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The Influence of Segmented Block Copolymers in Immiscible Polymer Blends

Doris Pospiech*, Liane Häußler, Kathrin Eckstein, Dieter Jehnichen, Antje Gottwald, Petra Pötschke

Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

SUMMARY: One mechanism for compatibilization of immiscible polymer blends is adding block copolymers (BCP) that consist of segments chemically comparable to the parent homopolymers in the blend. BCP do both, emulsify the disperse phase to give smaller particles as well as increase the interfacial adhesion between the phases. The influence of segmented BCP in blends of immiscible high-performance polymers was investigated systematically by variation of the flexibility of the BCP segments. It was shown that the stiffness of the second segment in polysulfone (PSU) block copolymers as well as the PSU segment molecular weight determine the intermixing between the BCP and the PSU matrix.

Introduction

Blends of high performance polymers have attracted considerable attention because they offer the opportunity to design new materials with unusual properties. However, compatibilization of these blends which can be achieved in different ways1) is essential to reduce the immiscibility and to improve the mechanical properties. One method for compatibilization is to add BCP consisting of segments chemically comparable to the blend partners, as suggested theoretically by Noolandi2) and proven experimentally for diblock copolymers and random copolymers, e.g., by Dai et al.3). We were interested to check this concept experimentally for segmented BCP synthesized by a melt transesterification polycondensation4). The work discussed here focused on the modification of PSU by blending with either a liquid crystalline main chain polymer (improvement of processability and E-modulus)5), a liquid crystalline side chain polymer (surface modification)6,7) or an amorphous polyether (hydrophilization)8,9).

Concept

The aim of this work was to investigate the influence of segmented BCP in different blend systems. Therefore, the BCP were synthesized separately, in contrast to Weber et al.10) and

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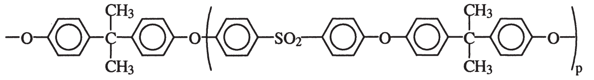
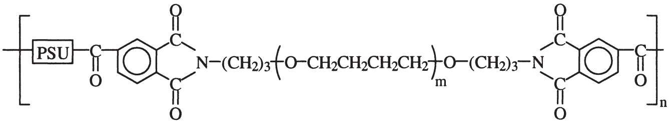
Inoue et al.[11)] who created PSU/polyamide block copolymers by reactive blending. Systematic investigations of binary solution casted blends of PSU with the segmented BCP were carried out in order to understand the interaction between the PSU matrix (**1**) and the PSU segments in the BCP in dependence on the molecular weight of the PSU segments. The molecular flexibility of the second segment incorporated in the BCP was changed systematically from amorphous-flexible [PSU-*b*-PTMO]$_n$ (**2**), to amorphous-nematic [PSU-*b*-(PET/HBA)]$_n$ (**3**) and introduction of a self-organizing layered structure [PSU-*b*-(SF-PES)]$_n$ (**4**). χ-Parameters for blends of the parent homopolymers calculated according to Ref.[12)] reflect that different degrees of phase separation in the blends have to be expected.

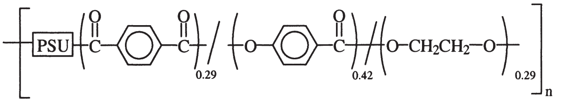


1



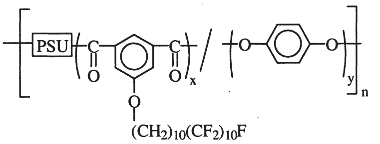
2

$\chi_{AB} = 0.89$



3

$\chi_{AB} = 0.07$

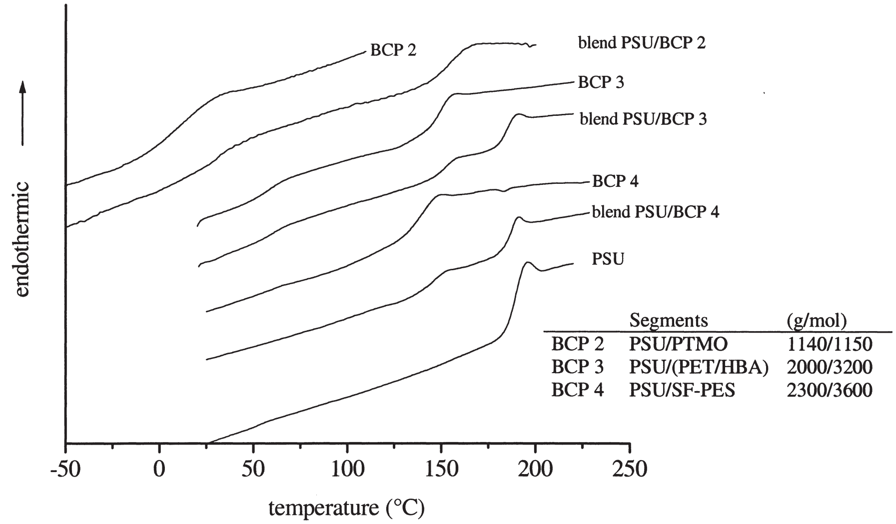


4

$\chi_{AB} = 13.68$

Results

The molecular weight of the PSU segments in the BCP was varied to verify the assumption that a certain critical molecular weight M_{cr} of the segments must be reached to achieve miscibility of the PSU segments of the BCP and the PSU matrix. M_{cr} should be related to the entanglement molecular weight M_e which was reported for PSU to be in the range of 1900 to 2500 g/mol[12-14)]. All blends investigated are mainly amorphous. Therefore, the occurrence of a single T_g in the DSC curves was used to characterize the state of phase separation in the blends. Fig. 1 illustrates the thermal behavior of blends (50/50 w/w) of the investigated systems of PSU with BCP having PSU segment molecular weights in the range of M_e. All of them show phase separation, although the phase structure of the BCP is different. BCP 2 and 4 are non-phase separated, whereas BCP 3 is. In this BCP, a glass transition caused by the liquid crystalline phase (LCP = PET/HBA) is found additionally to the T_g of the PSU phases.



	Segments	(g/mol)
BCP 2	PSU/PTMO	1140/1150
BCP 3	PSU/(PET/HBA)	2000/3200
BCP 4	PSU/SF-PES	2300/3600

Fig. 1: Detection of phase separation in blends containing high molecular weight PSU and different BCP (50/50 w/w) by DSC (2nd heating scan, heating rate 20 K/min)

Miscibility between the PSU phases is reached if the PSU segment molecular weight in the BCP is raised (Fig. 2). The different mobility of the second segment in the block copolymer is reflected by the critical molecular weights. In blends with BCP 2 having amorphous-flexible PTMO segments, M_{cr} is 3500 g/mol (~ $2 \cdot M_e$). Moreover, the phase separated blends show partial intermixing of the phases indicated by a shift of the T_g in comparison to the pure blend components[9)]. In contrast, blends with BCP 3 and 4 containing rigid-rod segments require higher M_{cr} (~ $4 \cdot M_e$), which is certainly caused by the high stiffness of these segments counteracting the entanglement of the PSU segments.

The influence of BCP 3 in blends of PSU and LCP has been examined in detail using model bilayer systems and melt mixed, injection moulded samples. NR studies of these bilayer systems (Fig. 3) revealed that the interfacial width between PSU and BCP is increased.

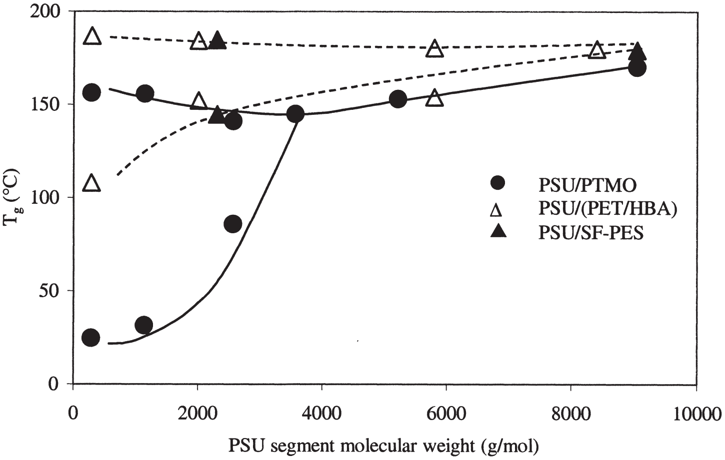


Fig. 2: Comparison of the glass transition temperatures of PSU/BCP (50/50 w/w) blends in dependence on the PSU segment molecular weight in the BCP (T_g values were determined using the Δc_p half step method)

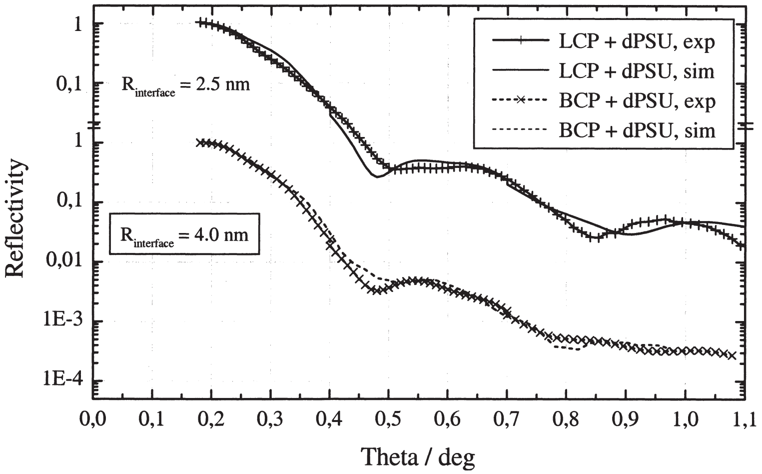


Fig. 3: Neutron reflectivity results for bilayers of deuterated PSU (M_w ~ 9000 g/mol) on LCP and BCP 3, respectively (as-prepared on wafers by spin-coating / floating procedures)

The partial miscibility between PSU matrix and PSU segments of the BCP is retained in ternary blends with LCP, resulting in morphology changes, better interfacial adhesion (Table 1) and finally in an improvement of mechanical properties of PSU/LCP blends[4,5).

Table1. Adhesion behavior, characterized by a critical crack extension force G_c (fracture toughness) [15) (samples prepared by hot pressing at 180°C for 30 min)

Sample:				
layer 1	PSU	PSU	PSU	PSU
interlayer	---	BCP 3, d: 0.07 μm	BCP 3, d: 30 μm	BCP 3, d: 200 μm
layer 2	(PET/HBA)	(PET/HBA)	(PET/HBA)	(PET/HBA)
G_c / J/m^2	0.0026	0.0058	0.0055	0.0850

BCP 3: [PSU 9800 - *b* - (PET/HBA) 7700]$_n$

A comparable result was obtained in blends of semicrystalline poly(p-phenylene sulfide) (PPS) with an LCP. Adding the corresponding segmented BCP leads to an improved impact strength and an decrease of particle size of the disperse phase[4,16,17).

Conclusions

Our systematical investigations allow to conclude that the mechanism of compatibilization by segmented BCP in immiscible PSU blends works by intermixing between the PSU segments of the BCP and the PSU matrix. The degree of intermixing depends on the chemical nature of the blend partners. In contrast, a partial intermixing could not be detected in blends of PPS with LCP and the corresponding segmented BCP which may by caused by the high crystallinity of PPS. However, the BCP works in this case as emulsifying part in the blend.

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