Reactive Compatibilization of Polyolefin/PET Blends by Melt Grafting with Glycidyl Methacrylate

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Summary: The melt free radical grafting of glycidyl methacrylate (GMA) onto high-density polyethylene (HDPE) was carried out in Brabender internal mixer. The GMA content of the grafted HDPE (HDPE-*g*-GMA) was determined through FTIR by means of a calibration curve. The influence of reaction procedure, radical initiator concentration and addition of a co-monomer (styrene) on the grafting efficiency was examined. Blends of poly(ethylene terephthalate) (PET) with HDPE and HDPE-*g*-GMA (75/25 w/w) were prepared by melt mixing in internal mixer. The morphology of the blends was then analysed by SEM microscopy. PET/HDPE-*g*-GMA blends displayed improved phase dispersion and interfacial adhesion as compared to unfunctionalized PET/HDPE blend.

Introduction

The study of compatibilization of immiscible polymer systems is of very great interest especially with respect to the development of recycling processes of post-consumer plastic materials (polyolefins, PET, etc.), aimed at the production of compounds with improved performances[1]). Effective compatibilization of these systems can be advantageously obtained by means of reactive mixing processes, through the modification of the polyolefin with functional groups which can react with the other blend component, giving rise to *in situ* compatibilization.

The free radical grafting of GMA onto polyolefins (PE, PP, EPR) has been investigated by a few authors in the recent years[2-5]). Among the vinyl monomers containing reactive groups, GMA can be considered a very suitable monomer as its epoxy group can easily react with other functional groups present in polar polymer, such as polyesters and polyamides. Moreover it has been reported that the compatibilization effectiveness of polyolefins grafted with GMA, in blends with polar polymers, is higher than that of the same polyolefins grafted with maleic anhydride (MA) or acrylic acid (AA)[1,6]).

The present communication reports on a study of melt free radical grafting of HDPE (both virgin and recycled) with glycidyl methacrylate monomer (GMA) and reactive mixing with recycled PET (R-PET). The effect of grafting procedures, radical initiator and co-monomer content on the grafting degree of HDPE and properties of PET/HDPE-*g*-GMA blends was investigated.

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Experimental

HDPE (MFI= 0.1 g/10min, 190°C/10kg) and R-PET (I.V.= 0.75 dl/g in phenol-tetrachloroethane, Mw= 4.4 10^3 g mol^{-1}, Mw/Mn≈ 1.7) were commercial products supplied respectively by Solvay and Replastic (Italy). R-PET had a content of COOH end groups of 3.4 10^5 mol $gram^{-1}$, as determined by titration with KOH in benzyl alcohol. GMA and styrene (STY) monomers (Aldrich) were used as received. Grafting reactions onto HDPE were carried out in a Brabender internal mixer, under nitrogen flux (175°C, 5 min, 50 rpm) in the presence of benzoyl peroxide (BPO) or dicumyl peroxide (DCP) as radical initiators. Different procedures were used for the grafting experiments. According to the *procedure A*, HDPE was first melted at 145°C for 2-3 min then GMA and initiator were added, simultaneously (*A1*) or separately (*A2*), at 175°C. In the *procedure B*, all components were feeded at 145°C and mixed at 175°C. The *procedure C* was carried out using the polymer (powder) premixed with the GMA and peroxide at room temperature and feeding the mixture in the internal mixer at 175°C. The reaction products were then purified by dissolution in boiling xylene and reprecipitation in ethyl acetate in order to remove residual monomer and other secondary products. The purified polymers (HDPE-*g*-GMA) were then compression moulded and examined by means of a Perkin-Elmer 1600 FTIR spectrometer. Melt viscosity of the polymers was measured at 275°C by a CEAST capillary rheometer (L/D= 40).

Blends of R-PET with HDPE and HDPE-*g*-GMA (containing about 3 wt.% GMA) were prepared in the Brabender mixer (270°C, 70 rpm, 5 min) under nitrogen flux. Before use all materials were carefully dried under vacuum at appropriate temperatures (120-170°C) in order to reduce the moisture content. Blend samples were fractured at liquid nitrogen temperature and examined by a Jeol T300 scanning electron microscope (SEM).

Results

In order to determine the amount of GMA grafted onto HDPE, $[GMA]_g$, the ratios of the FTIR peak areas corresponding to the stretching of the GMA carbonyl group (1735 cm^{-1}) and the bending of $-CH_2-$ sequences in HDPE (1462 and 720 cm^{-1}) were considered. Calibration curves, as shown in Fig. 1, were obtained by measuring the FTIR band ratios of commercial ethylene-*co*-glycidyl methacrylate copolymers (E-GMA) and their mechanical blends with HDPE, containing a known amount of GMA groups (8÷12 wt.%). This latter was determined both by H-NMR and non-aqueous back titration of trichloroacetic acid with sodium hydroxide[4].

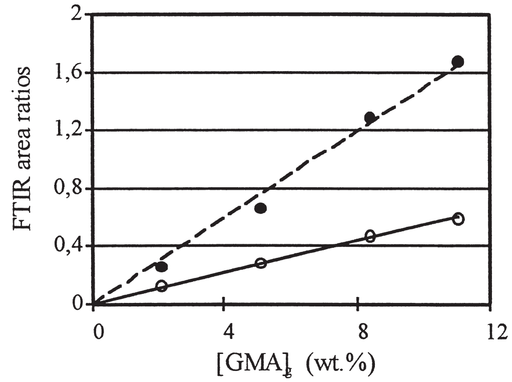


Fig. 1: Calibration curves obtained from FTIR peak area ratios of E-GMA and HDPE/E-GMA blends with known GMA contents: (•) A_{1732}/A_{720}, (o) A_{1732}/A_{1462}

The grafting degree of HDPE-*g*-GMA samples obtained by the various procedures (with initial monomer amount $[GMA]_i$=10 wt.%) is reported in Table 1.

Table 1. Amount of GMA grafted onto HDPE for different grafting procedures.

Procedure	A1	A2	B	C
$[GMA]_g$ (wt.%)	2	0,5	4,8	5,7

The *procedures B* and *C* display a relatively high grafting efficency as compared to the *procedure A*, suggesting that the level of dispersion of the components in the melt and the initial mixing temperature of reagents greatly affect the grafting yield.

Further, the addition of STY, as co-monomer, and the amount of peroxide are important parameters in controlling the grafting process[3,6]. As shown in Fig.2, the content of grafted GMA increases by increasing both the amount of co-monomer and that of peroxide (DCP).

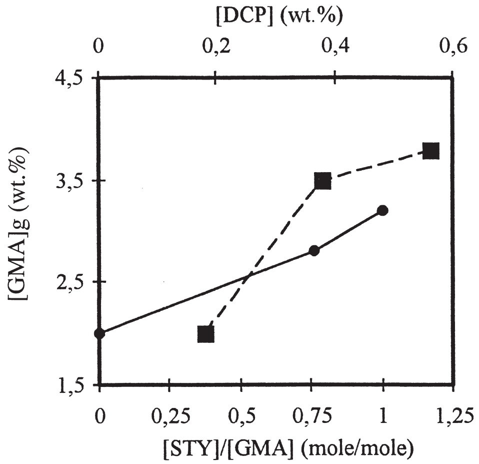


Fig.2: Amount of grafted GMA (*procedure B*) as a function of (■) peroxide concentration [DCP], and (●) molar ratio [STY]/[GMA] (initial concentrations: [GMA]i =10 wt.%; [DCP]= 0.16 wt.%)

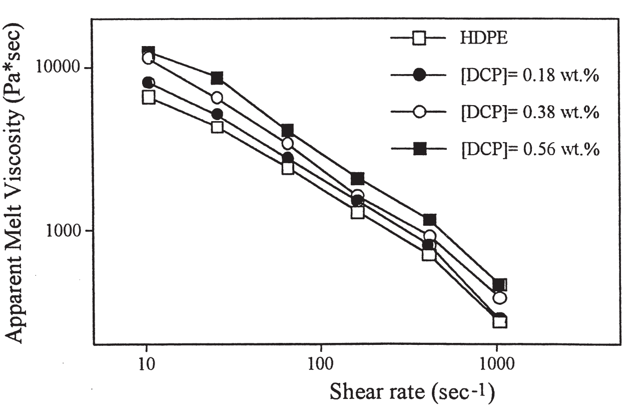
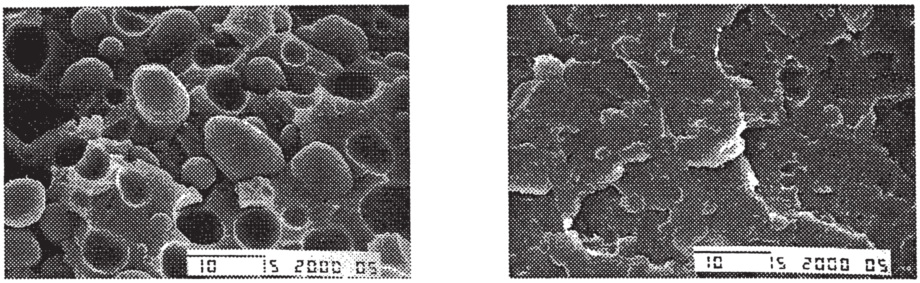


Fig.3: Apparent melt viscosity vs. shear rate of HDPE and HDPE-*g*-GMA prepared according to *procedure B*, using [GMA]i= 10 wt.% and different content of peroxide [DCP].

Rheological measurements carried out on various HDPE-*g*-GMA samples indicate an increase of melt viscosity with increasing the peroxide concentration (Fig.3). This can be accounted for by an increase of the GMA grafted on the polymer chain, even if crosslinking effects occurring during the grafting reaction cannot be excluded.



(a) (b)

Fig.4: SEM micrographs of fracture surfaces of (a) R-PET/HDPE [75/25] and (b) R-PET/HDPE-*g*-GMA [75/25] blends.

The morphology of blends of R-PET with HDPE and HDPE-*g*-GMA ($[\text{GMA}]_g \approx 3$ wt.%) at a composition ratio 75/25 is shown in Fig.4. The blend R-PET/HDPE-*g*-GMA shows a neat improvement of phase dispersion and interfacial adhesion as compared with the unfunctionalized blend, supporting a decrease of the interfacial tension in the melt. This can be related to the occurrence of interactions at the polymer interface. Similar effects were observed for blends R-PET/HDPE at same composition compatibilized with E-GMA copolymer7). FTIR analysis of R-PET/HDPE-*g*-GMA blend films showed the disappearance of the characteristic peak of GMA epoxy group at about 910 cm^{-1}, present in the grafted polyolefin. This can be assumed as an evidence of chemical reactions between the grafted GMA and the reactive end groups of PET8).

Conclusions

The effect of various melt grafting procedures of GMA onto HDPE was analysed. It was found that both concentration of radical initiator and addition of STY as co-monomer significantly affect the grafting yield. Blending of HDPE-*g*-GMA with R-PET allows to obtain a large improvement of polymer compatibility, giving rise to a higher phase dispersion and interfacial adhesion as compared to R-PET/HDPE blends. Due to the compatibilizing efficency of the grafted polyolefin an improvement of tensile and impact mechanical properties is expected, as found for compatibilized R-PET/HDPE/EGMA blends7). The results point out the great potential of melt grafting functionalization and reactive mixing for processing and upgrading of recycled polymers.

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