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Reactive processing of polymers: effect of in situ compatibilisation on characteristics of blends of polyethylene terephthalate and ethylene-propylene rubber

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Abstract

Ethylene-propylene rubber (EPR) functionalised with glycidyl methacrylate (GMA) (*f*-EPR) during melt processing in the presence of a co-monomer, such as trimethylolpropane triacrylate (Tris), was used to promote compatibilisation in blends of polyethylene terephthalate (PET) and *f*-EPR, and their characteristics were compared with those of PET/*f*-EPR reactive blends in which the *f*-EPR was functionalised with GMA via a conventional free radical melt reaction (in the absence of a co-monomer). Binary blends of PETand *f*-EPR (with two types of *f*-EPR prepared either in presence or absence of the co-monomer) with various compositions (80/20, 60/40 and 50/50 w/w%) were prepared in an internal mixer. The blends were evaluated by their rheology (from changes in torque during melt processing and blending reflecting melt viscosity, and their melt flow rate), morphology scanning electron microscopy (SEM), dynamic mechanical properties (DMA), Fourier transform infrared (FTIR) analysis, and solubility (Molau) test.

The reactive blends (PET/*f*-EPR) showed a marked increase in their melt viscosities in comparison with the corresponding physical (PET/EPR) blends (higher torque during melt blending), the extent of which depended on the amount of homopolymerised GMA (poly-GMA) present and the level of GMA grafting in the *f*-EPR. This increase was accounted for by, most probably, the occurrence of a reaction between the epoxy groups of GMA and the hydroxyl/carboxyl end groups of PET. Morphological examination by SEM showed a large improvement of phase dispersion, indicating reduced interfacial tension and compatibilisation, in both reactive blends, but with the Tris-GMA-based blends showing an even finer morphology (these blends are characterised by absence of poly-GMA and presence of higher level of grafted GMA in its *f*-EPR component by comparison to the conventional GMA-based blends). Examination of the DMA for the reactive blends at different compositions showed that in both cases there was a smaller separation between the glass transition temperatures compared to their position in the corresponding physical blends, which pointed to some interaction or chemical reaction between *f*-EPR and PET. The DMA results also showed that the shifts in the T_gs of the Tris-GMA-based blends were slightly higher than for the conventional GMA-blends. However, the overall tendency of the T_gs to approach each other in each case was found not to be significantly different (e.g. in a 60/40 ratio the former blend shifted by up to 4.5 °C in each direction whereas in the latter blend the shifts were about 3 °C). These results would suggest that in these blends the SEM and DMA analyses are probing uncorrelatable morphological details. The evidence for the formation of in situ graft copolymer between the *f*-EPR and PET during reactive blending was clearly illustrated from analysis by FTIR of the separated phases from the Tris-GMA-based reactive blends, and the positive Molau test pointed out to graft copolymerisation in the interface. A mechanism for the formation of the interfacial reaction during the reactive blending process is proposed.

Keywords: Reactive blending; Reactive processing; PET/EPR blends

1. Introduction

A cost effective approach to producing specialty materials with a new range of properties, is to combine the wide spectrum of properties that are normally only available in two or more existing polymers, by mechanical

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blending, to produce a new single modified material with improved characteristics. Unfortunately, however, most polymer pairs are immiscible and when blended together would result in phase separation giving rise to poor mechanical properties and undesirable performance for target end uses. In spite of this inherent drawback, a wide range of new useful materials with improved and unique properties have been obtained from such immiscible and incompatible polymer pairs either, by the addition of a third component, usually a graft or block copolymer, or by in situ formation of such copolymers during the blend preparation. These methods result in partial compatibilisation of the otherwise incompatible polymers [1–9]. A successful compatibilisation of immiscible polymer pairs would result in the compatibiliser locating at the interface between the discrete polymer phases so it can act as an emulsifier which reduces interfacial tension and improve adhesion between the phases, thus giving rise to improved mechanical properties and overall performance. Such compatibilisation often results in stabilised morphology with fine dispersion of the second (minor) phase in the matrix, and subsequently would have a direct effect on the final properties of the blends [10,11]. Blends based on polyalkyl terephthalates (e.g. polybutylene- and polyethylene terephthalate (PBT, PET)), have been compatibilised with a range of different functionalised second polymers; examples include use of GMA-functionalised PP in PP/PBT blends [12,13], rubber toughening of PBT by maleic anhydride-grafted EPR [14], GMA-grafted EPDM for the preparation of compatibilised and dynamically vulcanised thermoplastic elastomers of PBT and EPDM [15]. It has been shown that epoxy-containing polymers are probably the best candidates as reactive compatibilisers for polyester-related blends due to the fast reactions between epoxy and carboxylic acid or hydroxyl groups.

Compatibilisation in polymer blends is usually characterised by dynamic mechanical analysis (DMA), and the viscoelastic properties (e.g. storage modulus and the damping peak, or tan δ) are known to be influenced by the microstructure of the blends [16–18]. In this study, the compatibilising effect of GMA-functionalised EPR, with PET, was investigated by examining the dynamic mechanical properties (DMA) and the morphology of these blends. The effect of two different reactive processing routes to the functionalisation of the rubber, on the blends characteristics were examined. The first was based on the conventional free radical melt grafting reaction of GMA on the rubber backbone, and the second was based on an approach we have developed in our laboratory whereby the free radical melt grafting reaction takes place in the presence of a highly reactive co-monomer, e.g. Tris [19,20]. The GMA-functionalised rubbers (*f*-EPR) produced from these two reactive processing routes resulted in polymer materials having different microstructures. The effects of variations in the microstructure produced as a result of reactive processing of the rubber with GMA in the absence and presence of a co-monomer, on the DMA and morphology of PET/*f*-EPR blends are investigated. The nature and influence of the in situ graft copolymer produced during reactive blending of PET blends containing rubber functionalised in the presence of co-monomer, on the extent of compatibilisation were also examined.

2. Experimental

2.1. Materials

Granules of Tafmar P-0480, an ethylene-propylene rubber (EPR) with a melt flow rate of 1.7 g/10 min (at 230 °C/2.16 kg), and PET (a film grade-9921W) were supplied by Mitsui Chemicals, Inc. and Eastman Chemical, respectively. Glycidyl methacrylate (GMA) (97% purity) and trimethylolpropane triacrylate (Tris) were purchased from Aldrich Chemical Co, and used as received. The peroxide (2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane), T101, was kindly donated by AKZO Chemie and was used without further purification. All other chemicals and solvents were of reagent grade and were used without further purification.

2.2. Melt grafting of GMA on EPR by reactive processing methods and blending of PET with EPR-*g*-GMA

The peroxide-initiated melt grafting reactions of EPR with the monomer GMA in the absence (conventional reactive processing) and presence (Tris-assisted reactive processing) of the co-monomer Tris were carried out in an internal mixer (RAPRA-Hampden torque rheometer) as described before [19]. A set of GMA grafted EPR (EPR-*g*-GMA) samples having different grafting degrees and rheological properties were prepared (see Table 1).

Blends of PET and EPR (physical blends) or PET and EPR-*g*-GMA, from the different reactive processing routes described above (reactive blends) were then prepared in an internal mixer. Both polymers (PET and rubber) were initially dried before blending for more than 20 h in a vacuum oven at 135 °C (for PET) and 85 °C (for EPR). The rubber samples (EPR or EPR-*g*-GMA) were initially tumble mixed with PET (PET/EPR or PET/EPR-*g*-GMA) at different w/w ratios (50/50, 60/40 and 80/20) before melt blending in a closed chamber of the internal mixer under nitrogen at 275 °C for 10 min and a rotor speed of 65 rpm. The torque was recorded as a function of time during blending. The processed blend samples, which were cooled under nitrogen and dried in a vacuum oven at 85 °C for 24 h, were compression moulded in an electrically heated press into 2 mm thick plaques at 275 °C with 4 min pre-heating under minimum pressure followed by 30 s under a pressure of 100 kgf/cm^2. The plaques were cooled down to below 100 °C under pressure before removal from the press. For infrared analysis, thin polymer films were also compression