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# Melt reactivity of carboxylic acid functional polysulfone in polyamide/polysulfone blends: phase morphology and mechanical properties aspects

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Aliphatic polyamide (PA 6 or PA 66), polysulfone (PSU) and polysulfone copolymerized with 4,4′-bis(4-hydroxyphenyl)pentanoic acid bearing carboxylic acid functions (PSU copolymers) were melt blended in the MINI-MAX moulder. Morphology of the blends was characterized by image analysis on SEM pictures and light scattering. The particle size depends on the viscosity ratio and on the concentration of COOH functional units in the PSU. The carboxylic acid function indeed reacts with amino end groups of the polyamide, leading to the formation of a grafted copolymer concentrated at the interface. In this way, interfacial tension is reduced and interfacial adhesion enhanced. The mechanical properties of PA/PSU blends are also improved by the formation of this grafted copolymer. However, considering mechanical properties, particle size appears as the dominant parameter. Mechanism of deformation and fracture of these blends are also discussed. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: polyamide; polysulfone; melt reactive blend)**

## INTRODUCTION

The combination of amorphous and semi-crystalline polymers in multiphase polymer blends or alloys offers tremendous opportunities for the development of tailor-made materials[1]. These materials may exhibit the solvent resistance, high melting point and flow behaviour of the semi-crystalline component as well as the dimensional stability and the high glass transition of the amorphous component.

Although several commercial products based on polymer alloys of semi-crystalline and amorphous polymers have been successfully introduced to the market-place[2–4], there is still a great deal of research activity focused on these materials.

Polymer alloys of poly(aryl ether sulfone) and polyamide (PSU/PA) have been investigated by several research groups, especially because this combination of polymers promises a unique set of properties, comprising high dimensional stability, impact toughness, solvent resistance and good flow behaviour[5–12].

Polysulfone and aliphatic polyamides such as PA 6 or PA 66 are immiscible, but polymer blends of these components offer favourable flow properties and form tough films[5]. Owing to the immiscibility of PSU and PA, samples obtained by injection moulding show heterogeneous phase morphology and, therefore, undesirable mechanical properties. To overcome these problems, several types of compatibilizers, i.e. component promoting interfacial modification aimed at reduced interfacial tension, improved phase adhesion and inhibition of the coalescence process, have been used, especially block copolymers of PSU and PA 6[6–9]. A polymer like phenoxy was also used as a compatibilizer in these blends[10]. In addition, end-group chemistry was also applied for the interfacial modification in PA/PSU blends. Mechanical properties were significantly improved by blending PA and PSU with an anhydride terminated PSU[11].

In this study, poly(aryl ether sulfone)-copolymers, with different amounts of 4,4′-bis(4-hydroxyphenyl)pentanoic acid incorporated in the chains[12–14], have been used for reactive blending experiments with different polyamides. The aim of the present study is to investigate the interfacial modification brought by the possible reactions between the polyamide and the reactive PSU-copolymers.

## EXPERIMENTAL

4,4′-Bis(4-hydroxyphenyl)pentanoic acid was obtained from Aldrich Company. *N*-methyl-pyrrolidone was dried with $CaH_2$ and distilled.

The polyamides were Polyamide 6,6 (120 $\mu$mol g$^{-1}$ of amino end groups) from BASF AG and Polyamide 6 (22 K and 40 $\mu$mol g$^{-1}$ of amino terminal groups) from Sumitomo Chemical Company.

The PSU was Ultrason S 2010 from BASF AG and PSU-copolymers were synthesized as follows[11–13]. 4,4′-Bis(4-hydroxyphenyl)pentanoic acid, bisphenol A, bis(4-chlorophenyl)sulfone and $K_2CO_3$ were dissolved in

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**Table 1** PSU and PSU copolymers: composition and characterization

| Name | PSU 0 | PSU 1 | PSU 2 | PSU 3 | PSU 4 | PSU 5 |
|---|---|---|---|---|---|---|
| Grade number | Ultrason S | 27002/51 | 27002/52 | 27002/53 | 27002/61/1 | 27002/61/2 |
| Bis(4-chlorophenyl)-sulfone (mol) | | 0.1 | 0.1 | 0.1 | 1.0 | 1.0 |
| Bisphenol A (mol) | | 0.096 | 0.093 | 0.08 | 0.937 | 0.922 |
| 4,4′-Bis(4-hydroxyphenyl)pentanoic acid (mol) | | 0.002 | 0.0049 | 0.0098 | 0.019 | 0.048 |
| K2C03 (mol) | | 0.11 | 0.11 | 0.11 | 1.1 | 1.1 |
| N-methyl pyrrolidone (ml) | | 180 | 180 | 180 | 1800 | 1800 |
| Viscosity number | | 38.1 | 28.4 | 19.1 | 31.2 | 31.9 |
| *x*-units (mol.%) | 0 | 1.1 | 3.3 | 7.9 | 1.7 | 3.6 |
| Melt viscosity (Pa s) | | 800 | 100 | 20 | 200 | 400 |

dry *N*-methyl-pyrrolidone. *Table 1* summarizes the compositions used. The mixture was heated in a nitrogen atmosphere at 190°C for 6 h. During that time, the azeotropic mixture of *N*-methyl-pyrrolidone and water was continuously removed. The solution was cooled to room temperature, diluted with *N*-methyl-pyrrolidone and filtered. After this, an excess of acetic acid was added to the solution with further stirring (30 min), and the polymer was isolated by precipitation in water. The polymer was then extracted three times with hot water and dried at 130°C for 12 h.

The viscosity number of the polymers was measured at a concentration of 1 wt% in *N*-methyl-pyrrolidone at 25°C.

The $^1$H-n.m.r. spectroscopy was done using a Bruker 400 MHz instrument and $CDCl_3/CF_3COOD$ 50/50 solution. The amount of units derived from 4,4′-bis(4-hydroxyphenyl)pentanoic acid and bis(4-chlorophenyl)sulfone was calculated using the signal intensities in the $^1$H-n.m.r. spectra, taking into account the signal intensities of the $CH_2$-groups of 4,4′-bis(4-hydroxyphenyl)pentanoic acid ($\delta$ = 2.2 ppm and 2.5 ppm) with respect to the signal intensity of the $CH_3$ groups on the units deriving from bisphenol A ($\delta$ = 1.6 ppm).

Viscosity numbers and $^1$H-n.m.r. spectroscopic results are given in *Table 1*.

The mixing of blends was performed on a small-scale mixer MINI-MAX moulder from Custom Scientific Instruments Inc. This mixer was invented by B. Maxwell[15].

Before mixing, materials were dried overnight at 120°C under vacuum. Binary blends of PA with PSU-copolymers were mixed at 280 and 300°C under an average shear rate of 16 $s^{-1}$. Mixing in the MINI-MAX moulder was enhanced by the addition of three metal balls. Samples were withdrawn during mixing, allowing observation of the change of morphology during the processing. The PSU content was fixed at 20 wt%. For the ternary blends of PA/PSU/PSU-copolymer, the PSU and the PSU-copolymer were pre-blended by melt mixing at 270°C for 2 min. In this paper, the following notation will be used for these PSU/PSU copolymer pre-blends: PSU *xyy* means that the PSU 0 (see *Table 1*) has been blended with the PSU *x* (*x* = 1–5). The composition of this pre-blend is (100 − *yy*)% of PSU 0 and *yy*% of PSU *x*. For example, PSU 241 is a blend PSU 0/PSU 2 (59/41). It must be noted that PSU 200 is pure PSU 2.

Then these pre-blends and the polyamide were dried overnight at 120°C under vacuum. The pre-blends of PSU and PSU-copolymer and the PA were mixed at 280°C under an average shear rate of 16 $s^{-1}$. Good mixing in the MINI-MAX moulder was ensured by a periodic lifting of the rotor once every 5 s. After 2 min of mixing, test specimens were injected into a mould through the dye at the bottom of the mixer. The test specimens were then notched as illustrated in *Figure 1*.

Rapid estimation of the particle size of the blends can be obtained by light scattering. Tiny samples were cut and placed between two thin glass covers and melt pressed for about 5 s at 280°C. A thin film of material was formed and the sample was placed in the beam of a light-scattering analyser. The light-scattering analyser used 632.8 nm light from a Ne/He laser and a 46 photodiode linear array as detector[16]. A Debye–Bueche plot gave the straight line from which the correlation length $\xi$ was obtained[17]. From the correlation length, the specific interfacial area $S_{sp}$ and a mean particle diameter *d* can be calculated as the volume fraction of the dispersed phase $\Phi$ is known

$$S_{sp} = 4\Phi(1-\Phi)/\xi \qquad (1)$$

$$d = 1.5\xi/(1-\Phi) \qquad (2)$$

For the direct observation of the morphology of the dispersed phase, samples for scanning electron microscopy (SEM) were prepared by fracture in liquid nitrogen and solvent etching of the dispersed PSU with tetrahydrofuran (THF). From SEM pictures, image analysis was performed with a Macintosh microcomputer. The mean particle size was calculated on averaging at least 200 particles.

The melt viscosity of the materials was measured by a Rheometrics Dynamic Spectrometer RMS-605 at 180°C under periodical strain of 25%.

Whitening of the test specimen upon deformation was analysed by measuring the intensity of back-scattered light. The light source was a He/Ne laser beam slightly broadened by a divergent lens. The light spot of *ca.* 1 cm diameter was centred on the notch tip. A photo detector was used to determine the amount of light back-scattered by the sample. The incident and reflection angle were 30°. The reflected light varied only slightly during the deformation of a non-whitening sample, allowing the

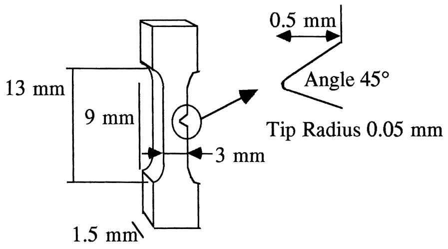

**Figure 1** Specimen dimension and notch of the test samples used in mechanical testing

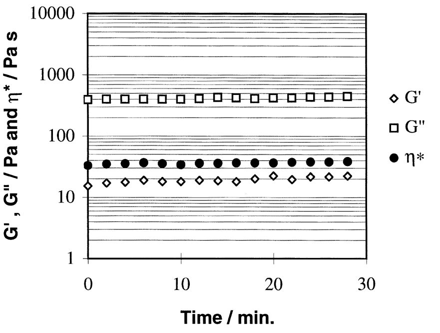

**Figure 2** Melt viscosity at 300°C of the PSU 2 as a function of time. The cyclic deformation sustained was 10% at a frequency of 1 Hz

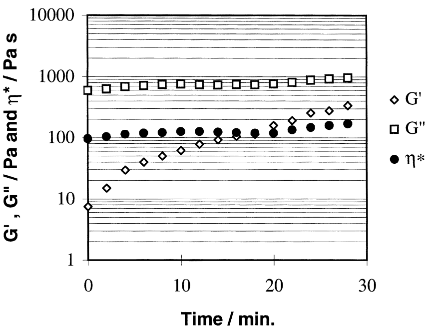

**Figure 3** Melt viscosity at 300°C of the PA 66 as a function of time. The cyclic deformation sustained was 10% at a frequency of 1 Hz

initial back scattering to be considered as the background. In this test, an increase in the back-scattered light is expected to be due to particle cavitation or debonding during the deformation.

The surfaces of fractured specimens were observed by SEM in order to consider the main mechanism of fracture.

The presence of grafted PA on the surface of the PSU particle was analysed by TEM, i.e. blends were solubilized in formic acid then filtrated and washed with fresh formic acid three times, and the remaining PSU particles were dried and dispersed in an epoxy resin for easier ultramicrotoming. Microtomes were stained with $RuO_4$ and observed by TEM. With $RuO_4$, the resin remains white, the PSU appears grey and the PA appears completely dark.

## RESULTS AND DISCUSSIONS

### Melt viscosity

*Table 1* reports the complex viscosity at 300°C of the different PSU under a cyclic deformation of 10%. Since the average shear rate developed in the mixer can be estimated to about 16 $s^{-1}$[18], only complex viscosity corresponding to this frequency is reported.

In *Figures 2* and *3*, the melt viscosity at 300°C is reported as a function of the time for the PSU 2 (*Figure 2*) and the polyamide 66 (*Figure 3*). The viscosity and the $G'$ and $G''$ of the PSU remains constant with time, which confirms the nice thermal stability of the polymer. For the PA, the $G'$ increases gradually, which can be related to the branching occurring during the PA degradation[24]. Since within the mixing times used during the preformed experiments the $G'$ remains far below the $G''$, it is expected that the viscosity ratio between the components of the blends do not change significantly during processing. This point is important for our proposal. Indeed, changes in the particle size during processing may arise from interfacial modification or from a progressive change in the viscosity ratio. The constancy of the viscosity of the materials allow us to rule out this latter possibility.

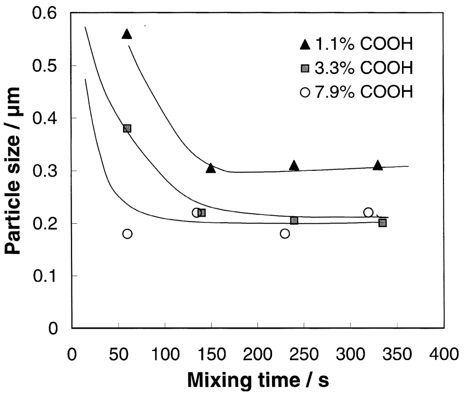

**Figure 4** Mean particle diameter measured by light scattering as a function of mixing time for PA 66/PSU-copolymers blends mixed with metal balls in the MINI-MAX molder at 280°C

### PA 66/PSU-copolymer blends

In a first step the progression during mixing of the particle size in PA 66/PSU-copolymer blends was characterized. *Figure 4* shows the particle size as a function of mixing time at 280 and 300°C. It is observed that the particle size rapidly decreases during the first 2 min of mixing, then it remains constant. Also, the PSU-copolymer with the lowest co-monomer content has the larger particles. Especially for the blends observed after 1 min of mixing.

Particle size may be more accurately observed by SEM. *Figure 5* shows SEM micrographs of PA 66/PSU-copolymers mixed at 280°C for 2 min. Clearly, the higher the co-monomer concentration, the smaller the particle size. However, as shown in *Figure 2*, the viscosities of the different PSU-copolymers are different. And presently, the effect of the co-monomer concentration cannot be definitely assessed, since the viscosity ratio deeply affects the particle size in melt-processed polymer blends[19–21].

The fact that, in *Figure 4*, the size of functional PSU particles remains constant after some time has to be explained. A first possibility is that PSU copolymers have better compatibility with the PA so that a steady state is rapidly reached and particle size does not change further. A second way to interpret this behaviour could be that PSU copolymer reacts with the PA, but after a few minutes the reaction rate is dramatically reduced. It must be stressed that in the small-scale mixer at high temperature, oxidative degradation is very likely to occur. The degradation of polyamides results in a strong reduction in the amino end group concentration[22,23]. The concentration of amino end groups in melt-processed polyamide 6 may become very low if oxidative degradation occurs[24]. Therefore, it is obvious that under such conditions reactions involving the amino groups of the PA are exceedingly slowed down. Whether the change of interaction parameter or interfacial reaction is dominant will be discussed later.

### PA 6/PSU/PSU-copolymer blends

The effect on the particle size and mechanical properties of the co-monomer content of the PSU-copolymers independent of the viscosity ratio has to be established. Therefore, PSU-copolymers were blended with PSU in

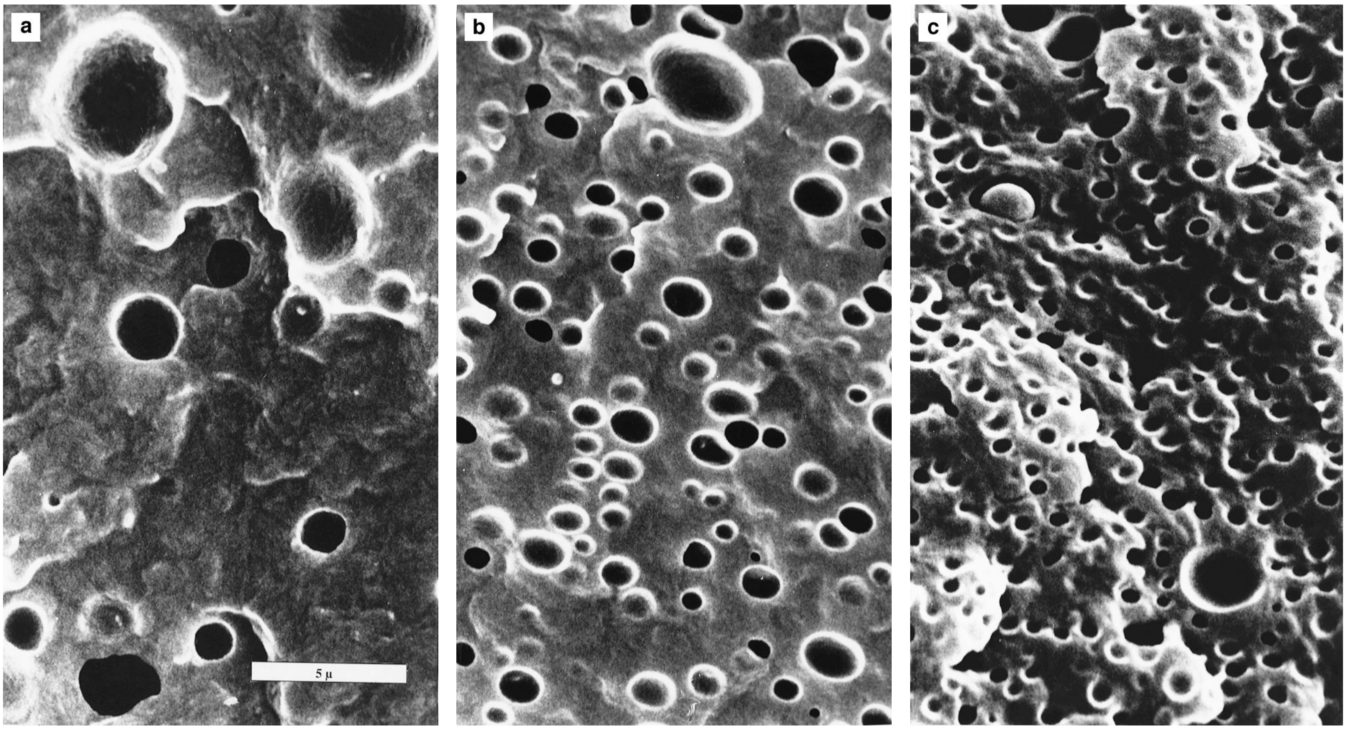

**Figure 5** SEM micrographs of the etched cryofractured PA 66/PSU-copolymers blends mixed in the MINI-MAX molder at 280°C for 2 min; (a) PA 66/PSU 1; (b) PA 66/PSU 2; (c) PA 66/PSU 3

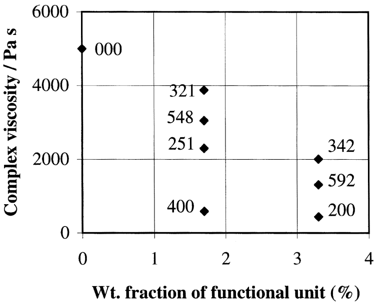

**Figure 6** Viscosity ratio as a function of the functional co-monomer content in the PSU phase of the PA 6/PSU/PSU copolymer blends

order to produce different PSU/PSU-copolymer 'pre'-blends with identical co-monomer content and different melt viscosity. *Figure 6* shows the melt viscosity as a function of the co-monomer content for the different PSU/PSU-copolymer 'pre'-blends. There is a nice overlap of the ranges of viscosity ratio, which will allow conclusions on the effect of the co-monomer content. Moreover, in order to rule out effects of oxidative degradation of the PA, the mixing conditions and mixing time were kept identical for all blends. Amino end group consumption by oxidative degradation is constant for all blends and this allows careful comparison of the effect of viscosity ratio and functionality.

*Figure 7* shows the mean particle size as a function of the viscosity ratio. For each degree of functionality, the dependence of the particle size on the viscosity ratio can be established. It is quite similar whatever the functionality is: going from a viscosity ratio of one to a viscosity ratio of three, the particle size is increased by approximately 30%. It must be stressed that the dependence of the particle size on the viscosity ratio is different to that described by Wu[18]. It is much smaller in the MINI-MAX moulder. A similar trend was also observed previously in a study considering the efficiency of the MINI-MAX moulder[25]. Such a difference could be explained by the different flow field developed in the extruder and in the MINI-MAX moulder.

Nevertheless, *Figure 7* shows the mean particle size as a function of the viscosity ratio for the PA 6/PSU/PSU-copolymer blends mixed for 2 min at 280°C: (*a*) 8% PSU/PSU-copolymers; (*b*) 16% PSU/PSU-copolymers; (*c*) 32% PSU/PSU-copolymers. For a given viscosity ratio, the particle size depends on the co-monomer content: with increasing co-monomer content, smaller particle sizes are found. This could be explained by a reaction between the PA and the carboxylic acid groups of the PSU-copolymers. The product of such a reaction is a grafted copolymer of PSU on which are grafted one or several PA 6 chains. In PA 66-based blends, the grafted copolymer structure could be more complex, with several PSU chains linked by PA 66 bridges. Nevertheless, the PSU-g-PA copolymer will tend to stay at the interface between PA and PSU. Considering *Figure 7*, there is a nice change of particle size resulting from the introduction of PSU copolymers. However, the biggest change in particle size is observed with 1.7% of functional unit. Then, only a small amount of grafted copolymer would be sufficient, provided it reacted and produced the *in situ* graft copolymer.

Such grafted copolymers are, at least partly, immiscible in selective solvents for PSU. Then the direct observation by TEM of PSU particles filtrated from a formic acid solution of a PA-rich blend can reveal the existence of a layer of grafted copolymer at the border of the PSU particles. As shown in *Figure 8*, PSU particles were dispersed in epoxy resin and stained with $RuO_4$. For the PA/PSU/PSU-copolymers blends (bottom picture), there is some grafted PA at the surface of the particles, while for the PA/PSU blend (upper picture) this is not found. Obviously some PA chains have reacted with the co-monomer of PSU-copolymers. Note that the double line surrounding

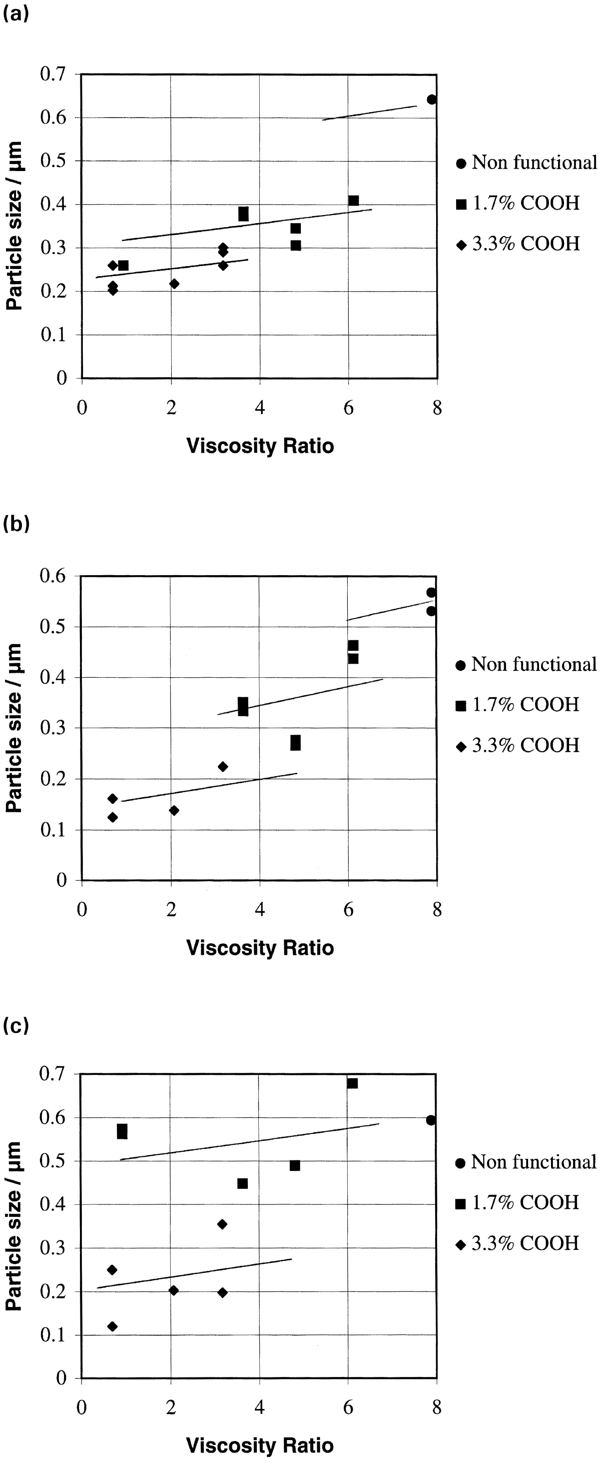

**Figure 7** Mean particle size as a function of the viscosity ratio for the PA 6/PSU/PSU-copolymer blends mixed for 2 min at 280°C; (a) 8% PSU/PSU-copolymers; (b) 16% PSU/PSU-copolymers; (c) 32% PSU/PSU-copolymers

the PSU particle in the upper picture may result from artefacts such as cut thickness effect or de-cohesion during cutting of slight swelling of the PSU by the epoxy.

The amount of copolymer formed at the interface does not cover all the interface, showing that, in this case, the reaction was not sufficient to promote interfacial saturation by grafted copolymer. Nevertheless, small amounts of block or graft copolymers are sufficient to promote large morphological changes. Then in our case, change of

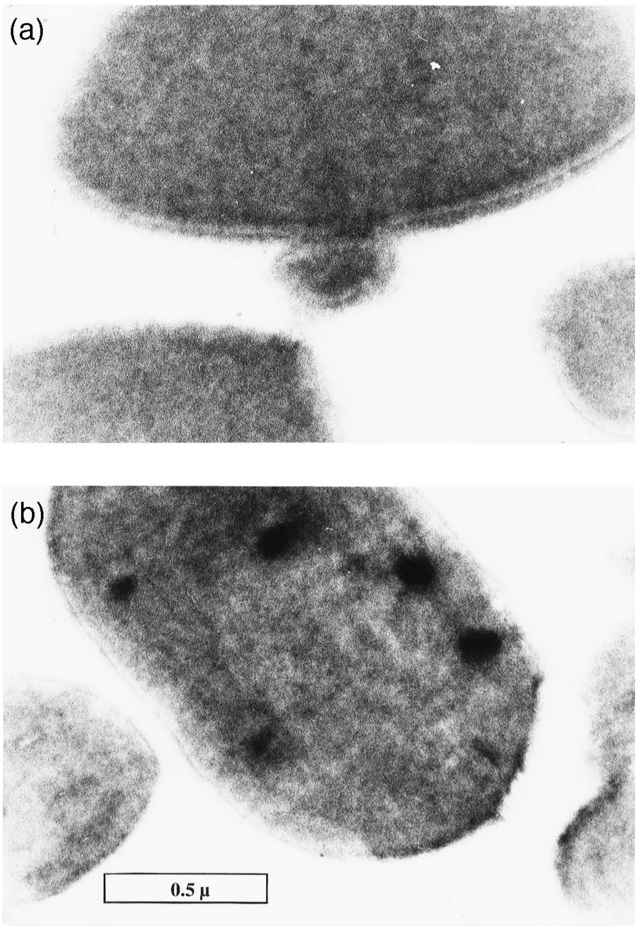

**Figure 8** TEM micrograph of the extracted PSU/PSU copolymer particles dispersed in epoxy and stained with $RuO_4$; (a) PA 6/PSU 0 and (b) PA 6/PSU 348

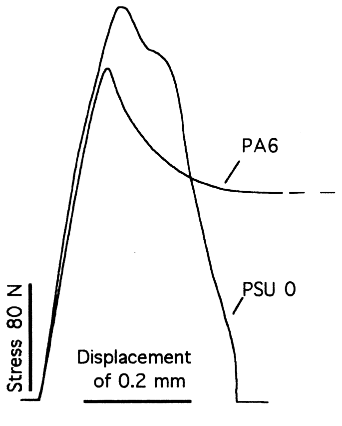

**Figure 9** Traction curves for the PA 6 and the PSU 0

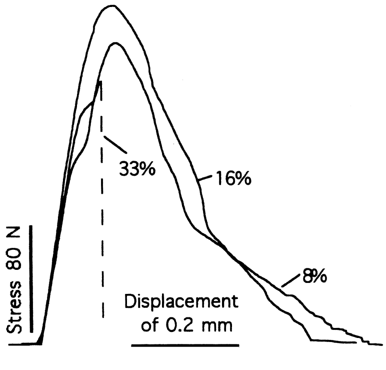

**Figure 10** Traction curves for the PA 6/PSU blends

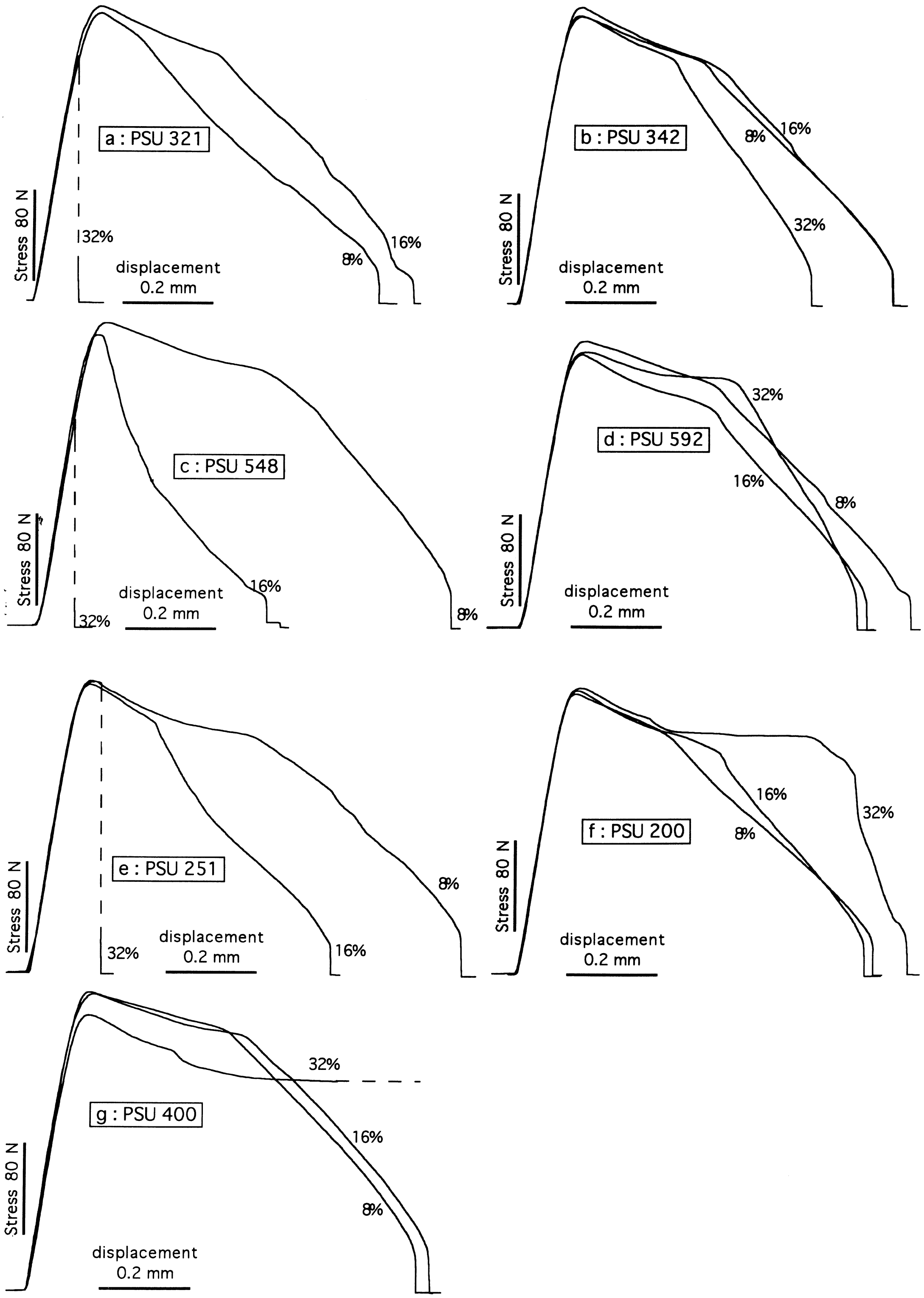

**Figure 11** Traction curves for the PA 6/PSU/PSU copolymer blends

interaction parameter due to the introduction of functional monomer in the PSU should not be responsible for large effects. This is expected, since only a few per cent of these functional monomers are added.

It is, nevertheless, remarkable that relatively low carboxylic acid functionality results in significant interfacial modification. At lower temperatures, in PA/rubber blends, concentration of carboxylic acid has to be of the order of 20–40%[26,27] to give interesting interfacial modification. In order to get larger amounts of grafted copolymer, the carboxylic acid functionality could be replaced by an anhydride functionality. The PA/carboxylic acid and PA/anhydride reaction have already been compared, showing that the anhydride groups have much faster reactions[28]. In this latter case, complete coverage of the interface was observed for PA 6/PP blends[29] and interfacial saturation could be shown in PA 6/EP blends[30].

The introduction of PSU copolymer brings a nice control of the blend morphology. However, the industrial development of these new materials is pushed by the

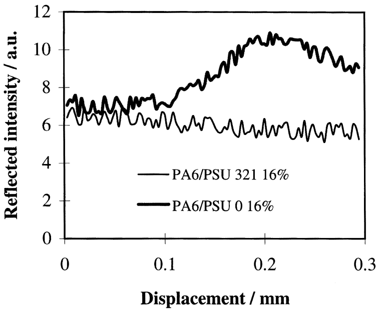

**Figure 12** Back-scattered intensity as a function of the traction for PA/PSU 0 (84/16) and PA/PSU 321 (80/16)

possibility of obtaining improved mechanical properties. *Figure 9* shows traction curves for PA and PSU polymers. The PSU has higher modulus and yield point, but the PA has a remarkable elongation at break. In *Figure 10*, it is observed for PA/PSU blends that the elongation at break of the PA is lost by the addition of PSU. In *Figure 11*, however, it is observed that by the addition of PSU-copolymers, toughness can be improved. However, going in the order of decreasing particle size one has *Figure 11a–g* which show increasing elongation at break. This is very important for the blends containing 32% PSU. Particle size is the dominant parameter controlling mechanical properties.

Improved toughness of polyamide/rubber blends comes from the cavitation or debonding of the rubber particles[31]. This results in the intense whitening of the material in the deformed region. *Figure 12* shows the surface whitening during deformation of the PA/PSU and PA/PSU/PSU copolymer blends. Only the PA/PSU blend exhibited surface whitening. However, as shown in *Figure 10* the PA/PSU blends were less ductile. In *Figure 9*, it is observed that the yield point of the PSU is much higher than that of the PA. Therefore, PSU particles are not likely to cavitate. When the stress concentration is high, only debonding of the PSU particles would release it and slight whitening is indeed observed.

**Figure 13** Fracture surface of the PA/PSU 251 (68/32) at low magnification

The back-scattered light only comes from a thin layer at the surface of the sample. Since PA and PSU have different refractive indexes, the fine dispersion of the PSU induces strong light scattering. *Figure 13* shows a global view of the fracture surface of a PA/PSU/PSU copolymer blend. It can

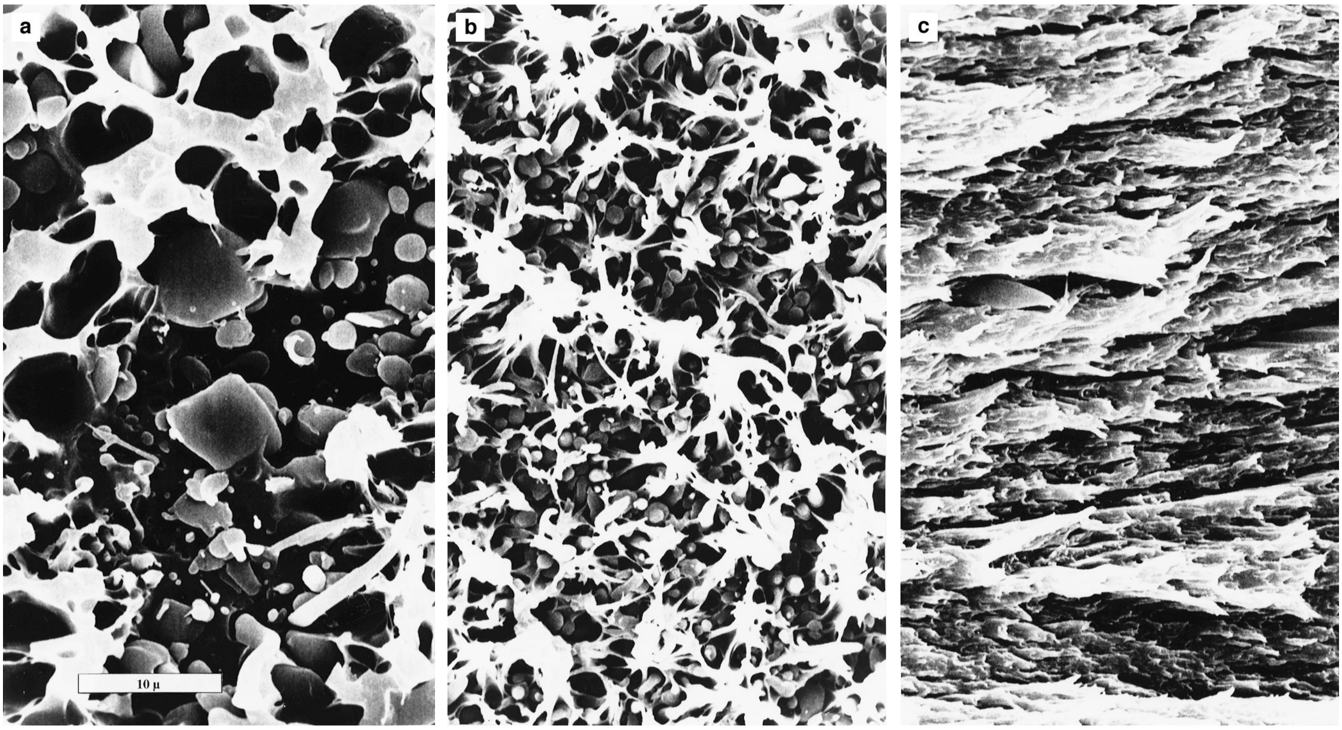

**Figure 14** Fracture surface of PA/PSU/PSU copolymers blends with 68% of PA for (a) PA 6/PSU 0; (b) PA 6/PSU 251 and (c) PA 6/PSU 200

be observed that along the surface of the sample, a thin layer of material has a different fracture mechanism and appears quite smooth. In this region, debonding of the PSU/PSU copolymer particles does not occur and the back-scattered light is not modified by the deformation and the bulk whitening of the sample. At the surface, in plane stress conditions, only a small improvement in the particle adhesion is required to avoid debonding. As stressed by Gent[32], the cavitation or the debonding of rubber depends on the size of the inclusion; then in our case, smaller particle size is also a reason why debonding of the PSU particles is not observed in the surface layer. Moreover, in addition to the change in the stress state at the surface of the sample, orientation of the chain and fast crystallization at the mould surface can induce changes in deformation mechanism. However, such an effect would be comparable whether PSU copolymer is present in the blend or not.

In a more plane strain region, that is, in the middle of the sample, significant differences of deformation mechanism are observed. In *Figure 14* fracture surfaces are compared for different blends. For the brittle fracture of the PA 6/PSU 32% blend, PSU particles and holes are found on the fracture surface without tearing or fibrillation resulting from the yielding of the PA. For a more ductile blend, small-scale yielding is observed between the PSU particles. It should be noted that for the eye the fracture surface is white. Nevertheless, the change in fracture mechanism with the increasing co-monomer content in the PSU can be due to both the reduction in particle size, which seems dominant, and the improved interfacial adhesion promoted by the graft-copolymer layer at the interface between the two components of the blends.

## CONCLUSIONS

Aliphatic polyamide, polysulfone and polysulfone copolymerized with 4,4′-bis(4-hydroxyphenyl)pentanoic acid bearing carboxylic acid functions were melt blended in the MINI-MAX moulder.

The morphology of blends strongly depends on the viscosity ratio of the components, but concentration of the carboxylic acid group in the PSU phase may also bring interesting control of the particle size. It was shown that the carboxylic acid function is able to react with the polyamide amino end groups. The result of this reaction is a grafted copolymer located at the interface. However, the amount of graft copolymer formed is relatively low compared with what is produced in toughened PA, but nevertheless sufficient to promote interesting interfacial modification resulting in lower interfacial tension and improved phase adhesion.

The introduction in PA/PSU blends of carboxylic acid functional PSU not only controls the morphology but opens the possibility of blending PA and PSU with interesting toughness with the advantage of the high yielding point of the PSU and the large elongation at break of the PA. Introduction of PSU in PA modifies the fracture mechanism. Without carboxylic acid, functionalized PSU adhesion is poor and particle size is large, resulting in reduced mechanical properties compared with the properties of the blend components. With 3.3% of functional units in the PSU phase, the particle size reduction and the improved interfacial adhesion lead to blends whose properties are intermediate to that of the components.

It is remarkable that such low concentration of carboxylic acid functionality may lead to significant interfacial modification and interesting mechanical properties.

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