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Bulk and Surface Properties of Blends with Semifluorinated Polymers and Block Copolymers

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Summary: The goal of the investigation presented here is the development of extremely hydrophobic materials based on polysulfone that can be applied, for instance, as fouling-resistant membrane materials. The concept used is the addition of semifluorinated polymers to polysulfone in suitable blend compositions. The influence of molecular parameters like chain structure of the semifluorinated polymer (segmented block copolymers, random copolymers) and segment molecular weight on the state of phase separation in the bulk and its influence on the surface properties have been systematically examined. It could be shown that segmented block copolymers with semifluorinated polyester segments with intermediate segment molecular weight are more suitable in blends with polysulfone than random polysulfone copolymers having semifluorinated side chains with respect to form homogeneous thin films (coatings) with highly non-wetting properties.

Keywords: blends, fluorinated polymers, polysulfone, self-organization, wetting

Introduction

Compounds with ultrahydrophobic properties are of special interest for materials with drastically reduced wetting, for instance for the development of self-cleaning or bioinert surfaces for implants that suppress adhesion of proteins in contact with blood. Semifluorinated low molecular compounds as well as polymers have extremely low surface free energy[1-7] which is the prerequisite for ultrahydrophobicity. On the other hand, they are expensive and, therefore, often applied only as an additive, using the ability of fluorinated compounds to segregate to the surface.[8-9] The quality of the surface depends significantly on the state of miscibility between additive and matrix polymer. Here, we want to discuss the influence of semifluorinated polymers with different chain structure on the state of miscibility in binary blends with polysulfone (bulk properties) and the influence of the solid state structure on the surface properties of thin spin-coated films of these blends in order to achieve stable and homogeneous films with low surface free energy (i.e., high contact angles versus water). The influence of chemical composition

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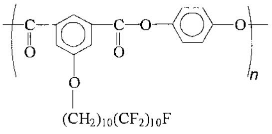
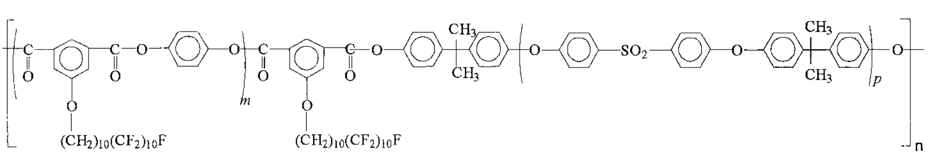
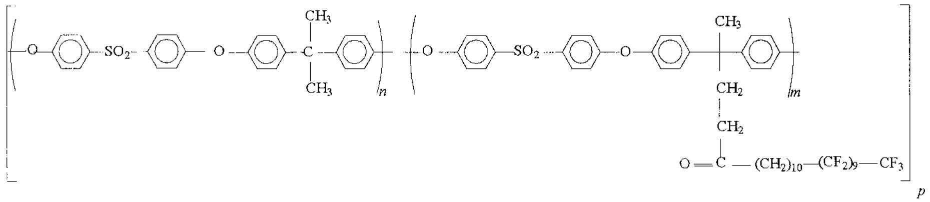
(concentration and distribution of side chains) and phase separation in the bulk on the phase separation in blends with polysulfone will be outlined for the pure semifluorinated polyester **1**, segmented block copolymers (BCP) having semifluorinated (SF) polyester segments and polysulfone blocks **2**, as well as for copolymers of polysulfone (PSU) having semifluorinated side chains attached to 4,4'-bis(oxyphenyl)pentanoic acid randomly distributed along the chain **3**.



1: semifluorinated polyester (SF-PES)



2: segmented semifluorinated polyester / PSU block copolymer (BCP)



3: random copolymer having semifluorinated side chains attached to 4,4'-bis(oxyphenyl)pentanoic acid

Experimental

The synthesis of segmented BCP[10-11] and copolymers[12] with semifluorinated side chains is described elsewhere. The blends were prepared by mixing the SF (block) copolymer and PSU in the appropriate weight ratio in a trifluoroacetic acid / chloroform mixture (1/1 v/v, c_{pol}: 60 mg / 20 ml), precipitation into methanol, filtering off and drying in vacuum at 50 °C for 5 h. DSC measurements were carried out with a Perkin Elmer DSC 7 (heating and cooling rate: 20 K/min). The blend compositions in the text are given in wt/wt%.

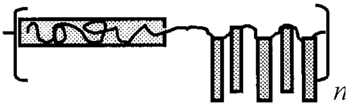
Thin films for surface characterization were prepared by spin coating (Headway Inc., USA, 2000 rpm/60 s) solutions of the blends (c_{pol}: 1 wt%, solvents: pentafluorophenol/ chloroform for BCP/PSU blends and chloroform for random copolymer / PSU blends) on pre-cleaned silicon wafer. The films were dried at 50 °C for 4 h in vacuum and then annealed at 200 °C in vacuum for 4 h. Dynamic contact angles were measured using ADSA-P[13] and water as probe. AFM measurements of the same surfaces were carried out by means of a Nanoscope III (Digital Instruments, USA) in tapping mode for both height and phase imaging (tapping frequency 70 kHz, free amplitude 4 V). The area roughness was estimated from $10 \times 10\ \mu m^2$ pictures by RMS. X-ray photoelectron spectroscopy was performed using an AXIS Ultra instrument (Kratos Analytical, UK) with $AlK\alpha_{1,2}$ radiation and pass energies of 160 eV or 20 eV, respectively.

Results and Discussion

Bulk Structure of the Semifluorinated Polyester and Block Copolymers

All polymers under investigation contain –oxydecylperfluorodecyl side chains ($-O(CH_2)_{10}-(CF_2)_9-CF_3$). The strong microphase separation in the pure semifluorinated polyester **1** is caused by the thermodynamic immiscibility between oxydecyl- and perfluorodecyl part of the side chains. The major reason for the extremely low surface free energy is the formation of a well-ordered surface layer of CF_3 groups which is supported by the highly ordered bulk structure.[14] This structure can be maintained in the segmented BCP **2** presumed a certain molecular weight of the semi-fluorinated blocks, i.e., the state of phase separation in the segmented block copolymers can be controlled by the molecular weights of both PSU and SF.[10,11] Three types of segmented BCP having different degrees of phase separation were examined with respect to their influence in blends with PSU (Figure 1).

Phase separated SF-PES/PSU block copolymers consist of domains containing the self-organized SF-side chains embedded in the amorphous PSU matrix (PSU segments).[10] This proposed structure model was confirmed by temperature-resolved SAXS/WAXS measurements.[10,11,20] A similar structure can be assumed based on WAXS/SAXS results for the random copolymers **3** independently on the concentration of SF-side chains.[12]



1) weakly phase separated BCP: SF-PES 3,600 g/mol / PSU 2,300 g/mol.
2) strongly phase separated BCP: SF-PES 9,000 g/mol / PSU 9,000 g/mol.
3) non-phase separated BCP: SF-PES 1,750 g/mol / PSU 9,000 g/mol.

Fig. 1. Schematic structure of the segmented polysulfone / semifluorinated polyester block copolymers (left: PSU block; right: SF-PES block).

Evaluation of Phase Separation in the Blends (Bulk Structure)

Blends of the semifluorinated polyester (poly(p-phenylene-oxydecylperfluorodecyl isophthalate) with PSU

Calculation of the Flory-Huggins interaction parameter χ between PSU and the semifluorinated polyester based on the solubility parameter concept [15,16] gave a χ of 13.6 referring to the strong demixing tendency between both polymers that should even be enforced by the self-organization of the SF-PES in domains. Accordingly, blends of **1** with polysulfone are completely immiscible, as illustrated in Figure 2 by the DSC curves (2nd heating) of solution precipitated blends.

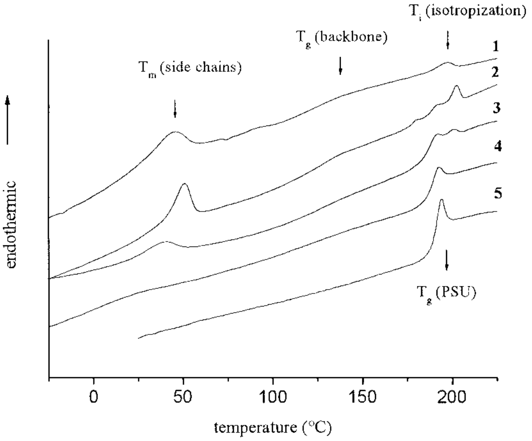


Fig. 2. DSC curves (2nd heating) of blends of semifluorinated polyesters and polysulfone with different composition (1: SF-PES; 2: SF-PES/PSU = 75/25; 3: SF-PES/PSU = 50/50; 4: SF-PES/PSU = 25/75; 5: PSU).

The SF-PES (curve 1) shows three distinct thermal transitions which were assigned recently by a combination of methods like DSC, temperature-resolved SAXS/WAXS, rheology and pVT measurements. [18,19] The first one is the melting of semifluorinated side chains that are then still trapped within the rigid lattice of backbones, the second one is the glass transition of the polyester backbone, causing simultaneously a smectic-smectic transition in the order, and the third one is the isotropization after that the polymer melt does not show signs of ordering, as detected by temperature-dependent SAXS. The blends of SF-PES and PSU show all transitions found in the SF-PES as well as the glass transition of PSU without change in temperature, referring to complete immiscibility.

Blends of segmented block copolymers with PSU

The influence of the segmented SF-PES / PSU block copolymers in binary blends with polysulfone was examined in dependence on the state of phase separation and the molecular weight of the block copolymer segments. It was expected that long PSU segments of block copolymers will mix with the PSU matrix while shorter ones form two phases (PSU matrix and PSU phase of the block copolymer). Semifluorinated polyester segments will, on the other hand, crystallize in their own domains if the BCP used in the blend is phase separated. DSC results obtained for blends with different composition are shown in Figures 3-5. The shift of phase behavior of the BCP in the blends is visible. Figure 3 shows the DSC curves of blends of PSU with the weakly phase separated BCP 1. The appearance of two glass transitions indicates the demixing of the amorpous phases of both PSU and SF-PES, whereas the crystallization (or self-organization in smectic layers) of semifluorinated side chains in the SF-block is suppressed due to the rather short block molecular weight. The blend of PSU with the strongly phase separated BCP 2 represents a partially miscible blend system. The DSC curves given in Fig. 4 show the typical melting transitions of side chain melting of SF-side chains at about 60 °C, which can additionally be detected by temperature-resolved SAXS. That means, extending the SF-block in comparison to BCP 1 induces an increased demixing not only in the block copolymer but also in the blend. Mixing PSU with a non-phase separated block copolymer (having only very short SF-blocks and long PSU blocks) results in a miscible blend, which can be detected by the appearance of only a single T_g.

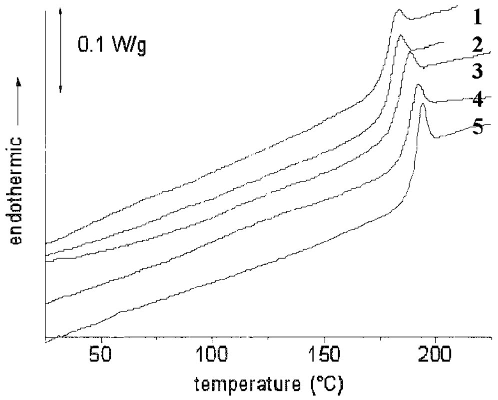


Fig. 3. DSC curves (2nd heating) of blends of a weakly phase separated block copolymer (SF-PES 3,600/PSU 2,300) and polysulfone with different composition (1: BCP; 2: BCP/PSU = 75/25; 3: BCP/PSU = 50/50; 4: BCP/PSU = 25/75; 5: PSU).

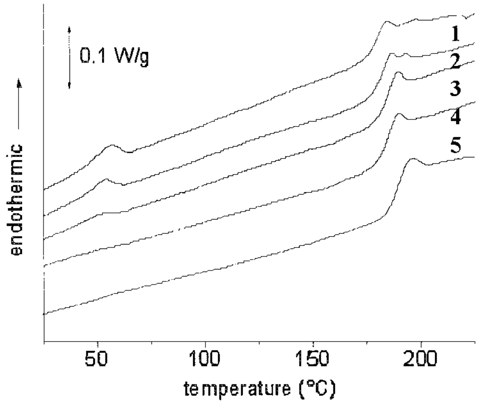


Fig. 4. DSC curves (2nd heating) of blends of a strongly phase separated block copolymer (SF-PES 9,000/PSU 9,000) and polysulfone with different composition (1: BCP; 2: BCP/PSU = 75/25; 3: BCP/PSU = 50/50; 4: BCP/PSU = 25/75; 5: PSU).

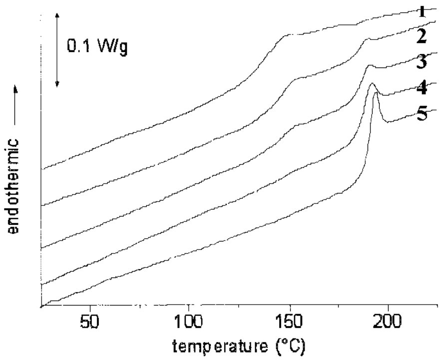


Fig. 5. DSC curves (2^{nd} heating) of blends of a non-phase separated block copolymer (SF-PES 1,750/PSU 9,000) and polysulfone with different composition (1: BCP; 2: BCP/PSU = 75/25; 3: BCP/PSU = 50/50; 4: BCP/PSU = 25/75; 5: PSU).

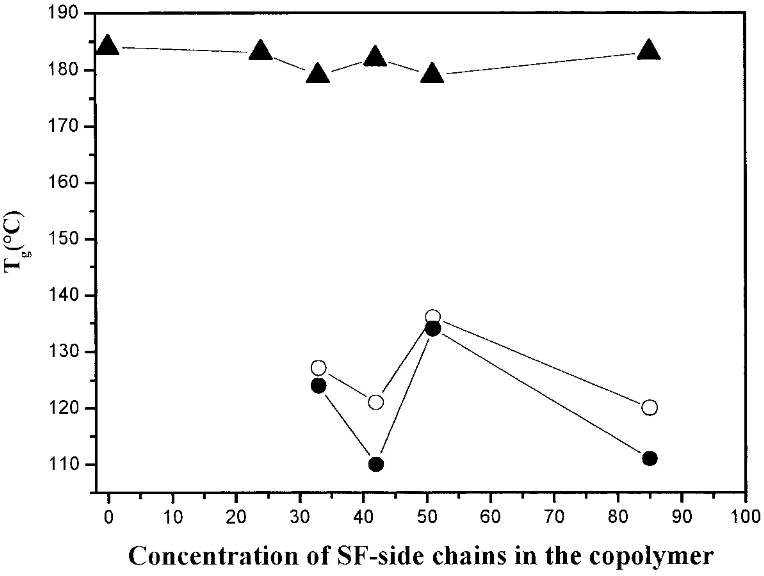


Fig. 6. T_g of blends (50/50 wt/wt) of polysulfone with copolymers of polysulfone with 4,4'-bis(oxyphenyl)pentanoic acid with -oxydecylperfluorodecyl side chains (○: T_g of copolymers; ● $T_{g,\ copolymer}$ in the blend; ▲: $T_{g,\ PSU\ matrix}$ in the blend).

Thus, it can be noted that the degree of phase separation in the blends can be controlled by the molecular weights of both, PSU and SF-PES segments in the BCP. The critical molecular weight of the PSU segments to achieve miscibility with the PSU matrix is in the region of 9,000 g/mol which is about four times the entanglement molecular weight of PSU and thus very high compared to other segmented PSU block copolymers investigated.[17] An explanation therefore is the self-organization tendency of the SF-PES enhancing the phase separation also in the blends enhancing the demixing in the blend.

Blends of semifluorinated random PSU copolymers with PSU

All blends of random PSU copolymers having different concentrations of SF-side chains are not miscible with PSU according to DSC results (Figure 6). Two glass transitions can be observed, the higher one caused by the PSU homopolymer and the second one by the random copolymer phase in the blend. Both T_g are only slightly shifted compared to the PSU matrix homopolymer and the pure random copolymers, indicating the strong immiscibility of the blend.

Surface Properties of the Blends

The surface properties of the blends were examined on thin films spin coated from a solution containing both blend partners on Si wafer. Thus, in most cases except the homopolymer blends smooth films with an averaged roughness between 5 and 30 nm were obtained. The roughness decreases after annealing above the glass transition of PSU (200 °C) to 2 – 16 nm. The roughness of these films does not influence the contact angles measured because it is well below the critical roughness in the order of several hundreds of nanometers up to 1 µm which was found in systematic contact angle investigations of polymer films.[21,22] The films were dried after spin coating at 50 °C and after measurement annealed to come closer to thermodynamic equilibrium. A real thermodynamic equilibrium in the samples will not be reached after procedure. The results obtained for the blends were interpreted using the results of wetting measurements of the block copolymer films reported recently. [10,11,20,22] For the segmented SF-PES/PSU block copolymers a dependence of the contact angle on the segment molecular weight of the semifluorinated segments was shown, i.e., the contact angle increases with raising molecular weight of the blocks.

The film thickness of the blend films were in the range of 150 to 250 nm, as determined by ellipsometry. We are well aware that in these thickness ranges influences of the film thickness, i.e., due to confinement effects, as described for diblock copolymers frequently (see, for instance, refs.[24,25] may play an important role. However, the thickness of all samples are comparable and the contact angles reported describe thus a certain, defined state after annealing. The situation may change if very thick films in the micrometer range are investigated.

Blends of the semifluorinated polyester (poly(p-phenylene-oxydecylperfluorodecyl isophthalate) homopolymer with PSU

Due to the high immiscibility of SF-PES and PSU the polymer films formed by spin coating on Si wafer are very heterogeneous. With only one wt% SF-PES, PSU films with high roughness having structural maxima of about 250 nm in height detected by AFM are obtained. The contact angle found here is 118° which is 13° higher than that of pure PSU and only 6° lower than that of the semifluorinated polyester. Higher concentrations of SF-PES in the blend cause highly rough surfaces with pretty low contact angles (see Figure 7) even after annealing which usually results in smoothing of spin coated films. Due to that reason films containing these semifluorinated aromatic polyesters **1** need indispensably compatibilization by block copolymers and cannot be used to get an exact information on surface free energies.

Blends of segmented block copolymers with PSU

Figure 7 summarizes the results of contact angle measurements (using water as probe) on surfaces of blends of block copolymers with PSU. It is obvious that the degree of phase separation in the blends also plays a major role for the wetting behavior of the films.

The wetting behavior of the completely immiscible PSU/SF-PES blend is strongly determined by the heterogeneous surface resulting from demixing during blend preparation, drying and annealing. The low contact angles are due to these heterogeneous surfaces. The miscible blend shows contact angles that almost follow an additivity rule between those of PSU and the respective block copolymer. Thus, the miscible blends behave like a copolymer. The good mixing of both polymers prevents obviously additional surface segregation of the SF-blocks of BCP 3. In contrast, higher contact angles than in the pure blend components are found on surfaces of partially miscible blends which can only be explained by segregation of SF-PES segments from their phase separated domains to the surface. A comparable effect was found earlier on films of the pure block copolymers having a phase separated surface morphology.[22]

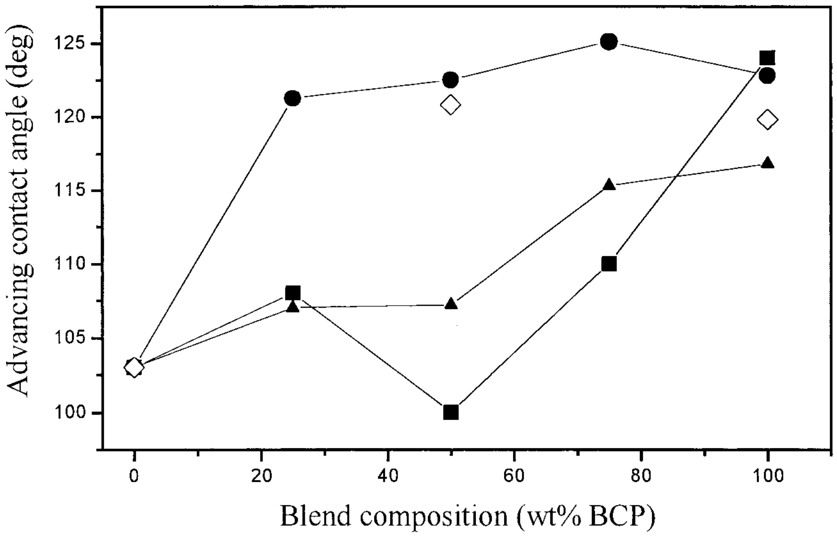


Fig. 7. Water contact angle on surfaces of thin films of blends consisting of PSU and segmented BCP (SF-PES/PSU), all samples annealed for 4 hrs at 200 °C in vacuum.

■: immiscible homopolymer blend of PSU with SF-PES
●: partially miscible blend of PSU with BCP 2
◇: immiscible blend of PSU with BCP 1
▲: miscible blend of PSU with BCP 3.

Surface segregation of the semifluorinated side chains was proven by XPS investigation. The results for blends of BCP 3 and PSU are given in Table 1. The surface segregation is stronger in the blends than in the pure BCP which might be due to the stronger fixation of SF chains in the ordered SF domains in the BCP than in the SF domains of the blend (lower degree of ordering).

Surface segregation is fostered by consecutive *annealing* of the samples. Annealing (temperature and time) of the partially miscible blends causes the decrease of roughness of the films (see as an example the development of roughness in the blend (BCP 2 (SF-PES 9,000 / PSU 9,000) / PSU in dependence on the annealing temperature in Table 2), and a slight change of contact angle. In contrast, the contact angles of miscible BCP/PSU blends (for example BCP 3/PSU) are increased by annealing which seems to be induced by a dewetting process of the miscible film from the substrate, as observed by AFM. The dewetting process causes a higher roughness than in the original sample, as reported earlier in ref. [24] The film roughness can also be controlled by the composition of the blend as illustrated in Figure 8 for different binary and ternary blends of PSU, SF-PES and block copolymers. The addition of BCP always results in smoothing of the films.

Table 1. [F]/[C] ratio found by XPS at different take-off angles in blends of BCP 2 (SF-PES 9,000 / PSU 9,000) / PSU after annealing at 200 °C for 4 h.

[F]/[C] ratio	Blend composition (BCP 2 / PSU) 25/75	50/50	72/25	BCP 2
take-off angle 60°	0.582	0.531	0.554	0.480
take-off angle 45°	0.550	0.542	0.553	0.450
take-off angle 0°	0.564	0.556	0.590	0.500

It could be shown that addition of 5 wt% of the block copolymer to the homopolymer blend results in a significant decrease of roughness of the samples (#6 in Fig. 8).

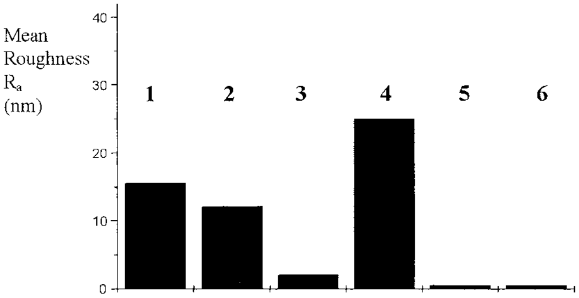


Fig. 8. Roughness R_a determined by AFM of binary and ternary blends of PSU, SF-PES and BCP with different composition.
(1: PSU / BCP (PSU 2300/SF-PES 1850), (25/75); 2: PSU / BCP (PSU 2300/SF-PES 1850), (50/50); 3: PSU / BCP (PSU 2300/SF-PES 1850), (75/25); 4: SF-PES / BCP (PSU 2300/SF-PES 1850), (95/5); 5: PSU / BCP (PSU 2300/SF-PES 1850 g/mol), (95/5); 6: PSU / SF-PES / BCP (PSU 2300/SF-PES 1850 g/mol), (75/20/5).

Table 2. Roughness of films of blends of BCP 2 (SF-PES 9,000 / PSU 9,000) and PSU in dependence on the annealing temperature (annealing time: 4 h).

R_a (nm)	Blend composition (BCP / PSU)		
	25/75	50/50	75/25
annealed at 90 °C	7.4	16.5	28.0
annealed at 150 °C	8.0	13.5	27.0
annealed at 200 °C	2.1	12.2	15.6

Blends of semifluorinated random PSU copolymers with PSU

In spite of the strong immiscibility of the blends smooth films could be prepared by spin coating the blend solutions. However, contact angles obtained on dried and annealed blend films showed a significant difference to the pure copolymers with semifluorinated side chains (Figure 9).

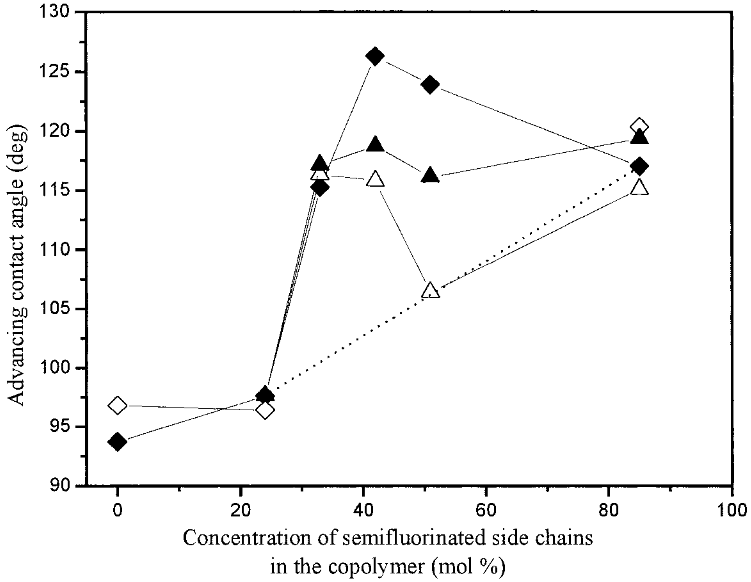


Fig. 9. Contact angles of PSU copolymers with semifluorinated side chains and their 50/50 (wt/wt) blends with PSU, dried (50 °C / 4 h / vac) and after annealing (200 °C / 4 h / vac) (◆: copolymers, dried; ◇: copolymers, annealed; ▲: blends, dried; Δ: blends, annealed).

The contact angles of 50/50 (wt/wt) blends of the copolymers with PSU are lower than those of the pure copolymers. Annealing only slightly affects the advancing contact angles of the copolymers.

Conclusion

Segmented block copolymers of polysulfone and semifluorinated polyesters with medium segment molecular weights are more effective to compatibilize blends with the PSU homopolymer than random PSU copolymers with semifluorinated substituents distributed along the polymer chain. The reason is the strong self-organization of the semifluorinated chains in the latter preventing the mixing of the phases. Partial miscibility between the segmented BCP and PSU matrix in a blend is a necessary requirement to obtain homogeneous, stable surfaces with low surface free energy because partial demixing allows surface segregation of non-self organized semifluorinated chains. Thus, control of phase separation in the bulk and at the surface is possible in such blends and can successfully be used to tailor surface properties of films.

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