Reactive Compatibilization of the Polyamide 6/Poly(phenylene oxide) Blend by Means of Styrene–Maleic Anhydride Copolymer

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ABSTRACT: The compatibilization of the polymer blend polyamide 6/poly(phenylene oxide) (PA-6/PPO) system has been studied using the reactive random copolymer styrene–maleic anhydride (SMA) as a compatibilizer precursor. SMA is miscible with PPO when the MA content of SMA is not higher than 8 wt %. The anhydride groups of SMA react with the amino end groups of PA-6 during melt blending to form a graft copolymer at the interface with a compatibilizing effect as a result. Two different blending procedures were compared to each other and the compatibilizing effect of the added SMA was evaluated for a matrix/dispersed particle type of morphology. The effect of the different material parameters such as the functionality of SMA (wt % MA in SMA) and the molecular weight of PA-6, and blending parameters such as the extrusion time was analyzed with respect to the blend phase morphology. Finally, the amount of reacted MA groups in the blends PA-6/(PPO/SMA) was determined with FTIR after the use of an extraction method to remove the PA-6 matrix phase. The comparison between the morphological data (particle size reduction of the dispersed PPO/SMA phase) and the FTIR data (amount of reacted MA groups) of the blends considered, turned out to be very logical. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 889–898, 1999

Key words: polyamide 6; poly(phenylene oxide); interfacial reactions; melt extrusion; reactive compatibilization)

INTRODUCTION

The method of reactive compatibilization is very often used to obtain blends with desirable properties. This method is based on the *in situ* formation of a block or graft copolymer at the interface between the blend phases during melt mixing. Because most polymer blends do not have the appropriate functional groups, functionalization of the blend components is very often required.[1,2] In some cases, it is possible to add a third polymer that is miscible with one of the blend phases and reactive with the other blend phase.[3]

Blends of polyamide 6 (PA-6) and poly(phenylene oxide) (PPO) are of interest as a high-performance alloy. PA-6 has a number of interesting properties such as a good melt processability and an excellent solvent resistance. However, its heat distortion temperature is low, and it has a poor dimensional stability and low impact strength. On the other hand, PPO has a high heat distortion temperature and very good dimensional stability because of its high T_g (218°C), but

its extremely bad melt-processability prohibits the wide use of PPO. Blending of PA-6 and PPO is interesting, due to their complementary properties. However, the PA-6/PPO blend is immiscible and a compatibilizing method is required.

In the literature, several methods are described to compatibilize the blend PA-6/PPO. A graft copolymer PPO-*g*-PA-6 has been synthesized and added to this blend.[4] This method is called "physical compatibilization," because the graft copolymer is not generated via reactive extrusion but synthesized separately and then added to the blend during extrusion. This method, however, has some disadvantages; the graft copolymer synthesis is complex and expensive, and the graft copolymer will not always be located at the PA-6/PPO interface. This was also observed by Lai;[4] the diblock copolymer is more efficient than a more complex graft copolymer. The reactive compatibilization method that will be used in this article has undoubtedly more potentialities than the physical compatibilization method.

A maleic anhydride-functionalized PPO was synthesized by Campbell et al.[5] to compatibilize the blend of the PA-6,6/PPO. The formation of a graft copolymer PPO-*g*-PA was proven using an extraction method; this compatibilization strategy is certainly interesting, and the results obtained by this method will be compared to our results.

Jo and Kim[6] have studied the compatibilization effect of the random copolymer styrene–acrylic acid (SAA) in the blend of the PA-6/PPO; a graft copolymer is formed by means of the reaction between the acid groups of SAA and the amino end groups of PA-6. It was found that only the addition of a very high functional SAA copolymer (35 wt % AA) results in a compatibilization effect; the reason for this phenomenon is still unclear. Furthermore, the miscibility of the blend PPO/SAA system was not investigated, and this is certainly a crucial factor with respect to compatibilization.

In this article, the possibilities of adding a third polymer (styrene–maleic anhydride copolymers) to compatibilize the blend system of PA-6/PPO are examined. This method obviously has a number of advantages compared to the other methods described: no separate copolymer synthesis or functionalization of PPO is required, the reaction of PA-6 with anhydrides is much easier than with acid groups, and the PPO/SMA system is completely miscible when the MA content of SMA is low (0 to 8 wt % MA). Furthermore, a

Table I Molecular Characteristics of the Blend Components Used

Materials	Method	M_w
PA-6	[η] in HCOOH/	18,000
PA-6	H$_2$O 85/15 at 25°C	44,000
PPO	GPC in CHCl$_3$	54,000
SMA2	[η] in THF	145,000
SMA8	at 25°C	280,000

method has been developed to determine the extent of reaction in the PA-6/(PPO/SMA) blends to get a better understanding of the compatibilization efficiency.

EXPERIMENTAL

Materials

The characteristics of the blend components are given in Table I. Two types (with a different M_w) of the semicrystalline polyamide 6 were used; they were provided by DSM research. PPO was supplied by General Electric; it is an amorphous polymer with a T_g of ±218°C. SMA2 was provided by Bayer, and SMA8 by Arco; both polymers are amorphous with a T_g of 105 and 116°C, respectively. The number after SMA denotes the wt % maleic anhydride in SMA. The molecular weight of the polymers was determined using gel permeation chromatography (GPC) and intrinsic viscosity measurements.

Blend Preparation

The PA-6/(PPO/SMA) blends were prepared in a double screw mini-extruder designed by DSM. The mixing chamber is saturated with nitrogen gas during melt blending to avoid oxidative degradation of the blend components.[7,8] The extrusion temperature was kept constant at 270°C during blending, and the screw speed was 100 rpm. Two different blending sequences have been used; they will be discussed further on. The residence time within the mixing chamber can be varied by means of a recirculation channel. This recirculation channel can be closed, and the blended material then leaves the mixing chamber via a die. After blending, the extruded polymer strand is quenched in a mixture of isopropanol/CO$_2$

($-78°$C) to freeze in the generated phase morphology. In all blends studied, PA-6 forms the matrix while the dispersed phase consists of the miscible components PPO and SMA.

Morphological Characterization

The extruded polymer strand of the blend PA-6/(PPO/SMA) was kept in liquid nitrogen for some time, and a brittle fracture was performed. The fracture surface was etched with chloroform for 48 h at room temperature to dissolve the dispersed phase PPO/SMA. Chloroform is a suitable solvent for PPO and SMA but a nonsolvent for PA-6. 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 XL-20 scanning electron microscope.

For each blend, several micrographs with a total amount of 200 up to 500 particles were analyzed with a camera, and the diameter of the particles was calculated.[9] No attempt was made to correct for not cutting the particles at their largest diameter. A weight-average diameter (D_w) was calculated according to the following formula:

$$D_w = \frac{\Sigma\ N_i \cdot D_i^2}{\Sigma\ N_i \cdot D_i} \quad (1)$$

The interfacial area (A_{3D}) per volume unit of the dispersed phase (V_{3D}) was calculated from the total perimeter of the particles (P_{2D}) divided by the total area of the particles (A_{2D}), as obtained from the micrographs:

$$A_i(\mu m^2/\mu m^3) = \frac{P_{2D}(\mu m)}{A_{2D}(\mu m^2)} = \frac{A_{3D}(\mu m^2)}{V_{3D}(\mu m^3)} \quad (2)$$

Extraction Procedure

In a previous article,[10] an extraction procedure was described in detail to remove the PA-6 phase from PA-6/(PS/SMA2) blends. The same extraction procedure can be used to remove the PA-6 phase from PA-6/(PPO/SMA) blends. This procedure is briefly described below. The blends are put in 100 mL HCl, 6N at 85°C for 40 h. This causes the hydrolysis of the PA-6 matrix into its PA-6 monomers, which are soluble in HCl, 6N.[11,12] The imide links formed during melt extrusion are stable under these conditions.[13,14] The dispersed PPO/SMA particles are not soluble in HCl, 6N, and flocculate together to form a solid precipi-

Figure 1 Part of the FTIR spectrum of pure SMA and pure PPO. The reference band of PPO is shown.

tated phase. This PPO/SMA phase is filtered and washed with water several times to remove all PA-6 monomers, and finally dried at 50°C. In the next step, the PPO/SMA phase is dissolved in chloroform and filtered. The goal of this step is to remove eventually residual PA-6 monomers (these monomers are insoluble in chloroform). Before measuring the amount of nonreacted anhydride groups in the PPO/SMA phase, there is still one problem that 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 PPO/SMA phase is heated at 240°C to close the eventually opened anhydride rings; this proved to be an effective procedure to convert a diacid back into an anhydride.[10] A relatively high temperature (240°C) is chosen so that the phase PPO/SMA is well above its T_g. However, it was proven that almost no anhydride groups were hydrolyzed in HCl, 6N because the anhydride groups that had not reacted with PA-6 are located inside the PPO/SMA particles and do not have contact with the solvent HCl, 6N.

Finally, the PPO/SMA phase is again dissolved in chloroform, and a drop of this solution is put on a KBr disk. Chloroform is evaporated at room temperature and the thin film thus obtained is analyzed by FTIR.

FTIR Analysis

FTIR spectra were recorded from 2200 cm^{-1} to 600 cm^{-1} at a resolution of 1 cm^{-1}. A part of the FTIR spectrum of neat PPO is shown in Figure 1, together with the spectrum of neat SMA. The

Figure 2 Part of the FTIR spectrum of the blend PPO/SMA2 80/20 (A) and of pure PPO (B).

band at 857 cm^{-1} is used as a reference band for PPO. This band is chosen because there are no absorptions of SMA in this part of the spectrum (Fig. 1). It is not possible to integrate over the full area of the band at 857 cm^{-1} due to the presence of another PPO band located at 830 cm^{-1}. For this reason, only half of the area of the band at 857 cm^{-1} is integrated and taken as a reference band for PPO after drawing a baseline on this part of the spectrum.

Another part of the FTIR spectrum of pure PPO and of a mixture PPO/SMA2 80/20 is shown in Figure 2. Maleic anhydride exhibits an absorption at 1780 cm^{-1} (and a much weaker band at 1860 cm^{-1}). The newly formed imide group shows an absorption at 1700 cm^{-1}, which is not as useful because a band from PPO is present in this part of the spectrum. Moreover, it is not so evident to obtain a calibration curve for the imide absorption. For these reasons, the decrease of the MA band at 1780 cm^{-1} is used to measure the amount of reacted MA groups during melt extrusion. A baseline is also drawn on this part of the spectrum, and the height of the maleic anhydride band (MA) is measured. This value is divided by half of the area of the PPO band. The ratio of both is called the "band ratio MA/PPO."

band ratio MA/PPO

$$= \frac{\text{Height MA band (1780 cm}^{-1})}{\text{Half of band area of PPO (857 cm}^{-1})} \quad (3)$$

The "band ratio MA/PPO" was measured for pure PPO. This should, in principle, result in a zero value, if the baseline would be perfect and other absorbencies were completely absent at 1780 cm^{-1}. The result of these measurements is given in Figure 3 for different film thicknesses of pure PPO (approximately different areas of the PPO reference band). It can be seen that the "band ratio MA/PPO" increases with increasing thickness of the film. This is probably caused by the PPO band at 1765 cm^{-1} (Fig. 2), which gives rise to a small absorbance at 1780 cm^{-1}; this absorbance becomes more important with increasing film thickness. All further used "band ratios MA/PPO" are corrected for this contribution; the expected background absorbance at 1780 cm^{-1} is estimated from the data of Figure 3 after measuring the PPO reference band, and this background is subtracted from the measured "band ratio MA/PPO." This correction is very essential for low MA concentrations (e.g. PPO/SMA2 80/20); the standard deviation on the "band ratio MA/PPO" is much lower after the background correction. For higher MA concentrations, the correction becomes negligible.

To obtain reliable data, the "band ratio MA/PPO" should only be affected by the imidization reaction between MA and PA-6, and not by any other reaction (degradation of SMA or PPO, reaction between OH end groups of PPO and MA, etc.). This was tested by comparing the "band ratio MA/PPO" of extruded PPO/SMA2 blends to that of solution mixtures of PPO/SMA2. It was concluded that the melt extrusion process does not affect the band ratio.

The "band ratio MA/PPO" can only be related to a real concentration of MA by means of a cali-

Figure 3 The "band ratio MA/PPO" for several films of neat PPO as a function of the half area of the PPO reference band.

Figure 4 The "band ratio MA/PPO" as a function of the weight ratio MA/PPO in the calibration mixtures.

bration curve. For this reason, different calibration mixtures PPO/SMA2 were dissolved in chloroform. These calibration mixtures have a known MA concentration. For each mixture of PPO/SMA2, the "band ratio MA/PPO" was determined by means of FTIR; at least six different thin films were prepared, and an average "band ratio MA/PPO" was calculated. In Figure 4, the "band ratio MA/PPO" is plotted as a function of the weight ratio MA/PPO in the calibration mixtures. For samples with an unknown MA concentration (the remaining amount of MA after reactive blending), the "band ratio MA/PPO" is measured by means of FTIR, and this can be related to a real concentration. In this way, the percentage reacted MA groups during reactive blending with PA-6 can be calculated.

% reacted MA groups

$$= 100 - \% \text{ nonreacted MA groups} = 100$$

$$- \frac{\substack{\text{weight fraction MA of the phase} \\ \text{PPO/SMA after reactive blending}}}{\substack{\text{initial weight fraction MA} \\ \text{of the phase PPO/SMA}}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Effect of Blending Sequence

Two blending sequences, which turned out to give completely different phase morphologies, are first compared to each other. The effect of the blending

sequence on the resulting phase morphology is described in the literature for different blend systems;[15–17] the resulting effect depends very much on the type of blend system.

A first blending sequence, which will be referred to as the "one-step extrusion," can be described as follows: the miscible components PPO and SMA2 are first premixed in the miniextruder for 10 min, and subsequently PA-6 is added to this premixed blend. The blending time is recorded from the moment all the PA-6 has been added. It should be noted that only 25% of the mixing chamber is filled during the premixing step. Various blends PA-6/(PPO/SMA2) (M_w PA-6 = 44,000) were prepared in this way, and the phase morphology was analyzed with SEM. First, it was noticed that the addition of SMA2 did not lead to a big particle size reduction. The blend with a composition 75/(25/0) has a D_w of 1.8 μm, while the blend with a composition 75/(15/10) has a D_w of 0.65 μm. This is only a limited reduction in particle size. Second, it was noticed that a second population of very small particles (micelles) was present in all the blends that contained SMA2. This is shown in Figure 5. These micelles probably consist of SMA2, which was not well mixed with PPO during the premixing. This fact also explains the limited particle size reduction discussed above; a part of the SMA2 is not present at the PA-6/PPO interface, and does not act as a compatibilizer. This problem originates from the very high viscosity of PPO, which makes the interdiffusion between PPO and SMA2 very slow.

A second blending sequence will be referred to as the "two-step extrusion." In the first step, the miscible components PPO and SMA2 are premixed for 10 min in the miniextruder. The mixing efficiency is much higher now because the mixing chamber is completely filled with blend material, whereas in the "one-step extrusion" only 25% of the mixing chamber is filled during the premixing step. After this first step, the premixed blend PPO/SMA2 is pelletized. During a second extrusion step, this PPO/SMA2 blend is blended with PA-6. Several blends PA-6/(PPO/SMA2) (M_w PA-6 = 44,000) were prepared according to this "two-step extrusion." The particle size reduction is much larger now; the blend with composition 75/(15/10) has a D_w of 0.13 μm, which is five times lower than in the case of the "one-step extrusion" (Fig. 5). The bimodal distribution as observed with the "one-step extrusion" is not observed here: the SMA2 is premixed well here with PPO

Figure 5 SEM micrographs of the blend PA-6/(PPO/SMA2) in a weight ratio 75/(15/ 10). (A) "one-step extrusion;" (B) "two-step extrusion." M_w PA-6 = 44,000. Extrusion time: 15 min.

and can react at the PA-6/PPO interface to form a graft copolymer with a compatibilizing effect as a result. It can be concluded that the blending sequence has a major effect on the resulting phase morphology of the PA-6/(PPO/SMA2) blend. In all further blends discussed, the "two-step extrusion" has been used.

Effect of Extrusion Time

Several blends PA-6/(PPO/SMA2) were extruded at different extrusion times (5, 15, and 30 min) and the particle size (D_w) was analyzed. It was found that the particle size is independent from the extrusion time. The percentage reacted MA groups was analyzed for the blend PA-6/(PPO/ SMA2) (M_w PA-6 = 44,000) with a composition of 75/(20/5); this parameter is also independent from the extrusion time (±25% reacted MA groups for all extrusion times). It can, thus, be concluded that the formation of graft copolymer occurs during the first minutes of extrusion and then stops.

Two different concepts can explain this kind of time dependence. First, if the diffusion of SMA2 is fast enough, all SMA2 chains can reach the PA-6/PPO interface within 5 min, and the interfacial reaction will be stopped after these 5 min. Second, if the diffusion of SMA2 is extremely slow, the interfacial reaction will be limited to the SMA2 located in the interfacial zone. According to this second concept, most of the SMA2 will not be used for the interfacial reaction because it cannot diffuse towards the interface. The extremely high melt viscosity of PPO favors this second concept.

Effect of Compatibilizer Concentration (SMA2)

Blends PA-6/(PPO/SMA2) (M_w PA-6 = 44,000) were extruded during 15 min. The weight-aver-

age particle size is shown in Figure 6 (together with the data of blends with a lower Mw PA-6). It is very remarkable that increasing the SMA2 concentration from 5 to 10 wt % leads to a big decrease in particle size from 0.45 to 0.13 μm. Calculations, based on the amount of interfacial area, revealed that the presence of 5 wt % SMA2 at the interface should give rise to an SMA2 layer at the interface of ±30 nm, which is a few times the coil size of the SMA2 copolymer. From this point of view it is very surprising that increasing the concentration of SMA2 (from 5 to 10 wt %) still leads to a big particle size reduction. The only valuable explanation is that only a small part of all SMA2 has diffused towards the interface due to the high melt viscosity of PPO.

Figure 6 The weight-average particle diameter of blends PA-6/(PPO/SMA2) as a function of the SMA2 content (extrusion time = 15 min). All blends contain 75 wt % PA-6. ($\square$) M_w PA-6 = 18,000; ($\blacklozenge$) M_w PA-6 = 44,000.

Table II   Morphological Data and FTIR Results of Different Blend Series PA-6/(PPO/SMA)

M_w of PA-6 + Type of SMA	$M_w = 44{,}000$ SMA2			$M_w = 44{,}000$ SMA8	$M_w = 18{,}000$ SMA2	
wt % PPO	20	15	0	20	20	15
wt % SMA	5	10	25	5	5	10
% MA reacted	26	46	25	35	<3	10
[imide][b]	2.6	9.4	12.6	14.1	<0.3	2.1
% NH_2 reacted	12	43	58	65	<1	6
D_w (μm)	0.45	0.13	±0.1	0.3	4.31	1.65
A_i (μm^2/μm^3)	8.9	30.9	—[a]	13.3	0.9	2.5

Extrusion time: 15 min.
[a] Percentage etched phase too low for accurate measurements.
[b] μmol/g blend.

The results of the molecular characterization of this blend series (M_w PA-6 = 44,000; SMA2) are given in Table II (columns 1, 2, and 3), together with other data that will be discussed in the next paragraphs. In this table, the percentage reacted MA groups is calculated according to eq. (4). The concentration of the imide groups is also given in Table II; this parameter is expressed in μmol/g blend. It is calculated according to the initial concentration of MA in the blends and the percentage reacted MA groups. The percentage amino end groups that have reacted with maleic anhydride is also given in Table II; this parameter is calculated on the basis of the initial amino end group concentration of PA-6 (given by the supplier) and the amount of formed imide groups. In these calculations, it is assumed that imide links can only be formed by reaction between amino end groups of PA-6 and MA. It was shown by Maréchal et al.[8] that the reaction between amide groups of PA-6 and MA is negligible. It should also be noted that the amino concentration will not only change due to the reaction with MA, but also due to degradation processes occurring during extrusion and eventually also due to hydrolysis.[8] So, the parameter "percentage NH_2 reacted," as given in Table II, represents the percentage of the initial NH_2 groups converted to imide. Calculating the remaining concentration of NH_2 groups from this parameter is not correct.

Concerning the results from Table II (columns 1, 2, and 3), the following remarks can be made:

1. For the blend with the composition 75/(20/5), the percentage reacted MA groups is 26%. This parameter should be considered as the result of two things: namely, the amount of SMA2 that has reacted at the interface, and the amount of reacted MA groups per SMA2 molecule at the interface. Concerning this last point, it has been proven in recent work[18] that all the MA groups of SMA2 can react with PA-6 without any conformational restrictions. Only 26% of the MA groups have reacted with PA-6 at the interface, because the other SMA2 molecules remain in the core of the dispersed particles on account of the high melt viscosity of PPO.

2. The percentage reacted MA groups reaches its highest value for an intermediate SMA2 content. At low SMA2 content (PPO/SMA2 20/5), the reaction extent is limited due to the small amount of interfacial area and the absence of diffusion (only 26% reacted MA groups). At intermediate SMA2 content (PPO/SMA2 15/10), the % reacted MA groups has increased to 46%. There are two important factors that can account for this increase. First, the amount of interfacial area is increased (see Table II) and, as a consequence, a higher percentage of SMA2 will be located close enough to the interface to react with PA-6. It can be stated that the interfacial reaction accelerates itself. As a result of the interfacial reaction occurring during melt mixing, the amount of interfacial area increases; in this way, more SMA2 molecules are located close enough to the interface to undergo the interfacial reaction. From this point of view it is very important to emphasize that all parameters that affect the amount of interfacial area (such as the amount of dispersed phase, the viscosity of the blend components, and the intensity of mixing) will in-

Figure 7 The imide concentration and the % reacted amino groups as a function of the SMA2-content in PA-6/(PPO/SMA2) blends with 75 wt % PA-6. M_w PA-6 = 44,000. Extrusion time: 15 min.

fluence the reaction extent. Second, the viscosity of the PPO/SMA2 phase will be decreased by increasing the SMA2 content, which will favor the diffusion of SMA2 towards the interface. Finally, at high SMA2 content (PPO/SMA2 0/25), the % reacted MA groups is again lower (25%). In this case, the reaction extent is limited because of the fact that a part of the SMA chains are located in the core of the dispersed particles and are unable to take part in the interfacial reaction. In a previous article,[10] the % reacted MA groups was also determined for PA-6/(PS/SMA2) blends. In this system, the diffusion of SMA2 is fast enough to reach the interface within the applied blending time. In such a system, an increase of the SMA2 content does not accelerate the interfacial reaction, and a continuous decrease of the % reacted MA groups as a function of the SMA2 content was found.

3. The amount of imide groups (or the amount of consumed NH_2 end groups) increases more than linearly by increasing the SMA2 concentration in the dispersed phase from 0.2 up to 0.4. This is shown in Figure 7. The reasons for this phenomenon were discussed in the previous paragraph: a higher amount of interfacial area through self-acceleration and/or decrease of the viscosity of the dispersed phase by increasing the SMA2 content.

An interesting comparison can be made between our results and the data of Campbell et al.[5] for the blend system PA-6,6/(PPO/PPO-g-MA). Copolymer analysis of this system showed a decrease in the % reacted PPO-g-MA as a function of the content PPO-g-MA. At low PPO-g-MA content, all these molecules react at the interface. These results are in contrast with our data, and correspond more with what is expected for a blend system in which the diffusion is fast.

Blends with Low Molecular Weight PA-6

All the blends reported in the previous paragraphs were also prepared with a low molecular weight PA-6 (M_w = 18,000) for 15 min of extrusion. The particle size diameter as a function of the SMA2 content is shown in Figure 6.

For the noncompatibilized blends, the particle size is very large. The lower molecular weight PA-6 matrix has a lower viscosity, and its dispersive force is too low to obtain a fine dispersion of the dispersed phase. According to our concept of limited diffusion that was presented in the previous part, the amount of SMA2 that will be located close enough to the interface to react with PA-6 will be very low. This was confirmed by the analysis of the % reacted MA groups in the blend with a composition 75/(20/5); the "band ratio MA/PPO" after extrusion was still unchanged compared to the original value. However, the particle size of this blend was decreased significantly compared to the blend without SMA2, which indicates that the interfacial reaction has certainly taken place to some small extent. Taking into account the accuracy of the FTIR method, the amount of reacted MA groups is certainly lower than 3%. In the blend with a composition 75/(15/10), the percentage reacted MA groups is increased compared to the blend with a composition 75/(20/5), and the concentration of imide groups has increased more than linearly. These trends are very comparable to the blends with the higher molecular weight PA-6, but the reaction extent is much lower due to the limited amount of interfacial area (see Table II). These data give additional confirmation that the graft copolymer formation is limited to the SMA, which is close enough to the interface.

Based on the data of Table II, one can calculate the amount of imide links per unit of interfacial area for different blends. This is not done here because of the following reason: for blends with a high reaction extent (e.g., 75/(15/10), high M_w PA-6), the amount of the dispersed phase etched

away with chloroform is much lower than 25% because the grafted SMA2 chains are attached to the PA-6 matrix and cannot be etched away. This will cause that the parameter A_i is not correct for reacted blends; it depends on the extent of reaction and calculating the amount of imide links per area unit is not very meaningful.

Functionality of the Compatibilizer

In the previous paragraphs, only SMA2 has been used as a reactive copolymer. Before using another SMA copolymer with another functionality, one first needs to have information about the miscibility between PPO and SMA. The miscibility of the blend PPO/SMA has been studied by Witteler et al.[19] This blend always shows an LCST behavior. The miscibility decreases rapidly as the MA content of SMA increases. The blend combination PPO/SMA8 in a ratio of 80/20 (which will be used in this paragraph) is still miscible at 270°C according to the data of Witteler.[19] This was also confirmed by our DSC analysis of this blend (only one T_g).

The only new blend that will be discussed in this paragraph is PA-6/(PPO/SMA8) in a ratio of 75/(20/5), making use of PA-6 with $M_w = 44,000$. The use of the "one-step extrusion" for this blend was even more dramatic than in the case of SMA2 ($D_w = 1.28$ μm compared to $D_w = 0.86$ μm for the same blend with SMA2). The interdiffusion between PPO and SMA8 is probably very slow due to the limited miscibility between PPO and SMA8. The higher T_g and the higher M_w of SMA8 compared to SMA2 will also reduce the interdiffusion. In the results discussed below, the "two-step extrusion" is used. The morphological data and the results of the molecular characterization of this blend are given in Table II.

The following conclusions can be drawn: (a) the particle size is significantly smaller when using SMA8 compared to SMA2. The reason for this effect must be the higher functionality of SMA8, which leads to a more pronounced compatibilization effect on the particle size. This is also proven by the FTIR data: the amount of imide links formed is more than five times higher in case of SMA8 compared to SMA2. This can be explained by the combination of a higher amount of interfacial area and a higher amount of imide links formed per SMA chain in case of SMA8. (b) Given 35% reacted MA for the blend considered (Table II), theoretically one can have two extreme points of view. The first possibility is that all the SMA8

Figure 8 The weight-average particle diameter of PA-6/(PPO/SMA) blends in a weight ratio 75/(20/5) as a function of the extrusion time. ($\square$) SMA2; ($\blacklozenge$) SMA8. M_w PA-6 = 44,000.

molecules have reacted at the interface; in this case, 35% of the MA groups per SMA chain have a PA-6 graft. The second possibility is that only 35% of the SMA chains have reacted at the interface, and that all the MA groups of these SMA chains have a PA-6 graft. The reality is probably in between these two extreme points of view. However, because of the very limited diffusion of SMA towards the interface, the second possibility is thought to match more with the real situation. (c) A very interesting comparison can be made between this PA-6/PPO blend with 5 wt % SMA8 and the blend with 10 wt % SMA2 (columns 2 and 4 of Table II). The first blend has a higher imide concentration but not a lower particle size compared to the second blend. Two arguments can be formulated for this observation. First, the dispersed phase viscosity of the blend with 5 wt % SMA8 is expected to be much higher because of the higher PPO content, which will make the particle break up process more difficult. Second, one should also see the following point: four fully grafted SMA2 molecules may have a higher compatibilization effect on the particle size than one fully grafted SMA8 molecule, although the imide concentration is the same.

The effect of the extrusion time was also analyzed for this blend. At very long extrusion times (30 min) a bimodal distribution was found. Very probably, the graft copolymer SMA-g-PA-6 has left the interface and lost its compatibilizing effect. This gives rise to the formation of very small particles (micelles) and an increase of the size of the other particles, as can be seen in Figure 8. This effect was not observed for blends with

SMA2 at long extrusion times. The limited miscibility between PPO and SMA8 is the most probable reason for this effect, which was also noticed for other blend systems in which SMA has a limited miscibility with the dispersed phase.[20]

CONCLUSIONS

The copolymer SMA can be used as a compatibilizer for PA-6/PPO blends, although there are several fundamental problems: (1) the premixing between PPO and SMA is difficult because of the slow interdiffusion between both blend components. A separate premixing extrusion step is required to obtain a well premixed PPO/SMA blend. (2) The diffusion of the SMA copolymer towards the PA-6/PPO interface is very slow. The formation of graft copolymer is limited to the SMA, which is close enough to the interface.

The combination of the morphological data of blends PA-6/(PPO/SMA) and the corresponding FTIR results about the interfacial reaction in these blends provides a number of very interesting view points concerning the compatibilization mechanism of this blend: (a) the interfacial reaction accelerates itself; increasing the SMA content leads to a more than linear increase in imide concentration. (b) The amount of imide links formed depends on the amount of interfacial area, and in this way on all parameters that affect this amount. This was shown by decreasing the M_w of PA-6; the amount of generated interfacial area is drastically decreased, and this effect caused an enormous drop of the imide concentration. (c) Increasing the functionality of the SMA copolymer leads to a higher imide concentration and a smaller particle size of the dispersed phase. However, at very long extrusion times, the graft copolymer leaves the interface and looses its compatibilizing effect.

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