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Reactive compatibilization of A/(B/C) polymer blends

Part 3. Quantitative analysis of the interfacial thickness and the interfacial reaction

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The interfacial thickness in reactively compatibilized polymer blends is analysed with ellipsometry for the blend system polyamide 12/(polystyrene/poly(styrene-co-maleic anhydride)) PA-12/(PS/SMA2) and the blend system PA-12/SMA for different SMA types. Bilayer specimens were prepared and the interfacial thickness was measured *in situ* during annealing in the melt. SMA2 is expected to react with the amino endgroups of PA-12 to form a graft copolymer. For the blend system PA-12/(PS/SMA2), the interfacial thickness displays a clear maximum as a function of the SMA2 content. An attempt is made to interpret this phenomenon. This study of the interfacial thickness in bilayer systems PA-12/(PS/SMA2) was compared with an analysis of the interfacial reaction in extruded blends PA-6/(PS/SMA2). An extraction procedure was developed to remove the PA-6 phase from the extruded blends PA-6/(PS/SMA2) and to characterize the remaining PS/SMA2 phase with *FT*i.r.. In this way, the amount of reacted MA groups can be determined. The effect of different parameters such as the SMA2 content in the blends, the amount of dispersed phase (PS/SMA2) and the molecular weight of PA-6 was analysed with respect to the amount of reacted MA groups. The amount of reacted MA groups is interpreted as a complex parameter depending on the particle size of the dispersed PS/SMA2 phase, the interfacial thickness and the concentration of available anhydride groups and amino endgroups in the interfacial region. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polymer blends; PA-12-/(PS/SMA2); interfacial thickness)

INTRODUCTION

Reactive compatibilization of polymer blends is a method which is very often used to obtain compatibilized blends with favourable properties[1,2]. The technique of reactive compatibilization is based on the *in situ* formation of a block- or graft copolymer at the interface between the phases of a polymer blend during melt-mixing. Since most polymer blends do not have the appropriate functional groups, a functionalization of the blend components is required. However, in some cases, a third polymer, which is miscible with one of the blend components and reactive with the other, can be used for the formation of a compatibilizing copolymer at the interface[1,2]. In most of the studies related to the compatibilization of polymer blends, the emphasis is on the characterization of the phase morphology and the evaluation of the mechanical properties. In this paper, special interest is given to the thickness of the interface and the characterization of the interfacial reaction in reactively compatibilized blends.

The technique of ellipsometry has been used in recent studies to measure the interfacial thickness between two polymer layers[3–6]. One of these studies[6] deals with the measurement of the interfacial thickness in a reactive bilayer system where one layer consisted of amorphous polyamide (a-PA) and the other layer of a miscible blend of poly (styrene-co-acrylonitrile) (SAN) and poly (styrene-co-maleic anhydride) (SMA). The bilayer system studied in our paper is a comparable reactive system in which one of the layers consists of polyamide 12 (PA-12) and the other layer of the miscible components polystyrene (PS) and poly (styrene-co-maleic anhydride) (SMA2; 98 wt% S, 2 wt% MA). The anhydride groups of SMA2 are expected to react with the amino chain ends of PA-12. PA-12 has been selected on account of its lower melting point (176°C) than that of other aliphatic polyamides (f.e. PA-6, $T_m = 221$°C). Due to the lower melting point of PA-12, the sample preparation and the ellipsometric measurement can be performed at a lower temperature at which degradation is negligible[7].

The characterization of the interfacial reaction in reactively compatibilized blend systems is a very important topic but adequate characterization methods are very rare[8–10]. For most blend systems, the amount of reacted groups or the amount of newly formed groups during extrusion cannot be measured by techniques such as *FT*i.r. or NMR. In most cases, the concentration of the reactive groups is too low to be accurately determined. Hence, a selective separation of the blend components is required, but this is not always possible.

The aim of this paper is to determine the amount of reacted MA groups or the amount of newly formed imide groups during melt-extrusion of the blend system PA-6/(PS/SMA2). A method was developed to remove the PA-6 phase

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from the blend in order to make the *FT*i.r.-spectrum less complex. The remaining phase PS/SMA2 appeared to be very suitable for *FT*i.r. analysis and the concentration of the remaining anhydride groups could be accurately determined. The effect of different parameters such as the molecular weight of PA-6, the concentration of SMA2, the percentage of dispersed phase and the extrusion time was analysed with respect to the amount of reacted anhydride groups: in a recent paper, the blend system PA-6/(PS/PS-g-MA) was studied by Park *et al.*[11] but the characterization of the interfacial reaction was very limited.

Table 1 The molecular characteristics of the different blend components

Material	Method	M_w
PA-6	$[\eta]$ in	18 000
PA-6	HCOOH/H_2O 85/15	24 000
PA-6	at 25°C	35 000
PA-6		44 000
PA-12	–	–
PS	GPC in THF	180 000
SMA2		145 000
SMA8	$[\eta]$ in	280 000
SMA14	THF at 25°C	190 000
SMA17		210 000
SMA20		125 000

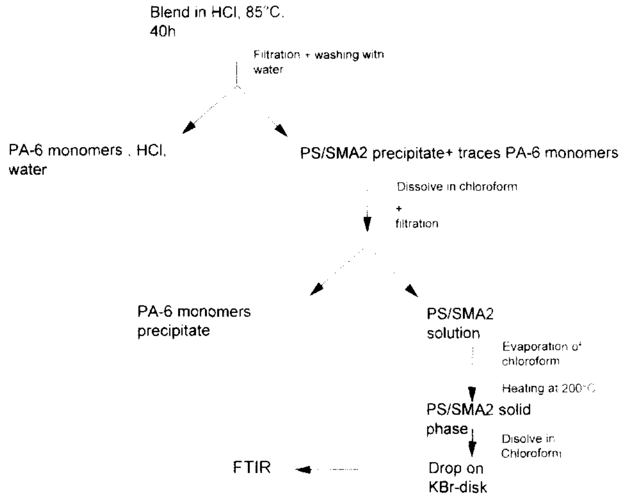

Figure 1 The complete extraction procedure to remove the PA-6 phase from the PA-6/(PS/SMA2) blend in order to determine the amount of unreacted MA groups

EXPERIMENTAL

Materials

The characteristics of the blend components are given in *Table 1*. Four different types of PA-6 and one type of PA-12 were used, which were all provided by DSM-Research. PS was provided by Denki Kagaku Kogoyu Co. under the commercial name Denka-Styrol GP-1. SMA2, SMA17 and SMA20 was supplied by BAYER. SMA14 was provided by Arco. SMA8 was provided by Arco. The number after SMA denotes the weight % maleic anhydride in SMA. The molecular weight of the polymers was determined using gel permeation chromatography (GPC) and intrinsic viscosity measurements.

Ellipsometry

A bilayer specimen composed of a thin PS/SMA2 film (*ca.* 600–700 nm) and a thick PA-12 substrate was prepared. The thick PA-12 substrate was prepared by melt-pressing PA-12 at 205°C between two silicon wafers to create an optically flat surface. The thin film was prepared by spin-coating a 6 wt% solution of PS/SMA2 in chlorobenzene onto a silicon wafer. Subsequently, the thin film was mounted on the thick substrate by the floating-on-water and pick-up technique[3,4]. The bilayer specimen thus prepared was dried at 50°C overnight. Besides the bilayer system PA-12/(PS/SMA2), the bilayer specimen PA-12/SMA was prepared with different SMA types. In these measurements, the thick substrate consisted of PA-12 and the thin film consisted of SMA.

The ellipsometric measurements were carried out using an automated ellipsometer (EL-8, Optec Co., Ltd.). Incident light from a He–Ne laser (632.8 nm) was applied to the bilayer specimen at an incident angle of 70°. The retardation Δ and reflection ratio tan ψ of reflected light were determined from ellipsometric readings. For data analysis, we used the four-layer model. With this four-layer model, the best set of data for d_2 and d_3 can be estimated by fitting the experimentally measured data Δ and tan ψ. The

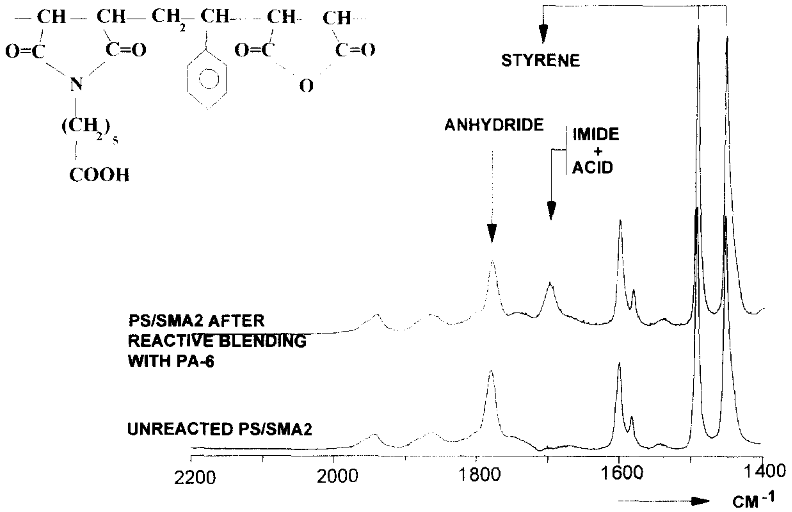

Figure 2 *FT*i.r. spectrum of PS/SMA2 before and after reactive blending with PA-6 (+ extraction of PA-6) together with the expected structure of SMA (after reactive blending with PA-6 + extraction procedure)

mathematical equations of this fitting procedure were discussed in previous papers[3-6]. The refractive indices of the different polymers were measured by ellipsometry as a function of temperature. To perform the refractive index measurements, the different materials were spin coated onto a silicon wafer from a 2 wt% solution. Chlorobenzene was used as a spin coating solvent for PS and SMA and *m*-cresol for PA-12. The refractive index data were used for the fitting procedure. The refractive index of the interface is approximated to be uniform and equal to $n_3 = (n_2 + n_4)/2$. Taking into account the composition profile at the interface layer, the interfacial thickness is determined as $\lambda = d_3/1.7$.

Blend preparation

Different compositions of the blend PA-6/(PS/SMA2) were prepared in a double screw mini-extruder designed by DSM-Research (Netherlands). The mixing chamber is saturated with nitrogen gas during blending to avoid oxidative degradation of the blend components. The extrusion temperature was always kept constant at 240°C during blending and the screw speed was 100 rpm.

A preblend of PS and SMA2 was prepared in the mini-extruder in order to obtain a miscible blend. This preblend was cut into small pieces, and used in the final extrusion step. In this final extrusion step, the PS/SMA2 preblend is firstly injected in the mini-extruder, immediately followed by PA-6. The mixing time is recorded from the moment all the PA-6 is added. This extrusion procedure in two steps is chosen to be sure that all the SMA2 is mixed with the PS-phase. After the first extrusion step, the MA content of the preblend PS/SMA2 was checked with *FT*i.r..

After blending, the extruded polymer strand was quenched in a mixture of isopropanol/CO_2 (− 78°C) in order to freeze in the phase morphology. In all blends studied, PA-6 forms the matrix while the dispersed phase consists of the miscible components PS and SMA2.

Morphological characterization

The extruded polymer strand of the blend PA-6/(PS/SMA2) was kept in liquid nitrogen for some time and a brittle fracture was performed. This brittle surface was etched with chloroform for 48 h at room temperature in order to dissolve the dispersed phase PS/SMA2. The etched surface was kept under vacuum before coating it with a gold layer of ± 40 nm. After gold coating, the morphology was examined with a Phillips X-20 scanning electron microscope.

Characterization of the interfacial reaction

A procedure was developed to remove the PA-6 phase from the blends PA-6/(PS/SMA2) and to quantify the amount of non-reacted maleic anhydride groups by means of *FT*i.r.. The complete procedure is schematically represented in *Figure 1*. Firstly, the blends are put in 100 ml solution of HCl, 6 N at 85°C for 40 h. This causes the hydrolysis of the PA-6 matrix and the resulting PA-6 monomers are soluble in HCl, 6 N[12,13]. It was shown in the literature[14,15] that the imide links are stable under these conditions and will not undergo hydrolysis. The dispersed PS/SMA2 particles flocculate together and form a solid precipitated phase. This phase is filtered and washed with water several times to remove all PA-6 monomers. The resulting PS/SMA2 phase is dried at 50°C to remove all water. In the next step, the PS/SMA2 phase is dissolved in $CHCl_3$ and filtered. The goal of this step is to remove eventually residual PA-6 monomers (these monomers are insoluble in $CHCl_3$).

Before measuring the amount of unreacted anhydride groups in the PS/SMA2 phase, there is still one problem which has to be taken into account: the anhydride groups (which had not reacted with PA-6 during melt-mixing) can undergo hydrolysis in HCl, 6 N, 85°C and give rise to a diacid function. For this reason, the PS/SMA2 phase is heated at 200°C for 45 min in order to close the eventually opened anhydride groups; this proved to be an effective procedure to convert a diacid back into its anhydride. This method has been further tested in the following way: SMA2 was dissolved in pyridine and then a small amount of water was added. This resulted in the complete hydrolysis of the anhydride groups, as proven by *FT*i.r.. Heating this hydrolysed SMA2 (after precipitation and filtration) under the above-mentioned conditions resulted in almost complete recovery of the anhydride groups. Thus, the heating procedure above is considered to be effective to close eventually opened anhydride groups. However, it was shown (by comparing the *FT*i.r.-spectrum of the PS/SMA2 phase before and after the heating procedure) that the hydrolysis of the anhydride groups in HCl is very limited. It is very likely that most of the (non-reacted) anhydride groups will be inside a PS/SMA2 particle and will not have contact with the solvent HCl during the extraction. Nevertheless, this heating procedure has always been applied.

Finally, the PS/SMA2 phase is again dissolved in $CHCl_3$, and a droplet of this solution is put on a KBr disk. $CHCl_3$ is evaporated at room temperature and the thin film thus obtained is analysed by *FT*i.r.. The *FT*i.r. spectrum and the expected structure of SMA after extraction is given in *Figure 2*. It is impossible to quantify the amount of imidelinks formed. The absorption of imide (1700 cm^{-1}) is too close to that of the acid (1705 cm^{-1}) and moreover, a calibration curve cannot be set up for this absorption peak. However, the absorption of the anhydride group (1780 cm^{-1}) is very suitable for quantification. The two styrene peaks at 1453 and 1492 cm^{-1} are chosen as reference peaks. A baseline is drawn on the *FT*i.r.-spectrum and the height of the maleic anhydride (MA) peak is divided by the area of the two styrene (S) peaks. The ratio of both is called the 'peak ratio MA/S'.

$$\text{Peak ratio MA/S} = \frac{\text{Height MA } (1780\ \text{cm}^{-1})}{\text{Area S } (1453\ \text{cm}^{-1} + 1492\ \text{cm}^{-1})} \tag{1}$$

This 'peak ratio MA/S' can only be related to a real concentration of MA by means of a calibration curve. For this reason, different calibration mixtures PS/SMA2 were dissolved in chloroform. These mixtures have a known MA concentration. For each mixture PS/SMA2, the 'peak ratio MA/S' was measured by means of *FT*i.r.; at least six different thin films were prepared and an average 'peak ratio MA/S' was calculated. This calibration curve is presented in *Figure 3*; the 'peak ratio MA/S' is plotted as a function of the mole fraction MA in the calibration mixtures.

For samples with an unknown MA concentration (i.e. the remaining amount of MA after reactive blending), the peak ratio MA/S can be measured by means of *FT*i.r. and this can be related to a real MA concentration. In this way, the percentage reacted MA groups during reactive blending

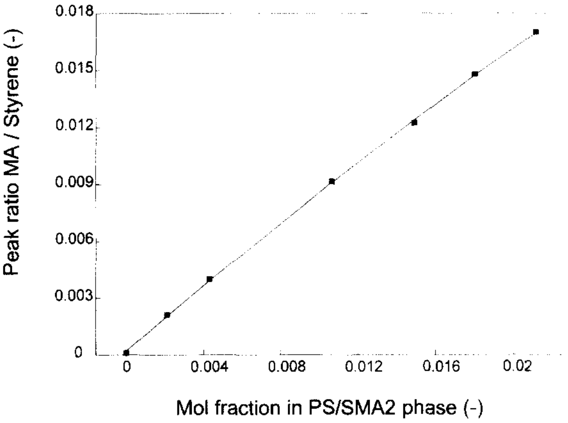

Figure 3 The calibration curve to determine the mol fraction MA in the phase PS/SMA2 from the peak ratio MA/S (*FT*i.r.)

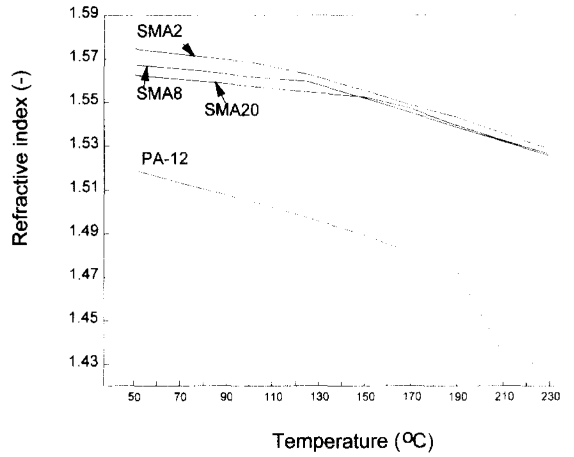

Figure 4 The temperature dependence of the refractive index of PA-12 and of some SMAs

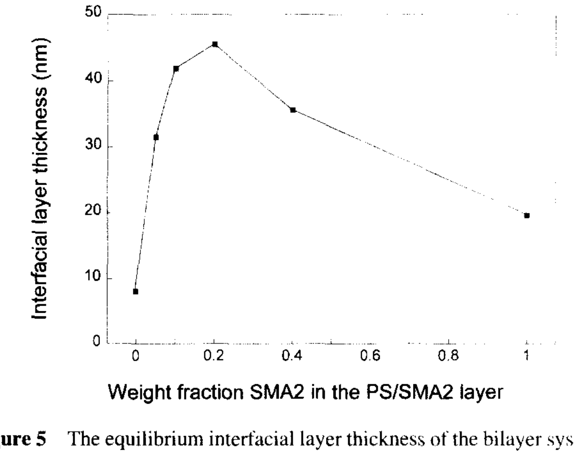

Figure 5 The equilibrium interfacial layer thickness of the bilayer system PA-12/(PS/SMA2) as a function of the SMA2 content

with PA-6 can be calculated.

$$\% \text{ reacted MAgroups} = 100 - \frac{\text{mol fraction MA of the phase PS/SMA2 after extrusion}}{\text{initial mol fraction MA of the phase PS/SMA2}} \times 100 \tag{2}$$

RESULTS AND DISCUSSION

Interfacial thickness of bilayer systems

The temperature dependence of the refractive indices is given in *Figure 4*. As can be observed, the refractive index of polymers usually decreases with increasing temperature. For the amorphous polymers (PS and all SMA types), the slope changes at T_g. For the semicrystalline PA-12, a discontinuity in refractive index is observed above the melting point (176°C). The difference in refractive index between PA-12 and the different SMA types (+ PS) is large enough for ellipsometric analysis. The temperature dependence of the refractive index of PS is not given in *Figure 4* because it is almost completely identical to that of SMA2.

Firstly, the evolution of the interfacial layer thickness of the bilayer sample PA-12/(PS/SMA2) (80/20) was studied as a function of the annealing time at 210°C. An increase in interfacial thickness was observed during the beginning of the annealing process but after some time ($<$ 10 min) the equilibrium interfacial layer thickness was obtained. It was not our goal to study the increase of the interfacial layer thickness at short times; for all other bilayer samples, the interfacial layer thickness was measured after an annealing time of 30 min at 210°C. This interfacial layer thickness is considered to be the equilibrium one.

A lot of different bilayer samples PA-12/(PS/SMA2) with a different ratio PS/SMA2 were prepared. The equilibrium interfacial layer thickness is presented in *Figure 5* as a function of the SMA2 content in the PS/SMA2 layer. As can be seen in *Figure 5*, very thick interfaces ranging up to 45 nm are obtained for the bilayer system PA-12/(PS/SMA2) (80/20). These thick interfaces suggest the formation of a core–shell particle structure in the case of reactively extruded blends with a matrix–particle morphology. It is very surprising that the interfacial layer thickness displays a clear maximum as a function of the SMA2 content. Comparable data were also found for the bilayer system amorphous a-PA/(SAN-25/SMA-23)[6]. In this case, the interfacial layer thickness was analysed as a function of the ratio SAN-25/SMA-23. The interfacial layer thickness also displays a maximum as a function of the concentration of the reactive copolymer SMA-23; the thickest interface in this system is found for the concentration (SAN-25/SMA-23) (80/20).

So, for both systems analysed with ellipsometry, the interfacial layer thickness displays a clear maximum as a function of the concentration of the reactive copolymer (SMA), and the interfacial layer thickness of the bilayer system consisting of polyamide and pure reactive copolymer is quite low. It is not easy to give a straightforward interpretation to this phenomenon. Nevertheless, an attempt is made in the following paragraph by taking into account the way in which the interface is formed.

Firstly, a bilayer system is considered in which the concentration of SMA2 in the thin film is low (i.e. PS/SMA2 80/20). The part of this thin film which is in contact with the PA-12 substrate will contain a high concentration of non-reactive PS-chains. These PS-chains are more mobile than the complex shaped graft copolymers resulting in a higher mobility of the interfacial region. During the annealing treatment in the melt, some SMA2 chains may diffuse towards the interface and some PS may be rejected from the interfacial region. However, in these static bilayer specimens, it is unlikely that all PS is rejected from the interfacial region. In reactively extruded blends, diffusion is probably

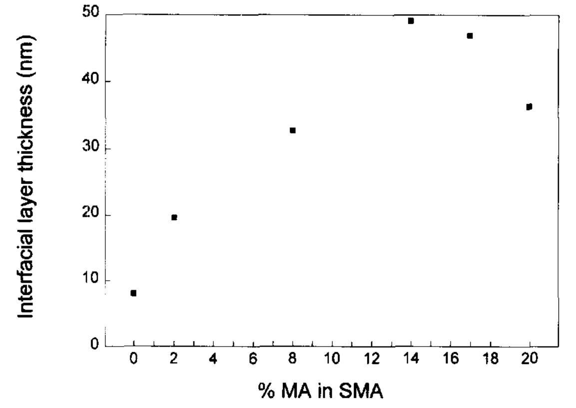

Figure 6 The equilibrium interfacial layer thickness of the bilayer system PA-12/SMA as a function of the MA content of SMA

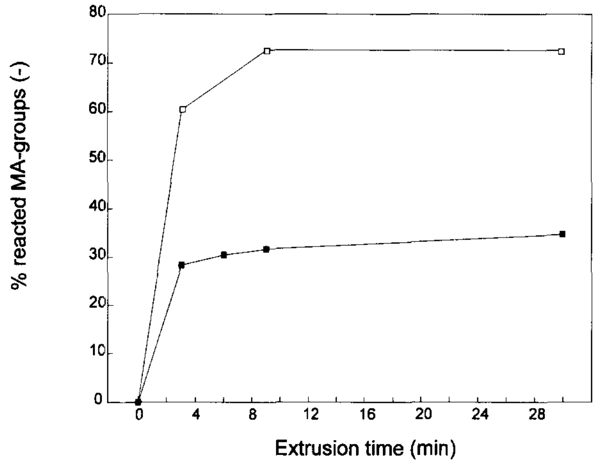

Figure 7 The percentage reacted MA groups in PA-6/SMA2 80/20 blends (■) and PA-6/(PS/SMA2) 80/(16/4) blends (□) as a function of the extrusion time M_w PA-6 = 44 000

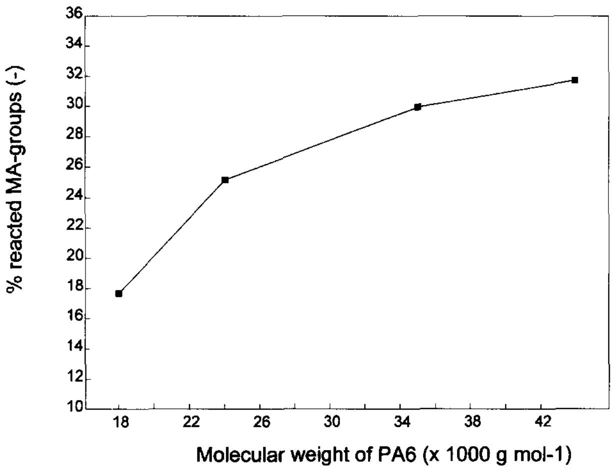

Figure 8 The percentage reacted MA groups in the PA-6/SMA2 80/20 blend as a function of the molecular weight of PA-6

much more important than in these bilayer systems and the final ratio PS/SMA2 in the interfacial region may be different. Secondly, we consider a bilayer system in which the thin layer consists of pure SMA2. In this case, all the chains at the interface are reactive and a very immobile interfacial region will be formed. It is assumed that the formation of a very thick interface is impossible in this system on account of the generation of an immobile interfacial region.

In another series of experiments, different bilayer specimens PA-12/SMA were prepared with a different MA content of SMA. The interfacial layer thickness was measured during annealing at 210°C; the interfacial layer thickness after 30 min of annealing was considered to be the equilibrium one. The equilibrium interfacial layer thickness is presented in *Figure 6* as a function of the MA content of SMA. As can be seen, the equilibrium interfacial layer thickness increases as a function of the MA content in SMA, reaches a maximum and then slightly decreases. With respect to the interpretation of these results, it is important to note that there is not only a difference in MA content between the different SMA types but also a difference in molecular weight (see *Table 1*) and a difference in T_g. The higher T_g of the SMA types with a higher MA content might partly explain the slight decrease of the interfacial layer thickness at very high MA content of SMA, as seen in *Figure 6*.

Analysis of the interfacial reaction

The extraction and characterization procedures discussed in the experimental part were applied to determine the amount of reacted MA groups in a series of blends PA-6/(PS/SMA2). Before interpreting the results, it is important to know whether the 'peak ratio MA/S' (measured with *FT*i.r.) will not change during the extrusion due to degradation of maleic anhydride or styrene. For this reason, pure SMA2 was extruded during 30 min at 240°C in the mini-extruder. The 'peak ratio MA/S' of SMA2 was still unchanged after 30 min extrusion, compared to the 'peak ratio MA/S' of SMA2 before extrusion. Therefore, it can be concluded that there are no degradation processes during extrusion which could affect the 'peak ratio MA/S' of SMA2.

The first parameter under examination is the effect of the extrusion time. PA-6/SMA2 80/20 and PA-6/(PS/SMA2) 80/(16/4) blends-were extruded at 240°C for different extrusion times. The highest molecular weight PA-6 ($M_w = 44\,000$) was used in this study. The percentage reacted MA groups is given in *Figure 7*, as a function of the extrusion time. As can be seen from this figure, for both blends, the interfacial reaction is almost completed after 3 min extrusion. This indicates that the interfacial reaction itself and also the diffusion of the SMA2 towards the interface is very fast. The effect of the extrusion time was also analysed for the above two blends with the lowest molecular weight PA-6 (M_w = 18 000). Again, the interfacial reaction was almost completed after 3 min. For all the other blends studied, an extrusion time of 9 min was always applied.

Another parameter under investigation is the molecular weight effect of the PA-6 matrix. PA6/SMA2 80/20 blends with a different molecular weight of PA-6 were prepared for a mixing time of 9 min. The percentage of reacted MA groups is plotted as a function of the PA-6 molecular weight in *Figure 8*. It is observed that the percentage of reacted MA groups gradually increases as a function of the molecular weight. This is a rather surprising result because the amount of reactive amino chain ends is higher for the low molecular weight PA-6 (see *Table 2*). However, SEM analysis of the phase morphology of these blends revealed that the average particle size is larger for the blends with a low molecular weight PA-6 matrix. This larger particle size and thus the lower amount of interfacial reaction area probably explains

Table 2 The concentration of end groups of PA-6 (mmol/g)

M_w of PA-6	[amino] (mmol/g)*	[acid] (mmol/g)*
18 000	0.043	0.081
24 000	0.046	0.052
35 000	–	
44 000	0.029	0.027

*As given by the supplier.

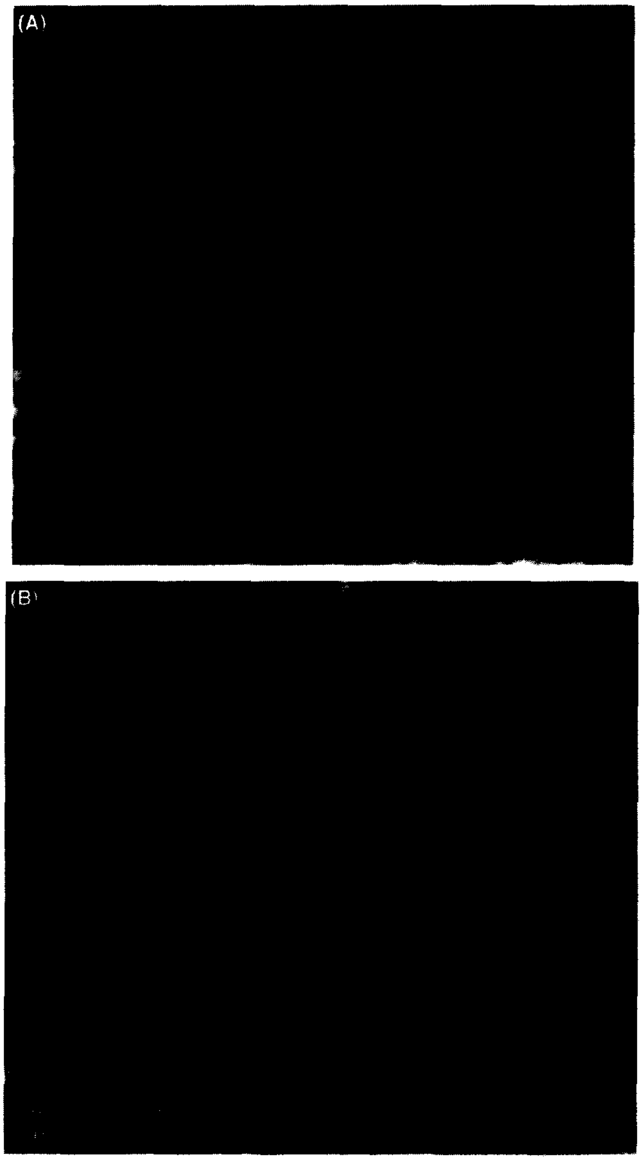

Figure 9 SEM micrographs of the PA-6/SMA2 80/20 blend for two different molecular weights of PA-6. (a) M_w = 24 000; (b) M_w = 18 000

the lower amount of reacted MA groups in the blends with the low molecular weight PA-6. The morphologies of some of these blends is presented in *Figure 9*. The larger particle size of the blends with the low molecular weight PA-6 can be accounted for by the lower viscosity of PA-6, resulting in a lower dispersive force of the PA-6 matrix. The higher rate of coalescence in a low molecular weight PA-6 is not expected to play a role of importance since coalescence is normally completely absent for well compatibilized blends.

As a third parameter, the effect of the amount dispersed phase was investigated. PA-6/SMA2 blends with different concentrations of the dispersed phase (SMA2) were prepared. Two different molecular weights of PA-6 were used (M_w = 44 000 and M_w = 18 000). As can be seen from *Figure 10*, the percentage reacted MA groups was found to increase with decreasing amount of the dispersed phase. The different factors that have to be taken into account for the interpretation of this result are discussed below:

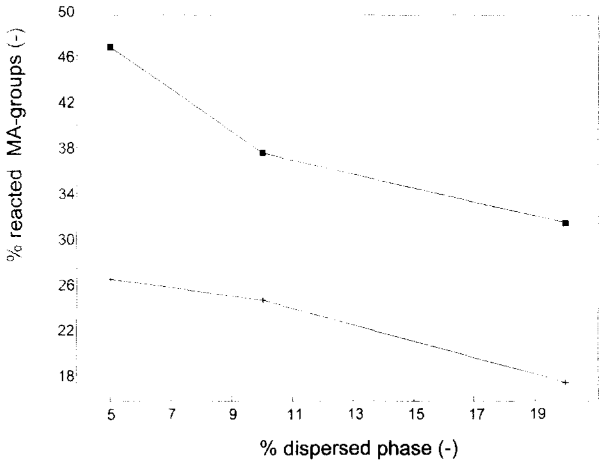

Figure 10 The percentage reacted MA groups in the PA-6/SMA2 blend as a function of the % dispersed phase (SMA2). (■) = M_w PA-6 = 44 000; (+) = M_w PA-6 = 18 000

Table 3 The concentration of reactive groups in various compositions of the PA-6/SMA2 blend for different molecular weights of PA-6

PA-6/SMA2	M_w of PA-6 (g/mol)	[amino] (mmol/g)	[MA] (mmol/g)	[amino]/[MA] (-)
80/20	44 000	0.0232	0.0408	0.568
90/10		0.0261	0.0204	1.279
95/5		0.0276	0.0102	2.701
80/20	18 000	0.0344	0.0408	0.843
90/10		0.0387	0.0204	1.897
95/5		0.0409	0.0102	4.005

(i) The observed trend could have resulted from a decreasing particle size and an increasing amount of interfacial reaction area as the percentage dispersed phase decreases. However, SEM analysis of the phase morphology revealed that the particle size is quite independent of the percentage dispersed phase, indicating that coalescence is suppressed in these kind of blends. The SEM micrographs are represented in *Figure 11*.

(ii) The concentration of reactive groups will be different for the different blends as shown in *Table 3*. For the blends with 5% and 10% dispersed phase, there is an excess of amino chain ends while for the blends with 20% dispersed phase, there is an excess of maleic anhydride groups. One should consider these concentrations of reactive groups with care. In fact, only the reactive groups that are available for reaction at the interface, are important. Steric hindrance will limit the amount of reactive groups available for interfacial reaction. So, the question is whether the excess of reactive amino end groups in the case of 5% dispersed phase will really lead to a higher concentration of amino groups available for reaction in the interfacial region (compared to the blend with 20% dispersed phase). This is discussed in the following point.

(iii) The interparticle distance will decrease as the amount of dispersed phase increases. When the interparticle distance becomes very short, the interfacial reaction zones of two particles can penetrate each other. This can result in a

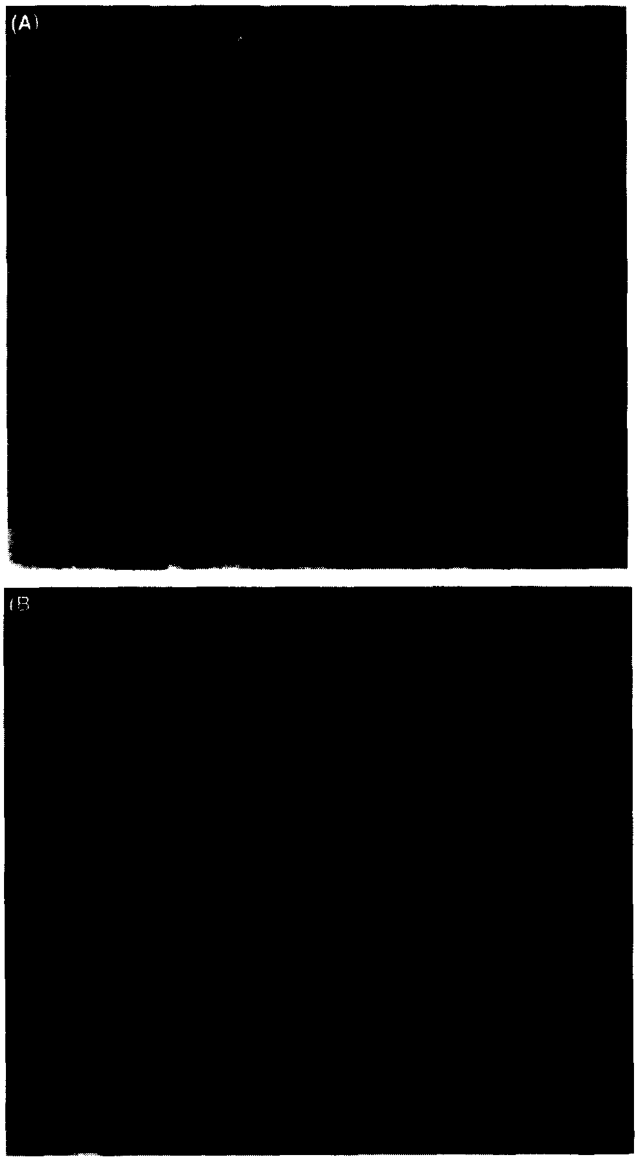

Figure 11 SEM micrographs of (a) PA-6/SMA2 95/5 and (b) PA-6/SMA2 90/10 M_w PA-6 = 18 000

situation where some PA-6 chains (with one amino chain end) are located in the interfacial reaction zone of more than one particle, which will decrease the amount of available amino chain ends and in this way also the percentage reacted MA groups. This is believed to be the predominant factor explaining the observed trend in *Figure 10*.

The fourth parameter that was varied is the concentration of SMA2 in the blend PA-6/(PS/SMA2). Different compositions were prepared: all blends have 80% PA-6 and 20% PS/SMA2 with varying PS/SMA2 weight ratios. Two different types of PA-6 were used (M_w = 44 000 and M_w = 18 000). Firstly, the phase morphology of these blends is discussed. For the uncompatibilized blends PA-6/PS, the dispersed PS particles are larger in the low molecular weight PA-6 matrix (*Figure 12a,b*). This can easily be explained on the basis of the lower dispersive forces and the higher coalescence rate in a low molecular weight matrix. However, this trend is inverted in the blend PA-6/(PS/SMA2) 80/(16/4); the dispersed particles are much larger in the higher molecular weight PA-6 matrix (*Figure 12c,d*). However, at a higher magnification, a second population of very small particles is observed in the case of the high molecular weight matrix (*Figure 12e*). This behaviour is interpreted in the following way:

(1) It is very likely that, in the case of the high molecular weight PA-6, the graft copolymer has left the interface, resulting in a bimodal particle size distribution as seen in *Figure 12e*. In a previous paper[16] it was concluded that, in the blend system PA-6/(PMMA/SMA), the graft copolymer is repelled from the interface due to the weak miscibility of the SMA main chain of the graft copolymer with the dispersed phase and the large forces exerted on the PA-6 side chains of the graft copolymer in an extruder.

(2) For the blend system PA-6/(PS/SMA2), the miscibility of PS and SMA2 can also be considered as relatively weak. In the literature, demixing was found between PS and SMA6[17].

(3) In the case of the low molecular weight PA-6, a bimodal distribution is not observed (*Figure 12f*). Very probably, the graft copolymer has not left the interface in this case, which is also indicated by the much better compatibilizing effect compared to the high molecular weight matrix (*Figure 12c–d*). It is not completely clear why the graft copolymer is only repelled from the interface in the case of the high molecular weight matrix but we assume that the higher viscosity and the higher shear forces in a high molecular weight matrix enhance this phenomenon.

In the blends PA-6/(PS/SMA2) with weight ratios PS/SMA2 40/60, 20/80 and 0/100, the particle size is again smaller for the high molecular weight matrix (as already discussed before); a bimodal distribution is not observed for these blends.

The percentage reacted MA groups for the blends PA-6/(PS/SMA2) is given in *Figure 13* as a function of the SMA2 content. The percentage reacted MA groups decreases with increasing SMA2 content. The observed trend in *Figure 13* can be explained by the two following factors. Firstly, when the concentration of SMA2 is increased, the interface will become saturated with SMA2, and as a consequence, some SMA2 molecules will not be able to reach the interface to react. This will of course decrease the percentage of reacted MA groups. Secondly, the steric hindrance between grafted PA-6 chains at the interface will increase as the concentration of SMA2 increases and the amount of grafted PA-6 chains increases. This will also decrease the percentage reacted MA groups.

The blend PA-6/PS/SMA2 80/(16/4) with the high molecular weight PA-6 (bimodal distribution) has a very high conversion level of MA. It should be noted that once the graft copolymer has left the interface, the steric hindrance will be lower at the interface and the other unreacted SMA2 chains can also diffuse from the core of a particle towards the interface.

In *Figure 13*, the results were plotted in a relative way: the amount of reacted MA groups is expressed as a percentage of the initial amount of MA groups [equation (2)].

The results can also be plotted in an absolute way: the amount of reacted MA groups can be expressed as the difference between the initial mol fraction MA in the PS/SMA2 phase and the mol fraction MA in the PS/SMA2 phase after extrusion.

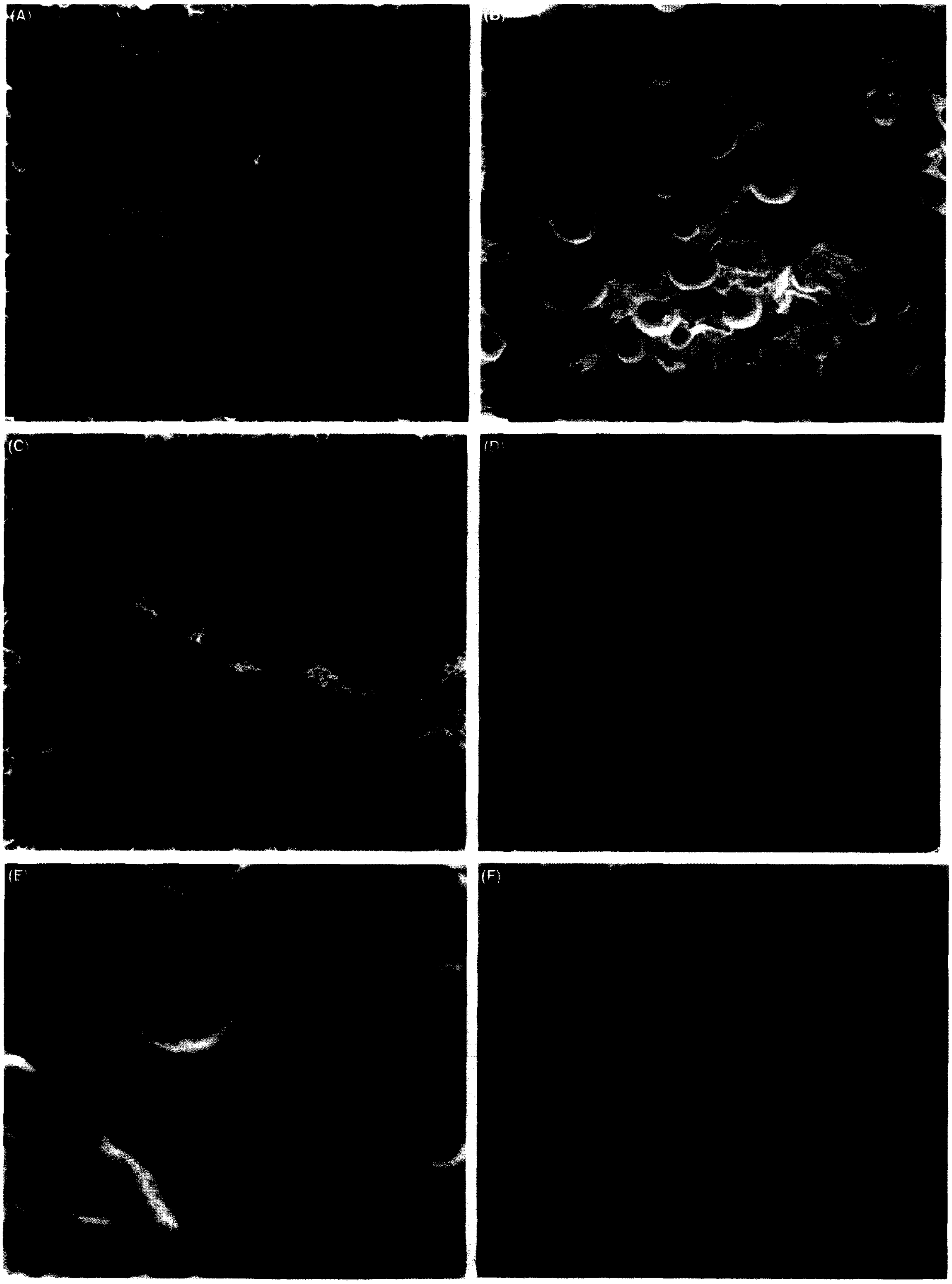

Figure 12 SEM micrographs of PA-6/(PS/SMA2) blends (80% PA-6; 20% PS/SMA2) with different weight ratios PS/SMA2 for two different molecular weights of PA-6 (a,c,e: $M_w = 44\,000$; b,d,f: $M_w = 18\,000$). (a + b) PS/SMA2 = 20/0 (Magn. × 2000); (c + d) PS/SMA2 = 16/4 (Magn. × 2000); (e + f) PS/SMA2 = 16/4 (Magn. × 20 000)

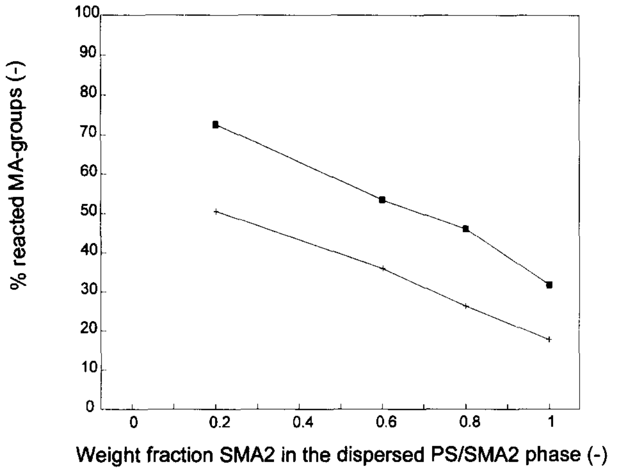

Figure 13 The percentage reacted MA groups in PA-6/(PS/SMA2) blends with 80% PA-6 as a function of the SMA2 content of the dispersed phase. (■) = M_w PA-6 = 44 000; (+) = M_w PA-6 = 18 000

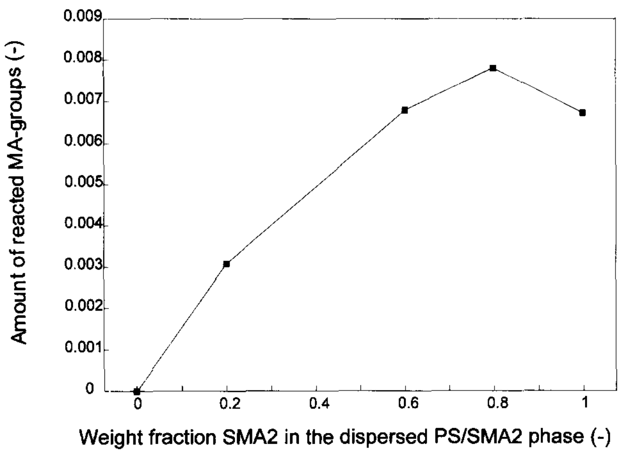

Figure 14 The amount of reacted MA groups (equation (3)) in PA-6/(PS/SMA2) blends with 80 % PA-6 as a function of the SMA2-content of the dispersed phase. M_w PA-6 = 44 000

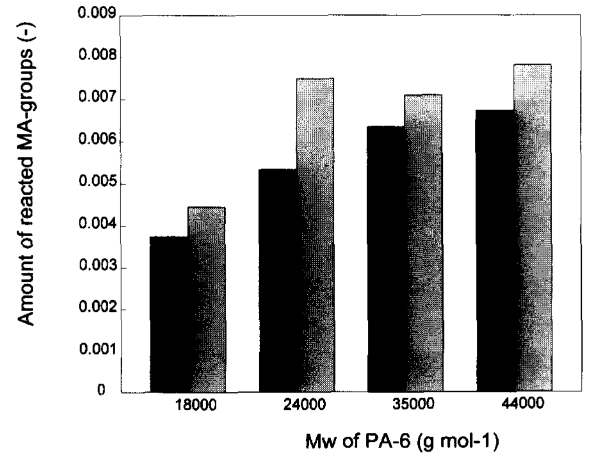

Figure 15 The amount of reacted MA groups (equation (3)) in PA-6/SMA2 80/20 blends (black bars) and PA-6/(PS/SMA2) 80/(4/16) blends (shaded bars) for different molecular weights of PA-6

$$\text{Absolute amount of reacted MA} - \text{groups} = \text{initial mol fraction MA} - \text{mol fraction MA after extrusion} \quad (3)$$

This parameter is plotted in *Figure 14* for the previous blend series with the high molecular weight PA-6. It was expected that the absolute amount of reacted MA groups would first increase with increasing SMA2 content and then become constant at higher concentrations of SMA2. However, as can be seen in *Figure 14*, the amount of reacted MA groups displays a slight maximum as a function of the SMA2 content. The PA-6/SMA2 80/20 blends and the PA-6/(PS/SMA2) 80/(4/16) blends were also prepared for the other available molecular weights of PA-6. In *Figure 15*, it can be seen that, for each molecular weight of PA-6, the absolute amount of reacted MA groups is higher for the PA-6/(PS/SMA2) 80/(4/16) blend than for the PA-6/SMA2 80/20 blend. The interpretation of this phenomenon is not so easy; the following factors have to be taken into account:

(i) The concentration of available MA groups in the interfacial region should increase with increasing SMA2 content in the blend. However, at higher SMA2 contents, steric hindrance may limit the interfacial reaction and the concentration of available MA groups in the interfacial region may become constant. So, one should expect that the absolute amount of reacted MA groups first increases as a function of the SMA2 content and then becomes constant at high SMA2 content. This is indeed the trend that is observed in *Figure 14* except for the slight maximum observed at high SMA2 content. An attempt is made to clarify this slight maximum in the following point.

(ii) The previous measurements of the interfacial thickness in the bilayer systems PA-12/(PS/SMA2) have to be taken into account. If we assume that, according to *Figure 5*, the interfacial thickness and thus the reaction zone, is slightly thicker for the blend PA-6/(PS/SMA2) 80/(4/16) than for the blend PA-6/SMA2 80/20, one can understand that this can give rise to a slightly higher amount of reacted MA groups for the PA-6/(PS/SMA2) 80/(4/16) blend.

CONCLUSIONS

The analysis of the interfacial layer thickness of bilayer specimens with ellipsometry revealed that:

(i) The interfacial layer thickness of the bilayer system PA-12/(PS/SMA2) displays a clear maximum as a function of the SMA2 content. Very thick interfaces up to 45 nm are formed.

(ii) The interfacial layer thickness of the bilayer system PA-12/SMA increases as a function of the MA content in SMA. At higher MA content, the interfacial layer thickness decreases again.

It is possible to remove the PA-6 phase in PA-6/(PS/SMA2) blends and to quantify the % reacted MA groups by means of *FT*i.r.. It was found that:

(i) The interfacial reaction is almost completed after 3 min extrusion.

(ii) The % reacted MA groups increases as a function of the molecular weight of PA-6. It was shown with SEM that this trend is related to the amount of interfacial reaction area.

(iii) The % reacted MA groups increases as the % dispersed phase decreases, the particle size being independent of the % dispersed phase.

(iv) The % reacted MA groups decreases as the concentration of SMA2 is increased. This can be interpreted on the basis of the increased steric hindrance at the interface as the SMA2 content increases.

(v) The absolute amount of reacted MA groups displays a slight maximum as a function of the SMA2 content which is a very surprising result. This was found for the different molecular weights of PA-6.

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