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Compatibilisation of PPE/SAN blends by triblock terpolymers: Correlation between block terpolymer composition, morphology and properties

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Abstract

Immiscible blends of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and poly(styrene-*co*-acrylonitrile) (SAN) with a weight composition of 60/40 were compatibilised by polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock terpolymers (SBM) using a two-stage melt-processing approach. In order to investigate the influence of the SBM composition on the compatibilisation efficiency, the block lengths of the triblock terpolymers were systematically varied. The resulting morphological features of the blend systems as function of SBM composition and processing parameters are correlated with the resulting thermal and thermo-mechanical properties. In the ideal case, SBM should be located at the interface as PS is miscible with PPE while PMMA is miscible with SAN. The elastomeric middle block as an immiscible component should remain at the interface. This particular morphological arrangement is known as the 'raspberry morphology'. A detailed TEM analysis of the blend morphologies following initial extrusion-compounding revealed a high compatibilisation efficiency of the SBM types with equal lengths of the end blocks and, furthermore, the desired raspberry morphology was achieved. In contrast, high PS contents in comparison to the other blocks led to a pronounced micelle formation in the PPE phase. Further evaluation of the blend structures following injection-moulding indicated that the morphologies remain relatively stable during this second melt-processing step. A detailed thermal analysis of all blend systems supports the interpretation of the observed morphological features. The fundamental correlation between SBM composition and blend morphology established in this study opens the door for the controlled development of interfacial properties of such compatibilised PPE/SAN blends during melt-processing.

Keywords: Polymer blend; Compatibilisation; Triblock terpolymer

1. Introduction

Blending of polymers provides an efficient route to develop new materials with tailored properties [1,2]. Due to the fact that an already existing range of base polymers is used, a large variety of new high-capacity polymers is readily and economically available. The highest market value and the strongest growth rate are predicted for blends based on both polycarbonate (PC) and poly(2,6-dimethyl-1,4-phenylene ether) (PPE). It should be noted that PPE is also frequently referred to as PPO (poly(2,6-dimethyl-1,4-phenylene oxide)), especially in the American-Pacific region, as the material was initially commercialised under this name. With regard to PPE in particular, blends of the most significant commercial interest are miscible PPE/polystyrene blends (PPE/PS) and reactively-compatibilised PPE/polyamide blends (PPE/PA). In contrast, blends of PPE and poly(styrene-*co*-acrylonitrile) (PPE/SAN) are expected to provide various advantages, combining the toughness, the flame-retardant behaviour, and the high heat distortion temperature of PPE with the chemical resistance, the low material cost, the resistance to stress cracking, and the high stiffness of SAN.

The miscibility of PPE and SAN is strongly dependent on the composition of SAN, more precisely, on the ratio between styrene and acrylonitrile (AN). Miscibility at all temperatures occurs up to 9.8 wt% of AN in SAN, whereas at higher contents above 12.4 wt%, phase separation occurs. This phase

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separation leads to a two-phase structure, independent of the temperature [3,4]. Intermediate compositions exhibit a lower critical solution temperature behaviour (LCST). Taking into account that SAN copolymers of technical relevance have AN contents between 19 and 35 wt% in order to ensure high chemical resistance compared to PS, such blends with PPE are not miscible and show a coarse morphology. A recent study by Merfeld et al. [4] has verified that the interfacial properties of PPE/SAN blends reflect the AN content. For example, an AN content of 20 wt% leads to an interfacial thickness of only 5 nm which demonstrates the strongly segregated behaviour. As a consequence of the low interfacial thickness and interfacial strength observed for such incompatible blends, the mechanical properties determining the fracture behaviour such as ultimate fracture strain, impact strength and fracture toughness of the blends should be lower than those predicted by the linear rule-of-mixtures.

Earlier works investigating PPE/SAN 40/60 (weight composition) and PPE/ABS 48/52 blends, respectively, support this assumption; blends prepared by both solvent-mediated processing as well as melt-processing showed a brittle behaviour [5–8]. Fekete et al. [9] showed that some mechanical properties such as modulus and strength of PPE/SAN blends can be described by a linear rule-of-mixture approach over a wide range of compositions. These experimental results for melt-blended samples were explained on the basis of a partial miscibility, deduced from observed shifts in the glass transition temperatures of both components by around 2–3 K. However, an earlier study [10] has shown that the presence of low molecular weight components (which are likely present in the used commercial polymers) can lead to similar shifts in the glass transition temperatures of such blends. Using purified materials in their work, Stadler et al. [5] did not report such behaviour for PPE/SAN.

A common approach to improve the toughness of incompatible blends is the chemical or physical compatibilisation [1,2,11]. In the latter case, surface-active block copolymers are often employed to control both the morphology and the resulting physical properties of immiscible blends [12–15]. The addition of block copolymers improves the dispersion due to a reduced interfacial tension and inhibition of collision-induced coalescence [16].

Diblock copolymers (A-*b*-B) with a defined composition have been shown to enhance the dispersion and the load transfer between PPE and SAN; a consequence of the selective entanglement of both end blocks in the interfacial region [4,5,8]. Although the mechanical properties such as stiffness and strength of such compatibilised PPE/SAN blends are significantly improved, the toughness remains insufficient. An efficient way to achieve a significant toughness increase is provided by the use of triblock terpolymers when appropriately composed. In particular, polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock terpolymers (SBM) and their hydrogenated version, poly(styrene)-*block*-poly(ethylene-*co*-butylene)-*block*-poly(methyl methacrylate) are advantageous as a compatibilising agent in PPE/SAN-blends [5,17]. A so-called 'raspberry morphology' of PPE/SAN/SEBM blends was reported by Stadler et al. for the first time [5], which was also found in PPE/SAN/SBM blends [6,7].

This raspberry morphology, obtained by solvent-mediated processing, is schematically shown in Fig. 1. Each end block of the SBM is selectively miscible with one blend component, in particular, an entanglement of PMMA in SAN (miscibility for AN content of 19 wt%) [18,19] and of PS in PPE [20] is observed. The incompatibility of the elastomeric middle block with both the blend components and the end blocks as well as the balanced chemical interaction parameters lead to a discontinuous distribution of PB and PEB spheres, respectively, within the interface. It is important to note that the investigated systems were close to or at thermodynamic equilibrium due to the fact that solvent-mediated processing was employed.

Nevertheless, Lach et al. [6] and Kirschnick et al. [7] have already demonstrated the feasibility of melt-processing of PPE/SAN 40/60 blends using SBM as a compatibiliser. Although the raspberry morphology could be observed, PPE formed the disperse phase in the SAN matrix, independent of SBM composition and processing conditions. In order to further improve the overall behaviour of such compatibilised blends, a continuous PPE phase is desirable, since PPE is the component with the higher glass transition temperature and toughness.

The aim of this study, therefore, was the systematic investigation of the influence of the composition of SBM compatibilisers on the resulting morphology of melt-processed PPE/SAN blends with a weight composition of 60/40. Melt-compounding of the base polymers and compatibilisation by four SBM types with varying block lengths with weight fractions of up to 20 wt% was carried out by twin-screw extrusion, followed by injection-moulding. The morphological features of these blend systems as function of the composition and processing parameters are correlated with the resulting thermal and thermo-mechanical properties. The observations described in this paper provide the necessary basis for a

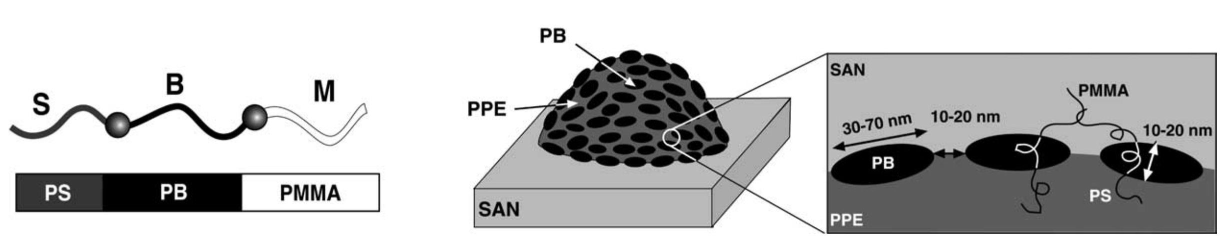

Fig. 1. SBM and model of the 'raspberry' morphology within a PPE/SAN/SBM blend [5].