

Improved compatibility between polyamide and polypropylene by the use of maleic anhydride grafted SEBS

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(Received 5 June 1997; revised 15 September 1997; accepted 5 November 1997)

Blends containing equal weight fractions of polypropylene (PP) and polyamide (PA-6 and PA-6.6) and up to 25% of a compatibilizing thermoplastic elastomer, either polystyrene-*block*-poly(ethylene-*stat*-butylene)-*block*-polystyrene (SEBS) or SEBS modified by maleic anhydride (SEBS-MA), were prepared by melt mixing. In all these blends, PP formed the continuous matrix phase. Even at high concentrations, unmodified SEBS was found to be a poor compatibilizer, affecting mainly the properties of the matrix. The graft copolymer formed, by reaction between SEBS-MA and polyamide during melt mixing, strongly influenced the blend morphology, by forming an interphase, separating the PA phase domains from the matrix. The crystallization behaviour of PP indicated that full coverage required between 3% and 5% SEBS-MA at the intense mixing conditions used. Above this level, the total surface area of the polyamide domains seemed to increase in direct proportion to the concentration of SEBS-MA. The thickness of the interphase layer was estimated to be about 15 nm. At high concentrations of SEBS-MA, the PA domains agglomerated and formed extended structures held together by the interphase polymer. This was reflected by the stress-strain and rheological behaviour of the blends. In blends with PA domains of small volume, crystallization of PA was delayed. The rate of water absorption was very low in blends containing SEBS-MA, much lower than in corresponding blends containing SEBS. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polymer blend; polypropylene; polyamide)

INTRODUCTION

Many polymer pairs are incompatible, both in the thermodynamic and engineering sense of the word. A typical example is the polymer pair polypropylene and polyamide, e.g. PA-6 or PA-6.6 which produces blends with very poor mechanical properties^{1,2}. The literature suggests there is a great interest in finding suitable ways to combine these polymers into useful materials^{1–12}. Compatibility problems are often overcome by using a suitable compatibilizing agent, normally a *graft* or *block* copolymer, containing polymer segments of different structures capable of interacting with each of the two polymers concerned. Such compatibilizing agents affects the morphology and properties of the blend, by adsorption at the interface between the immiscible polymers.

The present study was initiated in order to study both the morphology and morphologically dependent properties of PP-PA blends, as modified by different amounts of two self-assembling thermoplastic elastomers. One of these was polystyrene-*block*-poly(ethylene-*stat*-butylene)-*block*-polystyrene (SEBS) of high molecular weight, the other a lower molecular weight SEBS-polymer modified by reaction with maleic anhydride and referred to as SEBS-MA. During melt mixing conditions, the latter polymer may become grafted with the polyamide, in a reaction involving succinic anhydride groups on SEBS-MA and amino end groups on

the polyamide². The grafting reaction is an application of reactive processing, an area which has been recently reviewed by Xanthos^{13,14}. Because of the self-assembling property of thermoplastic elastomers, both compatibilizers have the potential of forming interphase layers binding together polypropylene and polyamide. The SEBS-MA has been shown to be a good compatibilizer in blends of PP and PA^{15–17}.

The amount of compatibilizer was varied from 0 to 25%, a concentration range beyond that normally considered in compatibilization studies⁶. All blends were prepared using a one step melt mixing processes. This was because a parallel study of PP-PA blends containing 5% SEBS-MA had shown that two-step mixing procedures imparted little advantage, or even produced a blend with properties inferior to that obtained by the one-step mixing¹⁸. In addition to the morphology, some further properties of the blends, which can be expected to depend on the morphology, were also studied. Therefore results from studies of the crystallization and melting behaviour of PP and PA in the blends, stress-strain properties, melt rheology and water absorption are reported. As will be shown polyamide is the dispersed phase in all blends studied. SEBS is not a very potent compatibilizer for PP-PA blends, whereas SEBS-MA grafted by polyamide strongly affects blend morphology, by assembling at the interface between PP and PA. At high concentrations of SEBS-MA and correspondingly smaller PA phase domains, the PA domains agglomerate into larger structures joined together by grafted SEBS-MA.

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Table 1 Composition of the two- and three-component blends studied^a

Blend	PA-6 (wt%)	PP (wt%)	SEBS-MA (wt%)	SEBS (wt%)
A6P	50.0	50.0	0	0
A6PSM-1	49.5	49.5	1	0
A6PSM-2	49.0	49.0	2	0
A6PSM-3	48.5	48.5	3	0
A6PSM-5	47.5	47.5	5	0
A6PSM-7	46.5	46.5	7	0
A6PSM-10	45.0	45.0	10	0
A6PSM-15	42.5	42.5	15	0
A6PSM-25	37.5	37.5	25	0
A6PS-15	42.5	42.5	0	15
A6PS-25	37.5	37.5	0	25
A6SM-26	73.9	0	26.1	0

Blend	PA-6.6(wt%)	PP (wt%)	SEBS-MA(wt%)	SEBS (wt%)
A66P	50.0	50.0	0	0
A66PSM-15	42.5	42.5	15	0
A66PSM-25	37.5	37.5	25	0
A66PS-15	42.5	42.5	0	15
A66PS-25	37.5	37.5	0	25
A66SM-26	73.9	0	26.1	0

^aIn the code used to designate the different materials the components are abbreviated as follows: PP as P, PA-6 as A6, PA-6.6 as A66, SEBS as S and SEBS-MA as SM. All materials containing PP and polyamide, contain equal amounts of PP and polyamide. The number given at the end of the code represents the amount of compatibilizer in percent by weight. Thus, A6PSM-15 refers to a material prepared from 15 parts by weight of SEBS-MA, 42.5 parts PA-6 and 42.5 parts of PP, and A66SM-26 a material prepared by mixing 26 parts of SEBS-MA with 74 parts of PA-6.6

EXPERIMENTAL

Materials

The following commercial materials were used: isotactic polypropylene (PP), PY 6100 (MFI = 5) from Shell, polyamide 6 (PA-6), Ultramid B3 ($M_n = 18\,000$) from BASF, polyamide 6.6 (PA-6.6), Maranyl A100 ($M_n = 18\,000$) from ICI and two triblock thermoplastic elastomers from Shell, Kraton G 1651, and Kraton FG 1901X. Kraton G 1651 is a polystyrene-*block*-poly(ethylene-*stat*-butylene)-*block*-polystyrene copolymer (SEBS), having polystyrene (PS) endblocks with a molecular weight of 29 000, and a midblock of poly(ethylene-*co*-butylene) (EB) with a molecular weight of 116 000¹⁹. Kraton FG 1901X, here referred to as SEBS-MA, is essentially a low molecular weight SEBS copolymer, functionalized by reaction with about 2% by weight of maleic anhydride. The parent SEBS copolymer is supposed to have a block length structure similar to that of Kraton G 165 which has PS endblocks with a molecular weight of 8 000 and an EB midblock with a molecular weight of 29 000^{16,17}. The functionalized SEBS contains approximately 2% by weight of succinic anhydride groups, attached to the EB midblocks. Before processing and rheological measurements, the polyamides, as well as blends containing polyamide, were dried at 80°C for 20 h to remove absorbed water.

Blend preparation

Blends were prepared from equal amounts (by weight) of

polyamide and polypropylene and from 0% to 25% of either SEBS or SEBS-MA. The compositions of these blends and two reference materials are presented in *Table 1*.

Blends containing PA-6 were prepared by melt mixing in a Berstorff ZE 25 × 43D co-rotating intermeshing twin screw extruder, fed by a dry mix of pellets of component materials. The temperature of the melt in the die zone was 250°C and the screw speed was 105 rpm. The feed rate was 3.5 kg h⁻¹ giving a residence time of about 2.4 min. The blends containing PA-6.6 were prepared by melt mixing in a Buss Ko-Kneader with a melt temperature in the die zone of 270°C. The extruded strands from both mixing devices had a circular shape with a diameter of about 3 mm. Granulates of the blends for injection moulding were prepared using a Scheer SGS/E pelletizer.

Tensile strength test bars (type 2 ISO/R527) and smaller test bars for water absorption studies (10 × 4 × 2 mm) were prepared in an Engel ES 200/50 HL injection moulding machine. The mould temperature was 60°C, the barrel temperature was 250°C when moulding blends containing PA-6, and 280°C when moulding blends containing PA-6.6.

Morphology

The morphology of the blends was studied by transmission electron microscopy (TEM) using a Jeol 100U instrument, and by scanning electron microscopy (SEM), using an ISI 100A instrument. Scanning electron microscopy was used to study cryo-fractured (liquid nitrogen

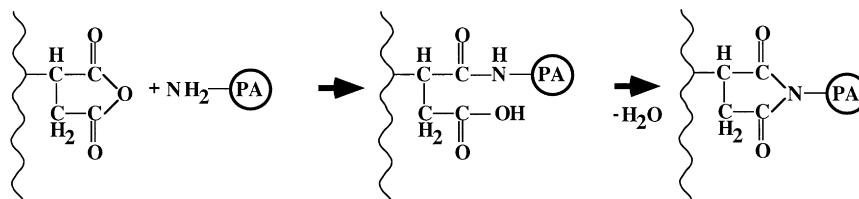


Figure 1 Grafting of SEBS-MA by reaction between a succinic anhydride group in the modified thermoplastic elastomer and a polyamide amino end group.

temperature) blend surfaces. These were extracted by formic acid (Merck pro analysis) for 24 h to remove the polyamide phase domains, or by xylene to remove ungrafted thermoplastic elastomer from the surface. The solvent treated samples were coated with a 20 nm thick conductive layer of Au–Pd alloy.

The samples for the TEM-study were thin sections, cut with a glass knife in a LKB Ultratome V ultramicrotome supplied with a cryo-kit. The sections were taken at right angles to the axial direction of the extruded blend strands. The sample temperature was -80°C and the knife temperature -40°C . A 50/50 (v/v) mixture of water and dimethyl sulfoxide was used as the trough liquid. The sections having a minimum thickness of 80 nm were exposed to vapor from a freshly prepared solution of ruthenium tetroxide for 20 min, in order to develop contrast, by staining the polystyrene domains in SEBS and SEBS-MA²¹. This treatment also slightly stained the polyamide phases. The average size of the polyamide domains in each blend was determined by measurement of approximately 500 polyamide domains from sets of TEM micrographs.

Solvent extraction

Solvent extraction may give information about blend structure and the extent of reaction between SEBS-MA and the polyamides²². Xylene was used to dissolve accessible domains of SEBS, or ungrafted SEBS-MA and formic acid to dissolve polyamide from the accessible polyamide phase domains. Granules of the blends were placed for 72 h in containers with xylene at room temperature. After washing with fresh solvent, the samples were dried at 50°C for 24 h and the weight loss determined. This procedure was repeated using formic acid as solvent. The reverse order of extraction was also used. A separate experiment showed that SEBS-MA, on immersion in formic acid for 72 h absorbs about 2% by weight of formic acid.

Stress–strain behaviour

Ten injection moulded tensile bars of each blend were tested in a JJ Instruments T30K tensile testing machine at room temperature, using a crosshead speed of 50 mm min^{-1} . The bars were dried for 20 h at 80°C before testing.

Water absorption measurement

Samples (10 pieces with dimensions $10 \times 4 \times 2\text{ mm}$) of the pure materials and of the blends, which have been conditioned at 80°C for 24 h, were placed in a container with distilled water at 23°C . The increase in weight by time was determined by weighing the samples (wiped dry with a dry cloth) at certain time intervals. The percentage of water absorption was calculated as follows:

Percentage water absorption

$$= \frac{\text{Weight of wet sample} - \text{Conditioned weight}}{\text{Conditioned weight}} \times 100$$

Differential scanning calorimetry (DSC)

The melting and crystallization behaviour of PP and PA in the blends were studied by differential scanning calorimetry (Mettler DSC 30) equipped with a low temperature cell, using samples (5–10 mg) sealed into aluminum pans. In order to avoid possible influence due to the thermal history of the sample, on crystallization and

melting phenomena, the sample was first heated to 300°C at a heating rate of $10^{\circ}\text{C min}^{-1}$. The crystallization process was then followed as the sample was cooled to -150°C at a rate of $10^{\circ}\text{C min}^{-1}$. The melting behaviour was studied by again heating the sample to 300°C at a rate of $10^{\circ}\text{C min}^{-1}$. The crystallization and melting temperatures were taken as the those corresponding to the peak values of the crystallization exotherms and melting endotherms, respectively.

Rheological measurements

Shear viscosity as a function of shear rate was determined, at 27WC using a Gbttfert Rheograph 2001 capillary rheometer (capillary diameter 1 mm, length/diameter ratio 30). The shear rate at the wall was calculated using the Rabinowitsch equation²³. Because of the large length/diameter ratio of the capillary, Bagley corrections were not applied.

RESULTS AND DISCUSSION

The present study is concerned with the morphology and properties of blends containing equal amounts of polypropylene (PP) and polyamide (PA) and, from 0% to 25% of a compatibilizing agent. In most blends the polyamide used was PA-6, although a few blends containing PA-6.6 were also included in the study. The compatibilizing agent was either SEBS of a high molecular weight or SEBS-MA. The latter polymer is essentially a SEBS three-block copolymer with shorter block lengths than the SEBS polymer, which has been modified by reaction with about 2% maleic anhydride, to give a polymer in which the EB midblock is substituted with succinic anhydride groups. On average each molecule of SEBS-MA would contain about 9 anhydride groups. During melt mixing with a polyamide, the succinic anhydride groups on SEBS-MA may react with polyamide amino end groups (see *Figure 1*), giving a PA-grafted thermoplastic elastomer, which has a strong tendency to be anchored at the PP–PA interface. In the different blends, the ratio between the number of succinic anhydride groups and the number of polyamide amino end groups varied with the amount of SEBS-MA used, and passed unity at about 12% SEBS-MA. All blends were prepared using a single mixing step, i.e. a dry mix of pellets of the component materials was fed to either a double screw extruder (blends containing PA-6), or to a Buss Ko-Kneader (blends containing PA-6.6). In either case, the blends were obtained in the form of cylindrical strands with a diameter of about 3 mm. Besides the PP–PA blends, two materials were prepared by melt mixing of SEBS-MA with PA-6 and PA-6.6, respectively. The compositions of the different materials prepared are presented in *Table 1*, which also defines the codes used in designating the different blends.

Blend morphology

In all of the present PP–PA blends, polypropylene seems to form the continuous phase. This conclusion is based mainly on the observation that small test pieces of the blends retained their shape and size when subjected to extensive treatment, first with xylene and then formic acid, or with formic acid and then xylene. This occurred even though a large fraction of the compatibilizer and a major portion of the polyamide was removed by these extraction steps (see *Table 2*). Inspection of the residue by SEM showed the presence of a continuous network containing large cavities, as well as, small holes representing the dissolved polymer phases. Moreover, studies by TEM of

Table 2 Blend sample weight losses on extraction first by xylene and then formic acid, in percent by weight of the original sample, and also the corresponding fraction (% by w.) of the amount of polyamide and SEBS, or SEBS-MA in the samples, removed by extraction with formic acid and xylene, respectively

Material	Extraction with xylene		Extraction with formic acid	
	% of original sample weight	% of SEBS or SEBS-MA	% of original sample weight	% of polyamide
A6P	0	0	50	100
A6PSM-1	1.0	100	50	100
A6PSM-2	1.4	71	45.6	93.0
A6PSM-3	1.8	59.2	31.2	64.2
A6PSM-5	1.4	28.5	44.5	93.8
A6PSM-7	2.3	33.5	43.6	93.9
A6PSM-10	3.2	31.6	36.8	81.8
A6PSM-15	5.1	33.7	33.5	78.7
A6PSM-25	11.5	46.2	27.7	73.8
A6PS-25	20.6	82.5	33.2	88.5
A6SM-26	2.2	8.4	^a	^a
A66P	0	0	50	100
A66PSM-15	3.4	22.4	28.6	67.2
A66PSM-25	15.3	58.5	28.6	76.2
A66PS-15	5.4	30.4	41.9	98.7
A66PS-25	9.8	35.1	33.7	90.0
A66SM-262	0	0	^a	^a

^aThe sample fell apart

Similar results were obtained when the order of the extraction steps was changed

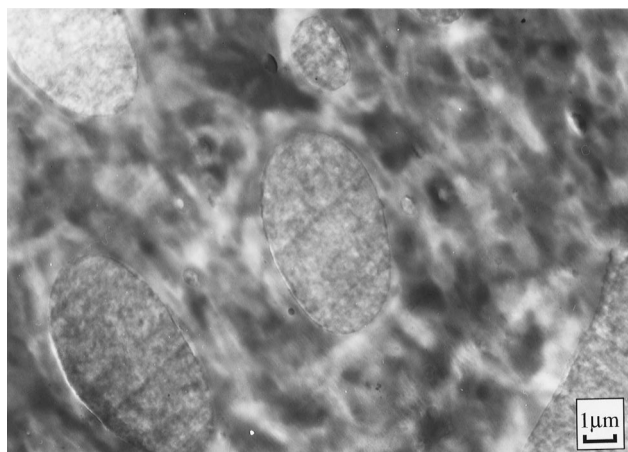


Figure 2 The morphology of an uncompatibilized blend containing equal amounts of PP and PA-6 (blend A6P of Table 1), as observed by TEM using an unstained thin section cut from an extruded strand of the blend at right angles to the flow direction. The greyish closed areas represent polyamide domains dispersed in the continuous polypropylene phase.

ruthenium tetroxide stained, thin sections, taken from uncompatibilized blends, or blends containing small amounts of compatibilizer, showed that the more easily stained of the major phases, polyamide, appeared as closed phase domains embedded in a brighter matrix of the less easily stained PP phase¹⁶.

Electron microscopy

Uncompatibilized blends. Studies by TEM of sections taken from a 50/50 (w/w) PP-PA-6 blend (Figure 2), showed that the polyamide was present in the form of large phase domains, with an approximate diameter (as measured across the flow direction) of about 5–10 μm, surrounded by the continuous polypropylene matrix. The PP-PA-6 blend, and the corresponding PP-PA-6.6 blend were very brittle. Close inspection of micrographs, from ultramicrotomed sections showed that the PP and PA phases were partly separated from each other by thin cracks, possibly created during high speed cutting of the extruded blend strands into pellets, or during ultramicrotome sectioning. The poor adhesion between the two

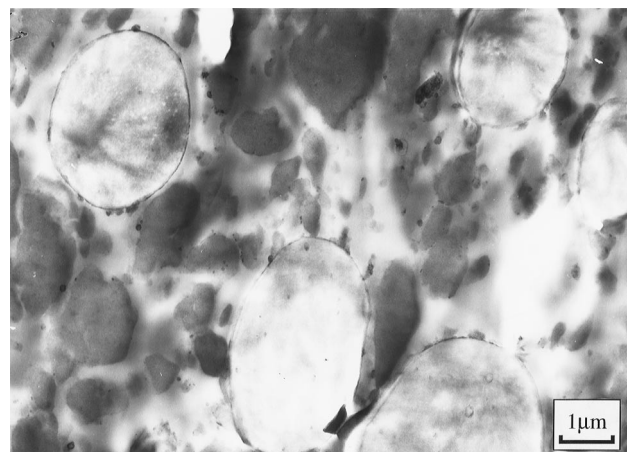


Figure 3 The morphology of blend A6PS-25 as observed by TEM using a thin section stained by ruthenium tetroxide. The stained (dark) SEBS phase is mainly embedded as a separate phase, in the continuous PP phase and is only to a small extent present at the surface of the dispersed polyamide domains.

phases was also evident from SEM studies of blend fracture surfaces. Injection moulded test pieces were easily split on bending, in a manner demonstrating that the polyamide phase domains were preferentially extended in the flow direction.

Blends compatibilized by SEBS. The addition of up to 25% SEBS led to a moderate decrease in the diameter of the polyamide phase domains. Thus, in the PP-PA-6 blend, with 25% by weight of SEBS (A6PS-25), most polyamide domains had diameters in the range 1–5 μm (Figure 3). The dark, or dark-dotted areas in this micrograph represent SEBS, the dark dots corresponding to strongly stained polystyrene micro domains²⁴. It is obvious that most of the SEBS is present as a separate phase, dispersed in the continuous PP matrix and that only a small fraction of the total amount of SEBS is located at the interface between the polyamide and polypropylene phases (Figure 3). This demonstrates that SEBS is a poor compatibilizer for PP-PA blends. The micrograph also shows that SEBS has a tendency to form a network structure in the PP matrix.

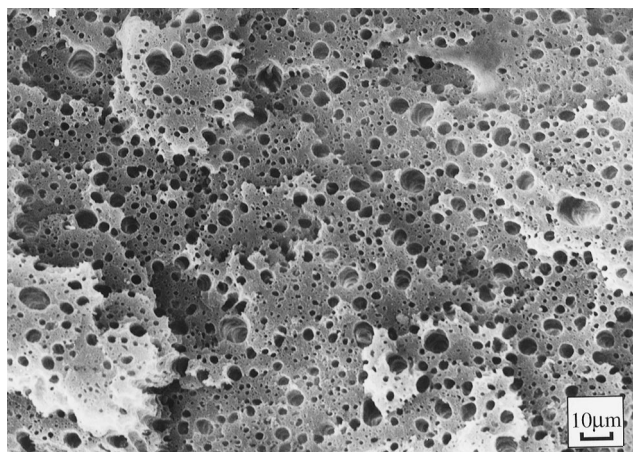


Figure 4 The morphology of blend A6PS-25 (cf. Figure 3) as observed by SEM of a cryo-fractured surface extracted by formic acid, showing a number of cylindrical holes representing extended polyamide phase domains removed by extraction.

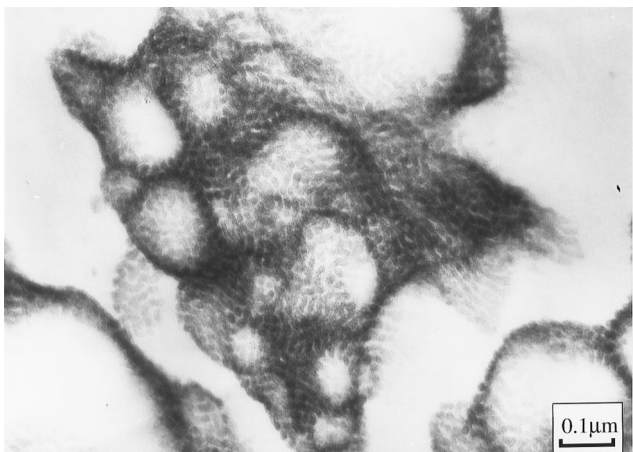
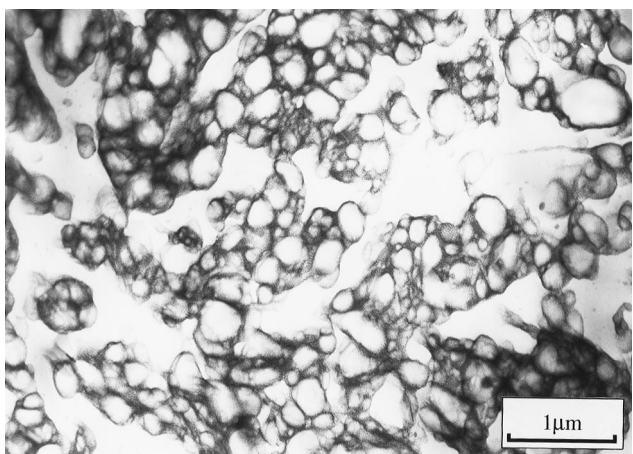


Figure 5 The morphology of blend A6PSM-25 as observed by TEM using a thin section stained by ruthenium tetroxide. a. The polyamide domains are completely encapsulated by grafted SEBS-MA and form extended agglomerates joined together by the compatibilizing phase. b. The dark dots represent PS microdomains in the self-assembling interphase polymer.

The SEM micrograph in *Figure 4* shows a fracture surface of the blend A6PS25. The sample was obtained by fracturing a strand of extrudate at liquid nitrogen temperature, which was then extracted by formic acid. The plane of the fracture surface was at right angles to the original flow direction. The cylindrical holes in the surface represent

polyamide domains removed by formic acid extraction. The presence of holes of this type demonstrates that the blend contained fibrillar polyamide domains oriented in the flow direction of the sample. Another SEM study of a similar fracture surface, extracted instead by xylene, showed polyamide domains separated from the surrounding PP phase, by tiny tubular voids, and a large number of etched cavities in the continuous PP phase, representing dissolved SEBS. This confirms the TEM results, which indicated that only a small amount of the SEBS was located at the interface between PP and PA (*Figure 3*).

Blends compatibilized by SEBS-MA. The use of SEBS-MA as a compatibilizer precursor for PP-PA blends has been previously described¹⁵⁻¹⁷. The PA-grafted thermoplastic elastomer formed under melt mixing conditions is an effective compatibilizer for PP-PA blends. The compatibilizing effect is not only due to the high affinity of the polyamide grafts for polyamide, but also to the rather high affinity of ungrafted EB midblocks for PP. In addition the presence of polystyrene endblocks, confer self-assembling properties to the compatibilizing polymer⁶.

The morphology of PP-PA-6 blends containing a small amount of SEBS-MA, prepared by both one- or two-step mixing, has been discussed elsewhere¹⁸. The phase structure of blend A6PSM-25, representing a blend with a high amount (25%) of SEBS-MA, is illustrated by the TEM micrographs of a stained section reproduced in *Figure 5*. A comparison with *Figures 2 and 3* demonstrates the large effect of SEBS-MA on blend morphology. The polyamide phase is present in the form of small spherical phase domains, completely encapsulated by polyamide grafted SEBS-MA. The two-phase structure of the interphase surrounding the PA-6 domains, which consists of SEBS-MA grafted by polyamide, is clearly seen in *Figure 5b*. The dark dots represent polystyrene micro domains stained by ruthenium tetroxide. The individual polyamide domains are agglomerated and form extended structures joined together by the interphase polymer. The tendency of PA-6 and SEBS-MA to form a common continuous two-phase structure is a consequence of the self-assembling properties of the interphase polymer and the high volume fraction (0.66) of PA6, plus SEBS-MA used in this blend. From measurements on a set of TEM micrographs, the average PA-6 domain size for blend A6PSM-25 (*Figure 5*) was estimated to be 0.11 μm. In this case, the PA-6 domains are mainly spherical. This is obvious from the fact that: (a) the diameter of the PA-6 domains is comparable to the thickness of the thin section studied; (b) very few of the PA-6 domains are cut through during sectioning; and (c) the upper surface of almost all PA-6 domains are covered by grafted SEBS-MA (*Figure 5*). The morphology of the blend presented in *Figure 5*, differs in several respects from that of the corresponding blend containing 5% SEBS-MA¹⁸. The latter blend, A6PSM-5, contained mainly nonadhering PA-6 domains, with an average diameter of 0.36 μm, as measured at right angles to the flow direction. Sections taken along the direction of flow, showed that a majority of these phase domains were preferentially extended in the flow direction, with a length to diameter ratio of up to 10¹⁸. An increase in the amount of SEBS-MA from 5% to 25% obviously leads to a large reduction of the average volume of the individual PA-6 phase domains, a corresponding increase in the specific surface area of PA-6, and also to an agglomeration of encapsulated PA-6 domains into larger structures held together by the compatibilizing polymer. An estimate of the

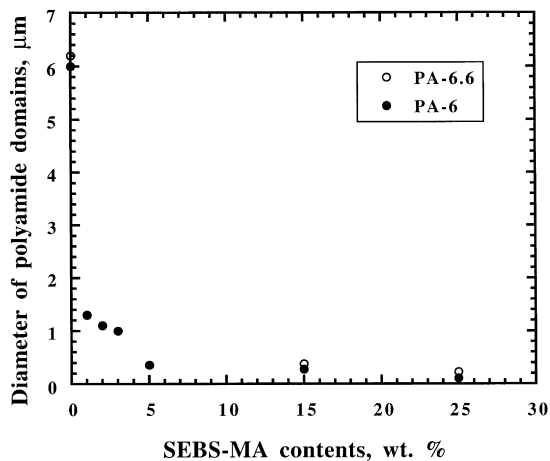


Figure 6 The number average cross-section diameter of polyamide domains in PP-PA blends containing various amounts of SEBS-MA, as calculated from sets of TEM micrographs of thin sections taken at right angles to the flow direction and stained by ruthenium tetroxide.

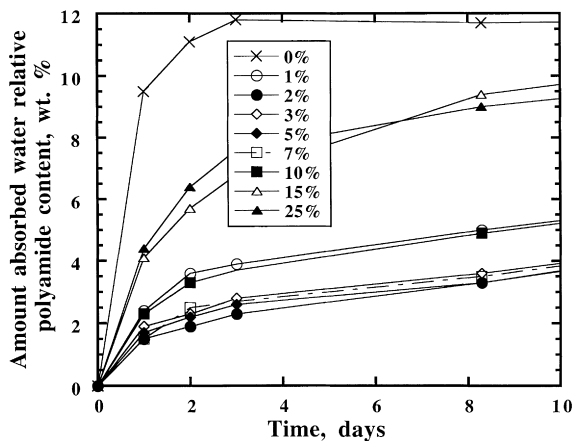


Figure 7 Amount of water absorbed (increase in weight) per unit weight of polyamide in the sample, as a function of immersion time in water, of injection moulded test bars prepared from PP-PA-6 blends containing 0% to 25% by weight SEBS-MA.

ratio between the total surface area of the PA-6 domains in the blends with 25% and 5% SEBS-MA can be made by assuming the PA-6 domains of blend A6PSM-25 to be spheres with a diameter of $0.11 \mu\text{m}$, and those of blend A6PSM5 to be cylinders with a diameter of $0.36 \mu\text{m}$ and a length of $3.6 \mu\text{m}$.

Considering also the different densities of the polymers, this gives a PA-6 surface area ratio of 3.9, a value not too far from 5, which corresponds to the ratio of the concentration of SEBS-MA in the two blends. Using the same assumption regarding domain sizes and shapes, the average thickness of the compatibilizing phase in the two blends can be calculated to be 11 nm for blend A6PSM-5 and 14 nm for blend A6PSM-25. These values are in good agreement with the size of the black dots in *Figure 5*, representing stained PS microdomains. The calculated thickness of the interphase layer is also in good agreement with the observation that the spacing between adjacent agglomerated PA-6 domains in blend A6PSM-25 seems to correspond to a double layer of PS domains. This observation was made by inspection of a set of TEM micrographs similar to that reproduced in *Figure 5*. It is obvious that individual or adjacent PS microdomains might contain PS endblocks of molecules whose grafted EB midblocks are anchored in two

adjacent PA-6 domains, thus serving as a cohesive bridge between the latter.

The diagram in *Figure 6* gives the average cross-sectional diameter of polyamide phase domains in blends prepared using different relative amounts of SEBS-MA. The data were obtained by measurements on sets of micrographs of thin sections cut at right angles to the flow direction. The data can be understood by considering the fact that the specific surface area of the polyamide domains increases with an increase in the concentration of SEBS-MA because: (a) the phase domains change shape from cylinder-like to spheres; and (b) the diameter of the spherical domains decrease. Assuming that the interphase layer surrounding the PA-6 domains is some 11–14 nm thick, an analysis of the data in *Figure 6* for blends containing PA-6 indicates that the transition from cylinder-like to spherical domains would be completed at a concentration of SEBS-MA of between 7% and 10%.

The effect of SEBS-MA on the morphology of PP-PA-6.6 blends was about the same as that for PP-PA-6 blends, although the domain sizes were somewhat different (*Figure 6*). Thus the PP-PA-6.6 with 25% SEBS-MA contained PA-6.6 phase domains of an average diameter of $0.23 \mu\text{m}$, a value that should be compared with $0.11 \mu\text{m}$ for the corresponding PP-PA-6 blend. The differences might be due to the higher mixing intensity in the extruder (PA-6 blends), than in the Ko-Kneader (PA-6.6 blends) and to the use of different mixing temperatures.

Solvent extraction. The compatibilizing additives used, SEBS and SEBS-MA, are both soluble in xylene, while the polyamides are soluble in formic acid and PP is insoluble in both at room temperature. Extraction with these solvents may thus provide information about blend properties. All samples of blends containing both polyamide and polypropylene, with and without compatibilizer, kept their original shape and size after extraction in xylene and formic acid. As referred to earlier, this shows that the blends contained a continuous polypropylene phase. Although the polyamide phase domains would be embedded in the PP matrix, an astonishingly large amount of polyamide could be extracted from all of the blends, see *Table 2*. This points at the presence of voids or cracks in the pelleted samples, which enabled the dissolved polyamide to be leached out to the sample surface. Such cracks may have been formed during preparation of pellets by high speed cutting of extruded strands.

Repeated extraction of two-component blends, prepared from SEBS-MA and polyamide (A6SM-25 and A66SM-25), by formic acid and xylene, showed that less than 10% of the original SEBS-MA could be recovered from the xylene extract (see also *Table 2*). Hence, most of the SEBS-MA was grafted during melt mixing with polyamide²², and to an extent rendering the product insoluble in xylene. These two-component blends fell apart on treatment with formic acid, but not with xylene, expectedly showing that the polyamide phase was continuous.

In the three-component blends containing SEBS-MA, TEM studies showed that the compatibilizer is almost entirely located at the PP-PA interphase. Therefore, the fact that a lower relative amount of SEBS-MA, than PA was removed by the extraction steps, is indicative of grafting, as grafted SEBS-MA would not be soluble in xylene.

Water absorption

Polyamides have a strong tendency to absorb moisture

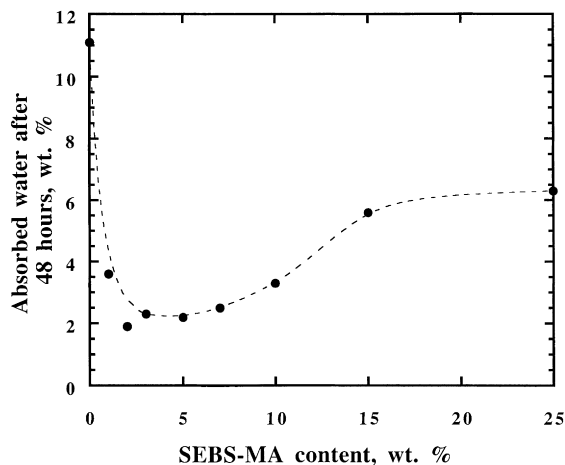


Figure 8 Amount of water absorbed per unit weight of polyamide during immersion in water over 48 h for PP-PA-6 blends containing various amounts of SEBS-MA (data from Figure 7).

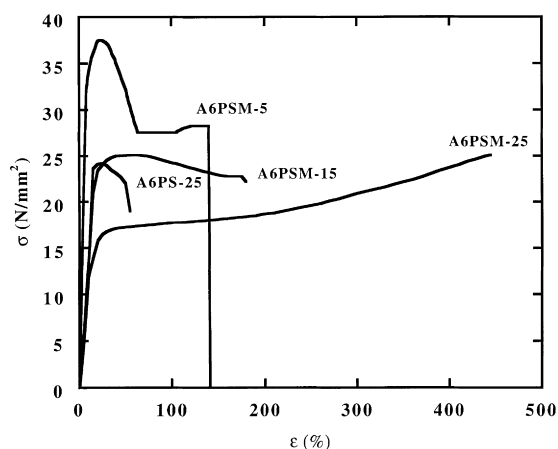


Figure 9 Tensile stress-strain curves at room temperature, comparing the properties of PP-PA-6 blends compatibilized by 25% SEBS, or 5%, 15% and 25% of SEBS-MA.

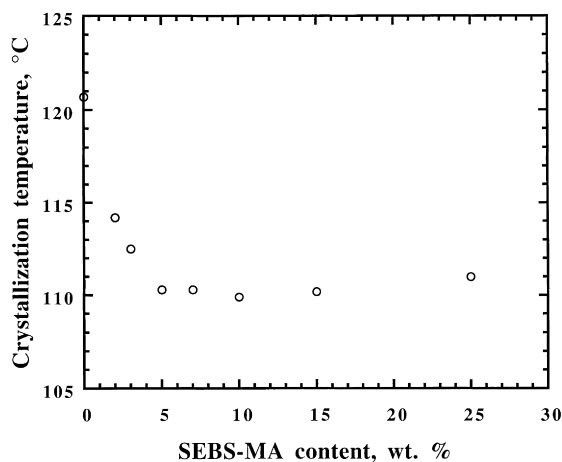


Figure 10 The crystallization temperature of polypropylene in PP-PA-6 blends containing various amounts of SEBS-MA.

from the environment. Water acts as a plasticizing agent and affects the thermal and mechanical properties of polyamides. Figure 7 shows that the rate of water absorption in injection moulded test bars during immersion in water, is much lower for blends compatibilized by SEBS-MA, than

for the uncompatibilized blend. For the compatibilized blends, a saturation level was not reached even after 100 days of immersion. The rate of water uptake was lowest for blends with an intermediate concentration of SEBS-MA. This is shown in Figure 8 where results for the amount of water adsorbed during 48 h of immersion are presented. The higher rate of water uptake for blends containing high amounts of SEBS-MA, is probably due to the presence of extended agglomerates of PA-6 domains, joined together by the grafted thermoplastic elastomer and also to a higher rate of water transport through the interphase polymer, than through PP. For blends compatibilized by SEBS, the rate of absorption was much higher and a saturation level was reached within about 12 days for blend A6PS-15 and A6PS-25

The uncompatibilized blend sample absorbed slightly more water than that corresponding to equilibrium uptake of water in relation to the amount of pure polyamide present in the sample. The excess water is probably due to filling of fine capillary voids separating the phases²⁶.

Stress-strain properties

The large difference in morphology observed for blends containing SEBS and SEBS-MA is also reflected in their stress-strain behaviour. Addition of SEBS to PP-PA-6 blends leads to a reduction of brittleness. This is demonstrated by the curve for blend A6PS-25 in Figure 9, which shows that this blend undergoes some plastic deformation before fracture. The effect is probably to a large extent caused by the presence of extended, rubbery SEBS domains in the PP phase, and not primarily related to interfacial phenomena.

With blends containing SEBS-MA, the deformation behaviour varied considerably with the amount of compatibilizer. Blend A6PSM-5 deformed by yielding and necking, in a manner resembling that of pure PP or PA-6, although the yield stress was lower (37 N mm^{-2} , as compared with 65 N mm^{-2} for PA-6 and 44 N mm^{-2} for PP) and fracture occurred at a much lower strain (140%, as compared with about 560% for PP and 400% for PA-6). The deformation behaviour of the blend with the highest concentration of SEBS-MA approaches that previously observed for PP-SEBS blends with a bicontinuous structure i.e. a typical yield point is absent, and the sample deforms and fractures in a more or less rubber-like fashion²⁷. This supports the suggestion that the blend contains an almost continuous network of agglomerated PA-6 domains, enclosed in a rubbery interphase of partially grafted SEBS-MA. The deformation behaviour and elongation at fracture of blend A6PSM-15 is clearly intermediate between those of blend A6PSM-25, which contains extensively agglomerated PA-6 domains and blend A6PSM-5, which contains mainly unagglomerated discrete polyamide phase domains.

Thermal properties

Blend structure, as controlled by the type and amount of compatibilizer, was found to have no marked effect on the melting behaviour (T_m and ΔH_m) of PP and PA in the blends. The crystallization behaviour of PP and PA was, however, found to depend on blend structure. Thus the crystallization temperature of PP in the uncompatibilized blends, in blends containing SEBS as compatibilizer, and also in blends containing low amounts of SEBS-MA, was found to be higher than that of pure PP, as determined using the same experimental conditions. This must be ascribed to

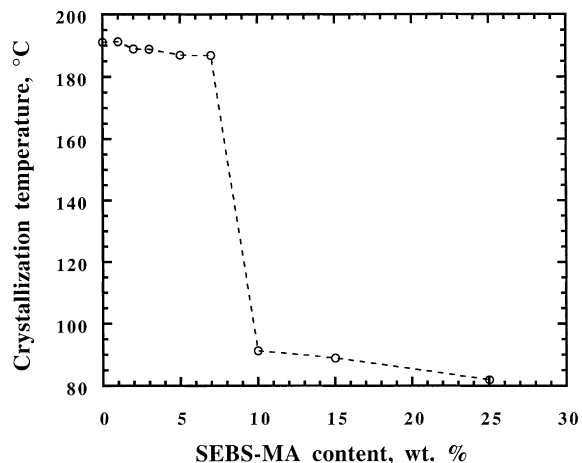


Figure 11 The crystallization temperature of polyamide in PP-PA-6 blends containing various amounts of SEBS-MA.

the effect of nucleation of PP, by contact with crystalline polyamide across the PP-PA interface. With SEBS as compatibilizer, the crystallization temperature of PP was about the same as in the uncompatibilized blend A6P, even at SEBS concentrations of 15% and 25%. Accordingly, the PP-PA-6 interface would not be completely covered by SEBS in any of these blends. In blends containing PA-6 and compatibilized by SEBS-MA, the crystallization temperature of PP varied with composition as presented in *Figure 10*. A nucleating influence of PA-6 was observed only at SEBS-MA concentrations lower than 5%. In blends containing 5% or more of SEBS-MA the crystallization temperature was about the same as for pure PP. In these blends, the PP and PA-6 phases would be completely separated by an interphase layer of PA-6 grafted SEBS-MA, a conclusion which is in agreement with the result from TEM studies (*Figure 5* and Ref. ¹⁸).

The crystallization behaviour of polyamide also varied with the amount of SEBS-MA used in preparing the blends. For blends containing PA-6, the crystallization temperature varied in the manner illustrated by *Figure 11*. In the concentration range from 0% to 7% SEBS-MA the crystallization temperature slowly decreased. This was accompanied by a broadening of the crystallization peak. A further increase in the concentration of SEBS-MA to 10%, caused a marked drop in crystallization temperature from about 180°C to below 100°C. The PA-6 crystallization peak for this blend and blends containing higher concentrations of SEBS-MA, appeared as a low temperature shoulder, or a peak overlapping the normal crystallization peak of PP¹⁹. The observed behaviour is most likely an effect of SEBS-MA on the polyamide domain volume. As each of the small polyamide domains has to be nucleated independently, crystallization occurs at a higher than normal degree of supercooling. This effect is referred to in literature as fractionated or cold crystallization²⁸⁻³².

A similar, but somewhat different behaviour was observed for blends containing PA-6.6. In this case the pronounced effect of compatibilizer concentration on crystallization of PA-6.6 first occurred at concentrations of SEBS-MA between 15% and 25%. Thus, the crystallization temperature of PA-6.6 in the blend containing 15% SEBS-MA was only slightly lower (about 10°C) than that of the uncompatibilized blend. However, no crystallization peak attributable to PA-6.6 appeared in the thermogram recorded as the blend containing 25% of SEBS-MA was

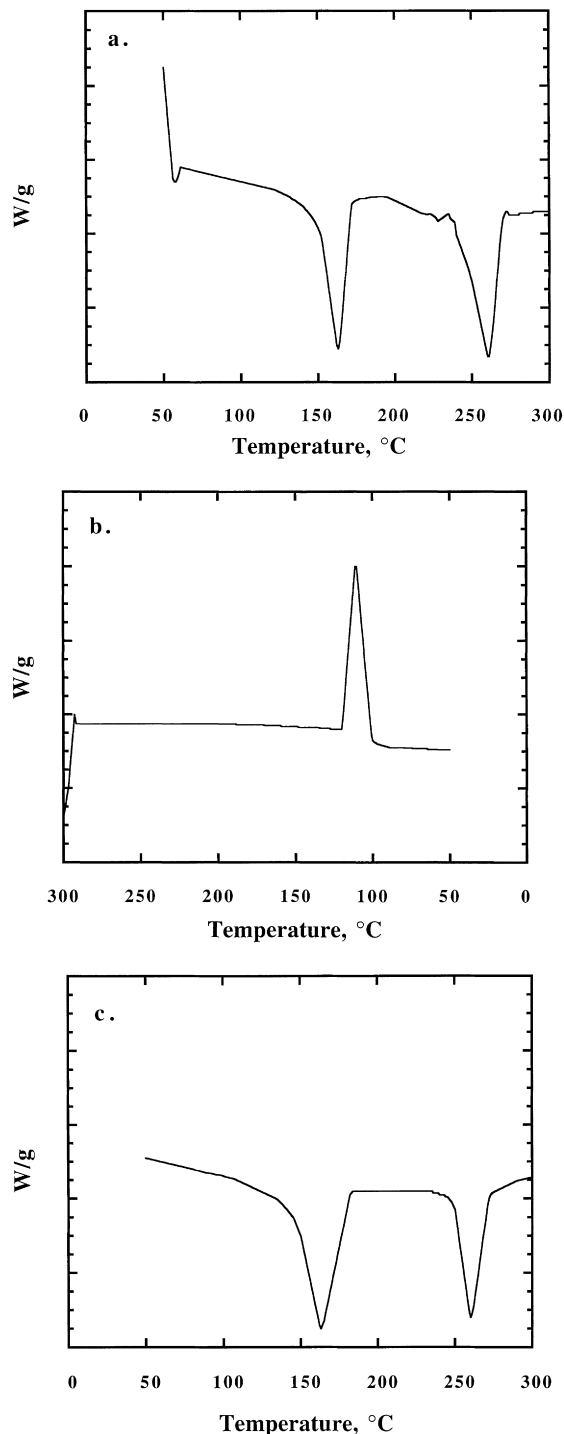


Figure 12 Thermograms showing melting endotherms and crystallization exotherms observed for blend A66PSM-25 in three successive DSC runs involving: (1) heating of the original blend (as delivered from the extruder) to 300°C; (2) cooling the molten blend from the first run after keeping it at 300°C for 5 min; and (3) reheating the cold melt from the second run.

cooled from the melt (see *Figure 12b*). In spite of this, a normal PA-6.6 melting endotherm was observed as the latter blend was reheated (*Figure 12c*). The heat of melting corresponding to the PA-6.6 melting endotherm in *Figure 12c*, is in good agreement with the expected value for the amount of PA-6.6 present in the sample. This means that crystallization of PA-6.6 in the A66PSM-25 blend was slow and must have occurred over a broad temperature interval. This conclusion is in agreement with the fact that in the

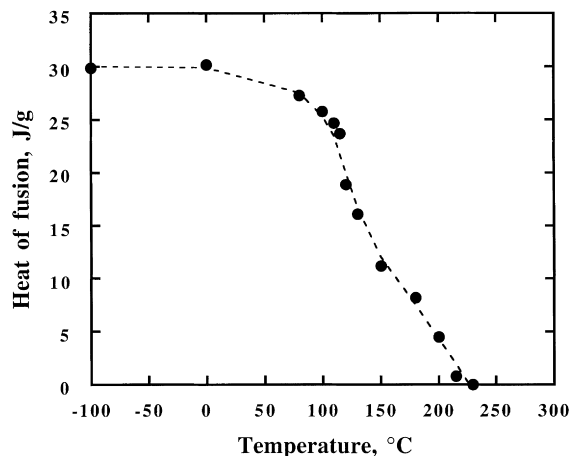


Figure 13 The heat of fusion of polyamide as derived from DSC thermograms from a set of samples of blend A66PSM-25, obtained by cooling the molten blend samples from 300°C at a rate of 10°C min⁻¹ to different temperatures. (The negative slope of the curve is proportional to the rate of crystallization of PA-6.6 in the blend, as a function of temperature under the cooling conditions used in *Figure 12c*.)

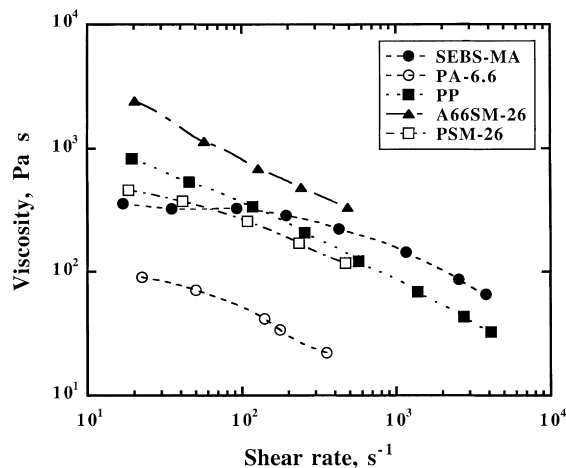


Figure 14 Apparent viscosities at 270°C as a function of shear rate for pure PP, pure PA-6.6 and pure SEBS-MA, and for two-component blends containing 25% SEBS-MA and either PA-6.6 or PP.

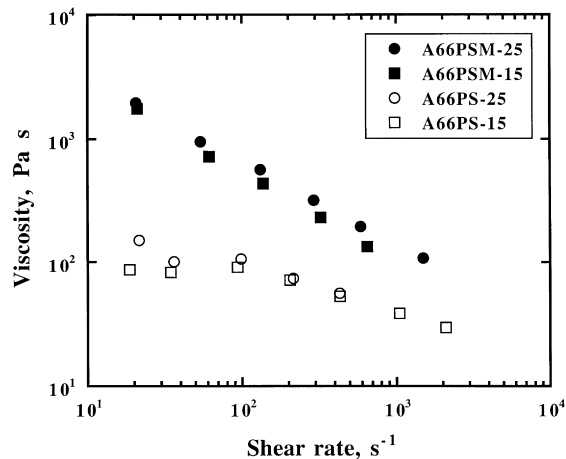


Figure 15 Apparent viscosities at 270°C as a function of shear rate for PP-PA-6.6 blends compatibilized with either SEBS or SEBS-MA.

interval from 290°C, to the temperature at which PP starts to crystallize, the thermogram in *Figure 12b* is almost linear and horizontal, and also somewhat displaced from the expected baseline level. The different behaviour observed for PA-6 and PA-6.6 blends indicates a difference in the nucleation and crystallization properties of the two polyamides. It might also partly be to the different distribution of polyamide domain volumes in the blends.

The crystallization behaviour of PA-6.6 in blend A66PSM-25 was further studied using DSC in the following way. A series of samples were crystallized from the melt by cooling from 300°C, down to different predetermined temperatures (turning point temperatures). In each case, the heat of melting of PA-6.6 was determined from the thermogram recorded as the individual sample was immediately reheated from the turning point temperature to 300°C. The results shown in *Figure 13* give the heat of melting for the individual samples as a function of their turning point temperatures (the lowest temperature reached during the cooling step). The slope of the curve in this diagram represents the rate of crystallization as a function of temperature at the cooling rate used (10°C min⁻¹). The specific heat of fusion of PA-6.6 in the samples cooled to 0°C and -100°C is in good agreement with the expected heat of fusion of the amount of PA-6.6 in the blend. The curve in *Figure 13* has an almost constant slope in the temperature range from about 220°C to 90°C. This indicates that PA-6.6 in the blend containing 25% of SEBS-MA crystallizes at a fairly constant rate over this broad temperature range, and explains the absence of a PA-6.6 crystallization peak in the thermogram reproduced in *Figure 12b*.

Rheology

The shear rate dependence of the steady shear viscosities of PP, PA-6.6, SEBS-MA, A66SM-26 and PSM-26 are shown in *Figure 14*. Addition of 26% SEBS-MA to PA-6.6 causes a large increase in viscosity. The viscosity of this blend, A66SM-26, is about 15 times higher than that of pure polyamide and more than twice that of pure SEBS-MA. The high viscosity at low shear rates and also the large shear rate dependence observed for this blend, are most probably related to the presence of extended aggregates of grafted SEBS-MA in the polyamide phase¹⁸. The low viscosity of PSM-26 indicates that similar structures are not formed when SEBS-MA is dispersed in PP. This is in agreement with results from TEM studies of PP containing 26% of SEBS-MA, which showed that, at low concentration, the thermoplastic elastomer was dispersed into small, well separated phase domains¹⁸.

The steady shear viscosities of some of the three-component blends are presented in *Figure 15*. A comparison with *Figure 14* shows that the viscosity of blends compatibilized by SEBS is considerably lower than that of the continuous PP phase. The low viscosities of these blends is probably due to the presence, in the melt, of large, easily deformable, low viscosity PA-6.6 droplets, which become oriented in the flow direction³³. The situation is quite different for blends containing SEBS-MA. At low shear rates, the viscosities of these blends are considerably higher than that of either pure PP or SEBS-MA. The shear rate dependence of these blends is rather pronounced and resembles that of blend A66SM-26 (see *Figure 14*). The results suggest that extended structures of polyamide domains joined together by grafted SEBS-MA (see *Figure*

3 for the structure of a similar blend based on PA-6), also exist in the melt.

CONCLUSIONS

In uncompatibilized, as well as, compatibilized PP-PA blends containing equal weight fractions of PP and PA, polypropylene forms the continuous matrix phase.

Even at high concentrations (25% by weight), SEBS is a poor compatibilizer for PP-PA blends. In such blends, most of the thermoplastic elastomer forms separate SEBS phase domains in the polypropylene phase, and only a small fraction becomes localized at the PP-PA interface. Accordingly, SEBS affects the properties of the blends mainly by modifying the properties of the matrix.

By grafting with polyamide during melt mixing, SEBS-MA forms an effective compatibilizer, having a strong tendency to develop a separate interphase, separating the polyamide domains from the matrix. In blends containing PA-6, the total surface area of the polyamide phase domains seems to increase in proportion to the concentration of SEBS-MA, indicating that the thickness of the interphase layer is almost constant and independent of compatibilizer concentration. The interphase layer thickness was estimated to be about 15 nm. At high concentrations of SEBS-MA (15% and 25%), the PA-6 phase domains form large aggregates, held together by a thermoplastic elastomer interphase network, which extends polyamide grafts into the adjacent phase domains.

The presence in the PP-PA-6 blend, with highest concentration of SEBS-MA (25%), of almost continuous aggregates of small PA-6 domains, surrounded by a layer of thermoplastic rubber, is in agreement with the observed stress-strain behaviour of the blend. The melt flow properties of this blend suggest that similar agglomerates are also present in the melt.

Blends compatibilized by SEBS-MA showed a low rate of water adsorption. The rate of water absorption was particularly low at intermediate concentrations of SEBS-MA i.e. for those where the blend contained separate dispersed polyamide domains, completely surrounded by an interphase layer of grafted SEBS-MA.

In several of the blends, crystallization of PP was nucleated by polyamide, indicating that the two crystallizing phases were not completely separated by an interphase layer. Full coverage was observed only in blends containing SEBS-MA and appears to require SEBS-MA concentrations between 3% and 5%.

In blends containing large amounts of SEBS-MA, the polyamides showed the phenomenon of cold crystallization

(crystallization at much lower temperatures than in the pure form), a characteristic which appears when polymers crystallize in small, separated phase domains.

REFERENCES

1. Paul, D. R., in *Polymer Blends*, Vol. 2, Chap. 12, ed. D. R. Paul and S. Newman. Academic Press, New York, 1978.
2. Ide, F. and Hasegawa, A., *J. Appl. Polym. Sci.*, 1974, **18**, 963.
3. Chen, C. C., Fontan, E., Min, K. and White, J. L., *Polym. Eng. Sci.*, 1988, **28**, 69.
4. Serpe, G., Jarrin, J. and Dawans, F., *Polym. Eng. Sci.*, 1990, **30**, 553.
5. Macknight, W. J., Lenz, R. W., Musto, P. V. and Somani, R. J., *Polym. Eng. Sci.*, 1985, **25**, 1124.
6. Utracki, L. A., *Polymer Alloys and Blends*. Hanser, New York, 1989.
7. Braun, D. and Eisenlohr, U., *Angew. Makromol. Chem.*, 1977, **58/59**, 227.
8. Cimmino, S., Coppola, F., D'Orazio, L., Greco, R., Maglio, G., Malinconico, M., Mancarella, C., Martuscelli, E. and Ragosta, G., *Polymer*, 1986, **27**, 1874.
9. Xanthos, M., Young, M. W. and Biesenberger, J. A., *Polym. Eng. Sci.*, 1990, **30**, 355.
10. Greco, R., Malinconico, M., Martuscelli, E., Ragosta, G. and Scarinzi, G., *Polymer*, 1987, **28**, 1185.
11. Baker, W. E. and Saleem, M., *Polym. Eng. Sci.*, 1987, **27**, 1634.
12. Borggreve, R. J. M. and Gaymans, R. J., *Polymer*, 1989, **30**, 63.
13. Xanthos, M., *Polym. Eng. Sci.*, 1988, **28**, 1392.
14. Xanthos, M. and Dagli, S. S., *Polym. Eng. Sci.*, 1991, **31**, 929.
15. Holsti-Miettinen, R., Seppälä, J. and Ikkala, O. T., *Polym. Eng. Sci.*, 1992, **32**, 868.
16. González-Montiel, A., Keskkula, H. and Paul, D. R., *Polymer*, 1995, **36**, 4587.
17. Rösch, J. and Mülhaupt, R., *Makromol. Chem., Rapid Comm.*, 1993, **14**, 503.
18. Ohlsson, B., Hassander, H. and Törnell, B., *Polymer* (in press).
19. Yee, A. F. and Diamant, J., *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.*, 1978, **192**, 92.
20. Oshinski, A. J., Keskkula, H. and Paul, D. R., *Polymer*, 1992, **33**, 268.
21. Montezinos, D., Wells, B. G. and Burns, J. L., *J. Polym. Sci., Polym. Lett. Ed.*, 1985, **237**, 421.
22. Gelles, R., Modic, M. and Kirkpatrick, J., *SPE ANTEC Tech. Papers* 1988.
23. Rabinowitsch, B., *Z. Physik. Chem. (Leipzig)*, 1929, **145A**, 1.
24. Ohlsson, B. and Törnell, B., *J. Appl. Polym. Sci.*, 1990, **41**, 1189.
25. Modic, M.J., *Soc. Plast. Engng, ANTEC*, 1993, **39**, 205.
26. Lee, J.-D. and Yang, S.-M., *Polym. Eng. Sci.*, 1995, **35**, 1821.
27. Ohlsson, B., Hassander, H. and Törnell, B., *Polym. Eng. Sci.*, 1996, **36**, 501.
28. Frensch, B., Harnischfeger, P. and Jungnickel, B.-J., in *Multiphase Polymer: Blends and Ionomers*, ed. L. A. Utracki and R. A. Weiss. ACS Symp. Ser. 395, Am. Chem. Soc., Washington, DC, 1989.
29. Tang, T. and Huang, B., *J. Appl. Polym. Sci.*, 1994, **53**, 355.
30. Morales, R. A., Arnal, M. L. and Müller, A., *J. Polym. Bull.*, 1995, **35**, 379.
31. Moon, H.-S., Ryoo, B.-K. and Park, J.-K., *J. Polym. Sci. Polym. Phys. Ed.*, 1994, **32**, 1427.
32. Jannasch, P. and Wesslén, B., *J. Appl. Polym. Sci.*, 1995, **58**, 753.
33. Han, C. D. *Multiphase Flow in Polymer Processing*. Academic Press, New York, 1981.