	-130.2	129.9	189.1	-34.2	38.1
R-PET/R-PE/SEBS-g-MA 75/25/5	115.8	-169.7	179.0	194.0	-35.4	34.3
R-PET/R-PE/SEBS-g-MA 75/25/10	116.1	-147.1	160.8	194.7	-35.8	35.6

Generally, the heats of transition (per gram of polymer) decrease as the amount of compatibilizer increases, the larger variations being observed for blends containing E-GMA. This is likely to be ascribed to the to the effect of miscibility of E-GMA with the PE phase and of the interactions of polyolefin functional groups with PET in the melt, which can influence the crystallization process and the crystalline structure of the phases. The crystallinity degree of the dispersed polyolefin phase in blends compatibilized with E-GMA (10 pph) is about 20% lower than that found in the blends without compatibilizer, whereas for PET phase the decrease of crystallinity is of about 6%. Minor variations are observed for the melting temperatures of both components.

The effect of the addition of functionalized polyolefins on the melt viscosity of R-PET/R-PE (75/25) blends has been analysed for different contents of E-GMA and SEBS-*g*-MA respectively.

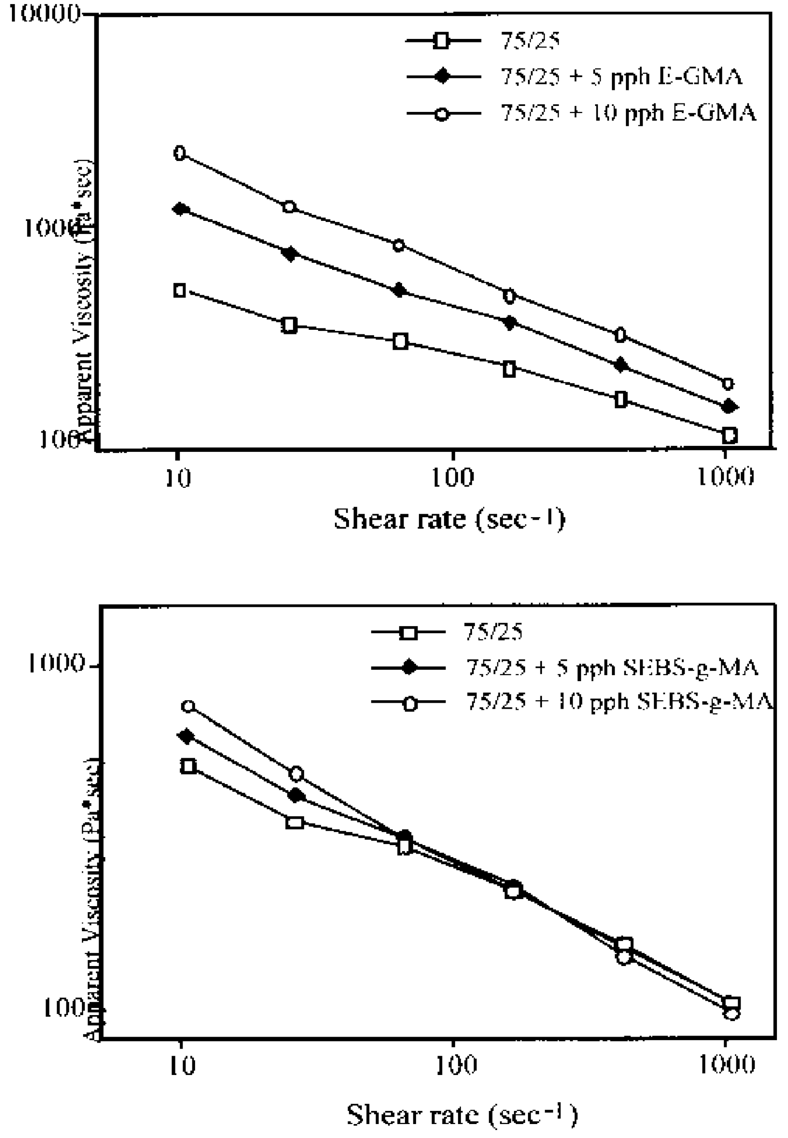

Fig. 2. Apparent melt viscosity of R-PET/R-PE (75/25) blends compatibilized with (a) E-GMA and (b) SEBS-g-GMA, as a function of shear rate at 275°C.

As shown in Figs. 2a-b, for the same blend composition, the melt viscosity of the compatibilized blends is higher than that of non-compatibilized blends and generally increases with increasing the amount of compatibilizer. However, blends with E-GMA display higher viscosity as compared with blends containing SEBS-g-MA over the shear range examined. Such an effect can be accounted for by the occurrence of strong interfacial interactions in the melt between the functional groups of E-GMA and PET, giving rise to less deformable particles [10].

The compatibilizing effect of E-GMA and SEBS-*g*-MA copolymers was analysed by tensile and impact mechanical tests on R-PET/R-PE (75/25 and 25/75) blends as a function of E-GMA and SEBS-*g*-MA content. For blends with R-PET matrix (75/25) the elongation at break of compatibilized blends is about 3 times that of non-compatibilized blends. A higher tensile modulus and yield stress were observed in the presence of E-GMA. For blends with R-PE matrix (25/75), a large increase of elongation at break up to about 250% was found upon addition of SEBS-*g*-MA (10 pph), in good agreement with literature data for PET/HDPE/SEBS-*g*-MA blends [2]. As shown in Fig. 3, the values of Izod impact strength indicated a marked improvement of the impact resistence for R-PET/R-PE (75/25) blends compatibilized with E-GMA. For blends with polyolefin matrix (25/75) the addition of 10 pph SEBS-*g*-MA increases the impact strength by about 4 times.

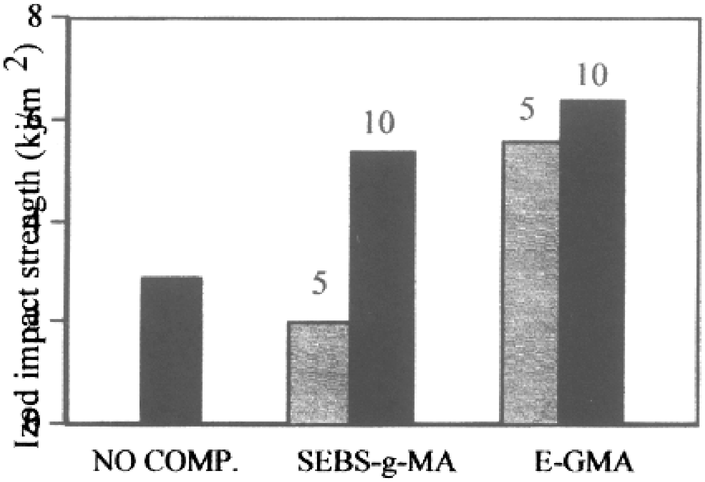

Fig. 3. Izod impact strength of R-PET/R-PE (75/25) blends compatibilized with 5 and 10 pph SEBS-*g*-MA and E-GMA, as compared with the non-compatibilized blend.

Binary blends of R-PET and various compatibilizers (HDPE-*g*-MA, EPR-*g*-MA, E-AA, E-GMA) at compositions of 5÷5 pph were examined in order to evaluate the effect of type and concentration of functional groups on the melt reactivity with PET. The variation of torque moment recorded during the blending process is reported in Fig. 4 as a function of compatibilizer content. A large increase of torque was observed for all R-PET/E-GMA blends, whereas blends with HDPE-*g*-MA, EPR-*g*-MA or E-AA displaied minor variations with composition. Dagli e Kamdar [3] reported similar effects of increasing torque for blends of HDPE and PET compatibilized with E-GMA. The variation of torque during melt mixing can be associated with a change of viscosity as a consequence of chemical reactions between the polyester chain-ends and the functional groups of the compatibilizer. Accordingly, rheological measurements by capillary viscosimetry exhibited a neat increase of melt viscosity for blends of R-PET with E-GMA as compared to those with MA or AA functionalized polyolefins, supporting that epoxy groups of GMA give rise to stronger interactions with the polyester chains [12]. Evidences of grafting reactions between PET and E-GMA in their blends were obtained by ^{13}C-NMR analysis after selective extraction of the polyolefin component with xylene; the spectra revealed the presence of characteristic signals of both PET and E-GMA carbons without variation of peak area ratios with respect to the unextracted blend [13].

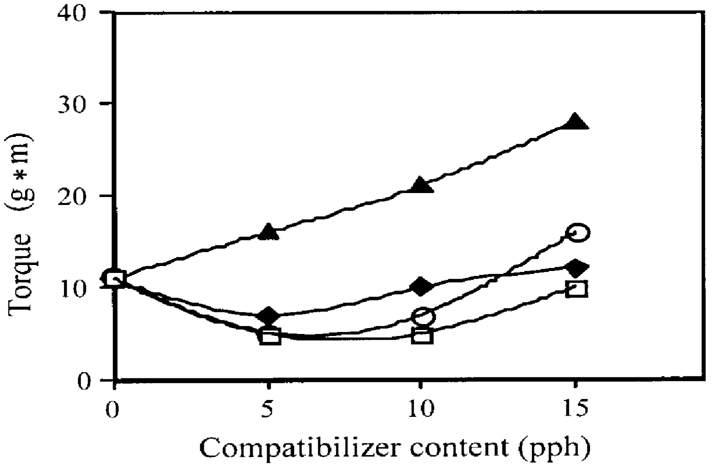

Fig. 4 Effect of compatibilizer content on the relative torque variation recorded during melt mixing (T=270°C) of binary blends of R-PET with: (▲) E-GMA, (◆) EPR-*g*-MA, (○) E-AA, (□) HDPE-*g*-MA.

The results obtained point out that the in situ compatibilization of R-PET/R-PE (and R-PET/HDPE) blends by melt mixing with suitable functionalized polymers is an effective method for improving the physical and mechanical properties of these systems. The compatibilizing effect of the various functionalized polyolefins is depending on the type and concentration of functional groups and is strictly related with their reactivity toward PET in the melt.

Among the compatibilizers examined, E-GMA copolymer (at a concentration of about 10 pph) promotes a finer dispersion of polyethylene phase - with particle size of one order of magnitude lower as compared to non-compatibilized blends - and better interfacial adhesion with PET matrix. Rheological measurements carried out on binary and ternary blends show that addition of E-GMA causes a neat increase of melt viscosity which can be accounted for by the occurrence of chemical reactions between the components, leading to the in situ formation of graft copolymer. The higher compatibilizing effectiveness of E-GMA is also supported by mechanical tests which indicate a considerable improvement of tensile and impact resistance for R-PET/R-PE blends with PET matrix. Such effects can be ascribed to a higher reactivity of the epoxy groups of GMA toward both the carboxyl and hydroxyl end-groups of PET, as compared with that of maleic anhydride (MA) and acrylic acid (AA) functionalities [14]. This is consistent with the results by Hu et al. [15] on reactive compatibilization of PBT/PP blends indicating that radical grafting of polyolefin with GMA monomer was more effective than MA or AA grafting in henancing the blend morphology and mechanical performances. Likewise, for PET/PP blends it has been shown that the compatibilizing efficency of SEBS copolymers grafted with GMA is higher than that of SEBS grafted with MA [16].

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