

## **Compatibilization of polysulfone/polyamide-blends by reactive polysulfones - evidence for copolymer formation**

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### **Summary**

In order to compatibilize polysulfone/polyamide-blends by reactive blending melt blending studies using polysulfones with different functional groups (carboxyl-, anhydride) and polyamide were performed in a batch-type mixer. The obtained materials were investigated by solvent extraction and transmission electron microscopy. Model experiments reveal the possibility to compatibilize polysulfone/polyamide-blends by reactive blending techniques using functionalized polysulfones. Extraction studies as well as the morphologies of the prepared samples give evidence for a copolymer formation during the melt blending experiments.

### **Introduction**

Blending of immiscible polymers has become a popular route to develop materials with new properties [1-2]. In order to increase the rather limited number of applications for high performance polymers like polysulfones, polyethersulfones and polyetherimides, blends with engineering thermoplastics like polyamides, polyesters or polycarbonates are of high potential. The amorphous polyarylethers (polyethersulfone, polysulfone) offer high heat resistance, dimensional stability and good mechanical properties. Like many other amorphous thermoplastic materials, these products have low stress crack resistance and high melt viscosities. Therefore blending of polyarylethers with partially crystalline polymers like polyamides, which have excellent stress crack resistance and good flow properties, could be an appropriate way to new materials with tailor-made properties.

Since polyarylethers and polyamides are completely immiscible the mechanical properties of the binary blends are very poor [3-4]. Different ways to compatibilize polyarylether/polyamide-blends are known from the literature. Several authors use PSU-b-PA prepared by anionic polymerization techniques starting from polysulfone or amino-terminated polysulfones and caprolactam [4,5-7] as compatibilizer. Reactive blending techniques have also been elaborated to compatibilize polyarylether/polyamide blends [8-10], mainly using reactions between attached anhydride functionalities and terminal amino-groups of polyamides.

In a previous paper we investigated the strength of polysulfone/polyamide interfaces

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which were modified by using polysulfones with different functional groups. Polysulfone grafted with maleic anhydride (PSU-g-MA) gave a significant increase in interfacial

strength between polysulfone and polyamide [11]. This effect was explained by an in situ copolymer formation during the annealing steps.

Starting from polysulfones with various functional groups (carboxyl-, different anhydride-), model experiments were performed to evaluate their reactivity towards polyamides during melt mixing.

### **Experimental part**

For the reactive blending studies polysulfones with different types of functional groups (Scheme 1) were synthesized [10-13]. 4,4'-bis(4-hydroxyphenyl) valeric acid (Diphenolic acid, DPA), maleic anhydride (MA), bisphenol A, 4,4'-dichlorodiphenylsulfone (DCDPS) and dicumylperoxide were obtained from Aldrich, 4-fluorophthalic anhydride was obtained from Fluorochem. N-methyl-2-pyrrolidone (NMP) was dried over  $\text{CaH}_2$  and distilled. The molecular weight ( $M_n$ ) of the polysulfones was determined by GPC ( $\text{CHCl}_3$ , Polystyrene-calibration). The glass transition temperatures were determined using a Perkin-Elmer DSC-7 operating at a heating rate of 20 k/min.

#### **nf-PSU:**

287,08 g (1 mol) 4,4'-dichlorodiphenylsulfone, 223,83 g bisphenol A (0,9805 mol) and 140,97 g (1,02 mol)  $\text{K}_2\text{CO}_3$  were dissolved in 1600 ml dry NMP. The mixture was heated to 190°C for 6 h in a nitrogen atmosphere. During this time the azeotropic mixture of NMP and water was continuously removed. The solution was cooled to room temperature, diluted with NMP (1600 ml) and filtered. After this procedure the polymer was isolated by precipitation in water. The polymer was extracted 3 times with hot water and dried. The amount of Chlorine-endgroups was 98 % (detected by elemental analysis). The properties of this product are summarized in Table 1.

#### **PSU-g-MA:**

50 g of nf-PSU were dissolved in chlorobenzene, the solution was heated to reflux. 11,3 g of maleic anhydride and 3,5 g dicumylperoxide were added over a period of 4 hours. After refluxing for another hour the solution was cooled to room temperature and the polymer was isolated by precipitation in ethanole. The polymer was filtered and redissolved in NMP and again precipitated in a mixture of NMP/ $\text{H}_2\text{O}$  (1:4). After filtration the polymer was extracted with hot water and dried. The amount of anhydride groups was determined by potentiometric titration. The properties of the product are given in Table 1.

#### **PSU-COOH:**

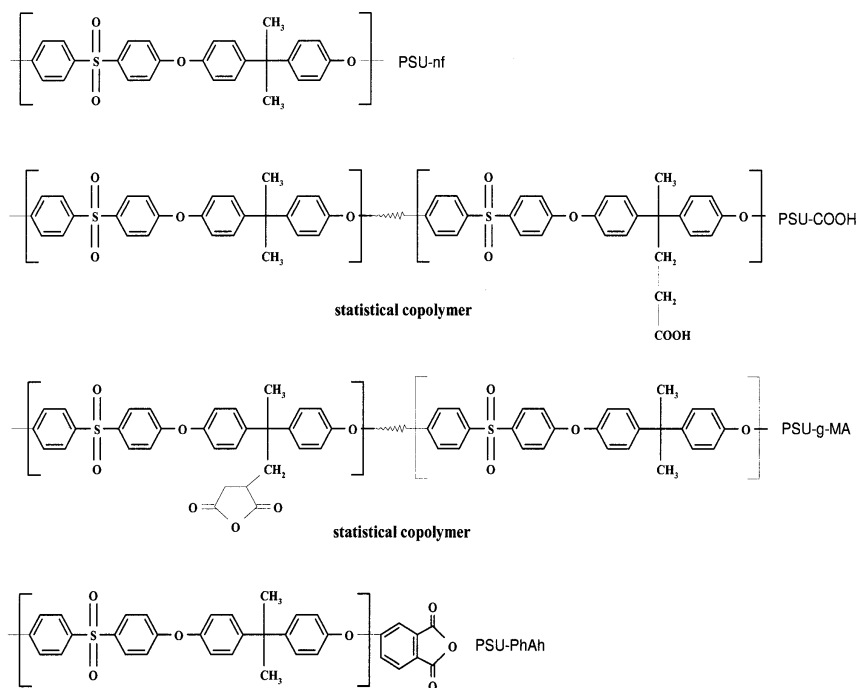
86,12 g (0,3 mol) 4,4'-dichlorodiphenylsulfone, 63,92 g (0,278 mol) bisphenol A, 4,21 g (0,0147 mol) diphenolic acid (DPA) and 42,29 g (0,306 mol)  $\text{K}_2\text{CO}_3$  were dissolved in 600 ml dry NMP. The mixture was heated to 190°C for 6 h in a nitrogen atmosphere. During this time the azeotropic mixture of NMP and water was continuously removed. The solution was cooled to room temperature, diluted with NMP (600 ml) and filtered.

After this procedure an excess of acetic acid was added to the solution and after further stirring (30 min) the polymer was isolated by precipitation in water. The polymer was extracted 3 times with hot water and dried. The amounts of incorporated DPA units were estimated using  $^1\text{H-NMR}$ -spectroscopy (in  $\text{CDCl}_3/\text{CF}_3\text{COOD}$  1:1). The ratio of monomer units derived from DPA and bisphenol A was calculated using the signal intensities in the  $^1\text{H-NMR}$ -spectra, taking into account the signal intensities of the  $\text{CH}_2$ -groups of DPA ( $\delta = 2,2$  ppm and  $2,5$  ppm) with respect to the signal intensity of the  $\text{CH}_3$ -groups of the units derived from bisphenol A ( $\delta = 1,6$  ppm). From this number the amount of incorporated DPA-units (wt.%) was calculated. The properties of this product are summarized in Table 1.

### PSU-PhAh:

274,65 g (0,9567 mol) 4,4'-dichlorodiphenylsulfone, 228,28 g (1 mol) bisphenol A and 140,97 g (1,02 mol)  $\text{K}_2\text{CO}_3$  were dissolved in 1600 ml dry NMP. The mixture was heated to  $190^\circ\text{C}$  for 7 h in a nitrogen atmosphere. During this time the azeotropic mixture of NMP and water was continuously removed. After this time 26,58 g (0,16 mol) of 4-fluorophthalic anhydride and 9,3 g (0,16 mol) of KF were added and the solution was further stirred for 10 minutes. The solution was cooled to room temperature, diluted with NMP (1600 ml) and filtered. After this procedure the polymer was isolated by precipitation in water. The polymer was extracted 3 times with hot water and dried. The amount of phthalic anhydride endgroups was determined by FT-IR. The properties of this product are also included in Table 1.

Scheme 1: Chemical structures of the used polysulfones



For the blending studies a copolyamide consisting of units derived from caprolactam, hexamethylene diamine and terephthalic acid (PA 6,6T,  $T_g=100^\circ\text{C}$ ,  $T_m=285^\circ\text{C}$ , 126  $\mu\text{mol/g}$   $\text{NH}_2$ -endgroups) was used. Melt blending experiments were performed using a Haake Mixer (Rheomix 600) operating at a temperature of  $310^\circ\text{C}$ . The materials were melt mixed for 5 minutes, quenched, dried and grinded. The compositions of the blends are given in table 2.

Table 1: Properties of the used polysulfones

product	Mn [g/mol]	Tg [ $^\circ\text{C}$ ]	equiv. functional groups [ $\mu\text{mol/g}$ ]
PSU-nf	5000	179	0
PSU-g-MA	5400	175	100
PSU-COOH	4400	173	37,0
PSU-PhAh	4900	175	205

The melt blended samples were analysed using a solvent extraction method, where dimethylformamide (DMF) was used to extract the polysulfone matrix phase. The insoluble material was separated using either filtration or centrifugation. In a subsequent step the insoluble material was analyzed by extraction with formic acid (HCOOH), which acts as a selective solvent for the polyamide. The insoluble material was again separated and counted as in situ formed copolymer. To separate polysulfone inclusions the insoluble material (after DMF and HCOOH extractions) was further extracted with DMF.

Table 2: Composition of the blends and results of the extraction experiments

sample	1	2	3	4
PSU-nf	80	---	---	---
PSU-g-MA	---	80	---	---
PSU-COOH	---	---	80	---
PSU-PhAh	---	---	---	80
PA	20	20	20	20
<b>DMF-extraction</b>				
soluble fraction [wt.%]	81,3	79,6	79,9	74
insoluble fraction [wt.%]	18,7	20,4	20,1	26
<b>HCOOH-extraction of the insoluble DMF-fraction</b>				
soluble fraction [wt.%]	99,7	85,7	90,6	67,0
insoluble fraction [wt.%]	0,3	14,3	9,4	33,0 (27)

Transmission electron microscopy (TEM) was used to image the particle size of the dispersed polyamide phase. The ultra thin sections were stained with  $\text{RuO}_4$ , which predominantly reacts with the polysulfone phase. TEM was performed in the bright field mode on a Hitachi H 7100 transmission electron microscope operating at 125 kV.

## Results and discussion

Blends with a 80:20 composition of polysulfone-compound to polyamide were prepared in the Haake Mixer. At this composition the matrix phase is formed by polysulfone, therefore selective extraction of the polysulfone using DMF as solvent is possible to separate unreacted polysulfone. In all blends with modified polysulfones a higher amount of insoluble material was detected compared to the blend of the polysulfone without reactive endgroups. The highest deviation was found in the case of sample 4, where the phthalic anhydride terminated polysulfone was used. To separate the unreacted polyamide, the insoluble material was further extracted with formic acid. As can be seen from table 2, in the case of blend 1 only a very small amount of insoluble material was observed, indicating that no copolymer formation has taken place. In the blends containing functionalized polysulfones much higher amounts of material remained insoluble, indicating the formation of copolymers during melt blending.

The highest amount of copolymer was formed in the blend using PSU-PhAh whereas the lowest amount of copolymer was detected in the system with PSU-COOH as reactive polysulfone. This result of course is related to the much higher reactivity of the anhydride-functionality as well as to the absolute number of reactive sites (table 1). All in situ formed copolymers were completely soluble in 1,1,1,3,3,3-hexafluoroisopropanole, indicating that no crosslinked products have been formed.

The influence of the functional groups on the particle size of the dispersed polyamide phase can be seen from the TEM-images of the samples (figure 1 to 4).

In the sample where non-functionalized PSU was used, the dispersed PA-particles have a ellipsoidal shape with a size (long axis) up to 2  $\mu\text{m}$  (figure 1), whereas all samples which contain modified polysulfones have much smaller dispersed particles (figure 2 to 4).

Although only a small amount of copolymer was formed in sample 3, the particle size of the dispersed PA-phase is significantly reduced compared to the blend with non-functionalized PSU (figure 3). Beside the very small particles with 0,2 to 0,4  $\mu\text{m}$  diameter some bigger particles are also visible. The sample with PSU-g-MA modifier has a very homogeneous particle size distribution with a particle size of the dispersed phase from 0,2 to 0,5  $\mu\text{m}$ . In all these samples almost no polysulfone inclusions could be detected. Sample 4, where PSU-PhAh was used as reactive polysulfone has a particle size of the PA-particles between 0,2 and 0,8  $\mu\text{m}$ . The TEM-image of this sample (figure 4) also shows a significant amount of polysulfone inclusions in the PA-phase.

To separate the inclusions from the in situ formed copolymers, the insoluble material of sample 4 after DMF and HCOOH extraction was again extracted with DMF. The final amount of copolymer is also given in table 2 (value in brackets).

Although a qualitative correlation between the amount of formed copolymer and the particle size of the dispersed phase was observed several features have to be discussed in more detail. Taking into account the big difference in reactivity towards amino-groups between carboxyl- and anhydride-groups as well as the difference in available reactive sites, the small particle size of sample 3, which contains COOH-modified polysulfone is unexpected. Possible explanations for the observed morphology might be the existence of H-bonds between PA and PSU-COOH as well as a more favourable

viscosity ratio in that blend due to the significantly lower molecular weight of PSU-COOH [14]. Further studies will deal with these questions.

Fig. 1: PSU-nf/PA 80/20, stained with  $\text{RuO}_4$

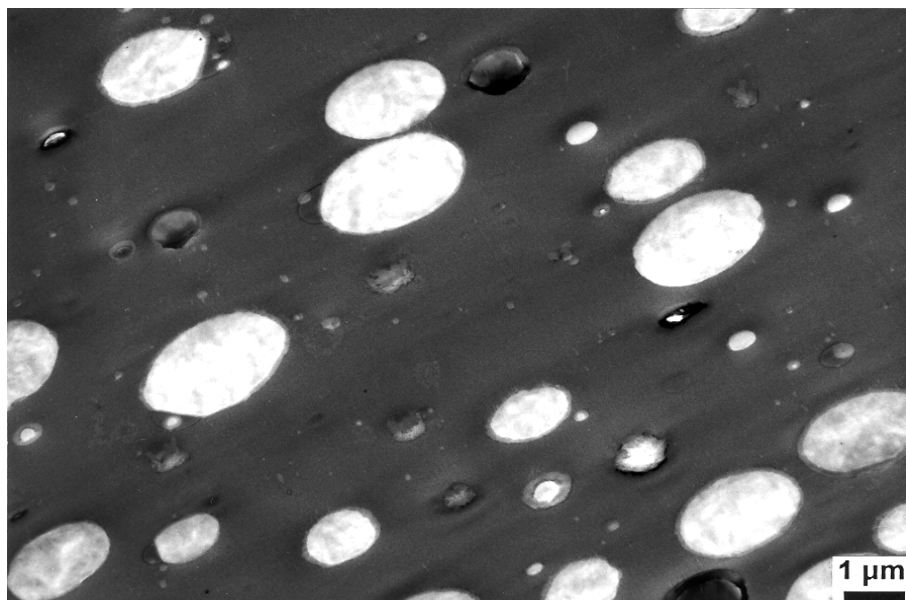


Fig. 2: PSU-g-MA/PA 80/20, stained with  $\text{RuO}_4$

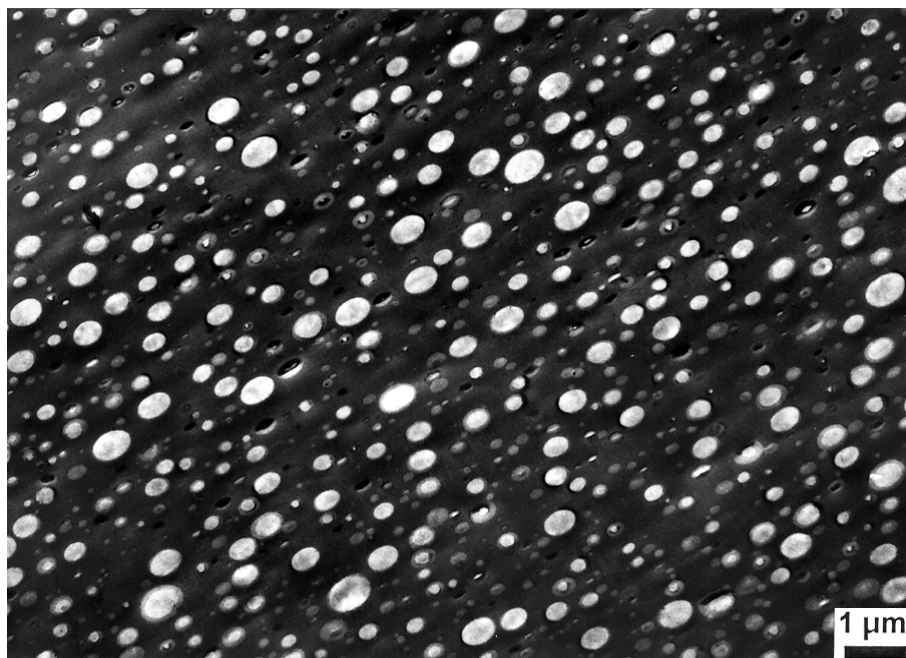


Fig.3: PSU-COOH/PA 80/20, stained with  $\text{RuO}_4$

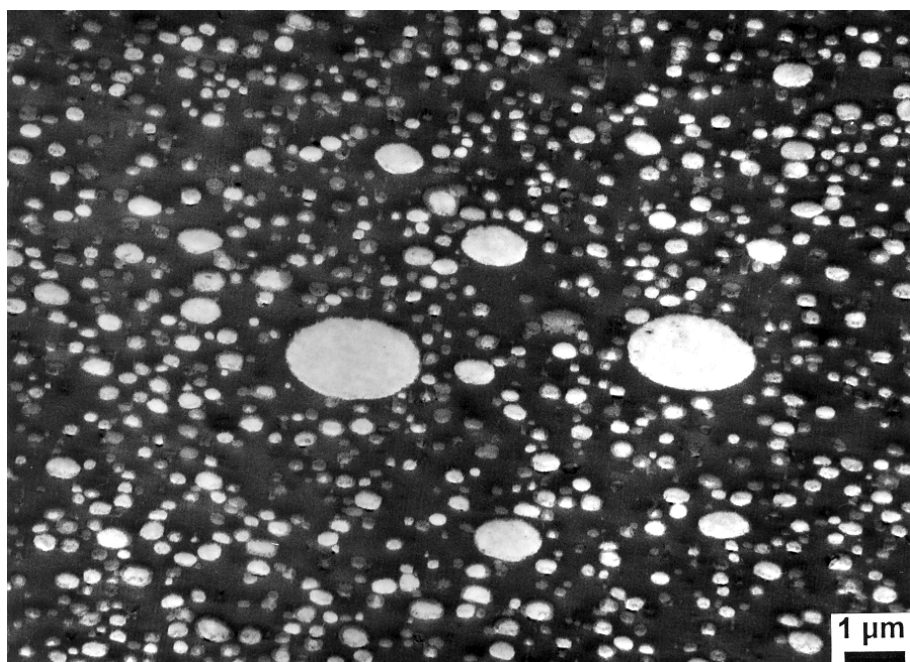
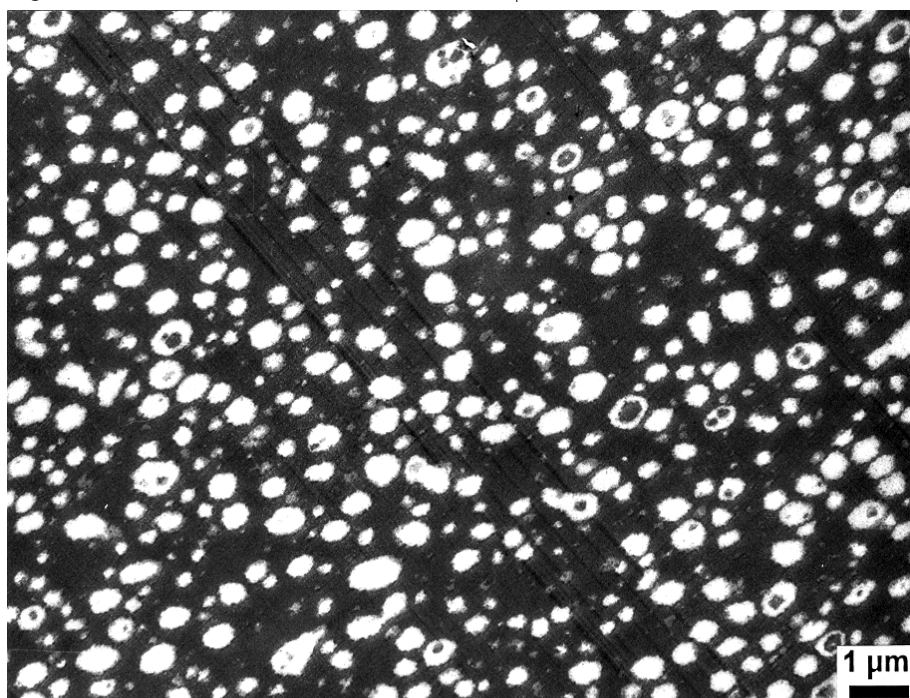


Fig. 4: PSU-PhAh/PA 80/20, stained with  $\text{RuO}_4$



The comparison between the morphologies of samples 2 and 3, where the in situ formed copolymers should be PSU-g-PA, with the morphology of sample 4, where a PSU-b-PA should have been formed, suggest an influence of the chain topology of the in situ formed copolymer on the final morphology of the blend. To clarify this question we will also study the morphology of the in situ formed copolymers.

## Conclusions

Model experiments reveal the possibility to compatibilize polysulfone/polyamide blends by reactive blending techniques using functionalized polysulfones. Extraction studies as well as the morphologies of the prepared samples show evidence for a copolymer formation during the melt blending.

## Acknowledgement

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