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The influence of wettability on the morphology of blends of polysulfones and polyamides

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In this paper we are presenting structural investigations on the phase separation behaviour of a novel high temperature stable polymer blend of a polysulfone (PSU) and a perfectly amorphous polyamide (PA). The phase separation kinetics of thin films cast onto glass slides and of bulk samples was observed by means of various microscopic methods such as optical, laser scanning confocal, scanning electron and transmission electron microscopy. The phase separation process was found to be suppressed by adding a small amount of compatibilizers such as chemically modified PSU, i.e. introducing a small amount of carboxylic groups, which causes the formation of covalent bonds with the PA at the interface of the PSU and PA or by adding a third component, phenoxy, which is supposed to be mainly located at the interface of the PSU and PA and to freeze the phase separation due to its attraction to both the PSU and PA. © 1997 Elsevier Science Ltd.

(Keywords: polysulfone; polyamide; blend)

INTRODUCTION

In order to obtain a polymer material with special properties, i.e. thermoplastic elasticity, high temperature stability, etc., it is advantageous to blend polymers in order to combine the features of the different components. If two polymers have very different physical properties, they are usually also immiscible, meaning that they will phase-separate if we keep them in the two phase region of their phase diagram. This is the case for a large number of industrially interesting polymer mixtures.

A phase separation, however, even if it is very slow, is practically not wanted, as it will lead to macrophase separation and therefore to a change of the original thermal and mechanical properties of the material. Block or graft copolymers can act as compatibilizers[1,2] similar to surfactants in oil and water systems, by lowering the interfacial tension between two immiscible polymers. Introducing covalent bonding between the two polymers at the interface[3,4] the growth of the phase-separated structure of a polymer blend in the interactive blending process can be frozen. At the same time the chemical connection of the two phases is usually increasing the mechanical strength of the material[5].

In this paper we first describe results on the attempt to compatibilize a novel high-temperature-resistant polymer alloy of a polysulfone (PSU) and a polyamide (PA) by functionalization of the PSU and grafting the PA onto this modified PSU. We will discuss the influence of the compatibilization on the phase separation of thin films cast on a glass substrate and of bulk samples by using various microscopic methods such as transmission optical (TOM), laser scanning confocal (LSCM), scanning electron (SEM) and transmission electron microscopy (TEM).

In bulk samples the Flory–Huggins segmental interaction parameter of the component polymers is mainly responsible for the phase-separating domain structure at a given time and temperature for a given set of molecular weights and compositions. If very thin films of the mixtures are attached to a substrate, the interaction between the substrate and the polymers also becomes very important and will strongly affect the structure formation in the film. This phenomenon is well known as wetting. The physicochemical parameters controlling the thermodynamic wettability were first described in detail by Zisman and Fowkes[6]. A review was given by de Gennes[7].

One of the parameters describing the wettability is the contact angle Θ_e, which is formed at the edge of the liquid/substrate interface and depends on the surface energy of the two components against the substrate, which again is correlated to their chemical constitution. In principle one can say, the closer the chemical constitution of a liquid and substrate is, the better the wettability and the smaller the contact angle will be in the thermodynamical equilibrium.

Here we do not want to discuss quantitative features in

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detail, but concentrate more on the kind and stability of a structure, which is formed from a mechanically mixed and as-cast sample during annealing at temperatures above the glass transition temperatures T_g's of the component polymers, which are usually very high. In the second step the influence of compatibilization on the morphologies will be evaluated.

EXPERIMENTAL

The polysulfone has an average molecular weight (M_w) of 3.78×10^4 and a glass transition temperature (T_g) of 188°C. The modified PSU was obtained by introducing carboxylic acid functions (COOH) to the aromatic ring by a two step reaction as given in *Scheme 1*. Details are given elsewhere[8,9]. Modified PSU carrying different amounts of COOH-groups (3.7 wt% and 4.6 wt%) were used. They have T_g's of 178°C and 176°C, respectively. The amorphous PA[10] with an average molecular weight (M_w) of 1.4×10^4 (*Scheme 2*) has a T_g of 130°C. Phenoxy (*Scheme 3*) is supposed to be a compatibilizer and has an average molecular weight (M_w) of 2.50×10^4 and a glass transition temperature (T_g) of 100°C.

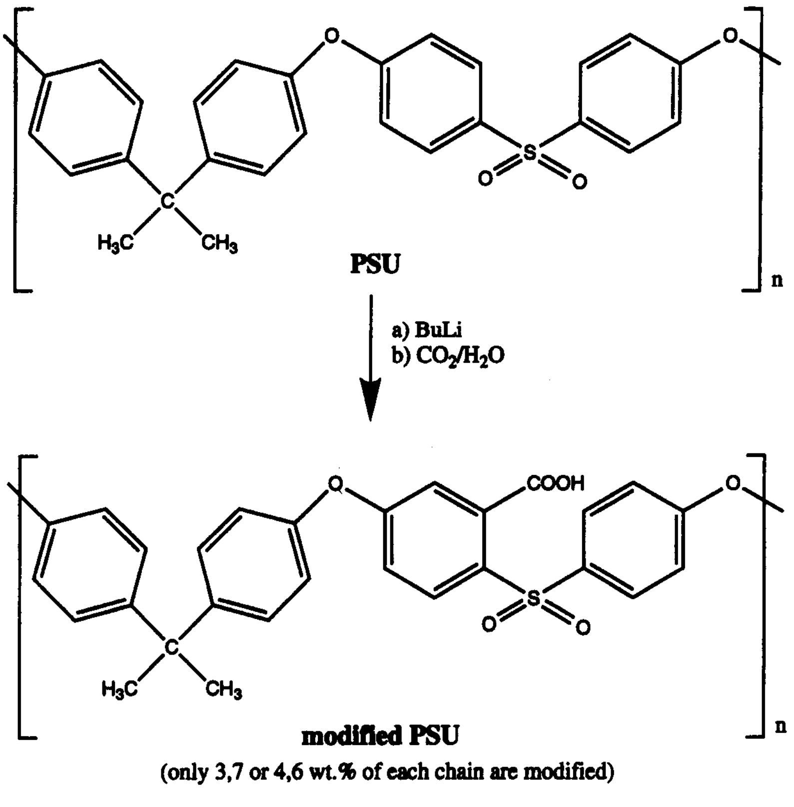
The blending was done using a twin-screw-extruder ZSK3 for 2 min at 300°C (10 kg h^{-1} throughput, 250 rpm). The thus obtained samples were used for either preparing a bulk-sample specimen (i) or after dissolution for preparation of thin films (ii). The compositions of the respective blends are listed in *Table 1*; (i) the bulk sample was prepared by mounting the as-extruded specimen between two glass slides and mixing them under slight pressure for a few seconds at 250°C and afterwards allowed to cool down to room temperature. The thus obtained polymer layer was about 50 μm thick. (ii) For the preparation of the solution-cast thin films the blends were dissolved in N-methyl pyrrolidone (NMP), which is a good common solvent for all polymers, total polymer weight being approximately 1 wt%. A few drops of each solution were put onto glass slides and allowed to evaporate at 90°C under vacuum for about 5 min to form thin films of about 5 μm thickness.

The specimens were annealed using a microscope hot stage (Linkam TH-600R; Hitech Co. Ltd., Japan) and the coarsening process of the blends during annealing at high temperatures (250–300°C) was observed by an optical microscope (Optiphot-pol; Nikon) in transmission mode.

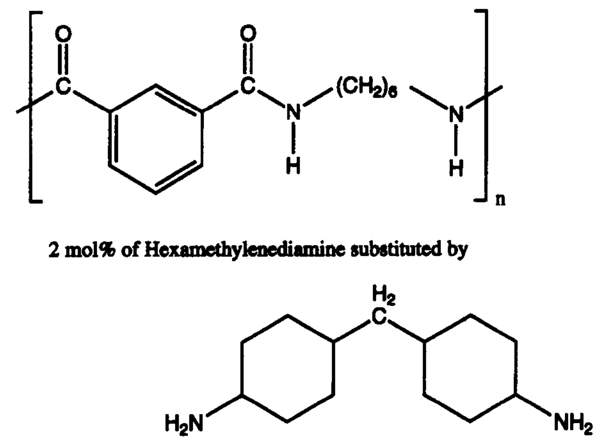
For laser scanning confocal microscopic investigations no further special treatment of the sample was required. LSCM was done with a LSM320 (Zeiss) using a He/Ne laser with $\lambda = 632.8$ nm wavelength and image processing was done with the optional firm software. A detailed description of the apparatus[11] and the image generation can be found in literature[12].

Scanning electron microscopy (Hitachi S4000) was done after cooling of the respective samples to room temperature, which is far below the T_g of the components. To avoid electrostatic charging and to optimize the compositional contrast, the sample surfaces were coated with a thin carbon layer. No further special treatment was necessary. Element dispersive X-ray spectroscopy (EDX) was performed with the optional detection system using an acceleration voltage of 10 keV.

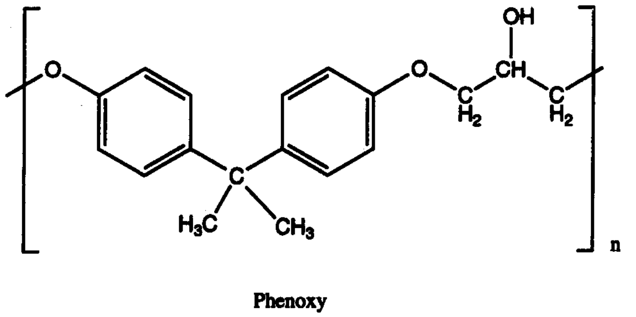
Transmission electron microscopy was performed with a Hitachi H-7100 using an acceleration voltage of 100 kV. The ultrathin sections were obtained using an ultramicrotome Reichert and Jung at room temperature. The presented TEM image showed a natural compositional contrast and therefore no further staining was required. In case of the sample SUAph the phenoxy



Scheme 1



Scheme 2



Scheme 3

Table 1 Characteristics of the polymer blends used in this work and their specimen codes

Specimen code	PA amorphous (wt%)	PSU (wt%)	PSU modified 3.7 wt% COOH (wt%)	PSU modified 4.6 wt% COOH (wt%)	Phenoxy (wt%)
SUA	33.4	66.6	—	—	—
SUA37	33.4	53.3	13.3	—	—
SUA46	33.4	53.3	—	13.3	—
SUAph	33.4	53.3	—	—	13.3

could not be made visible neither by staining with RuO_4 nor with phosphoric tungsten acid (PTA).

RESULTS AND DISCUSSION

Wetting phenomenon of as-cast samples

Pure PSU/PA blend. The morphology of the thin as-cast film of SUA developed during the phase separation process at 290°C as observed by TOM is shown in *Figure 1. Figure 1a* was recorded immediately after the sample reached 290°C: droplet-like phase corresponds to the PA and the matrix to the PSU as evaluated from their volume fractions. During annealing these structures show a coarsening process. At first the droplets are growing until about 2 min have passed (*Figures 1b,c*) and the PSU matrix remains to be a continuous phase. After 4 min (*Figure 1d*), however, the matrix begins to break up to form a new dispersed phase after 10 min (*Figures 1e,f*). The dimensions of these structures are several times larger than those obtained at the initial state. We will call this phenomenon 'phase inversion'.

In *Figure 2* we probed the structures formed after annealing for 10 min at 290°C (see *Figure 1f* for TOM) by SEM (*Figures 2a* and *2b*). The microscopy was performed after quenching from 290°C to room temperature which is far below the T_g of all of the components. For the detection of the SEM images (*Figure 2a*), an annular backscatter detector was used. This detector is sensitive to high energy elastically scattered electrons, the intensity of which strongly depends on the atomic number. Therefore a backscattered electron image has a compositional contrast. In our samples, the PSU-phase is expected to be bright compared to the PA-phase, as the PSU contains sulfur with the heaviest atom of the two components. As a matter of fact, however, the contrast is just the opposite. We interpret this puzzle as follows: we assume that the PA-phase is thinner than the PSU-phase and that the major amount of the detected backscattered electrons are released by the glass substrate. Hence more backscattered electrons are detected from the PA phase than from the PSU phase because the backscattered electrons from the substrate are absorbed less through the former phase than the latter one. Our assumption is verified by the EDX spectra as given in *Figure 3*. The dotted line corresponding to a scan of the dark area shows a strong sulfur peak, which identifies this phase as the PSU, and the solid line represents the spectrum of the bright area, which is then the PA. The very strong silica peak as well as the signals of sodium, calcium and magnesium are caused by the glass substrate. In the case of the PSU the polymer layer is much thicker, therefore the silica peak is much weaker.

As we can see in *Figure 2a*, the SEM image gives a 3-dimensional impression showing that the dark phase sticks out. More detailed information about the 3-dimensional structure of the surface was obtained by analysing the fractured surface of the sample as depicted in *Figure 2*. The scheme given in *Figure 2c* illustrates the orientation of the specimen in *Figure 2b*. We can estimate the thickness of the polymer layer by simply measuring the dimensions on the SEM image. The height of the out-sticking phase corresponding to the PSU can be estimated to about 5 μm, while the lower PA-phase is only around 2 μm.

By detecting the strong reflection of the polymer/air interface with the LSCM we can obtain useful information about the shape and dimensions (topology) of the surface of the polymer layer. In order to obtain such a 3-dimensional topographic image, a series of 20 LSCM slices with a step width from one slice to the other of 0.5 μm was recorded and stack along the z-axis. The corresponding scanning geometry is given in *Figure 4*. The result is a topological image as seen in *Figure 5a*. By plotting the points showing maximum within a 3-dimensional Cartesian coordinate system we obtain *Figure 5b*. One of the y, z-cross section is given in *Figure 5c* and therefrom we can estimate the height difference of the out-sticking phase to the lower one with about 3 μm, which is in agreement with the data we obtained using SEM.

Since the thickness of the film specimen is only a few micrometres, the wetting behaviour of the different polymers on glass should have a tremendous influence on the morphology which is obtained during the

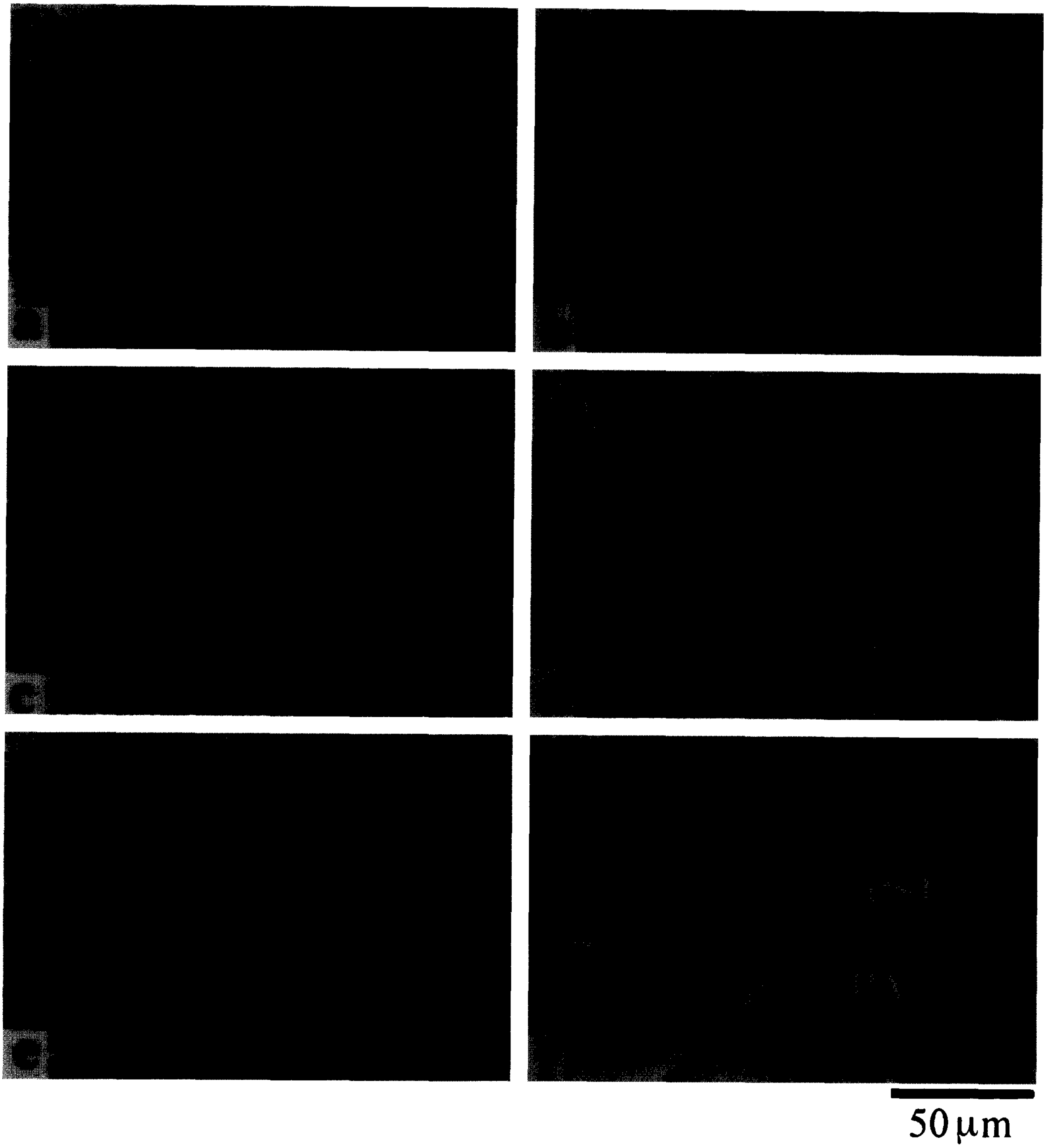


Figure 1 Series of TOM micrographs obtained on the same field showing the time evolution of the phase separated domain structures of SUA annealed at 290°C. (a) As cast sample and the samples annealed for (b) 45 s, (c) 2 min, (d) 4 min, (e) 5 min and (f) 10 min

annealing procedure. Wetting phenomena originate from the polarity of molecules. In order to get information about the attraction of the two polymers to a polar substrate like glass, we measured the contact angles of the respective polymers against water at room temperature. For PSU and PA we found 78° and 57° respectively. From the much larger contact angle observed for the PSU, we can conclude that the contact surface of the PSU is much smaller than that of the PA. As the glass surface is very polar like water, we may conclude that the PSU will be less wettable to the glass than the PA. It is therefore reasonable that the PSU forms the out-sticking phase, if we assume that the interface of the PSU domain to the glass substrate covers the same area that is visible at their air-surface (*Figure 5d*). As evident from the microscopic investigations this structure formation is the most reasonable one, although some different kinds of structure formation should be possible. For example one of them is given in *Figure 5e*.

The PA is more wettable to glass than the PSU, as the PA and the glass contain groups with strong polarity (NH, CO, SiO, etc.) and is able to build hydrogen

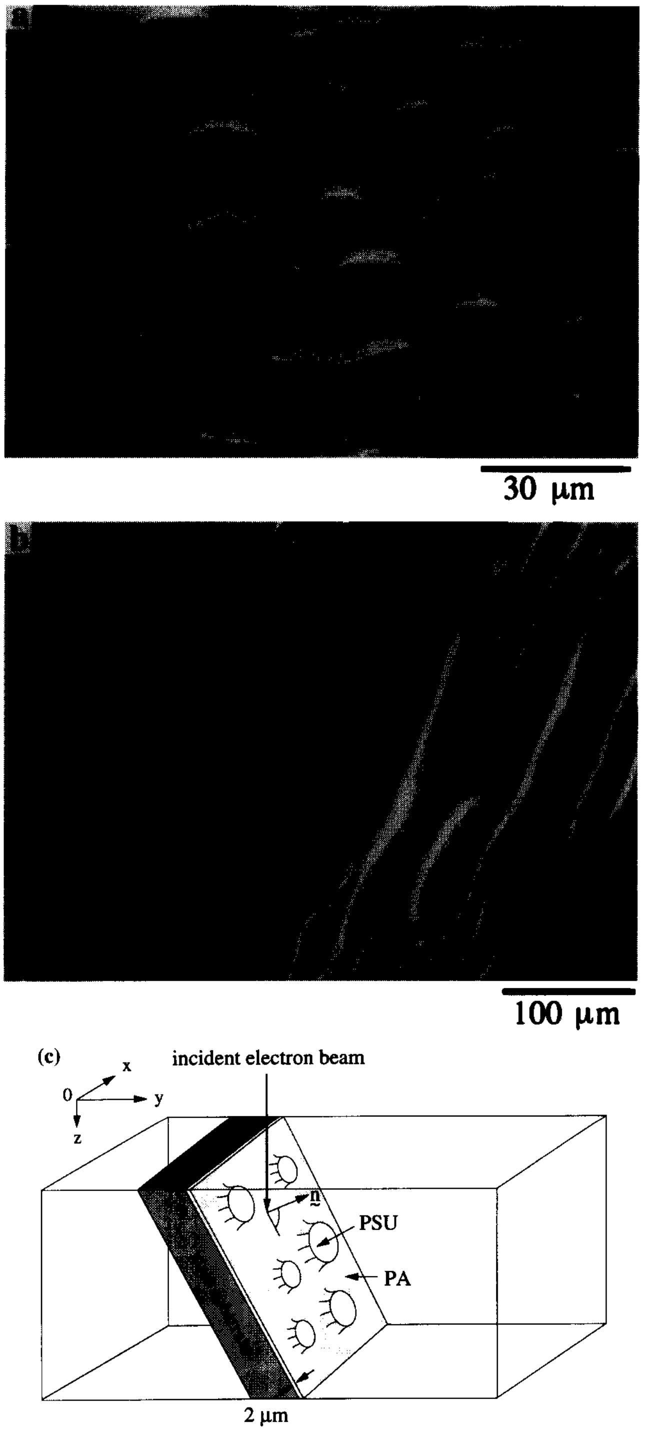


Figure 2 SEM micrographs of SUA annealed for 10 min at 290°C (corresponding to TOM micrograph of *Figure 1f*): (a) SEM image obtained in the top view with an annular RE-detector; (b) of a cut perpendicular through the glass slide; the polymer is visible as a bright layer on the right side of the glass slide. (c) Schematic diagram showing the optical arrangement of the SEM observations shown in (b)

bonding. The polarity of the SO-group of the PSU, however, is weaker, as it is localized between the two aromatic phenyl units. Therefore the PSU-phase turned into a droplike shape and the PA-phase spread on the glass surface.

Blends with compatibilizer. *Figures 6*, *7* and *8* show a series of TOM and SEM micrographs of SUA37, SUA46 and SUAph, respectively. The TOM micrographs in *Figures 6a*, *7a* and *8a* were recorded immediately after the onset of the annealing at 300°C; TOM micrographs shown in *Figures 6b*, *7b* and *8b* and SEM micrographs shown in *Figures 6c*, *7c* and *8c* were obtained after annealing of each specimen at 300°C for 30 min. In the case of the modified PSU the interaction with the PA is not very different compared to the blend with the pure PSU. Therefore the as cast samples with the modified PSU show a morphology and domain size similar to that of the PSU (compare *Figures 1a*, *6a*, *7a*). According to the TOM micrographs of SUA37 (*Figures 6a*, *b*), some changes of the originally obtained structure are observable during the annealing time as for the pure blend SUA (see *Figure 1*). In other words, a tendency for a phase inversion is visible in *Figure 6c*, although the phase inversion was not yet completed. Compared to the growth of the domain size of the pure blend (SUA), however, the growth of the domain size of SUA37 is suppressed. The blend SUA46 (*Figures 7a*, *b*), containing the highest amount of COOH-groups, shows no change of the morphology during the annealing and hence no phase inversion. The SEM micrographs (*Figures 6c* and *7c*) show the same features like the pure blend SUA (*Figure 2a*), i.e. the PSU phase appears darker than the PA phase and forms the out-sticking phase, meaning that the wetting behaviour is not or only weakly influenced by the chemical modification of the PSU.

The slowing down or freezing of the phase separation in the case of SUA37 and SUA46 is probably caused by a grafting reaction of the COOH-groups of the modified PSU with the amide groups of the PA as illustrated in *Scheme 4*. Due to the high annealing temperature a covalent bond can be formed between the PSU and PA at their interface building a grafted copolymer, which slows down or interrupts the phase separation process due to a reduction of the interfacial tension between the PSU and the PA-spheres. It is reasonable that the morphology of SUA37 changes to some extent in comparison to the SUA46 due to the lower content of COOH-groups.

Interestingly the sample SUAph containing phenoxy as compatibilizer, which is originally obtained by a reaction of bisphenol-A and epichlorhydrin, shows a much finer morphology even after the annealing procedure. The chemical structure of this compatibalizer shows two principal features in correlation to the PSU and the PA. While the bisphenol-A-part is chemically equal to one unit of the PSU (compare *Schemes 1* and *3*), the hydroxyl-groups of the aliphatic part are able to form hydrogen bonds to the amide groups of the PA. The phenoxy can therefore act similar to a surfactant and decrease the interfacial free energy, leading to an even smaller domain size than the samples containing the modified PSU after the casting procedure. Even after annealing at high temperatures the morphology of the SUAph is maintained, which strengthens the idea of the location of the phenoxy at the interface, although we have no direct proof at this moment.

Bulk samples

Figures 9a–d are the TEM micrographs of the original samples obtained by extruding SUA, SUA37, SUA46 and SUAph, respectively. In each image the bright phase corresponds to the PA-rich phase, while the dark phase is the PSU-rich phase as concluded from their volume fractions. Also the ternary blend SUAph (*Figure 6d*) shows only two phases in the electron microscopic image.

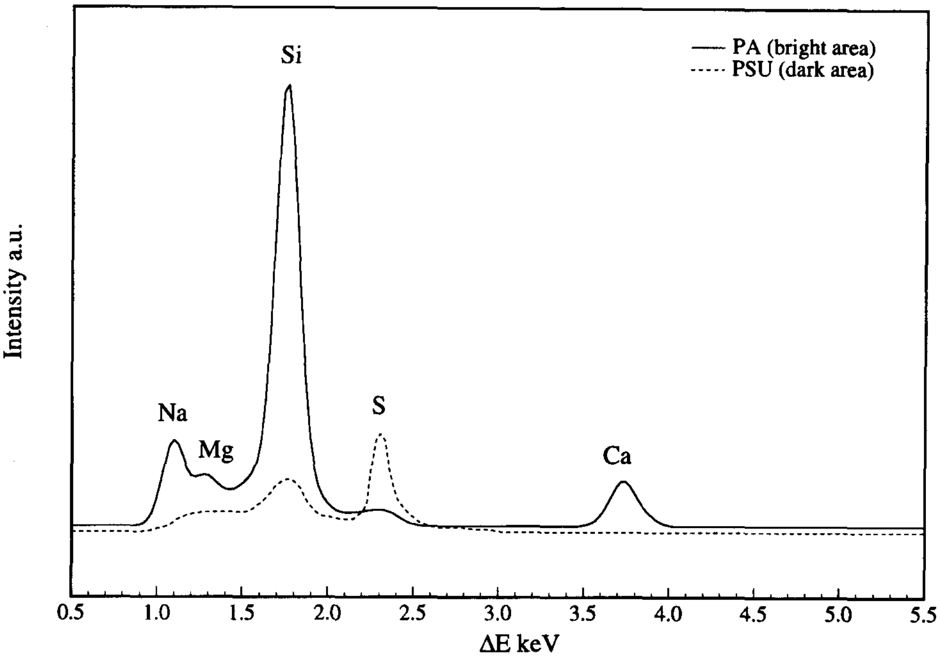


Figure 3 EDX-spectra of the dark area of the PSU phase (dotted line) and bright area of the PA phase (solid line) seen on the SEM image of *Figure 2a*

Attempts to obtain a contrast by staining with RuO_4 or PTA, however, failed.

In case of the bulk samples SUA, SUA37 and SUA46, the PA domains are much smaller than those of the solution cast film (*Figures 1a, 2a, 6a, 7a* and *8a*). A comparison of the morphologies obtained by solution-casting or melt-extrusion process is difficult as the parameters which control the structure formation are very different in both cases.

In the case of the bulk sample, the temperature, the mixing time and the extrusion speed mainly control the morphology. Therefore the samples SUA, SUA37 and SUA46 show a quite similar morphology. The domain size of the samples containing modified PSU (*Figures 9b, c*) is smaller compared to SUA (*Figure 9a*). As the modified PSU is expected to be randomly distributed in the PSU at molecular level and therefore some fractions of them to be naturally located at the interface, it has some influence on the compatibility of the PSU and PA: the COOH-groups of the modified PSU and the amino groups of the PA can react with each other at the interface of the two coexisting domains to form the graft copolymer acting as a compatibilizing agent for the PSU and PA.

The sample SUAph shows a completely different behaviour. During the melt-mixing and extrusion process the phase morphology was developed at a much larger length scale than the SUA, SUA37 and SUA46. The phenoxy will not cover the whole interface of the PSU and PA, as the viscosity of this component polymers is very high even at high temperatures and therefore the diffusion is very slow. Therefore the phenoxy has only a little chance to form a perfect layer around the PA-droplets. For this reason the phenoxy cannot act as the strong compatibilizer as in the case of the solution cast samples (*Figure 8a, b*), where the phenoxy has a better chance to find its place at the interface during the casting process. It is crucial to find the phase where the phenoxy exists in the melt-processed specimens, the investigation of which is, however, left for future work.

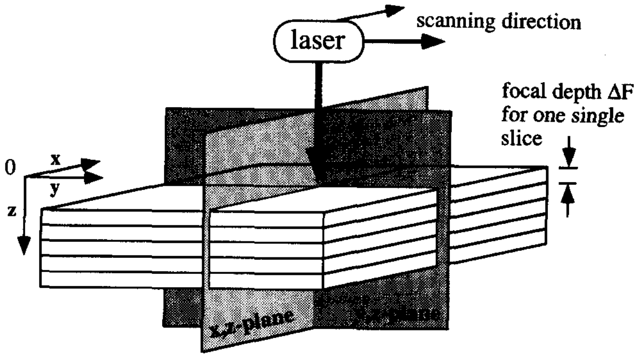


Figure 4 Sketch of the scanning geometry used to obtain the 3-dimensional information about the surface and inner structure of the images given in *Figures 5, 10* and *11*

The structural evolution for the binary blend of PSU and PA (SUA) was observed by using LSCM. The outline of the scanning geometry of the LSCM, which leads to the images shown in *Figures 10* and *11*, was given in *Figure 4*. Compared to *Figure 5*, where we used the strong reflection at the air surface of the sample to reconstruct its surface topology, we now use the reflection of the interface of the two phases (due to a difference of the refractive indices of the two phases) to obtain information about the bulk morphology inside the sample.

The LSCM image of the as-extruded SUA is given in *Figure 10*. According to the TEM image given in *Figure 9a* the PA forms clusters of droplets in the PSU-matrix with a diameter between a few hundred nanometres up to about 5 μm. As the LSCM contrast is mainly caused by the interface and especially by the interface which is perpendicularly oriented to the incident beam, the white spots in *Figure 10a* correspond to the top or bottom interface of PA droplets. The appearance of a single cluster depends very much on its size compared to the focal depth ΔF of the optical set-up

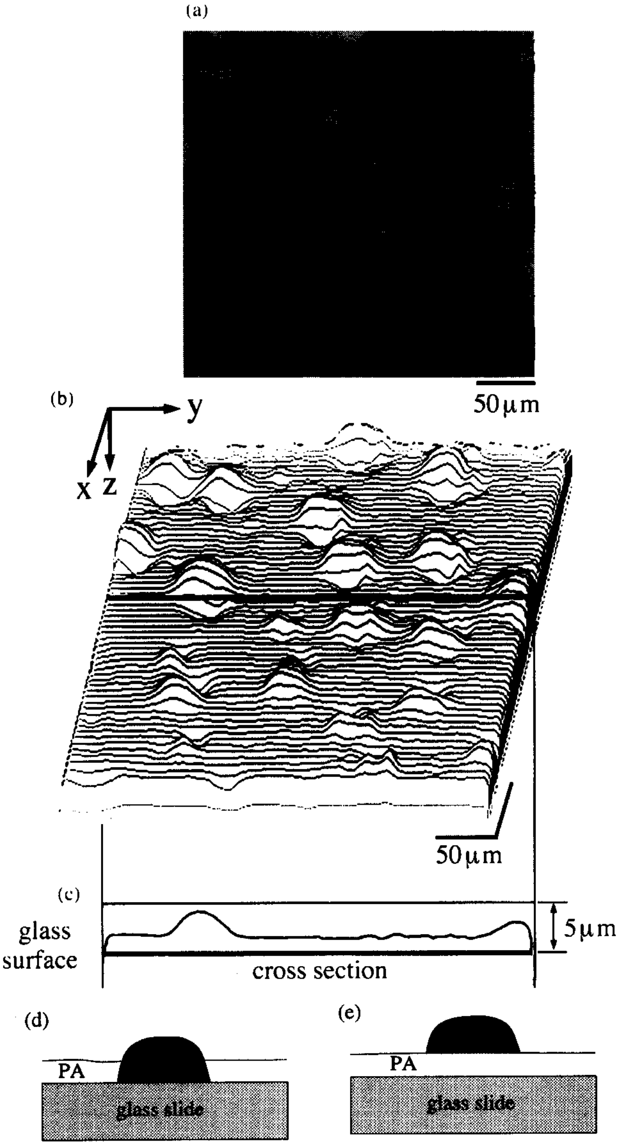


Figure 5 LSCM images of SUA annealed for 10 min at 290°C (corresponding to TOM micrograph of *Figure 1f*): (a) topographic image obtained by LSCM in reflection mode and (b) 3-dimensional reconstruction of the surface with a cross section (c) (height profile) obtained along the line marked in parts a and b. The out-sticking phase corresponds to the PSU. (d, e) Sketch of two morphologies in the thin film samples, which fit to the microscopic observations

and its location relative to the single slices. As we described in detail elsewhere[13], the droplets close to the focal depth show the strongest contrast and an artificial elongation in the z-direction parallel to the incident beam. We observe those elongated spheres in the x, z (*Figure 10b*) and y, z-plane (*Figure 10c*) (marked by an arrow) which is caused by the scanning procedure. A very detailed explanation of this phenomenon, however, is given in the above-mentioned paper and shall not be discussed further here.

The morphology of this blend sample which was sandwiched between two glass slides and annealed at 250°C for 1 h is given in *Figure 11*. The dark droplet-like phase corresponds to the PA and the bright matrix to the PSU as concluded from their volume fractions. In the projections along the x, z- (*Figure 11b*) and y, z-plane (*Figure 11c*) we again observe the strongest reflections at the interface, which is oriented perpendicular to the incident beam as marked by the bright arrows. The dimensions of the droplets with a diameter around 20 μm are observed several times larger than those in the as-extruded samples. Thus the SUA shows a quite rapid phase separation and domain growth.

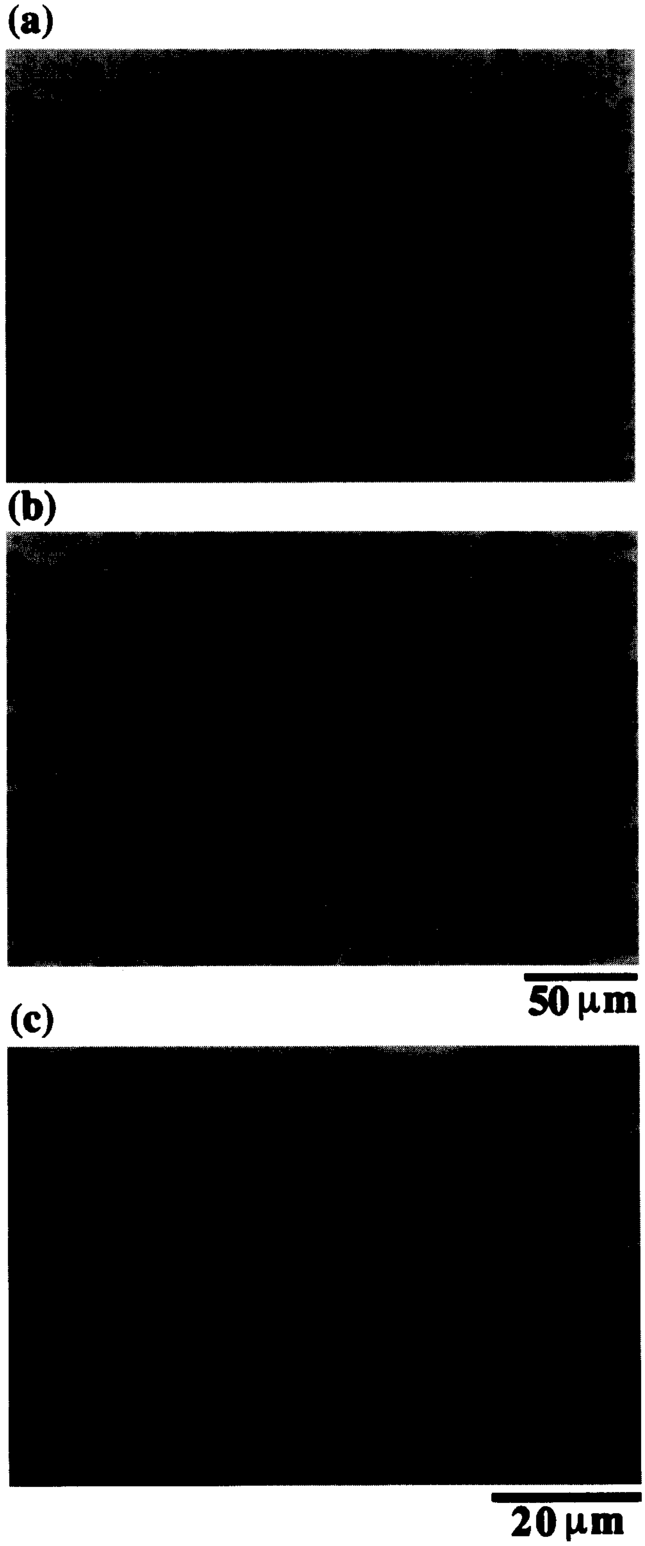


Figure 6 (a, b) TOM and (c) SEM micrographs of the as cast sample SUA37 (a) and annealed at 300°C for 30 min (b, c)

CONCLUSIONS

The highly immiscible blend of PSU and PA shows rapid

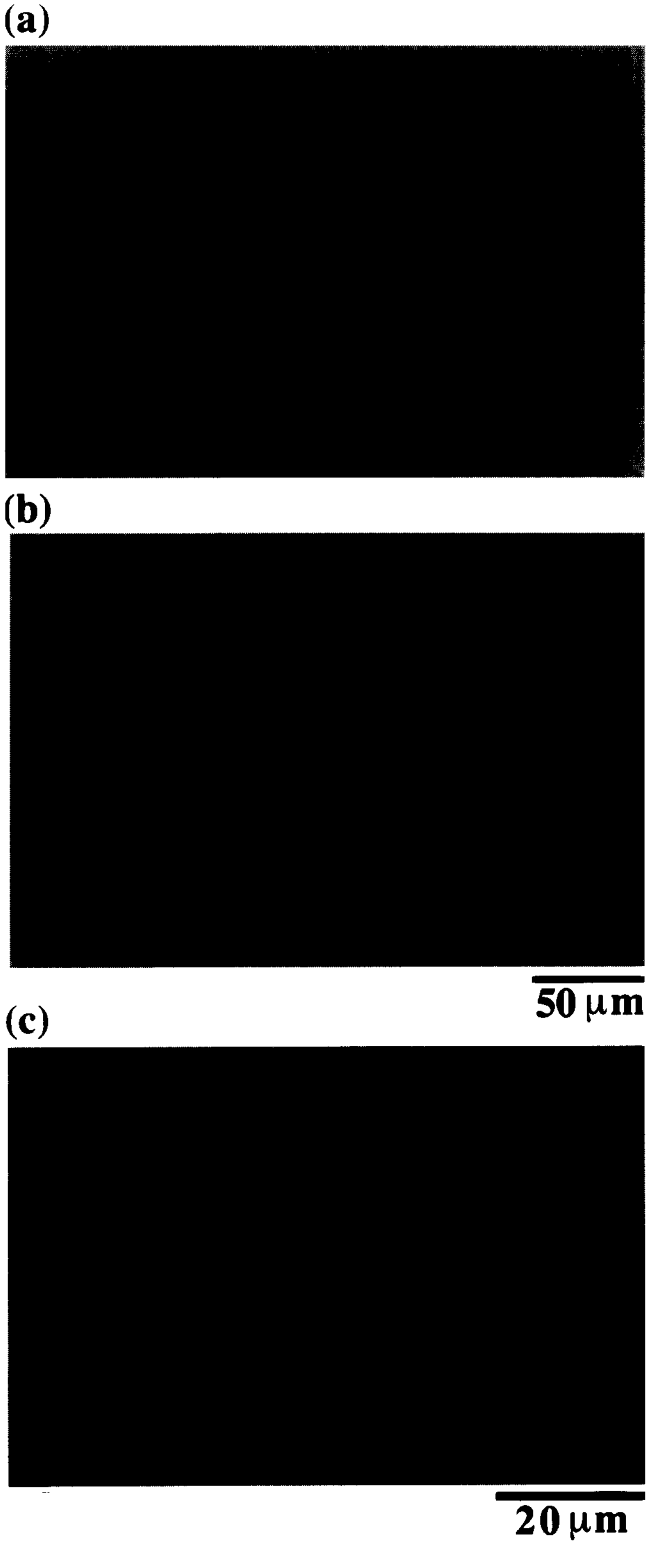


Figure 7 (a, b) TOM and (c) SEM micrographs of the as cast sample SUA46 (a) and annealed at 300°C for 30 min (b, c)

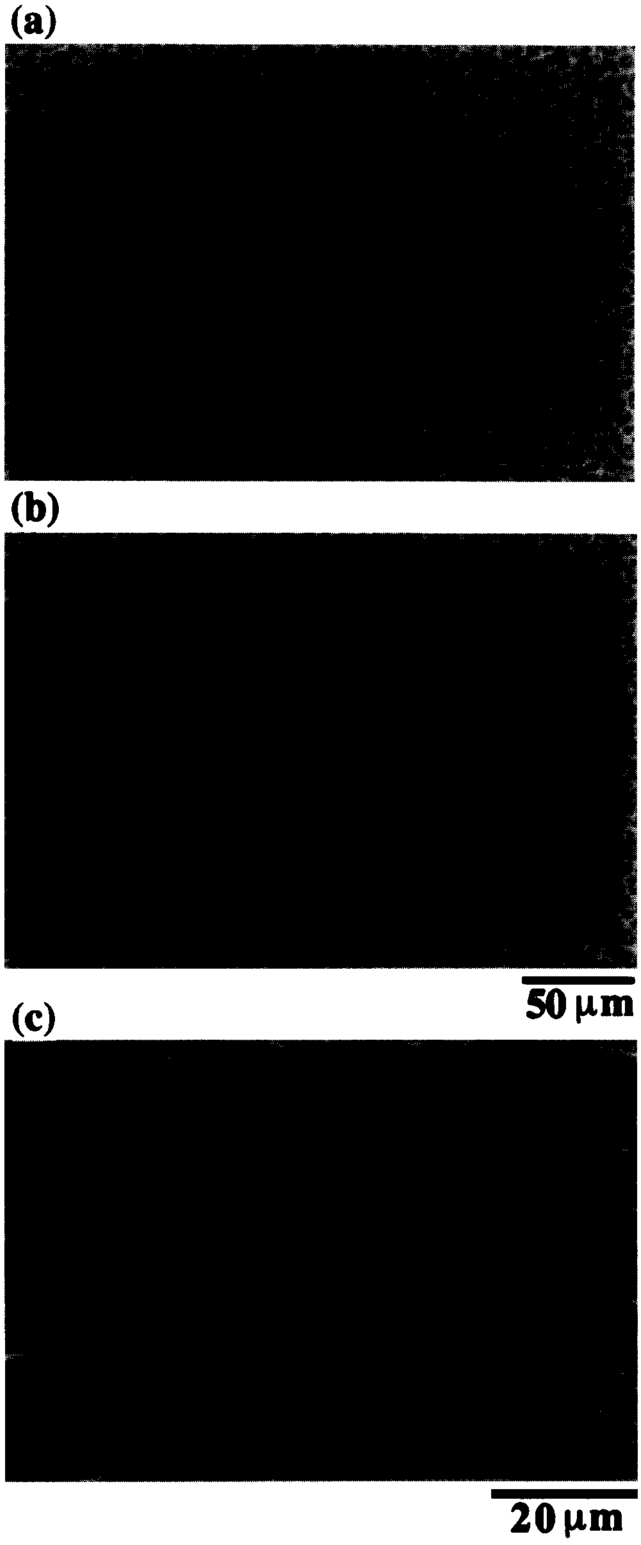
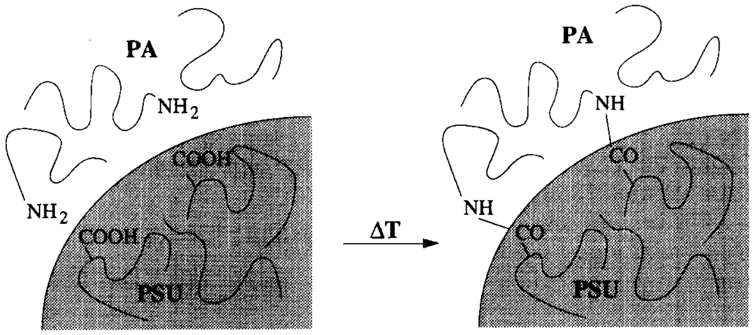


Figure 8 (a, b) TOM and (c) SEM micrographs of the as cast sample SUAph (a) and annealed at 300°C for 30 min (b, c)



Scheme 4

Scheme 4

Figure 9 TEM micrographs obtained from samples prepared by melt blending and extrusion at 250°C and slowly cooling down to room temperature: (a) SUA, (b) SUA37, (c) SUA46 and (d) SUAph. Ultramicrotomed samples without staining

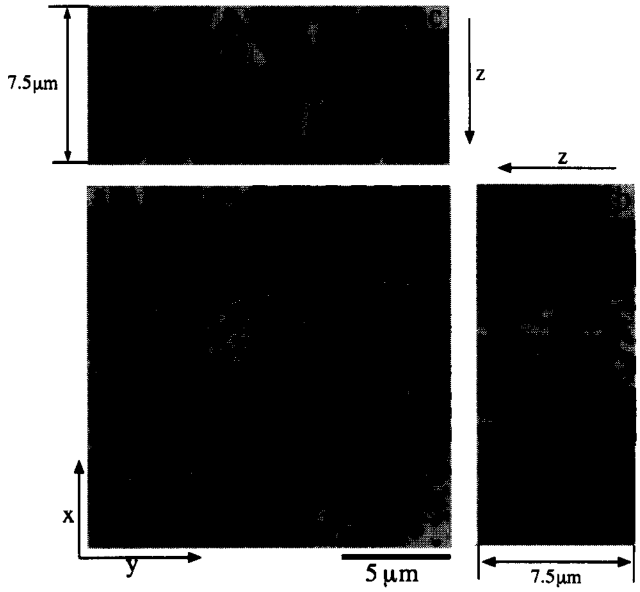


Figure 10 LSCM image of the bulk as extruded SUA sample in oxy-plane (a) and those in the x, z- (b) and y, z- (c) plane reconstructed from 30 slices with 1 μm distance (magn. 63×, N.A. 1.4, focal depth $\Delta F = 800$ nm). The white lines show the area where the images are cut as illustrated in the sketch in *Figure 4*

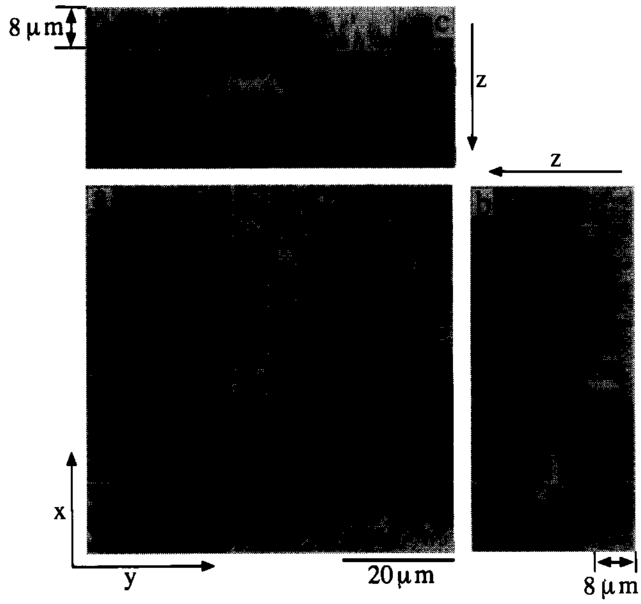


Figure 11 LSCM image of the bulk SUA sample annealed at 250°C for 1 h in the x, y-plane (a) and those in the x, z- (b) and y, z- (c) plane reconstructed from 30 slices with 1 μm distance (magn. 63×, N.A. 1.4, focal depth $\Delta F = 3\,\mu$m). The white lines show the area where the images are cut as illustrated in the sketch in *Figure 4*

phase separation in thin films cast from solution and bulk samples obtained from mixing in melt.

The morphology of thin films cast on glass slides of a pure blend of PSU and PA show strong phase separation although the structure formation is strongly influenced by the interaction with the glass and air interface, i.e. wetting. The morphology of the thin film can be determined as risings of PSU in a PA matrix by means of LSCM and SEM. Adding a small amount of a reactive component, a modified PSU, to the blend, the phase separation process can be suppressed completely. Although the influence of the interaction with the glass interface in this case is not clear at the moment, we assume that the formation of a graft copolymer at the interface is responsible for the interruption of the domain growth.

A bulk sample of PSU and PA undergoes phase separation as well while annealing. The phase separation process can be visualized by LSCM and TEM. The visualization of the morphology of a bulk sample containing modified PSU to control the morphology, i.e. domain size, is currently in progress and will be the topic of future publications.

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