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Functionalization of Styrene-Olefin Block Copolymers by Melt Radical Grafting of Glycidyl Methacrylate and Reactive Blending with PET

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Summary: Blocks copolymers styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS) and styrene-*b*-(ethylene-*co*-propylene) (SEP, SEPSEP), with different styrene content and number of blocks in the chain, were functionalized with glycidyl methacrylate (GMA) by melt radical grafting. The influence of monomer concentration, radical initiator and copolymer structure on the grafting degree was examined. The grafted copolymers were characterised by DSC and capillary rheometry. Blends of PET with functionalized SEBS and SEPSEP showed a marked improvement of phase morphology and elongation at break when compared to blends with unfunctionalized copolymers.

Keywords: blend compatibilization; block copolymers; glycidyl methacrylate; poly(ethylene terephthalate); radical grafting

Introduction

In the recent years thermoplastic elastomers have gained great interest for their peculiar properties and their wide application potential in technological sectors. In particular, A-B-A type block copolymers having polystyrene end-blocks and unsaturated (polybutadiene, polyisoprene) or saturated (ethylene-butylene, ethylene-propylene random copolymers) midblocks are thermoplastic elastomers which exhibit physical properties typical for rubber and melt processability similar to thermoplastics. The performances of these block copolymers can be significantly enhanced by grafting on the chain unsaturated functional monomers (i.e., anhydrides, esters, etc.) capable of reacting with the polar groups of other polymers, such as polyamides or polyesters, and thus improving the compatibility and mechanical properties of their blends.[1] Styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS) copolymers grafted with

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maleic anhydride (MAH) have been successfully used as impact modifiers for several thermoplastics as polystyrene (PS), polyamide-6 (PA6), poly(ethylene therephthalate) (PET) and polypropylene (PP).[2-4] In addition, these copolymers have been shown to act as compatibilizers for different polymer blends, especially for PP/PS,[5, 6] PA6/PP [7, 8] and PET/PP.[9]

Sofar, only a few studies have been dedicated to the functionalization processes of SEBS with MAH,[10] diethyl maleate[11] and oxazoline.[12] In particular, the functionalization of styrene-olefin block copolymers by melt grafting of glycidyl methacrylate (GMA) has not been reported in literature, even if grafting reactions of GMA onto melt polyolefins (PE, PP, EPR, etc.) have been described in several reports.[13-18]

Grafting of GMA presents several advantages due to easy grafting process in the melt, to the high reactivity of epoxy groups toward both amino, carboxyl and hydroxyl end-groups, as well as to a reduced enviromental impact, as compared to other reactive monomers. GMA modified polymers can be effectively exploited for the reactive compatibilization of various polymer systems, as blends of polyolefins with polyamides or polysters.[9, 19-22]

In the present paper, a study on the melt functionalization of SEBS and styrene-*b*-(ethylene-*co*-propylene) (SEP, SEPSEP) block copolymers, having different number of blocks and styrene content (STY), by means of radical grafting with GMA is reported. The influence of reaction procedure and copolymer structure on the grafting yield has been analysed and the properties of the grafted copolymers have been then compared with those of neat copolymers. The study was aimed at examining the role of the chemical structure and functionalization degree of the block copolymers on the compatibilization of thermoplastic polymer blends and composites. For this purpose, the compatibilizing effectiveness of the GMA modified block copolymers was also tested in reactive mixing with PET and PA6.

Experimental part

Materials

Commercial samples of styrene-olefin block copolymers, kindly supplied by Shell Italia, were used: SEBS (Kraton G1652), SEP01 (Kraton G1701X), SEP02 (Kraton G1702 X) and SEPSEP (Kraton G1730 M). SEBS (30 wt.-.% STY, viscosity= 1.4 Pa•s, MFR=10 g/10min) is a linear triblock copolymer with two PS end blocks; SEP01 (37 wt.-% STY, viscosity >50 Pa•s) and SEP02 (28 wt.-% STY, viscosity >50 Pa•s) are linear di-block copolymers and SEPSEP (21 wt.-

% STY, viscosity= 0.62 Pa·s, MFR=11 g/10min) is a linear tetra-block copolymer. Polymer viscosities were measured in 20% toluene solution at 25 °C; melt flow rates (MFR) were recorded at 230 °C/5 kg. GMA monomer (97% purity, Aldrich) and bis-[1-(tert-butylperoxy)-1methylethyl] benzene (BTP, Aldrich), as radical initiator, were used as received.

Binary blends of PET (SINCO Engineering, I.V.=0.74 dl/g) with block copolymers at composition (75/25 wt./wt. %), both functionalized and not, were obtained by melt mixing in a Brabender Plasticorder internal mixer at 260 °C, with a roller speed of 50 rpm, for 7 min under nitrogen stream.

Grafting procedure

Grafting of GMA onto SEBS, SEP and SEPSEP was carried out in the Brabender internal mixer, under nitrogen flux. The copolymer samples, GMA and the radical initiator were pre-mixed at room temperature, then charged into the pre-heated mixer and blended for 5 minutes at 200 °C using a roller speed of 50 rpm. The reaction products were purified by dissolution in boiling xylene, then filtered to determine the presence of gel and re-precipitated with ethanol in order to remove the unreacted monomer and homopolymerized GMA.[9] The precipitate was filtered, washed with ethanol and dried under vacuum at 80°C overnight. A non-aqueous back titration method was used to determine the GMA grafting degree of the various samples.[23] The purified polymers were compression moulded and examined with a Perkin Elmer 1600 FT-IR spectrometer.

Characterization of copolymers and blends

Melt viscosities of both grafted and neat copolymers were measured by a CEAST capillary rheometer over a shear rate range $10^1 \div 10^3$ sec^{-1} at 260 °C. A die length of 40 mm and diameter 1 mm (L/d= 40) was used. All measurements included Rabinowitsch correction.

The thermal behaviour of the copolymers was examined with a Perkin-Elmer Pyris Diamond DSC in the range 0÷120 °C at standard heating/cooling rate of 10 °C/min, under nitrogen flow. Melting temperatures (T_m) were determined at the maximum of the endothermic peaks. Glass transition temperatures (T_g) were recorded either at the onset point or at the half-width of the transition. The morphology of blends was examined on the surfaces of samples freeze-fractured in liquid nitrogen; the samples were sputter-coated with gold and analysed with a Jeol T300 scanning electron microscope (SEM). Tensile mechanical tests were carried out at room temperature by an Instron tensile machine (model 4302) according to standard conditions, using a speed of 5 %/min. The test specimens were prepared by compression moulding in a proper shape (ASTM D412).

Results and Discussion

GMA grafting

The grafted GMA content on the copolymers was determined by FTIR analysis. FTIR spectra of SEP01 and SEP01-*g*-GMA copolymers are compared in Figure 1a. The peak at 1601 cm^{-1}, (benzene ring stretching) due to the styrene blocks in the copolymers, was chosen as internal references while the peak corresponding to the stretching of the carbonyl in the ester group of GMA (1736 cm^{-1}) was used as the target for determining the amount of grafted GMA. Peak heights rather than peak areas were chosen because of the overlapping between the carbonyl stretching peak and the aromatic ring stretching overtone band (1745 cm^{-1}). The relative amount of grafted GMA was calculated from the ratio $H_g = H_{1736\ cm-1}/H_{1601\ cm-1}$. The degree of grafting, $[GMA]_g$ (wt.-% grafted GMA), was thus determined for each copolymer by calibration curves of the relative amount obtained by FTIR with the amount of grafted GMA as determined by the titration procedure.[23]

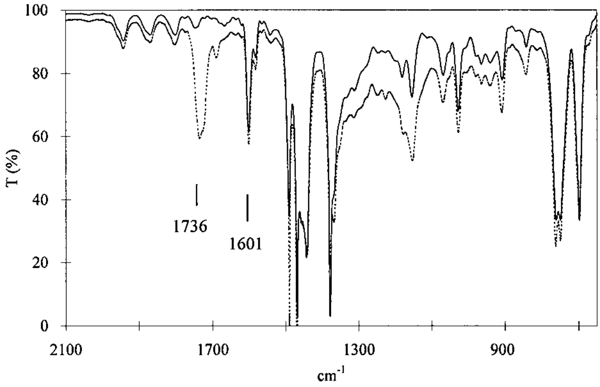

Figure 1: FT-IR spectra of SEP01 (continuous line) and SEP01-g-GMA block copolymers (dashed line)

An example of calibration plot is shown in Figure 2 for SEP01-*g*-GMA copolymers. The variation of grafting degree was examined as a function of the concentration of radical initiator, [BTP], and of monomer, $[GMA]_m$ (in part per hundred ratio).

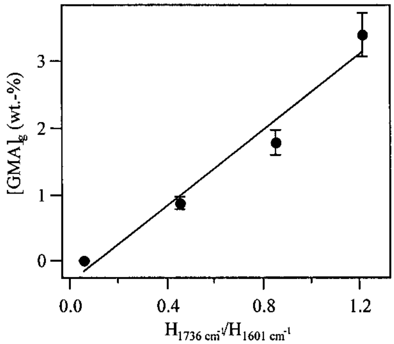

Figure 2: FT-IR calibration plot for the quantitative measurement of GMA grafted content onto SEP01

As shown in Figure 3, for a same value of $[GMA]_m$, the amount of grafted GMA increases with increasing the amount of peroxide in the range 0-1.5 phr. For [BTP]=1.5 phr, a continuous increase of $[GMA]_g$ with the monomer content is observed.

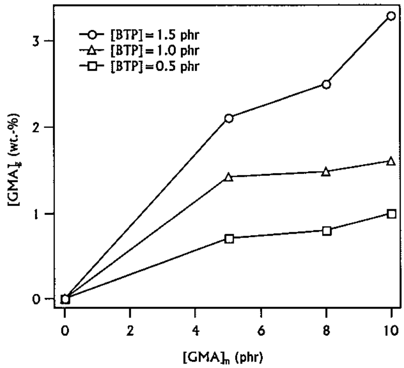

Figure 3: Effect of amount of monomer $[GMA]_m$ and radical initiator [BTP] on the grafting degree $[GMA]_g$ of SEP01-*g*-GMA copolymers

In these conditions the grafting yield (i.e. the ratio $[GMA]_g$/ $[GMA]_m$) reaches a maximum for $[GMA]_m$=5 phr, then decreases mainly because of the occurrence of GMA homopolymerization reaction.

For all grafting reactions no gel formation was detected indicating the absence of cross-linking phenomena, as the grafted samples were completely soluble in xylene. Moreover, the results of rheological analysis did not indicate any significant decrease of the molecular weight of the polymers after the reaction, which supports a limited occurrence of chain degradation during the melt grafting. It should be noticed that in the case of GMA grafting reactions onto polyolefins (HDPE, LDPE, PP) the effect of concentration of radical initiator on cross-linking or chain degradation phenomena resulted much more marked.[20, 24]

Table 1: GMA grafting degree $[GMA]_g$ of block copolymers as a function of initial monomer content $[GMA]_m$, ([BTP]=1.5 phr)

Polymers	STY	$[GMA]_g$ (wt.-%)		
	(wt.-%)	$[GMA]_m$=5 phr	$[GMA]_m$=8 phr	$[GMA]_m$=10 phr
SEP01-*g*-GMA	37	2.4	2.5	3.3
SEBS-*g*-GMA	30	2.9	3.9	4.4
SEP02-*g*-GMA	28	4.3	4.7	5.2
SEPSEP-*g*-GMA	21	2.9	5.6	5.8

In Table 1 the values of grafting degree of the various copolymers are listed as a function of GMA monomer concentration. For the same initial content of monomer (and radical initiator), the grafting degree results to be decreased as the overall styrene content in the chain increases: the tetrablock copolymer SEPSEP displays higher $[GMA]_g$ values (5÷6 wt.-.%), as compared to the diblock copolymer SEP01 (2÷3 wt.-.%) and to SEBS (3÷4 wt.-.%). This could suggest that the grafting reaction of GMA occurs preferentially on the polyolefin blocks. Such a conclusion is in agreement with the findings by Passaglia *et al.*[11] for SEBS functionalized with diethylmaleate and MAH, which resulted to be substantially grafted in the aliphatic blocks, although the styrenic blocks have the same probability to undergo grafting. This effect has been ascribed to a higher stability of benzylic radicals with respect to aliphatic ones and therefore to a lower reactivity of the formers toward the monomer grafting. As a consequence, the reduced presence of cross-linking and/or chain degradation in the GMA grafted copolymers may be related with a decreased tendency of the macroradicals on the PS blocks toward degradation and recombination.

Rheological and thermal characterization

The block copolymers, both grafted and not, were characterized by melt viscosities measurements at 260°C, as shown in Figure 4. Grafted samples obtained in the same grafting conditions ($[GMA]_m$ =10 phr, [BTP] =1.5 phr) display higher melt viscosities and a more pseudo-plastic type behaviour as compared to the unfunctionalized ones, in particular in the low shear rate range which is more sensitive to inter-chain interactions. Similar effects have been found for GMA grafted polyolefins.[24, 25] and have been mostly ascribed to polar interactions between GMA groups in the polymers chains. However, the marked increase observed in the melt viscosity of SEP-g-GMA samples can not be only accounted for by the effect of the grafting degree of the di-block copolymers and suggests the possible occurrence of crosslinking reactions between the grafted chains (via epoxy groups) in the melt.[25]

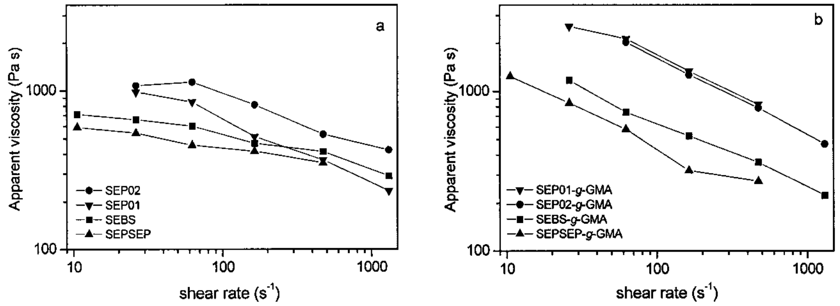

Figure 4: Apparent melt viscosity of (a) neat copolymers and (b) GMA grafted copolymers vs. shear rate at 260 °C

The results of the calorimetric analysis of the block copolymers are summarized in Table 2. The DSC heating thermograms of SEBS samples show two transitions, characteristics of the elastomeric and PS blocks respectively. The first transition appears as a shallow endothermal peak with maximum at about 17 °C and seems to be associated with the melting of very small crystalline zones in the sample, depending on the composition of the copolymer.[26]

In the functionalised SEBS, the peak is recorded at about 16 °C. No melting peak was observed for SEP and SEPSEP copolymers, at least in the examined temperature range.

Table 2: DSC transition parameters of neat and GMA grafted block copolymers.

Polymer	$[\mathrm{GMA}]_g$ (wt.-%)	T_m (°C)	$T_{g\,\mathrm{onset}}$ (°C)	T_g (°C)
SEP01	-	-	59	66
SEP01-*g*-GMA	3.3	-	60	65
SEBS	-	17.2	61	66
SEBS-*g*-GMA	4.4	16.0	54	60
SEPSEP	-	-	56	61
SEPSEP-*g*-GMA	5.8	-	51	56

The second transition, at higher temperatures, is related to the glass transition (T_g) of PS blocks and depends on the styrene content: it ranges from about 66 °C for SEP01 (and SEBS) to 61 °C for SEPSEP, and it is lower than in pure PS (about 100 °C). This is likely a consequence of a plastifying effect in the copolymers and of the reduced size of styrenic domains, with a consequent decrease of the softening temperature.[26] The functionalised samples show a further shift of T_g to lower temperature: the higher decrease is observed for the copolymers (SEPSEP-*g*-GMA and SEBS-*g*-GMA) with higher GMA content.

Blends of PET with block copolymers

Binary blends of PET with both functionalised and neat copolymers were examined by SEM microscopy and mechanical tests to evaluate the effect of the GMA grafting on the blend compatibility. The morphology of blends with non-functionalized copolymers shows that generally the elastomer phase is poorly dispersed in the PET matrix with large coalescence phenomena. In the blends with grafted copolymers an improvement of morphology is observed with a better dispersion and adhesion between the phases, indicating the presence of strong interactions at the interface which contribute to decrease the interfacial tension.

The tensile behaviour of plain PET and of binary blends (75/25 wt/wt) is shown in Figure 4. As compared to pure PET, the presence of the elastomers dispersed in the PET matrix decreases the elastic modulus and the yield strength.[27]

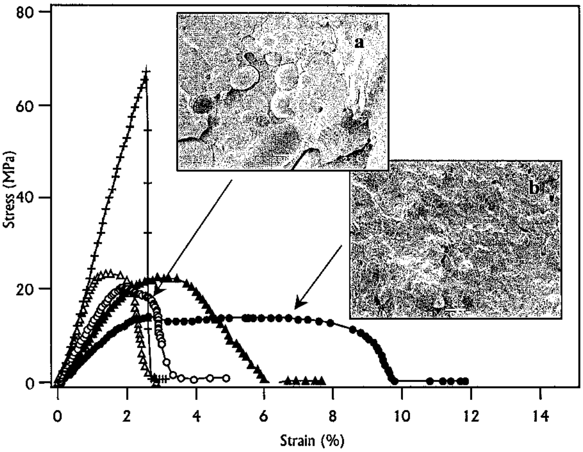

Figure 5: Tensile behaviour of PET (+) and binary blends PET/SEBS (Δ), PET/SEBS-*g*-GMA (▲), PET/SEPSEP (○), PET/SEPSEP-*g*-GMA (●) and SEM micrographs of fracture surfaces of (a) PET/SEPSEP and (b) PET/SEPSEP-*g*-GMA blends (bar length: 20 μm)

The blends PET/SEBS and PET/SEPSEP display a very low elongation at break due to their coarse phase morphology and to a lack of interfacial interactions with PET, which leads to debonding and premature rupture, as often observed for incompatible systems. The blends with SEP copolymers showed a very poor tensile behaviour. On the contrary, a significant increase in the elongation at break can be observed in the blends with functionalised copolymers. For the blend with SEBS-*g*-GMA the elongation at break is twice that of blend with SEBS and a larger effect is seen for the PET/SEPSEP-*g*-GMA blend, where the grafted GMA content is the highest. These results can be accounted for by an improvement of the adhesion at the interface (see micrographs in Figure 4), which is consistent with the in situ formation of a graft copolymer by reaction of the epoxy groups of GMA and the (carboxyl, hydroxyl) end-groups of PET.[19]

Conclusions

The melt grafting of GMA onto SEBS, SEP and SEPSEP block copolymers was studied by analysing the effect of monomer and radical initiator concentration on the grafting degree. Under the same grafting conditions the grafting degree ($[\text{GMA}]_g = 3 \div 6$ wt.-%) was found to be influenced by the styrene content and the type of elastomer in the copolymer chain, likely owing to a different stability of the macroradicals formed on aliphatic and styrenic blocks during the reaction. Copolymers with ethylene-propylene blocks (SEP02 and SEPSEP) displayed a higher grafting degree.

Blending of PET with GMA grafted copolymers resulted in an improvement of the phase dispersion and interfacial adhesion as compared to the blends with neat copolymers. A marked increase of the elongation at break was observed for the blends with SEPSEP-*g*-GMA and SEBS-*g*-GMA, which show values of about three times higher than those recorded for pure PET and blends with neat copolymers. The compatibilizing effectiveness of the grafted copolymers was related to the occurrence of chemical reactions between the epoxy groups of GMA and the end groups of PET.

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