

Effect of Multiblock Copolymers in Polymer Blends

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ABSTRACT: The use of multiblock copolymers for the compatibilization of immiscible polymer blends is controversially discussed in the literature. Investigations have been carried out to estimate the effect of multiblock copolymers containing segments of a liquid crystalline polyester (LCP) and polysulfone (PSU) segments in blends of the based homopolymers. One goal was to determine whether multiblock copolymers provide an opportunity for compatibilizing PSU/LCP blends. By using PSU/LCP multiblock copolymers with different molecular weights of the blocks in the appropriate binary, solution-casted blends, it was shown that the interpenetration of the polysulfone phase of the block copolymer and the PSU matrix leads to an improved miscibility of the blend. This effect is retained in ternary blends of PSU, LCP, and the multiblock copolymer, assuming a certain critical molecular weight of the multiblock copolymer segments. In addition, some mechanical characteristics of PSU/LCP melt blends such as the *E*-modulus and fracture strength are improved by adding long-segmented multiblock copolymers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2293–2309, 1997

Key words: multiblock copolymers; blends; polysulfone; phase behavior; morphology

INTRODUCTION

Thermotropic main-chain liquid crystalline polymers (LCP) have been the subject of scientific interest for many years (e.g., refs. 1–4). Beside this, the orientability of LC macromolecules in the melt and the formation of uniaxially oriented domains cause a high level of ultimate properties, e.g., high tensile strength and *E*-modulus, leading to considerable technological interest.^{5–8}

Blending of LCP with flexible chain polymers has come into consideration with the intention to increase the mechanical properties of conventional polymers and, simultaneously, to use the low melt viscosity of LCP for decreasing their viscosity, consequently enhancing the processability. It has been shown that even small amounts of

LCP result in a significant drop of the melt viscosity of conventional polymers.^{9–14} Of special interest is the generation of LCP fibers within the matrix polymer, generating *in situ* composites.¹⁰

However, the general problem of LCP blends is their immiscibility with flexible polymers, theoretically predicted by Flory,¹⁵ which is not only caused by differences in the chemical structure, but also by differences in the phase behavior of these polymers. The immiscibility of the blend partners results in phase separation within the polymer blend and in reduced mechanical properties due to the demixed morphology. Therefore, compatibilization of the immiscible polymers is necessary. Even in the case of *in situ* fibrils, a certain “connection” of LCP fibrils and matrix increases the effect of reinforcement.¹⁶

The common approach of compatibilization of polymer blends is to decrease the interfacial tension between the blend partners, causing an increase of interfacial width or mixing, thereby enhancing the phase-size uniformity and stability.¹⁷ In other words, the two separated polymer phases

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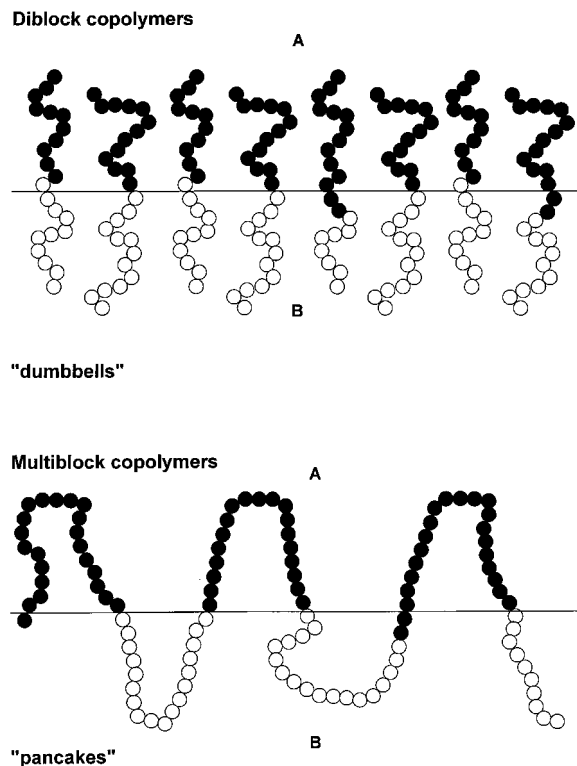


Figure 1 Arrangement of diblock copolymers and multiblock copolymers at the interface between immiscible polymers, according to Dai et al.³⁸

have to be brought together by a so-called stitching.¹⁸ In terms of this idea, two general routes of compatibilization of immiscible polymer blends were pointed out by Xanthos¹⁹:

1. Compatibilization by reactions between the blend partners or by using specific interactions between them (e.g., hydrogen bonding, ion-ion, and ion-dipole interactions^{20,21}). Reactions between the blend partners usually lead to the formation of block copolymer structures at the interfaces, therefore increasing the interfacial width and the intermixing between the phases.

In the case of polyesters to be blended, transesterification reactions between the polymers as reported for poly(ethylene terephthalate) (PET)/LCP and polycarbonate (PC)/LCP blends, resulting in a chemical coupling of the phases are useful to enhance phase adhesion.^{9,11,22-29} Reactions between the ester bonds or the end groups of LCP with carboxylic groups of polypropylene (PP) grafted with acrylic

acid or maleic anhydride were described previously for the compatibilization of PP/LCP blends.³⁰

2. Compatibilization by *block copolymers* containing segments chemically similar to the blend partners has become an important feature in blends containing polymers which are not able to undergo reactions between each other, e.g., blends of LCP with polysulfone, poly(phenylene oxide), or polystyrene (PS). In this approach, it is assumed that each of the different block copolymer segments is miscible with one of the blend components, therefore leading to an interdiffusion of these segments and the matrix phases within the interfaces.

The practical importance of diblock copolymers as polymeric surfactants and emulsifying agents has been known for several years, in particular, by investigations of Ouhadi et al.,³¹ Koning et al.,³² Vilgis and Noolandi,³³ Noolandi and Chen³⁴ proved theoretically only some years ago that the placement of the compatible blocks in the appropriated homopolymer phases actually lowers the interfacial free energy. The calculated interfacial tensions dropped with increasing molecular weight of the blocks, consequently resulting in the conclusion that a certain molecular weight of the segments is necessary to induce an intermixing. This molecular weight is strongly related to the entanglement molecular weight according to investigations of different PS blends containing the corresponding diblock copolymers done by Creton et al.³⁵ They noted that, since the diblocks are too short, they still act as surfactant, but do not cause a reinforcement of the interface. For a true com-

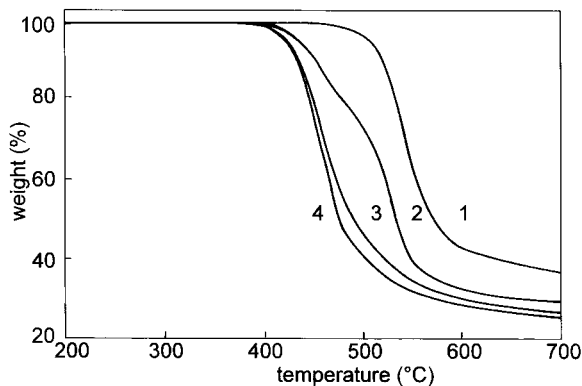


Figure 2 Thermal stability of selected polymer blends: (1) PSU; (2) PSU/BCP 1 50/50 (wt %/wt %); (3) LCP/BCP 1 50/50 (wt %/wt %); (4) LCP.

Table I Summary of Blend Compositions Investigated

Blend Sample	Segment Molecular Weight (g/mol)	LCP (wt %)	PSU (wt %)	BCP (wt %)
LCP	13,000	100	0	0
PSU	30,000	100	0	0
BCP 1	(PET/HBA) 3,200/PSU 2,000	100	0	0
BCP 2	(PET/HBA) 5,900/PSU 5,800	100	0	0
BCP 3	(PET/HBA) 7,400/PSU 8,400	100	0	0
PSU/PSU	30,000/2,000	0	50/50	0
PSU/PSU	30,000/8,400	0	50/50	0
PSU/LCP	30,000/13,300	80	20	0
		50	50	0
		20	80	0
PSU/BCP 1, 2 or 3		0	20	80
		0	50	50
		0	80	20
LCP/BCP 1 or 3		20	0	80
		50	0	50
		80	0	20
LCP/PSU/BCP 1		17.5	77.5	5
		47.5	47.5	5
		77.5	17.5	5
		17.0	68.0	15
		42.5	42.5	15
		68.0	17.0	15
LCP/PSU/BCP 3		35.0	35.0	30
		17.5	77.5	5
		47.5	47.5	5
		77.5	17.5	5
		42.5	42.5	15
		35.0	35.0	30

patibilizer, both effects are needed. Replacement of A–B diblock copolymers in AB blends by C–D diblocks (in which each of the blocks is thermodynamically miscible with one of the blend components, but chemically different) was furthermore shown theoretically,³³ as well as experimentally,³⁶ to give results comparable to A–B diblocks, demonstrating that thermodynamic reasons are the driving force for the arrangement of such block copolymers at the interphase.

Then, the question arose whether copolymers with a random chain segment distribution or even multiblock copolymers do affect immiscible polymer blends in a similar manner. The situation in comparison to diblock copolymers is illustrated in Figure 1.

In 1992, Noolandi suggested that multiblock copolymers which form such a pancake structure at the interface between two incompatible homopolymers would be more efficient as compatibilizers than would di- and triblock copolymers.³⁷ Noolandi pointed out that the avoiding of micelle formation of the block copolymer (i.e., by introduction of some irregularities into the multiblock copolymer architecture) would increase the interfacial activity of the block copolymer. This theory also assumes a certain critical length of the multiblocks in order to form loops which are large enough to penetrate into the homopolymer phases.

The first experimental evidence for Noolandi's suggestions was given by Dai et al.,^{38,39} again using the PS/(PVP) system containing the corre-

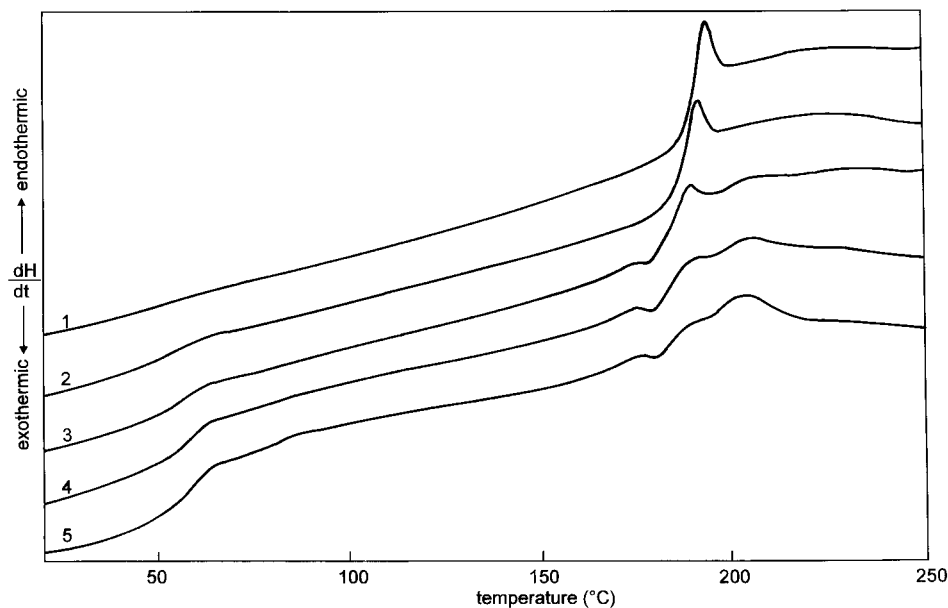


Figure 3 DSC curves of PSU/LCP (30,000/13,300 g/mol) blends in dependence on composition: (1) PSU; (2) PSU/LCP 80/20 (wt %/wt %); (3) PSU/LCP 50/50 (wt %/wt %); (4) PSU/LCP 20/80 (wt %/wt %); (5) LCP.

sponding random copolymer, leading to the conclusion that for mechanically strengthening the interface random copolymers with symmetric monomer fractions are a reasonable alternative to diblock copolymers. However, Noolandi and Shi questioned the validity of the conclusions mentioned above for melt-processed blends.⁴⁰

Therefore, we became interested in investigations of the effectiveness of LC multiblock copolymers in blends of the based homopolymers. Only rare, brief reports have been given on the use of multiblock copolymers. Kaufhold et al.⁴¹ noted the emulsifying effect of nonphase-separated, single-phase PC/polysulfone (PSU) multiblock copolymers in PC/PSU blends, leading to a more uniform size distribution of PC particles in the blend and, consequently, to improved mechanical properties. The compatibilizing effect of the block copolymer is discussed in terms of transesterification reactions between the PC blend partner and the PC segments of the block copolymer. Further reports are given by Heitz et al.⁴² and Schulze et al.⁴³ for LCP/PS blends. However, detailed investigations, especially of LC blends, are lacking.

Therefore, the influence of recently reported polysulfone–poly(ethylene terephthalate-*co*-oxybenzoate) multiblock copolymers (BCP) in blends of polysulfone and LC polyesters have been studied by using three BCP with different segment molecular weights. The molecular weight of PSU

and LCP units coupled in the BCP were comparable, reflecting the “symmetric” case discussed by Dai et al.³⁸ Both PSU and LC segments in the BCP have a polydispersity of about two.

Since it has been observed that the morphology of PSU/LCP multiblock copolymers is controlled by the coupled segment lengths (i.e., coupling of short segments results in a less phase-separated structure and coupling of very long ones in a strong phase-separated morphology), not only the block copolymer molecular weight but also the corresponding BCP morphology have to be taken into consideration in order to discuss the effect of the BCP in the blend. Moreover, the possibility of transesterification reactions of the LC polyester blend partner and the LCP segments of the BCP could not be neglected.

To obtain serious results, basic investigations of solution-casted films were started regarding first the binary blends of the multiblock copolymer with PSU and LCP, respectively, and then the ternary blends of PSU/LCP and BCP. The results obtained for the solution-casted blends are used to interpret the behavior of the BCP in injection-molded samples.

EXPERIMENTAL

Materials

The blend components used were high molecular polysulfone (PSU, MW 30,000 g/mol) from Poly-

science Europe GmbH (Eppelheim, Germany), poly(ethylene terephthalate-co-oxybenzoate), referred to as LCP (PET/HBA 40/60, MW 13 300 g/mol), prepared according to ref. 44, and poly(ethylene terephthalate-co-oxybenzoate)/polysulfone multiblock copolymers, referred to as BCP (PET/HBA)/PSU, synthesized and chemically characterized as described elsewhere.⁴⁵ Block copolymers with the following segment molecular weights were selected for the investigations: BCP 1 (3,200/2,000 g/mol), BCP 2 (5,900/5,800 g/mol), and BCP 3 (7,400/8,400 g/mol). Multiblock copolymers 1 and 3, respectively, form a uniform LC phase in the melt, whereas BCP 2 with intermediate segment lengths shows a biphasic structure under the polarizing microscope (coexistence of LC and isotropic phase). Some experiments were carried out with Vectra A 750 (Hoechst Celanese Corp.) as the LCP component.

Solution-casted blends were prepared as follows: Blend components were dissolved together in a mixture of trifluoroacetic acid/CHCl₃ (50/50 vol %/vol %). The blend solutions were precipitated into an excess of ethanol, then filtered and finally dried *in vacuo* (8 h/50°C).

Melt blends were obtained using a melt kneader (Brabender Plasticorder®) by mixing at 260°C for 20 min. The blends were then injection-molded using an Engel injection moulding machine Es 200H/80V/HL-2F (Germany) with a screw diameter of 15 mm, equipped with a special mold for small amounts, at temperatures in the range of 300–340°C (nozzle temperature).

Analytical

Thin polymer films were obtained by spreading of a trifluoroacetic acid/chloroform solution onto water. *Transmission electron microscopy* (TEM) investigations were carried out using a Zeiss EM 912 (Germany) in the zero-loss-mode ($\Delta E = 0$, elastic-scattered electrons only).

Cryofractures (liquid nitrogen) of injection-molded melt blends were investigated by *scanning electron microscopy* (SEM) using a Zeiss DSM 982 Gemini (Germany).

DSC measurements were carried out in a DSC 7 (Perkin-Elmer) in a nitrogen atmosphere. The temperature and transition enthalpy calibration were done with indium at a heating rate of 10 K/min. The heating rate for the experiments was 20 K/min; the cooling rate was 10 K/min. The determined temperatures were not corrected, because all samples were investigated under comparable conditions. For an identical thermal history,

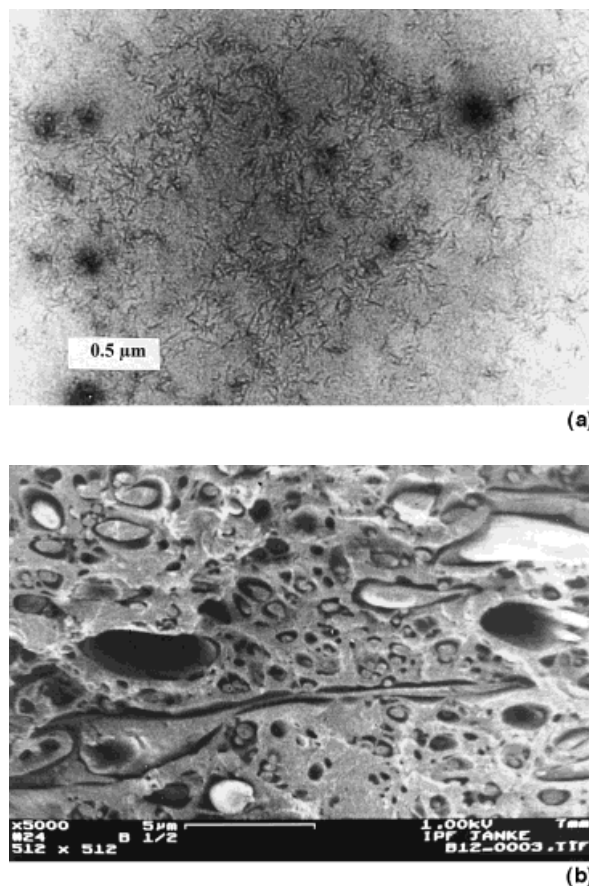


Figure 4 Morphology of the incompatibilized PSU/LCP blend (50/50 wt %) demonstrating the complete demixing: (a) TEM of the solution injection-casted blend; (b) SEM of the cryofracture of an injection-molded specimen.

the data were determined from cooling and the second heating run.

Complex melt viscosities were obtained using an RMS 800 rheometer (Rheometrics Inc., USA) with a disc and plate device (ϕ 25 mm, 2 mm gap, 30% strain amplitude) in a small oscillatory shear within the frequency range of 0.1–100 rad/s. Tensile tests were carried out using a Zwick test machine.

RESULTS AND DISCUSSION

Thermal Stability of the Blends

The thermogravimetric investigations of the blend components, published previously,⁴⁶ showed that the thermal stability of all samples is high. The temperature at which 1% weight loss has occurred is above 380°C for all samples except the pure LCP.

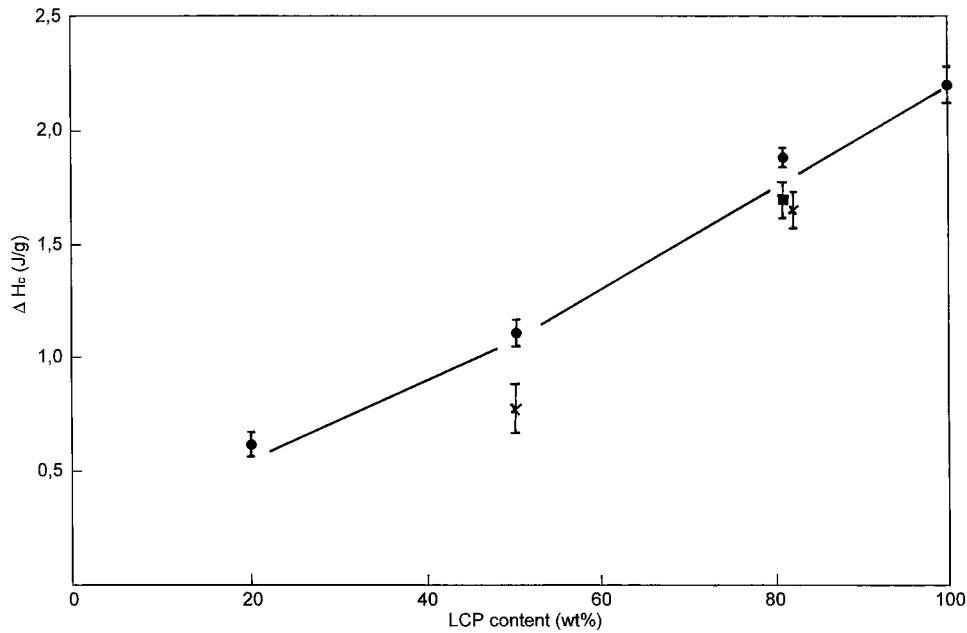


Figure 5 Crystallization enthalpy of LCP in LCP/BCP and LCP/PSU blends in dependence on composition: (■) LCP/BCP 1; (●) LCP/BCP 3; (×) LCP/PSU.

The blends show a similar behavior corresponding to their composition. The curves of some selected samples are illustrated in Figure 2.

Solution-Casted Binary Blends

Solution casting is a reliable method of obtaining homogeneous blends from immiscible polymers.

To separate the influence of the multiblock copolymers in PSU/LCP blends carefully, DSC and morphological investigations were carried out basically with such blends. For a satisfactory interpretation of the influence of multiblock copolymers in ternary blends of PSU/LCP/BCP, binary blends of the components were investigated first.

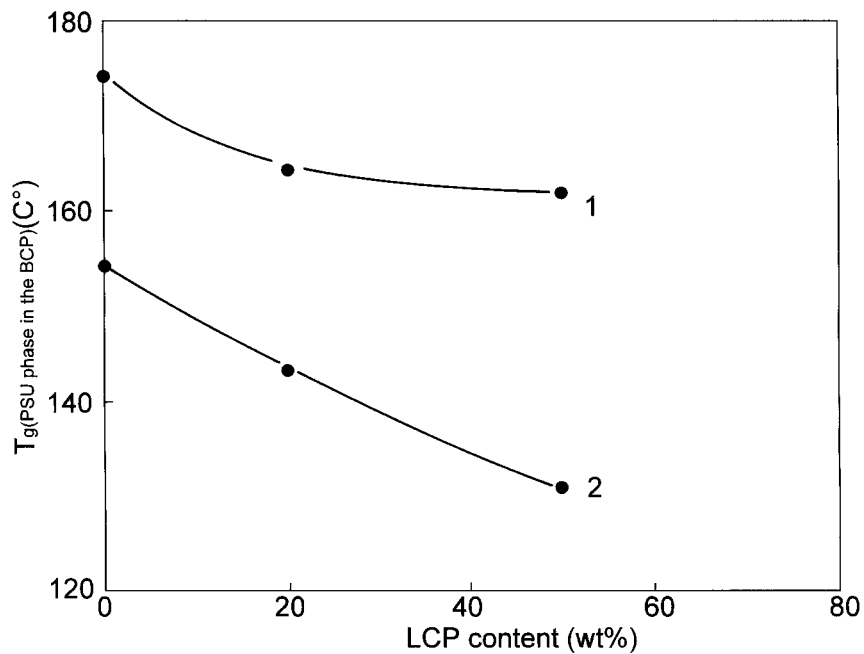


Figure 6 Glass transition temperature (PSU phase in the block copolymer) in blends of LCP with BCP in dependence on composition: (1) LCP/BCP 3; (2) LCP/BCP 1.

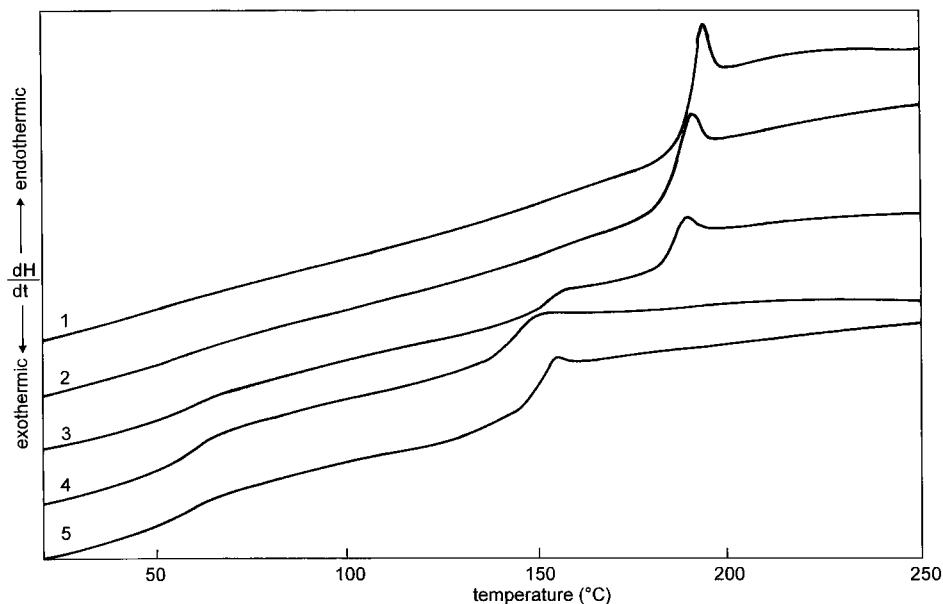


Figure 7 DSC curves of PSU/BCP 1 blends in dependence on the BCP content: (1) PSU; (2) PSU/BCP 1 80/20 (wt %/wt %); (3) PSU/BCP 1 50/50 (wt %/wt %); (4) PSU/BCP 1 20/80 (wt %/wt %); (5) BCP 1.

All sample compositions are listed in Table I.

DSC measurements of blends of high molecular PSU with PSU oligomers of different chain lengths revealed a single T_g positioned between the T_g 's of both according to the known mixing rules, meaning that PSUs of different molecular weight are misci-

ble. The DSC curves of the PSU/LCP blends (Fig. 3) reflect a superposition of the curves of the two polymers corresponding to their content in the mixture. The glass transitions of the initial components (T_g (PET-rich phase) and T_g (oxybenzoate-rich phase) of LCP, and the T_g of polysulfone) are not influ-

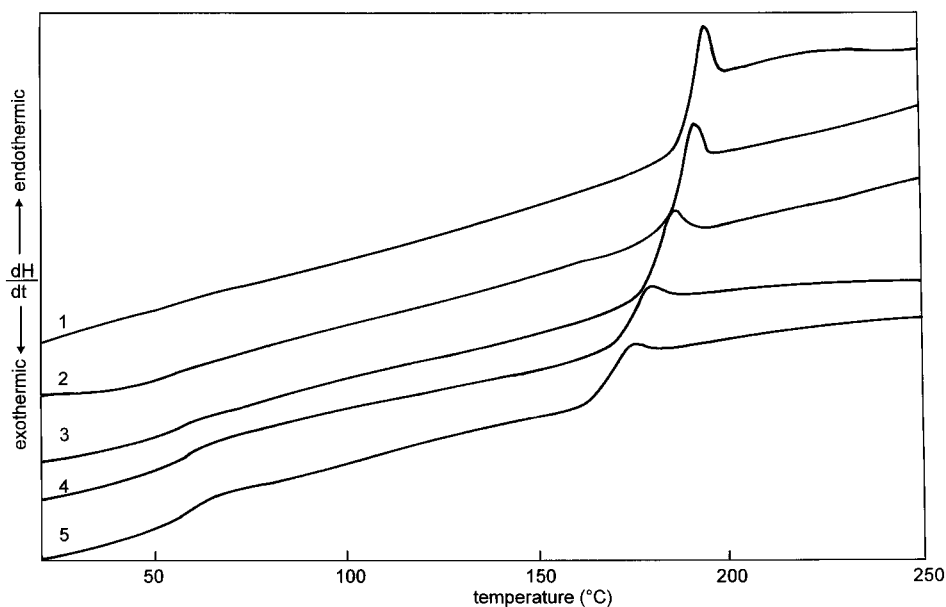


Figure 8 DSC curves of PSU/BCP 3 blends in dependence on BCP content: (1) PSU; (2) PSU/BCP 3 80/20 (wt %/wt %); (3) PSU/BCP 3 50/50 (wt %/wt %); (4) PSU/BCP 3 20/80 (wt %/wt %); (5) BCP 3.

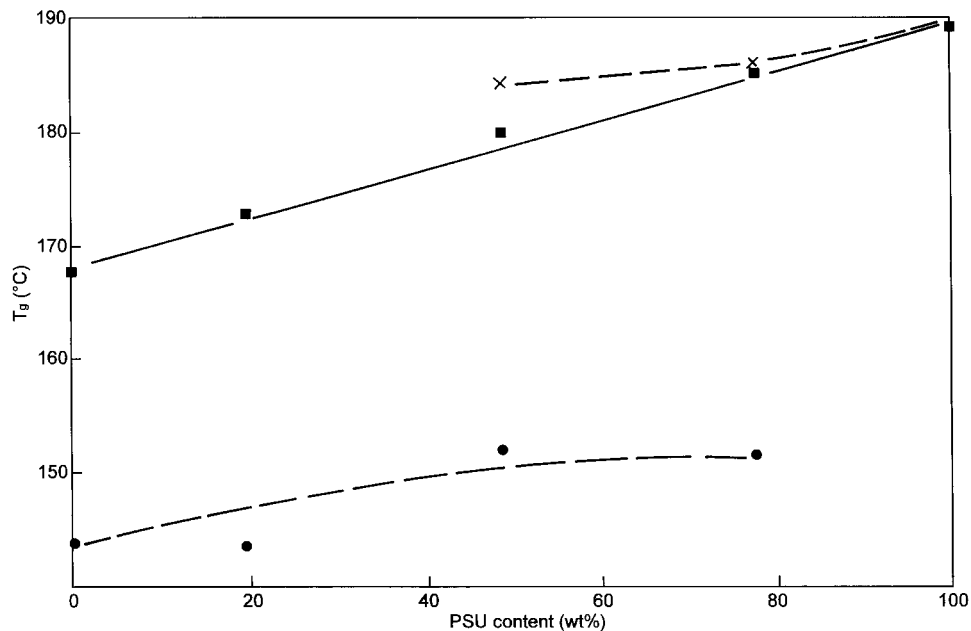


Figure 9 Comparison of the glass transition behavior of PSU in PSU/BCP blends with BCP containing different PSU and LCP segments: (■) PSU/BCP 3 (single T_g); (●) PSU/BCP 1 [T_g (PSU phase in the BCP)]; (×) PSU/BCP 1 [T_g (PSU blend partner)].

enced due to the complete immiscibility of the blend system. The T_g of the oxybenzoate-rich phase of the LCP is not detected. In blends with a high content of LCP, the PSU T_g is overlapped by the LCP melting. The complete immiscibility can be impressively illustrated by the morphology of the incompatibilized PSU/LCP blend as seen in the SEM and TEM pictures (Fig. 4).

However, the DSC cooling curves in which the crystallization and glass transition of PSU can be

separated more reliably demonstrate that the LCP crystallization is influenced by the PSU. The crystallization enthalpies, determined within the error of calculation and corrected with respect to the LCP content, are summarized in Figure 5, showing a drop with increasing PSU content. At a content of > 50 wt % PSU, the LCP crystallization is not further detected. In contrast, in the multiblock copolymers consisting of chemically coupled segments of LCP and PSU as described

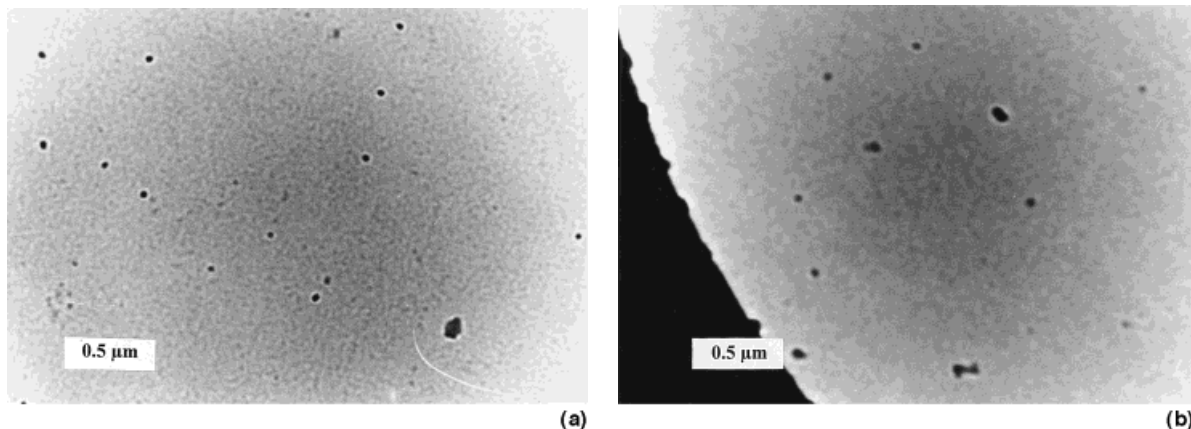


Figure 10 TEM micrographs of solution-casted binary in comparison to the starting polymer: (a) LCP; (b) BCP 1; (c) LCP/BCP 1 50/50 (wt %/wt %); (d) PSU/BCP 1 50/50 (wt %/wt %); (e) BCP 3; (f) LCP/BCP 3 50/50 (wt %/wt %); (g) PSU/BCP 3 50/50 (wt %/wt %).

previously,⁴⁵ the crystallization of the LCP part is completely suppressed. This is not observed in LCP that are chain-extended by short di(oxyphenylene) sulfone units (as a model for PSU).

Now, binary blends of LCP with different types of BCPs were examined. Lenz et al.⁴⁷ pointed out that the different phase behavior of LC and non-LC polymers with chemically comparable structural units is the main reason for their immiscibil-

ity. All multiblock copolymers used were found to form LC melts above their glass transitions matching the melting range of the LCP used. From that, miscibility between BCP and LCP was expected.

However, all glass transitions occurring in the pure blend partners are observed in the blends of the LCP with all three BCP. At this point, the multiphase structure of the LCP itself should be

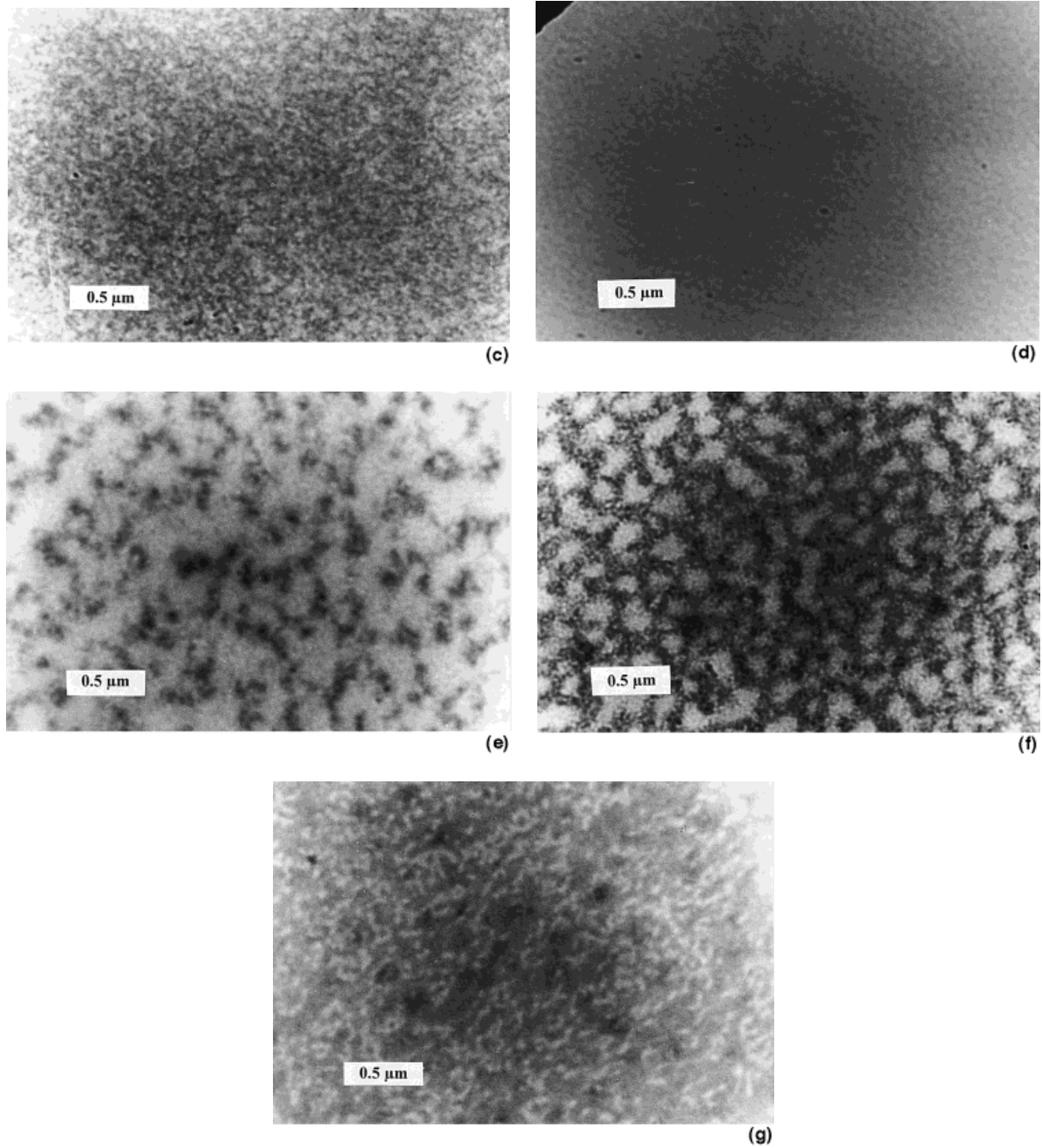


Figure 10 (Continued from the previous page)

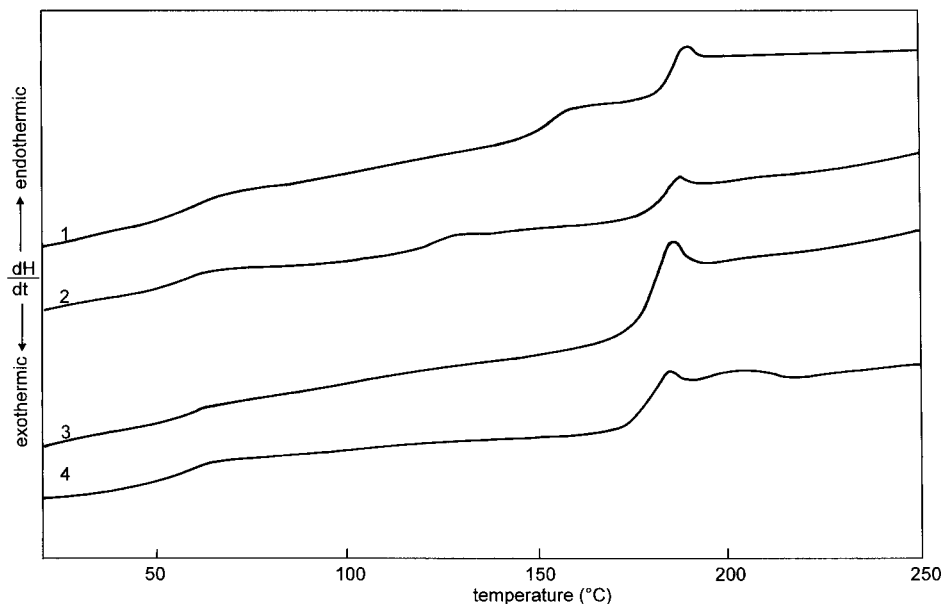


Figure 11 DSC curves of ternary LCP/PSU/BCP blends in comparison to binary PSU/BCP blends: (1) PSU/BCP 1 50/50 (wt %/wt %); (2) LCP/PSU/BCP 1 35/35/30 (wt %/wt %/wt %); (3) PSU/BCP 3 50/50 (wt %/wt %); (4) LCP/PSU/BCP 3 35/35/30 (wt %/wt %/wt %).

remembered, which is characterized by a PET-rich and an HBA-rich phase.⁴⁴ The T_g of the PSU phase in the BCP shifts to lower temperatures with increasing content of LCP, indicating, in contrast to the expectations, only a weak interaction between both polymers (Fig. 6). This fact might be caused by the difference in melt viscosities of LCP and BCPs (which is due to their different molecular weights and the incorporation of PSU into the multiblock copolymer chains, as well), preventing an intermixing of both blend phases. If this is true, a transesterification between LCP and BCP could be ruled out. Unfortunately, transesterification cannot be proved directly because the random chain structure of the starting LCP and the BCP is similar.

As already shown in Figure 5, the crystallization of the LCP is suppressed by the BCP which is unambiguously due to the suppression of the crystallization in the BCP as discussed above. Crystallization is not detected in blends of short-segmented BCP starting with a BCP content of 20 wt % and in the blends with long-segmented BCP starting at a BCP content of 80 wt %, respectively. If the BCP contains diphenylene sulfone units, then a small amount of LCP can crystallize in the blend, provided that the LCP segment lengths in the BCP are above 5,800 g/mol. It has

to be stated that the LCP is immiscible with PSU/LCP multiblock copolymers, but a certain interaction takes place.

The behavior of PSU/BCP blends depends significantly on the segment lengths coupled within the BCP. As illustrated in Figure 7, blending of PSU and the short-segmented BCP (2,000/3,200) causes the T_g of PSU and the T_g of the polysulfone phase in the BCP to come closer to each other. This can be discussed in terms of a certain interpenetration between the blend partners. A similar tendency, not demonstrated in the figure, was found for blends containing BCPs with intermediate segment lengths (5,900/5,800). In contrast, blends of PSU and the long-segmented BCP (8,400/7,400) show only a two-phase structure (Fig. 8). Besides the glass transition of the PET-rich phase of the LCP segments in the BCP, only a single T_g for PSU was observed, referring to an intermixing between the PSU phase of the block copolymer and the PSU matrix. This glass transition temperature corresponds to the composition (Fig. 9), showing an additive behavior that indicates a partial miscibility of the PSU phase of the BCP with the PSU blend partner.

The different miscibility behavior of the short- and long-segmented multiblock copolymers with LCP and PSU, respectively, is also reflected by

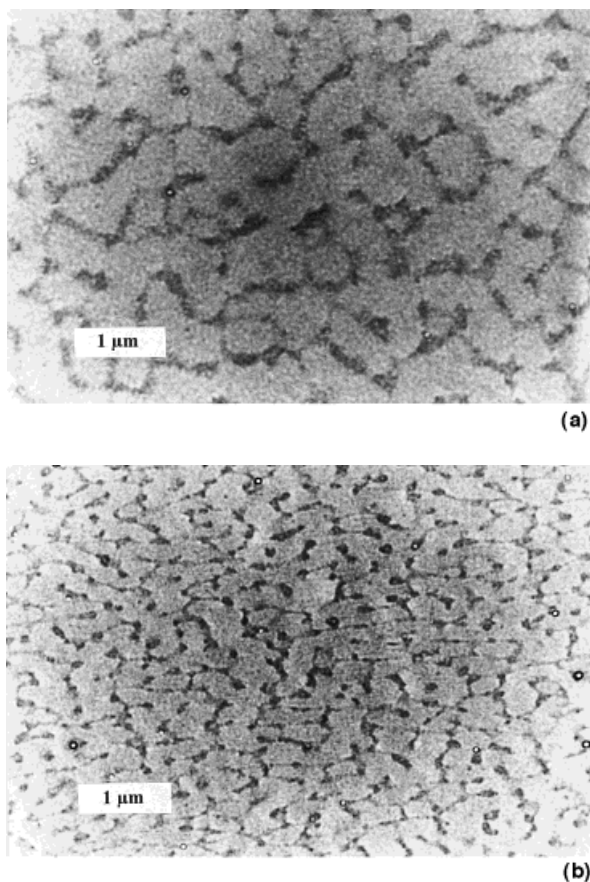


Figure 12 TEM micrographs of solution-casted ternary PSU/LCP/BCP blends: (a) PSU/LCP/BCP 1 35/35/30 (wt %/wt %/wt %); (b) PSU/LCP/BCP 3 35/35/30 (wt %/wt %/wt %).

their morphologies as examined by TEM.

Figure 10 shows the morphology of blends of BCP 1 with short molecular segments [(PET/HBA)/PSU = 3,200/2,000 g/mol] with LCP (c) and PSU (d) in comparison to the morphology observed in the pure LCP blend partner (a) and the pure BCP 1 (b). The fine disperse phase structure of the BCP is unchanged in blends with PSU, whereas in blends of the long-segmented BCP 3 [(PET/HBA)/PSU = 7,400/8,400 g/mol] with LCP, a stronger phase separation is also found (f). In contrast, the morphology of the blend with PSU (g) is significantly altered. Large domains in the TEM micrograph can be characterized by a one-phase structure. The second phase is essentially smaller compared to that found in pure BCP (e).

Therefore, it has to be noted that the phase separation occurring already in the long-segmented BCP is reduced by blending with PSU and

that their PSU segments are able to interpenetrate. This result is confirmed by both DSC and TEM observations.

From Dai's results³⁸ it was assumed that such a behavior can be found with BCP containing segments with molecular weights above the entanglement molecular weight. The entanglement molecular weight of PSU was calculated by Soliman et al.⁴⁸ to be approximately 2,500 g/mol. The partial miscibility of PSU with PSU/LCP multiblock copolymers was detected with PSU segment molecular weights of 8,400 g/mol, more than twice of the value given by Soliman et al. This might be due to the chemical coupling of the long PSU segments with rigid chain LCP segments, resulting in a reduced flexibility of the PSU segments, consequently shortening the "effective" available PSU length. From these, the question arose whether the partial miscibility of PSU with long-segmented BCP could be maintained in the ternary blend of all components, resulting in an improved intermixing of LCP and PSU.

Solution-Casted Ternary Blends

The behavior of the different binary blends is also reflected in ternary blends of LCP/PSU/BCP. This was proven for different blend compositions, i.e., for different contents of PSU and LCP as well as different contents of the block copolymer. The result for the selected blend composition PSU/LCP/BCP (35/35/30 wt %) is illustrated in Figure 11. The effects are more visible with a higher content of BCP. Nevertheless, the same behavior is observed in blends with lower BCP contents (15 and 5 wt %, respectively).

Blends with short-segmented BCP 1 show the T_g (PET-rich phase) of LCP, the T_g (PSU phase in the BCP), and the T_g (PSU blend partner) at a BCP content of more than 30%. The T_g of PSU in the BCP shifts to the T_g of the PET-rich phase of LCP, again reflecting a certain interaction between both phases.

In blends with the long-segmented BCP 3, only a single T_g of both the PSU blend partner and the PSU phase of BCP is found. Therefore, it can be concluded, taking the result for the binary PSU/BCP blend into account, that the long-segmented BCP shows a certain interpenetration of its PSU phase with the PSU matrix also in the presence of LCP in the blend. This can also be seen in the corresponding TEM micrographs (Fig. 12).

Summarizing the results obtained by investigations of solution-casted LCP/PSU blends con-

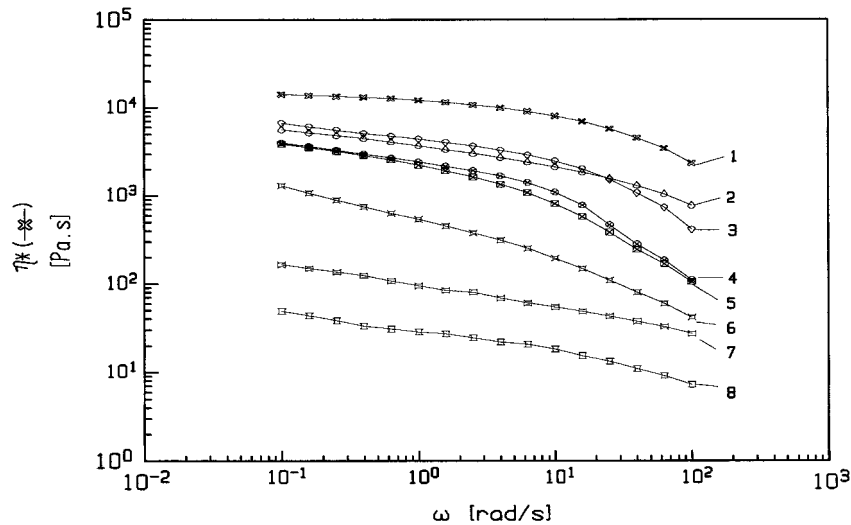


Figure 13 Complex melt viscosities of different blends vs. shear rate: (1) PSU; (2) PSU/BCP (50/50 wt %); (3) PSU/LCP (59/41 wt %); (4) PSU/LCP/BCP (47.5/47.5/5 wt %); (5) PSU/LCP (50/50 wt %); (6) PSU/LCP (29/71 wt %); (7) LCP/BCP (50/50 wt %); (8) LCP.

taining a multiblock copolymer, it can be stated that multiblock copolymers with certain segment lengths exceeding more than twice the entanglement molecular weight of PSU and LCP are able to generate a partial interaction be-

tween the original blend partners. In the last part of this investigation, it was intended to determine whether or not this interaction plays a role in melt-blended samples known as immiscible.

Table II Mechanical Characteristics of Injection-Molded Specimens of Melt-Blended PSU/LCP Blends Containing Multiblock Copolymers

Composition			Properties				
PSU (wt %)	LCP (wt %)	BCP (wt %)	Processing Temperature (°C)	<i>E</i> -modulus (GPa)	Tensile Strength (MPa)	Elongation (%)	Fracture Strength (MPa)
100	—	—	300	2.57	72.38	5.74	48.26
—	100	—	300	14.45	141.24	1.82	138.86
—	—	100	300	6.64	78.69	2.00	77.64
50	50	—	300	4.26	51.13	1.84	51.02
50	—	50	300	3.71	76.48	3.20	76.38
—	50	50	300	6.22	84.44	2.24	84.15
47.5	47.5	5	300	3.78	49.26	1.94	49.12
			340	4.46	61.93	2.40	61.72
48.75	48.75	2.5	300	3.85	47.46	1.84	46.86
			340	3.94	55.16	2.21	54.68
45	45	10	300	5.54	78.67	2.26	77.02
			340	4.15	60.02	2.31	59.60

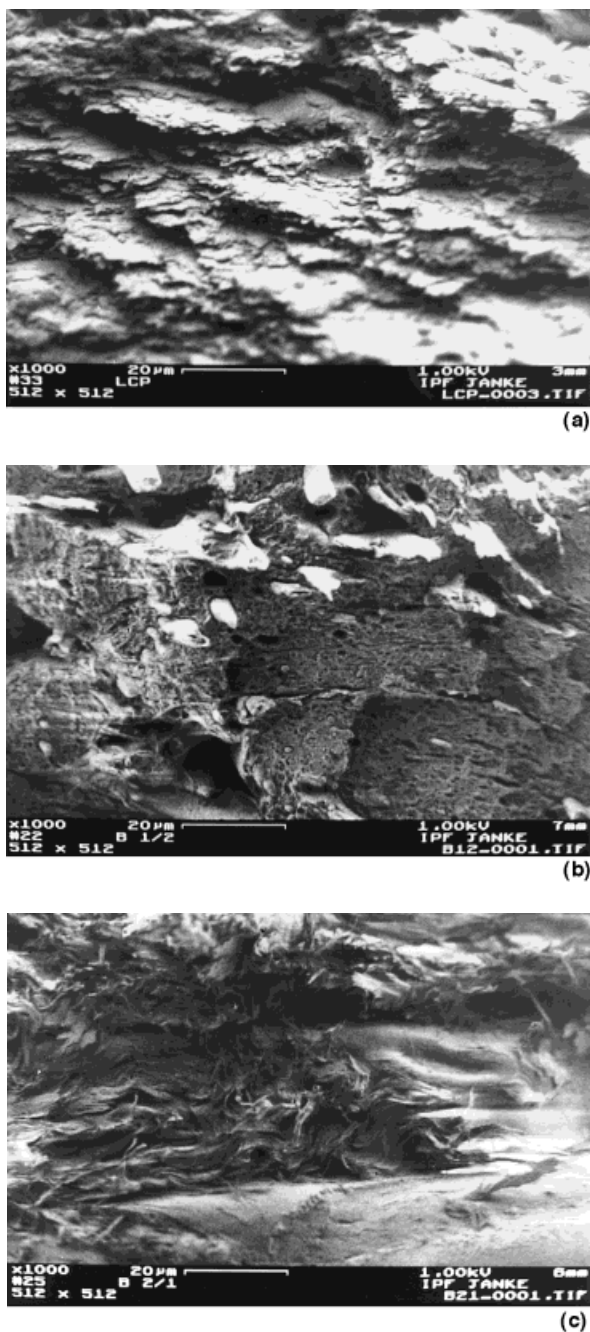


Figure 14 SEM micrographs of injection-molded specimens of PSU/LCP blends (cryofractures): (a) LCP; (b) PSU/LCP (50/50 wt %); (c) PSU/LCP/BCP (47.5/47.5/5 wt %).

Melt Blends

The morphology of polymer blends obtained by melt mixing is significantly influenced by the ratio of the melt viscosities of the blend partner. Basically, it is known from literature reports that a large difference exists between LCP and polysul-

fone melt viscosities. Magagnini et al.⁴⁹ already demonstrated that both polymers deviate from Newtonian behavior and show shear thinning over the whole shear range. This gave rise to a biphasic character of the respective blends with poor interphase adhesion for all compositions. Additionally, we noted in a previous report⁴⁶ that the coupling of both LCP (PET/HBA) and PSU segments in the corresponding multiblock copolymers resulted in melt viscosities ranging between those of the homopolymers. Compared to multiblock copolymers consisting of segments with equal molecular weights, the melt viscosity of a 50/50 (wt %/wt %) physical blend is lower, but an order of magnitude higher than the curve for the pure LCP. The BCP viscosities could be pushed under the blend curve only by coupling of very long LCP segments with much shorter PSU units. For evaluation of melt blends, some additional rheological investigations were carried out. All melt blends were prepared by melt mixing PSU and LCP in a Brabender plasticorder at 260°C for 20 min at 80 rpm, followed by granulation.

Figure 13 shows the melt viscosity vs. shear rate curves for different blend compositions at 280°C, approximating the processing temperature. The melt viscosities of the blends depend on the percentage of PSU. A higher content of PSU increases the melt viscosity toward that of pure PSU. Note that it does not matter whether the PSU is added as a blend component or, in the other case, as a structural component of the multiblock copolymer. Addition of 5 wt % BCP to a 50/50 (wt %/wt %) blend of PSU and LCP does, consequently, not alter the melt viscosity.

From that rheological point of view, it might be concluded that the block copolymer would not have significant influence on the blends. To investigate this, PSU/LCP blends with a composition of 50/50 wt % and different contents of multiblock copolymers were prepared and injection-molded using comparable processing conditions (nozzle temperature 300°C).

Table II summarizes the mechanical properties of the blends obtained by tensile tests (tensile strength, E -modulus, fracture strength, elongation). As expected, the mechanical characteristics of the blend dropped below the level of the homopolymers. Remembering the results found for the solution-casted samples, at first, binary blends of PSU and a long-segmented BCP [PSU/(PET/HBA) 7,100/7,400] as well as LCP and BCP, respectively, 50/50 wt %, were examined.

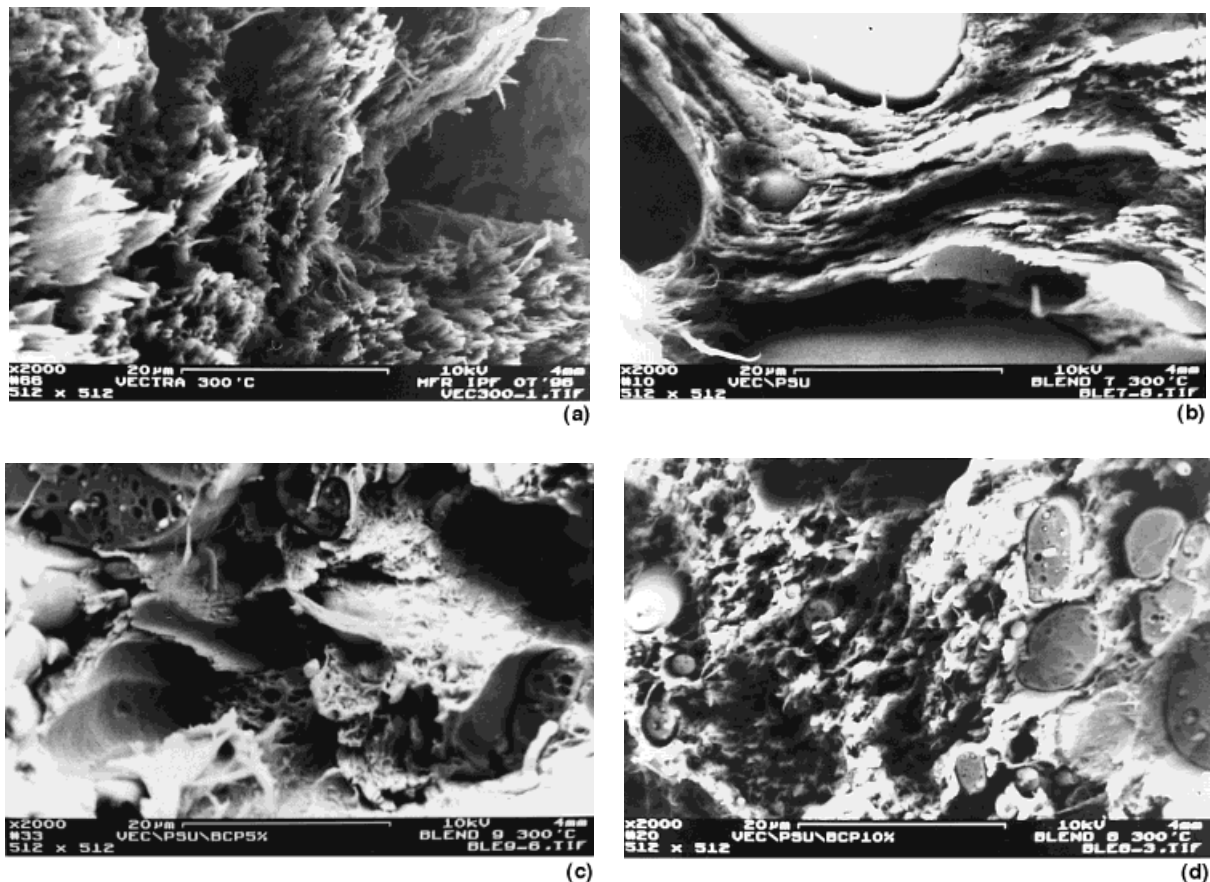


Figure 15 SEM micrographs of injection-molded specimens of PSU/Vectra blends (cryofractures): (a) Vectra; (b) PSU/Vectra (50/50 wt %); (c) PSU/Vectra/BCP (47.5/47.5/5 wt %); (d) PSU/Vectra/BCP (45/45/10 wt %).

Both PSU/BCP and LCP/BCP blends show increased mechanical characteristics as compared to the PSU/LCP blend. This could be expected with respect to the solution-casted samples. The values of the LCP/BCP blend reflect that under the conditions of an external mechanical flow field an intermixing of both LC phases can be forced, resulting in values slightly higher than those of the pure multiblock copolymers.

Ternary blends containing 5% BCP have only a slightly increased E -modulus and fracture strength values compared to the PSU/LCP blend. It is expected that they might be further increased by optimizing the processing conditions.

Despite this, the morphology indicates unambiguously a better adhesion of PSU and LCP, which has to be discussed as an effect of the multiblock copolymer added. Figure 14 compares SEM pictures taken from cryofractures of injection-molded bars. (a) The LCP displays the typi-

cal layered structure, and (b) the LCP/PSU blend (50/50 wt %), poor adhesion between LCP fibrils and PSU matrix, resulting in an inhomogeneous blend. (c) Adhesion of 5 wt % of BCP results in a better distribution and adhesion of the blended phases.

A similar effect was obtained when using the commercial Vectra A 750 LCP [poly(1,4-oxycarboxybenzoate-*co*-2,6-oxynaphthoate)] instead of (PET/HBA) (Fig. 15), i.e., the multiblock copolymers consisting of poly(ethylene terephthalate-*co*-oxycarboxybenzoate) and polysulfone segments (7,700/8,740 g/mol) seem to act as a phase compatibilizer in blends of PSU and LCP with compositions other than the LCP segments of the BCP. The mechanical characteristics of these blends (LCP/PSU = 50/50 wt %) show a significant increase in all values determined at a block copolymer content of 5 wt % at a final processing temperature of 340°C (Fig. 16).

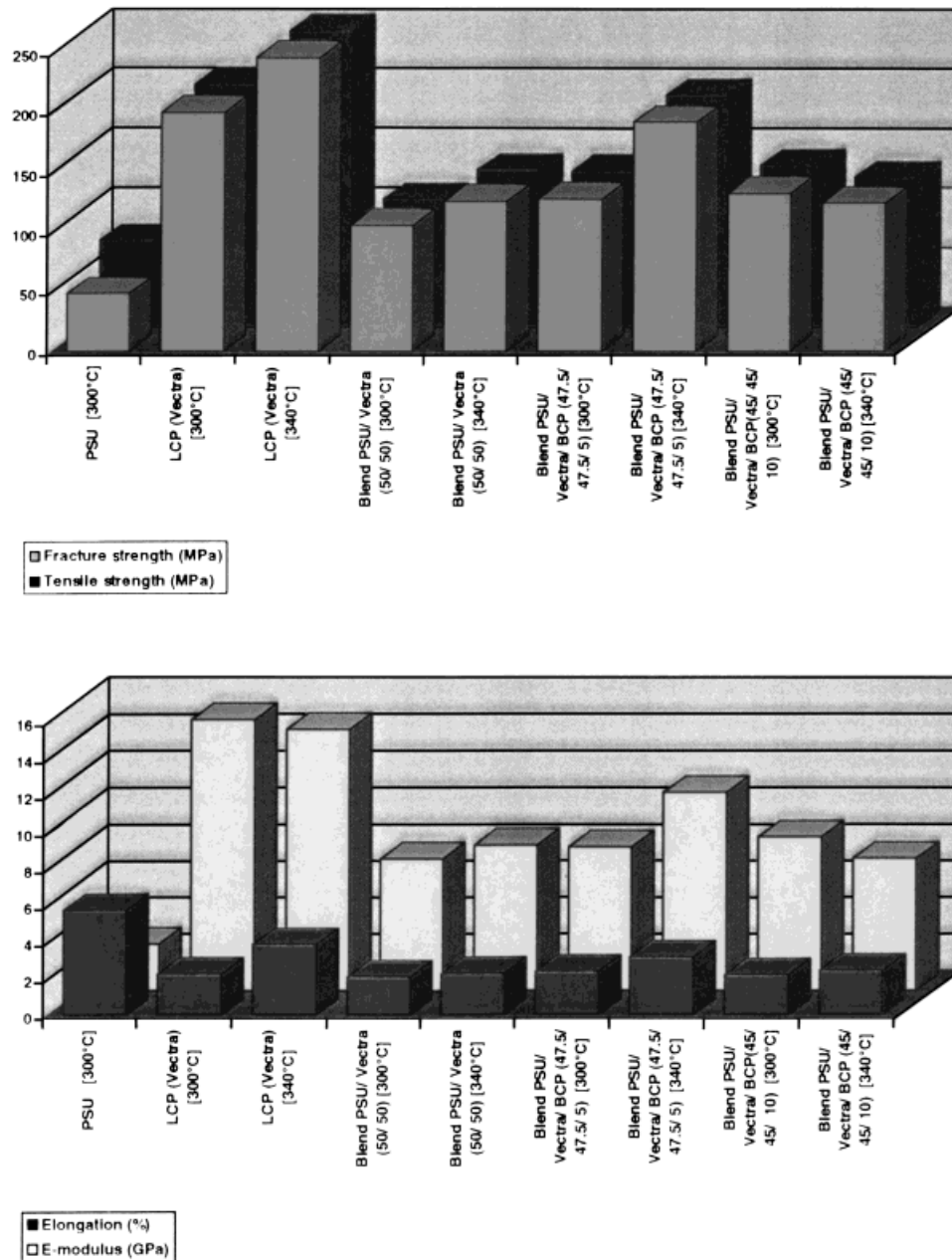


Figure 16 Mechanical characteristics of PSU/Vectra blends with different contents of PSU/(PET/HBA) multiblock copolymer as the compatibilizer.

CONCLUSIONS

Blends of PSU and LCP are representative of a wide class of blends of immiscible polymers which are not able to undergo reactions between each other. Compatibilization in such blends might be achieved by lowering the interfacial tension between the polymer phases by adding block copolymers which consist of segments of the based homopolymers.

In our approach, the effectiveness of multiblock copolymers containing PSU and aromatic polyester segments was examined assuming that both of the two segments are miscible with the corresponding homopolymer. Additionally, the influence of the segment molecular weights was investigated taking Noolandi's finding into account that a certain molecular weight higher than the entanglement molecular weight is necessary to form loops through the polymer.

The investigation of binary, solution-casted blends revealed a basic understanding of processes that happen in PSU/LCP/multiblock copolymer blends. In LCP/BCP blends, only a weak interaction was found, represented by a small shift of the glass transition temperatures. Although both polymers are LC, no indication for miscibility was detected, which, consequently, excludes transesterification between the blend partners. In PSU/BCP blends, miscibility between both PSU phases was observed, assuming a segment molecular weight of PSU of $\geq 8,400$ g/mol, which is more than twice of the entanglement molecular weight, i.e., the compatibilizing effect takes place in the amorphous phase of polysulfone. This should cause an increased interface width between PSU and LCP. Investigations using X-ray reflectometry are in progress to obtain a more detailed knowledge about the interface structure and the influence of the multiblock copolymer structure. The basic results in binary blends are also valid for the ternary PSU/LCP/BCP blends.

Furthermore, the addition of PSU/LCP multiblock copolymers resulted in altered mechanical characteristics of injection-molded blends: *E*-modulus and fracture strength are higher than the corresponding values of the noncompatibilized blends. Summarizing the results, it can be stated that addition of a PSU/LCP multiblock copolymer with high molecular segments offers a possibility for compatibilizing immiscible PSU/LCP blends, resulting in a better adhesion of the PSU and LCP phase.

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