Interfacial Graft Copolymer Formation during Reactive Melt Blending of Polyamide 6 and Styrene−Maleic Anhydride Copolymers

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ABSTRACT: Binary blends of polyamide 6 (PA-6) and the copolymer styrene−maleic anhydride (SMA) have been prepared via melt extrusion. The amino end groups of PA-6 and the anhydride groups of SMA react with each other during melt blending; this leads to the formation of a comblike graft copolymer at the interface between PA-6 and SMA. The aim of this paper is to investigate in detail the factors affecting the graft copolymer formation. An extraction procedure has been developed to remove the PA-6 phase from the blends, and the remaining SMA phase has been analyzed with FTIR to determine the amount of reacted anhydride groups. Several material parameters such as the M_w of PA-6, the MA content of SMA, and the amount of dispersed phase were varied to get a better insight into the graft copolymer formation. It was found that the number of grafted PA-6 chains per SMA chain is not much limited by conformational restraints; very complex graft copolymers can be formed. On the other hand, it was found that the concentration of amino end groups of PA-6 is a crucial parameter with respect to the chain microstructure of the graft copolymer formed. The amount of generated interfacial area between the immiscible phases is also an important parameter for the reaction extent. Calculations were made for estimating the thickness of the interfacial zone in these reactively compatibilized blends; these calculations are based on the FTIR data, the dispersed-phase particle size, and model assumptions. Finally, the relation between the MA content of SMA as reactive compatibilizer and the particle size of the PA-6/SMA blend was investigated.

Introduction

The method of reactive compatibilization is very often used to obtain blends with desirable properties. This method is based on the formation of a block or graft copolymer at the interface between the blend phases during melt mixing. Since 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 which is miscible with one of the blend components and reactive with the other blend component.[3] This method (addition of a third polymer as a reactive component) is not very frequently used because there are not many polymers that meet the above-mentioned requirements. However, the reactive copolymer styrene−maleic anhydride (SMA) is miscible with PS, PPO, PMMA, and SAN at certain concentrations of MA functionality. The immiscible binary blends of all these polymers with PA-6 can be compatibilized through addition of SMA as a third component. In all these ternary blends PA-6/(X/SMA), the amino end groups of PA-6 will react with the anhydride groups of SMA during melt mixing, giving rise to the formation of a graft copolymer and resulting in a compatibilizing effect. These ternary blends PA-6/(X/SMA) have been studied by our group[4,5] and also by other authors;[3,6] their dispersed-phase morphology was analyzed with scanning electron microscopy (SEM), and for some blends, the graft copolymer formation could be analyzed with FTIR.[5] In the present paper, reactive binary blends PA-6/SMA are prepared, and the graft copolymer formation is characterized by FTIR after extracting the PA-6 phase.

In these binary blends, the SMA copolymer does not have to diffuse toward the interface as is the case in the ternary blends; this makes the interpretation of the FTIR data much easier. Another problem often encountered in ternary blends PA-6/(X/SMA) is the bimodal particle size distribution; the graft copolymer is repelled from the interface matrix/dispersed particle and forms a separate micelle phase. This problem can also be avoided here.

The chemical reaction between polyamides and SMA during melt mixing has been the scope of many studies in the past. The melt-extruded blend PA-6/SMA has been investigated by Kim and Park.[7] Their FTIR study, however, is only qualitative; the decrease of the anhydride absorption band after extrusion is noticed, but no attempts have been made to quantify this effect. The addition of SMA to polyamide leads to an increase in the melt viscosity; this effect was also studied by Teyssié et al.[8]

Interesting FTIR experiments have been performed by Scott and Macosko.[9] Bilayer films of SMA and amino-terminated PA-11 were prepared, and the imide formation was followed in situ during heating by means of FTIR. It was found that higher temperatures and lower molecular weights of the components result in a faster imide formation and also in a larger amount of reaction. Similar FTIR experiments have been performed by Mülhaupt et al.[10] on the bilayer system amino-terminated poly(tetrahydrofuran)/SMA. The disadvantage of these bilayer experiments is that at least one of the components must have a very low molecular weight in order to have enough interdiffusion in the bilayer systems and an interfacial zone that is thick enough for analysis.

Another important contribution was done by Maréchal et al.[11] It was proven that the reaction between

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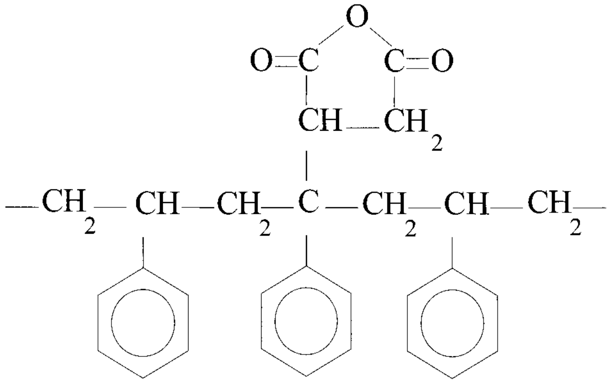

Figure 1. Molecular structure of PS-*g*-MA.

Table 1. Molecular Characteristics of the Blend Components Used

material	T_g (°C)	M_w	method
PA-6		18 000	[η] in HCOOH/H_2O 85/15 at 25 °C
PA-6		44 000	
PS	100	120 000	GPC in THF
SMA2	105	145 000	[η] in THF at 25 °C
SMA8	116	280 000	
SMA17	134	210 000	
SMA25	149	220 000	

amide groups of PA-6 and anhydride groups is negligible compared to the reaction between the amino chain ends of PA-6 and anhydride groups. The reaction extent in blends of PA-6 and SEBS-*g*-MA was recently elucidated by Paul et al.[12] The grafting reaction between various alkylamines with a variable alkyl length has been studied by Vermeesch et al.[13] The blend of vinyl oxazoline modified PS and amorphous PA has been studied by Briber et al.[14] Recently, the blend phase morphology and interfacial graft copolymer formation in blends PA-12/SMA has been studied by Hellmann et al.[15]

Experimental Section

Materials. The characteristics of the blend components are given in Table 1. Two different PA-6 types with a different molecular weight were used; they were both provided by DSM-Research. SMA2, SMA17, and SMA25 were supplied by BAYER; SMA8 was provided by Arco. PS was supplied by Dow Chemical. The number after SMA denotes the weight percent maleic anhydride (wt % MA) in SMA. All these SMA copolymers are amorphous; each extra wt % MA causes a T_g increase of 2 °C as determined with differential scanning calorimetry (DSC). The molecular weights of these polymers were determined using gel permeation chromatography (GPC) and intrinsic viscosity measurements.

Synthesis of PS-*g*-MA. As can be seen from Table 1, SMA2 has the lowest functionality from all commercially available SMA copolymers. It was our goal to obtain SMA copolymers with a much lower MA content in order to study the effect of the MA content of SMA on the phase morphology of PA-6/SMA blends. This was performed by grafting maleic anhydride (MA) onto PS in the melt by means of a peroxide. In this way, MA is not present as a comonomer as was the case with the SMA copolymers mentioned in Table 1, but the MA monomer is grafted onto the PS main chain as shown in Figure 1. For this reason, the obtained MA-grafted polystyrenes are noted as PS-*g*-MA instead of SMA. Two different methods for MA-grafting were used: a melt extrusion and a solution method.

In the melt extrusion method, PS was mixed with MA and dihydroxybenzoyl peroxide (DHBP) for 4 min using a miniextruder. The mixing temperature was set at 185 °C. Typical concentrations used are 6 wt % MA and 1 wt % DHBP; however, these concentrations were varied in order to obtain PS-*g*-MA polymers with a varying MA functionality. One cannot use very high (>2 wt %) peroxide concentrations without obtaining a colored PS-*g*-MA after extrusion. For this reason, a solution grafting method was also performed in order to obtain a higher functionalized PS-*g*-MA. Mixtures of 1,2-dichlorobenzene/PS/MA/dicumyl peroxide in a weight ratio 10/1/0.1/0.025 were kept at 150 °C under N_2 atmosphere for 1 h. In this way, a higher functionality of PS-*g*-MA could be obtained.

After MA grafting, the PS-*g*-MA was dissolved in THF and precipitated in ethanol in order to remove nonreacted MA. It was shown that all the nonreacted MA can be removed in this way by applying this method to mixtures of PS/MA. The obtained PS-*g*-MA was dried and heated at in an oven at 240 °C to close hydrolyzed anhydride groups. After this procedure, the MA content of PS-*g*-MA was determined by means of FTIR. A calibration curve, which was described in a previous paper,[5] was used to relate the band absorbance ratio MA/S to a real MA concentration.

Blend Preparation. The blends PA/SMA were prepared in a double-screw miniextruder designed by DSM-Research (The Netherlands). It consists of a mixing chamber with a capacity of 4 g and two corotating conical screws. By means of a recirculation channel within the mixing chamber and a valve to open the mixing chamber, the residence time can be varied. The mixing chamber can be saturated with nitrogen gas during melt blending. The extrusion temperature was always kept constant at 240 °C during blending, and the screw speed was 100 rpm. After blending, the extruded polymer strand was quenched in a mixture of 2-propanol/solid CO_2 (−78 °C) in order to freeze in the blend phase morphology.

Morphological Characterization of the Blends. The extruded polymer strands were held in liquid N_2 for some time, and a brittle fracture was performed. This surface was etched with chloroform for 48 h at room temperature in order to dissolve the dispersed-phase SMA. 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.

If the particles were large enough for accurate analysis, different micrographs with a total amount of ±300 particles were taken. These micrographs were analyzed with the aid of image analysis software, and the diameter of each particle was calculated. A weight-average diameter (D_w) and a number-average diameter (D_n) were calculated according to the following formula:

$$D_w = \frac{\sum N_i D_i^2}{\sum N_i D_i} \quad D_n = \frac{\sum N_i D_i}{\sum N_i} \tag{1}$$

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:

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

Extraction Procedure. In a previous paper,[5] an extraction procedure was described in detail to remove the PA-6 phase from PA-6/(PS/SMA2) blends. The same extraction procedure can of course be used to remove the PA-6 phase from PA-6/SMA blends. This procedure is shortly described here below. The blends are put into a 100 mL solution of 6 N HCl at 85 °C for 40 h. This causes the hydrolysis of the PA-6 matrix, and the resulting PA-6 monomer in the form of its hydrochloride salt is soluble in 6 N HCl.[16] The imide links formed during melt extrusion are stable under these conditions.[17] Every PA chain bound to SMA is degraded to one remaining monomer unit bound through the imide linkage and terminating in a carboxylic acid group. The dispersed SMA particles are not soluble in 6 N HCl, flocculate together, and form a solid precipitated phase. This SMA phase is filtered and washed

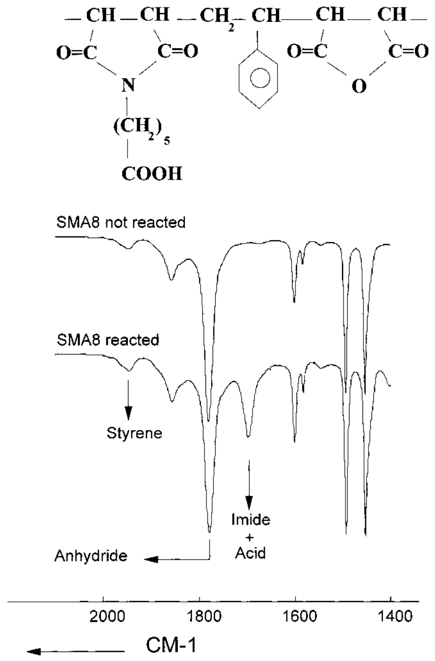

Figure 2. FTIR spectrum of SMA8 before and after melt blending with PA-6 (+ extraction of PA-6). The expected structure of SMA after melt blending and extraction is also given.

with water several times to remove all PA-6 monomers and finally dried at 50 °C. In the next step, the SMA phase is dissolved in chloroform and filtered. The goal of this step is to remove residual PA-6 monomer in the form of its hydrochloride salt. (This ionic species is insoluble in chloroform.) It has been confirmed that all PA-6 monomers are removed by applying the whole extraction procedure to PA-6/PS blends; no FTIR absorption at 1700 cm^{-1} related to the acid of the PA-6 monomer could be found in the extracted PS phase.

Before measuring the amount of nonreacted anhydride groups in the 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 6 N HCl at 85 °C and give rise to a diacid function. For this reason, the SMA phase is heated at 240 °C to close the opened anhydride rings; this proved to be an effective procedure to convert a diacid back into an anhydride.[5] In fact, only the anhydride groups that are close enough to the interface will be hydrolyzed; anhydride groups in the core of the dispersed particles will not have contact with the solvent HCl and will not be hydrolyzed.

Finally, the SMA phase is again dissolved in chloroform, and a droplet 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.

Quantitative FTIR Analysis. FTIR spectra were recorded from 4000 to 600 cm^{-1} at a resolution of 1 cm^{-1}. A part of the FTIR spectrum of SMA8 is shown in Figure 2; the FTIR spectrum of neat SMA8 is compared to the spectrum of an SMA8 phase after melt blending with PA-6 and the complete extraction procedure. As a verification of the method, the complete extrusion and extraction procedure was applied to neat SMA, and no change in the MA content of SMA was found. The height of the band at 1945 cm^{-1} is used as a reference band for styrene. This band is chosen because it is very easy to draw a baseline on this part of the spectrum. The band at 1700 cm^{-1} is the combination of the imide and the acid, as seen in Figure 2. At 1780 cm^{-1}, the absorption of the anhydride is seen. It is worth mentioning that the maleic anhydride which is copolymerized in the PS chain does not have its double bond anymore; the correct name for the copolymerized MA group is "succinic anhydride". Our goal is to quantify the increase of the (imide + acid) band or the decrease of the anhydride band after melt extrusion and extraction. This is not easy on account of the following problems:

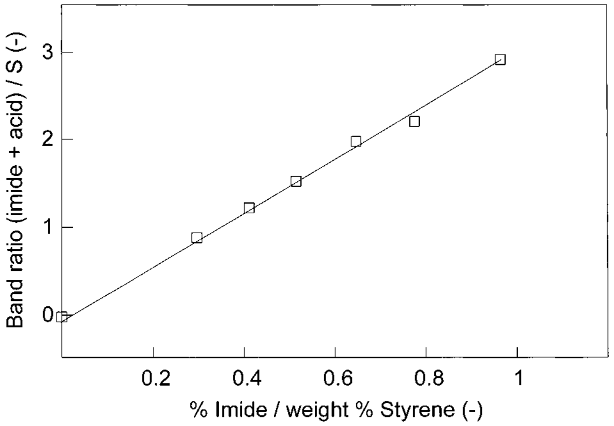

Figure 3. The "band ratio imide + acid/S" as a function of the "% imide/wt % styrene" of different blends PA-6/(PS/SMA2) from a previous paper.[5]

(i) In some cases, the decrease of the anhydride band (after extrusion and extraction) will be too low to be measured accurately. Furthermore, the anhydride band will not only be decreased due to the reaction with the amino chain ends; hydrogen bonding between the acid and anhydride will shift the absorption of some H-bonded anhydride groups to another frequency. These problems will not be important for SMA2 because the percent reacted anhydride groups is high in this case (see further) and the probability for hydrogen bonding is low. However, for SMA25 (low percent reacted anhydride groups, high probability for hydrogen bonding), these problems become dramatic.

(ii) The (imide + acid) band at 1700 cm^{-1} can be quantified more easily, but the problem here is to obtain a calibration curve that relates this band absorption to a real imide concentration.

This problem can be solved in the following way: the FTIR results of the blend series PA-6/(PS/SMA2)[5] are used to obtain a calibration curve for the FTIR results of the blend system PA-6/SMA. For the blend series PA-6/(PS/SMA2), the decrease of the anhydride band after extrusion is measured and related to a decrease in anhydride concentration by means of a calibration curve. So, for this blend series, the amount of reacted anhydride groups (and thus the amount of newly formed imide groups) is known. It is assumed that the anhydride band is not decreased due to hydrogen bonding for this blend series, as mentioned above. Then, for the blend series PA-6/(PS/SMA2), the height of the band at 1700 cm^{-1} is measured after drawing a baseline on the FTIR spectrum. The absorption at 1700 cm^{-1} is the combined absorption of the imide and the acid, as already mentioned. The "band absorbance ratio (imide + acid)/S" is defined in the following way:

$$\text{band ratio (imide + acid)/S} = \frac{\text{height of band (imide + acid) (1700 cm}^{-1}\text{)}}{\text{height of band S (1945 cm}^{-1}\text{)}} \tag{3}$$

This band ratio is plotted for different blends PA-6/(PS/SMA2)[5] as a function of the percent imide in the phase PS/SMA2 divided by the weight percent styrene; this is shown in Figure 3. The percent imide is defined in the following way:

$$\%\ \text{imide} = \frac{\text{initial wt \% MA of phase PS/SMA2} \times \text{\% reacted anhydride}}{100} \tag{4}$$

A linear relationship is found between the band ratio and the concentration of imide groups as can be seen from Figure 3.

Table 2. Data of the Morphological Characterization of PA-6/SMA 80/20 Blends (M_w PA-6 = 18 000)

wt % MA of SMA	notation	synthesis method	D_w (μm)	A_i (μm^2/μm^3)
0	PS	commercial polystyrene	3.08	1.3
0.075	PS-*g*-MA(0.07)	MA grafting of PS during extrusion	0.46	8.7
0.11	PS-*g*-MA(0.11)	MA grafting of PS during extrusion	0.32	12.4
0.22	PS-*g*-MA(0.22)	MA grafting of PS during extrusion	0.17	22.9
0.34	PS-*g*-MA(0.34)	MA grafting of PS in solution	0.14	29
2	SMA2	commercial copolymer	0.13	31.5
8	SMA8	commercial copolymer	0.18	22.6

The fitted equation from Figure 3 makes it possible to determine the imide concentration of blends PA/SMA from which the decrease of the anhydride band could not be measured accurately. However, the measured band ratios from blends PA/SMA will mostly be higher than those in Figure 3; the higher anhydride functionality of SMA compared to those of mixtures PS/SMA2 gives rise to a higher imide concentration. For this reason, the calibration curve has to be extrapolated to higher imide concentrations. It was proven that this extrapolation is allowed; this point will not be discussed further here.

It was also noticed that some background absorbance will be present at 1700 cm^{-1} due to the band of anhydride at 1780 cm^{-1}. This background absorbance is negligible for SMA2; it becomes more relevant when the weight percent anhydride of SMA increases. This background absorbance has always been subtracted from the measured band ratios.

Results and Discussion

Phase Morphology of PA-6/SMA Blends. PA-6/SMA blends in a weight ratio 80/20 with a different functionality for SMA have been prepared via melt extrusion. The results of the morphological characterization of these blends are presented in Table 2. Our first goal is to study the effect of the MA content of SMA on the particle size of these blends. PA-6/SMA blends with a M_w of 44 000 for PA-6 always show extremely small dispersed SMA particles. Even at a magnification of 20 000, these SMA particles can hardly be seen. For this reason, PA-6 with a M_w of 18 000 was used. The dispersive forces of this low molecular weight PA-6 during melt blending with SMA are much lower, and the resulting SMA particle size will be larger.[5]

The following conclusions can be made:

(i) A very low MA content of SMA gives already rise to a large particle size reduction. An MA content of 0.11 corresponds to only one grafted MA group for a chain with a molecular weight of 100 000. This very low MA content gives rise to a 10-fold reduction in particle size for the blend PA-6/PS-*g*-MA(0.11) as compared to the PA-6/PS blend (see Table 2). SEM micrographs are represented in Figure 4. It is important to note that PS and PS-*g*-MA have a very comparable molecular weight and melt viscosity because this can also influence the particle size.

(ii) As can be seen from Table 2, a further increase of the MA content results in a further decrease of the particle size (and increase of the amount of interfacial area). At low MA content (between 0 and 0.4 wt % MA), there is a good correlation between the amount of interfacial area and the MA content of SMA; this is shown in Figure 5. However, at higher MA content (>0.4 wt % MA), the amount of interfacial area becomes constant. The blend with SMA2 shows only a slightly higher amount of interfacial area than the blend with PS-*g*-MA(0.34).

(iii) For the blend PA-6/SMA8, the particle size is slightly higher than for the blend with SMA2. SMA8 cannot be well dispersed by this low viscous PA-6 due to its higher viscosity (combined effect of higher T_g and higher M_w of SMA8).

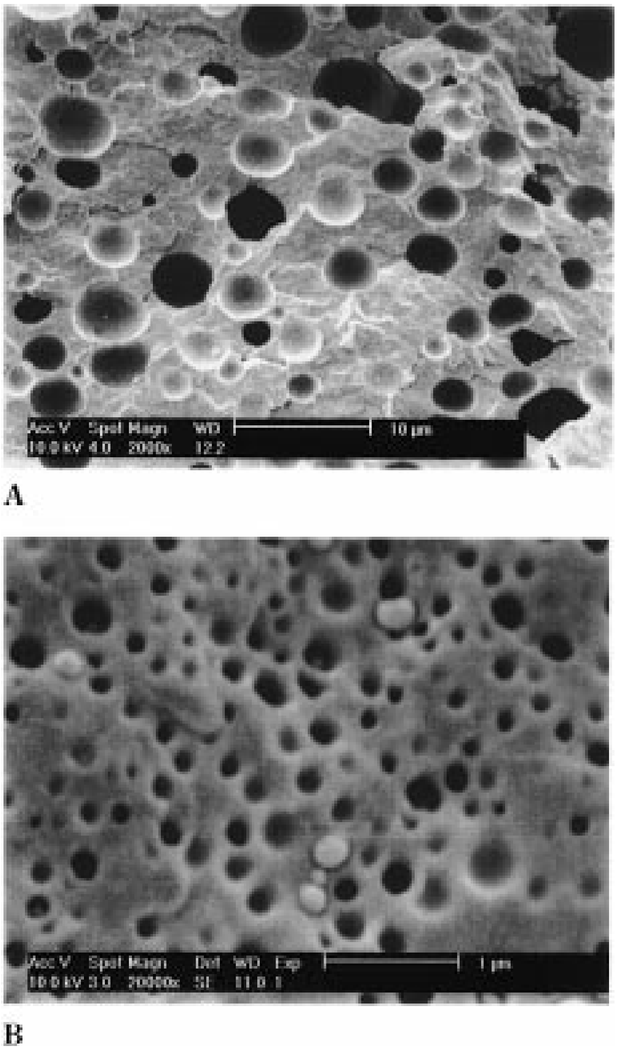

Figure 4. SEM micrographs of the blends PA-6/PS (A, top; magnification 2000) and PA-6/PS-*g*-MA(0.22) (B, bottom; magnification 20 000) in a weight ratio 80/20. M_w PA-6 = 18 000.

For the blend PA-6/SMA25, the resulting phase morphology is very coarse. In this way, the particle size of the blend PA/SMA displays a minimum as a function of the MA content. For PA-6 with M_w = 44 000, this last effect was not observed; the higher dispersive force of this high molecular weight PA-6 leads to a very fine dispersion even for the SMA types with a high T_g and a high viscosity.

FTIR Results of the Graft Copolymer Formation. The results from the FTIR characterization of the different PA-6/SMA blends after extraction of the PA-6 phase are given in Table 3. The results are divided into four topics which will be discussed in this order. First of all, the parameters on top of Table 3 will be defined.

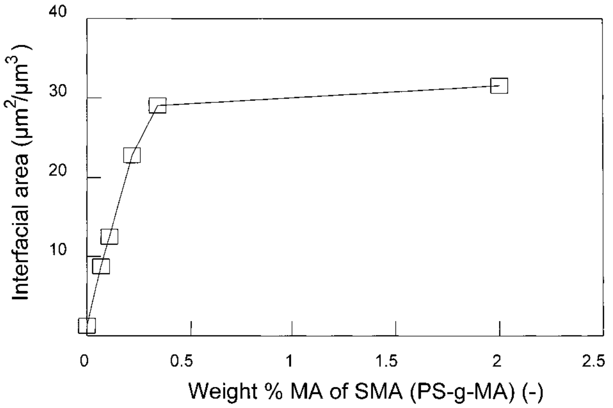

Figure 5. Interfacial area (eq 2) as a function of the wt % MA of SMA for blends PA-6/SMA (or PS-*g*-MA) in a weight ratio 80/20. M_w PA-6 = 18 000.

Table 3. Data from the FTIR Characterization of All the PA-6/SMA Blends after Extraction of the PA-6 Phase

% SMA in blend	wt % MA of SMA	[MA],i (μmol/g)	$[NH_2]$,i (μmol/g)	[imide] (μmol/g)	% imide of SMA	% react. NH_2	% react. MA
Topic 1: effect of MA functionality of SMA (M_w PA-6 = 44 000)							
10	2	20	26	7.7	0.8	30	38
10	8	82	26	14.5	1.4	55	18
10	17	173	26	19.5	1.9	75	11
10	25	255	26	19.9	2	77	8
Topic 2: effect of wt % dispersed phase for SMA2 and SMA8 (M_w PA-6 = 44 000)							
5	8	41	28	11.7	2.3	43	29
10	8	82	26	14.5	1.4	55	18
20	8	163	23	13.7	0.7	59	8
5	2	10	28	4.8	0.9	17	47
10	2	20	26	7.7	0.8	30	38
20	2	41	23	12.9	0.6	56	32
Topic 3: effect of wt % dispersed phase for SMA2 and SMA8 (M_w PA-6 = 18 000)							
5	8	41	41	5.1	1	12	12
10	8	82	39	8.1	0.8	21	10
20	8	163	34	13.3	0.65	39	8
5	2	10	41	2.7	0.5	7	27
10	2	20	39	5.1	0.5	13	25
20	2	41	34	7.2	0.35	20	18
Topic 4: effect of wt % dispersed phase for SMA25 (M_w PA-6 = 44 000)							
2.5	25	64	28	17.1	6.7	60	27
5	25	128	28	19.8	3.9	72	16
10	25	255	26	19.9	2	77	8
20	25	510	23	19.4	0.95	83	4

The parameter "% SMA in blend" refers to the weight percent dispersed phase (SMA) in the blend PA-6/SMA. The "wt % MA of SMA" refers to the functionality of SMA. The parameter "[MA],i" is the initial concentration of maleic anhydride in the whole blend before extrusion. This parameter is expressed in micromoles of MA per gram of blend. This parameter is calculated on the basis of the two previous parameters and the molecular weight of MA (98 g mol^{-1}). The parameter "$[NH_2]$,i" represents the initial concentration of amino end groups of PA-6 in the blend before extrusion; this parameter is expressed in micromoles of NH_2 per gram of blend. The concentration of amino end groups of the two PA-6 types used was given by the supplier (M_w PA-6 = 44 000, $[NH_2]$ = 29 μmol g^{-1}; M_w PA-6 = 18 000, $[NH_2]$ = 43 μmol g^{-1}). These numbers have not been further checked, but other information such as molecular weight data given by this supplier was very consistent with our measurements.

So, the first four parameters of Table 3 are material parameters; the other four parameters are related to the graft copolymer formation as a result of reactive blending. Starting from the "acid + imide band ratio" obtained with FTIR, the parameter "% imide of the SMA phase divided by the weight % styrene of SMA" can be calculated via the fitting already discussed (see Figure 3). From this last parameter, the percent imide of SMA can easily be calculated. This parameter is defined in the same way as it was defined in eq 4 for the blends PA-6/(PS/SMA2):

$$\%\text{ imide of SMA} = \frac{\text{wt \% MA of SMA} \times \%\text{ reacted anhydride}}{100} \tag{5}$$

This parameter can be made more clear by the following example. When 25% of the anhydride groups of SMA8 react, the percent imide of SMA is said to be 2. The parameter "% reacted MA" (last column of Table 3) can be calculated from eq 5. The parameter "[imide]", which is expressed in μmol/ g of blend, is calculated according to eq 6.

$$[\text{imide}]\ (\mu\text{mol g}^{-1}) = \frac{[\text{MA}],\text{i}\ (\mu\text{mol g}^{-1}) \times \%\text{ reacted MA}}{100} \tag{6}$$

Finally, the percent reacted NH_2 is calculated according to eq 7.

$$\%\text{ reacted NH}_2 = \frac{[\text{imide}]\ (\mu\text{mol g}^{-1})}{[\text{NH}_2],\text{i}\ (\mu\text{mol g}^{-1})} \tag{7}$$

In this last equation, 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.[11] that the reaction between amide groups of PA-6 and MA is negligible. It should also be noted that the amino concentration will change not only due to the reaction with MA but also because of degradation processes during extrusion and eventually also due to hydrolysis.[11,18] So, the parameter defined in eq 7 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.

Factors Affecting the Graft Copolymer Structure. One should realize that the reaction extent is always the combined result of the volume of the reaction zone (amount of interfacial area × thickness of the interface) and the amount of reacted anhydride groups per SMA molecule in this reaction zone. Most likely, the amount of interfacial area will increase with several orders of magnitude due to the interfacial reaction while a more moderate increase of the interfacial thickness is expected. As the particles get smaller and the interface thicker, a measurement of the particle size with SEM after extracting the dispersed phase becomes irrelevant. It is also important to note that the FTIR results from Table 3 are always average results for all the SMA chains (nonreacted SMA chains in the core of a particle + reacted SMA chains at the interface).

PA-6/SMA blends in a weight ratio 90/10 were prepared (M_w PA-6 = 44 000); SMA types with a varying weight percent MA of SMA have been used (Table 3, topic 1). As it was expected, the percent reacted anhydride groups decreases as the weight percent MA of

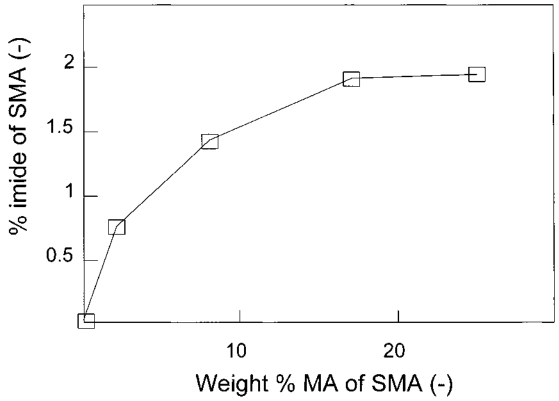

Figure 6. Percent imide of SMA (and the percent reacted NH_2) as a function of the weight percent MA of SMA for blends PA-6/SMA in a weight ratio 90/10. M_w PA-6 = 44 000.

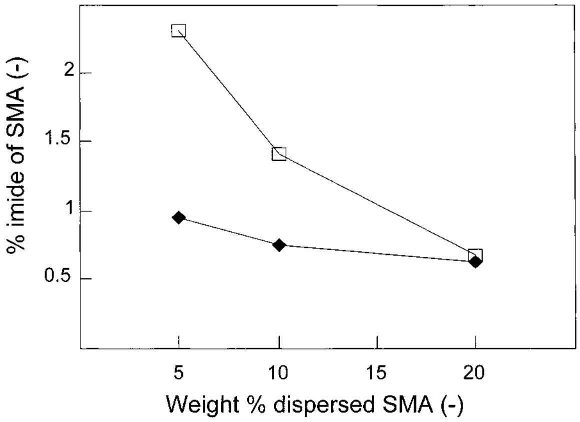

Figure 7. Percent imide of SMA as a function of the weight percent SMA in PA-6/SMA blends. (□) = SMA8; (◆) = SMA2. M_w PA-6 = 44 000.

SMA increases. This can also be expressed in the following way: the percent imide of SMA increases less than linearly as a function of the weight percent MA of SMA. This is shown in Figure 6. There are two possible reasons for this behavior. First, the concentration of amino end groups is limited. In the blend PA-6/SMA25 in a weight ratio 90/10, the [MA],i is 10 times higher than the [NH_2],i. Second, the amount of PA-6 grafts per SMA chain is limited on account of conformational restraints. Let us consider an SMA25 chain with a molecular weight of 100 000. Such a chain contains roughly 250 anhydride groups. It is very hard to imagine that all the anhydride groups can react with a PA-6 chain even if enough amino chain ends are present. In the following experiments, we sought to get a better understanding of the relative importance of these two parameters.

The second topic in Table 3 is the variation of the amount of dispersed phase (SMA) in the blends PA-6/SMA. This was done for SMA2 and SMA8 (M_w PA-6 = 44 000). The effect of the weight percent dispersed phase is very much different for SMA2 compared to SMA8. For SMA8, the [imide] in the total blend is not much dependent on the amount of dispersed phase. This also means that the complexity of the graft copolymers (~percent imide of SMA) will be much higher at a low weight percent dispersed phase. This is shown in Figure 7. The most probable reason for this effect is the limited amount of amino end groups of PA-6. Increasing the weight percent dispersed phase causes that the amount of available amino end groups have to be distributed over a larger amount of SMA, which will of course decrease the percent imide of SMA. In case of SMA2, the [imide] increases as a function of the weight percent dispersed phase. On the other hand, the percent imide of SMA is only slightly decreased when increasing the weight percent dispersed phase (Figure 7). For the blend with 5 wt % SMA2, the percent reacted NH_2 groups is only 17%; increasing the weight percent dispersed phase will not give rise to a shortage of amino end groups, and the percent imide of SMA will not be much affected. For the blend with 20 wt % dispersed phase, the percent imide is almost the same for SMA2 and SMA8. It can be concluded that the higher functionality of SMA8 only leads to a higher percent imide when enough amino end groups are present (at low weight percent dispersed phase).

The third topic in Table 3 concerns the use of another PA-6 with M_w = 18 000. All the blend compositions from the previous topic were also prepared with this PA-6. As already mentioned, the dispersed SMA particles will be larger with this PA-6 as a matrix due to the lower dispersive forces. The lower amount of interfacial area (~reaction zone) of these blends and the higher concentration of amino end groups will cause a shortage of amino chain ends cannot easily occur for these blends. According to the concept discussed under topic 2, the [imide] of all the blends with this low molecular weight PA-6 will increase markedly as a function of the weight percent dispersed phase, while the percent imide of SMA decreases only slightly with increasing weight percent dispersed phase. An interesting comparison can be made for the blend PA-6/SMA8 between the high and the low molecular weight PA-6. At 20 wt % dispersed phase, the average percent imide of SMA is almost the same for both PA-6 types. However, the blend with the low molecular weight PA-6 has a much lower amount of interfacial area. So, the blend with this low molecular weight PA-6 will probably have a relatively low amount of reacted SMA, but this SMA contains a high percent imide per reacted SMA chain. The blend with the high molecular weight PA-6 will probably have a higher amount of reacted SMA, but this SMA contains a relatively low percent imide per reacted SMA chain.

The fourth topic studied is the effect of the weight percent dispersed phase for PA-6/SMA25 blends (M_w PA-6 = 44 000). For the blend with 20 wt % dispersed phase (SMA25), there is of course a shortage of amino end groups and the percent imide of SMA is low. Decreasing the weight percent dispersed phase leads to an increase of the average percent imide of SMA while the [imide] remains nearly constant as was also observed for the blend PA-6/SMA8. However, it is very surprising that the percent imide of SMA can increase up to 6.7 for the blend with 2.5 wt % dispersed phase and that 60% of the amino end groups are consumed for such a low amount of dispersed phase. The following comments can be made about these data:

(i) The average percent imide of SMA increases from 0.95 to 6.7 by decreasing the percentage dispersed phase from 20 to 2.5 wt %. This increase is not only due to the formation of more complex graft copolymers but also because the percentage SMA chains taking part in the interfacial reaction is higher in the case of 2.5 wt % dispersed phase. For the blend with 20 wt % dispersed phase, some very small particles can still be observed with SEM while for the blend with 2.5 wt % dispersed

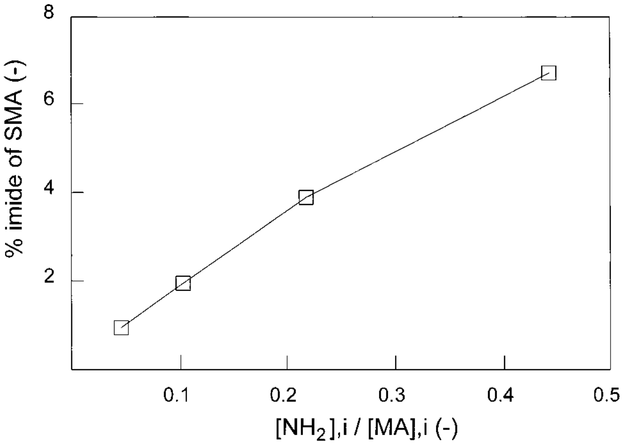

Figure 8. Percent imide of SMA as a function of the ratio $[NH_2]$,i/[MA],i for PA-6/SMA25 blends. M_w PA-6 = 44 000.

Table 4. Band Ratio "Diacid/S" for the Blends of Topic 1 and Topic 4

wt % SMA in blend	wt % MA of SMA	band ratio diacid/S	% imide of SMA
Topic 1: effect of MA functionality of SMA			
10	2	0	0.8
10	8	1.5	1.4
10	17	4.1	1.9
10	25	6.4	2
Topic 4: effect of wt % dispersed phase for SMA25			
2.5	25	13	6.7
5	25	10.9	3.9
10	25	6.4	2
20	25	5.2	0.95

phase, no particles can be observed because they are too small.

(ii) In Figure 8, the percent imide of SMA is plotted versus the ratio $[NH_2]$,i/[MA],i for blends with PA-6 (M_w = 44 000) and SMA25. It can be seen that the percent imide of SMA increases almost linearly as a function of this ratio. The conformational restraints for graft copolymer formation are thus very limited.

(iii) The formation of very complex comblike graft copolymers results in a very high viscosity for the blend with 2.5 wt % SMA25. Due to this high viscosity, this blend could only leave the mixing chamber of the miniextruder after raising the temperature to 260 °C.

Additional Information Obtained from FTIR. After extraction of the PA-6 phase from blends PA-6/SMA with HCl, the anhydride groups in the interfacial region will be hydrolyzed. The formed diacid also absorbs at 1700 cm^{-1}. An FTIR spectrum is also taken at this stage of the procedure, and a "band ratio (imide + acid + diacid)/S" is measured. By subtracting the "band ratio (imide + acid)/S" (this is the value after heating the sample) from this value, one obtains the absorbance of the diacid; the resulting value is named "band ratio diacid/S". This band ratio cannot be related to a real concentration of diacid because we do not have a calibration curve for this diacid, but some information can be obtained by comparing these values for different blends. This is shown in Table 4 for topics 1 and 4 of Table 3. The amount of diacid is related to the amount of anhydride groups that have not reacted with PA-6 and also to the amount of interfacial reaction zone. Concerning topic 1, it can be concluded that in the case of SMA2 all the anhydride groups in the interfacial region have reacted with PA-6. By increasing the MA content of SMA, the amount of nonreacted anhydride in the interfacial zone increases. Concerning topic 4, it is observed that the amount of nonreacted anhydride is the highest for the blend with 2.5 wt % SMA25 although the percent imide is also the highest for this blend. This fact can only be explained by the higher amount of interfacial area for this blend, as already suggested in the previous paragraph.

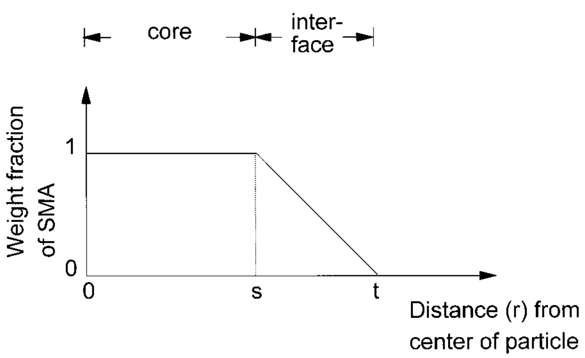

Figure 9. Weight fraction of SMA in PA-6/SMA blends as a function of the distance from the particle center. A linear concentration gradient is assumed.

Model Calculations of the Interfacial Thickness. On the basis of the particle size of the dispersed phase and the amount of reacted groups in the PA-6/SMA blends, some information can be obtained about the thickness of the interfacial reaction zone. The dispersed SMA particles are considered as perfectly spherical and uniformly sized. (Both assumptions are considered to be very close to the real situation.) The dispersed particles have a core which consists of nonreacted SMA and an interfacial zone in which the composition gradually changes from pure SMA to pure PA-6. In our model, a linear concentration gradient is used. This is schematically depicted in Figure 9. The concentration of SMA is described by a mathematical function. This function is 1 for $r < s$ and can be described by the function $(t - r)/(t - s)$ for $s < r < t$. For $r > t$, the function is zero. The amount of SMA2 in the core (M_c) and the amount of SMA2 in the interfacial region (M_i) can be calculated via the following integrals:

$$M_c = 4\pi\int_0^s r^2\,dr \tag{8}$$

$$M_i = 4\pi\int_s^t \frac{t - r}{t - s} r^2\,dr \tag{9}$$

The ratio $M_i/(M_i + M_c)$ represents the percentage of SMA that is located in the interfacial region. This parameter is the same as the percent reacted anhydride groups obtained from FTIR data if we make the assumption that all the anhydride groups in the interfacial zone have reacted. For this reason, the blend PA-6/SMA2 80/20 is studied because the previous assumption seems very realistic for this blend system, as discussed in the previous paragraph. In this way, it is possible to calculate the interfacial thickness $(t - s)$ for a certain particle diameter $(2s)$. This is done in Figure 10 for the PA-6/SMA2 80/20 blend for two different molecular weights of PA-6. The particle diameter $(2s)$ is considered as a parameter because there are several uncertainties about the particle size information obtained from SEM. The following remarks have to be made:

(i) The particles are not always cut at their largest diameter. A correction can be made for this fact by multiplying the average particle diameter as measured

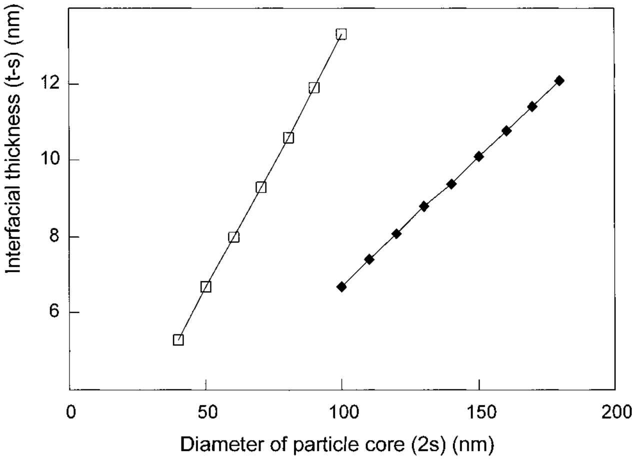

Figure 10. Interfacial thickness ($t - s$) as a function of the diameter of the particle core ($2s$) for PA-6/SMA2 blends in a ratio 80/20. (□) M_w PA-6 = 44 000; (◆) M_w PA-6 = 18 000.

by a factor $4/\pi$.[19] For the blend with the low molecular weight PA-6, D_n was 110 nm; after applying this correction, one obtains 140 nm. This corresponds to an interfacial thickness ($t - s$) of 9.3 nm.

(ii) For the blend with the higher molecular weight PA-6, the particle size could not be measured because the particles are too small. The distance $2s$ is thought to be in the range 50−80 nm for this blend. This corresponds to an interfacial thickness ($t - s$) in the range 6.7−10.6 nm.

(iii) Only the nonreacted core of SMA can be etched away; the reacted SMA chains are covalently bounded to the PA-6 and cannot be etched away. So, in theory, the particle diameter observed with SEM is $2s$, but in reality it might be less; some nonreacted SMA molecules that are physically entangled with the reacted ones might also not be etched away.

For all these reasons, the interfacial thickness is calculated for the two discussed blends as a function of the particle diameter $2s$ (Figure 10).

Conclusions

An extraction method was developed to remove the PA-6 phase of PA-6/SMA blends and to determine the amount of reacted anhydride groups via FTIR. We concluded the following:

(i) At fixed PA/SMA ratio, increasing the MA content of SMA leads to a higher percent imide of SMA if enough amino end groups of PA-6 are present (at low weight percent dispersed phase).

(ii) At fixed PA/SMA ratio and at a fixed MA level, the use of a lower M_w PA-6 results in a larger average particle diameter for the dispersed SMA phase. This leads in general to a lower imide concentration.

(iii) By varying the amount of dispersed SMA25 in the PA-6/SMA25 blend, it was found that the $[NH_2]$,i is the determining factor for the graft copolymer complexity, rather than conformational restraints. At very low weight percent dispersed SMA25, the imide concentration is still high. This is only possible via the formation of extremely small particles and very complex comblike graft copolymers.

Some other very interesting results could also be obtained:

(i) A very low amount of functional groups (0.4 wt % MA for blends with PA-6, M_w = 18 000) is enough to obtain the minimum particle size in the PA-6/SMA 80/20 blend.

(ii) Calculations based on the percent reacted groups and on some very realistic assumptions made it possible to estimate the thickness of the reaction zone. For the PA-6/SMA2 80/20 blend with the low molecular weight PA-6, a value of 9.3 nm was obtained. However, this interfacial thickness was plotted as a function of the particle diameter due to some uncertainties concerning the particle diameter.

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