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Impact-modified nylon 6/polypropylene blends: 2. Effect of reactive functionality on morphology and mechanical properties

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The morphology of nylon 6/polypropylene blends modified with maleated rubbers, such as styrene–ethylene/butylene–styrene triblock copolymers (SEBS-*g*-maleic anhydride (MA)) and ethylene–propylene random copolymers (EPR-*g*-MA), is affected by changes in the level of functionality of the rubber. By adjusting this level of functionality it is possible to induce drastic changes in the morphology of blends with fixed composition. Unfunctionalized versions of these elastomers are difficult to disperse in the nylon 6 phase, even in the presence of maleic anhydride–polypropylene, and lead to blends with low toughness. The use of polypropylene (PP) grafted with maleic anhydride (PP-*g*-MA) in addition to the maleated rubbers improves the degree of dispersion of the polypropylene phase and the low temperature toughness of the blends. Blends with up to 16% PP-*g*-MA showed ductile–brittle transition temperatures as low as the transition temperature of toughened nylon 6 (−30°C). The degree of heterogeneity of mixtures of PP and PP-*g*-MA has a profound effect on the low temperature toughness and morphology of the rubber-modified nylon 6/PP blends, particularly in blends with compositions in the transition region of phase continuity. A fine degree of dispersion of the PP-*g*-MA in PP is desired in these mixtures, since it leads to the best low temperature toughness in blends of fixed composition.

(Keywords: nylon 6; polypropylene; blends)

INTRODUCTION

Blends of polyamides and polypropylene, when properly compatibilized, can combine some of the best characteristics of both materials: good chemical resistance, low water sorption, high heat deformation temperature and reduced cost. Functionalized polyolefins, such as maleic anhydride (MA) grafted polypropylene (PP), are effective compatibilizers for these blends[1–5]; however, high levels of toughness can only be achieved by addition of an appropriate rubber that can function as an impact modifier[6–10].

Maleated rubbers, such as ethylene–propylene random copolymers (EPR-*g*-MA) and styrene–ethylene/butylene–styrene triblock copolymers (SEBS-*g*-MA), are known to act both as impact modifiers and compatibilizers for nylon 6/polypropylene blends[4,6–12]. The maleic anhydride groups grafted to the rubber react with the amine end-groups of the nylon 6, forming a graft copolymer that helps to disperse the rubber in the nylon 6 and to strengthen the nylon 6/PP interface. Changes in the degree of reactive functionality of the rubber would no doubt affect both functions. It has been reported that changes in the degree of functionality of grafted SEBS rubbers can affect the morphology of 50/50 blends of nylon 6 and polypropylene[10]. Manipulation of the level of functionality in the rubber may provide a way to control the morphology and properties of these blends without the need to modify the ratio of their components. Incorporation of maleated polypropylene (PP-*g*-MA) into nylon 6/PP blends, in addition to the maleated elastomer, offers additional control over blend morphology and interfacial strength.

Grafting of maleic anhydride to the polypropylene is usually accompanied by chain scission or molecular weight loss[13–15]. Thus, there is generally an inverse relationship between the level of MA grafted and the final molecular weight of this material. To compensate for this, it is common to blend a highly grafted polypropylene of low molecular weight with virgin polypropylene of high molecular weight; this allows the manufacturer to tailor independently the melt viscosity and functionality of such products. It has been recently reported that the degree of grafting (MA content) in the PP may affect the homogeneity of such blends[5,16]. Polypropylene and PP-*g*-MA materials with low MA content give rise to homogeneous blends, whereas highly grafted PP-*g*-MA materials form heterogeneous mixtures with PP. The degree of homogeneity of the PP/PP-*g*-MA mixture has been shown to affect the morphology and properties of blends with polyamides[5], and may also influence the morphology and mechanical properties of rubber-modified nylon 6/PP blends.

This paper focuses on the changes in blend morphology and mechanical properties caused by the amount of

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*To whom correspondence should be addressed grafted maleic anhydride in the polypropylene and rubber phases. The effect of the degree of heterogeneity of the PP/PP-*g*-MA mixture on the morphology and toughness of rubber-modified nylon 6/PP blends is also considered.

EXPERIMENTAL

Table 1 shows pertinent information about the different polypropylene materials used in this study. Unless otherwise stated, the virgin polypropylene used throughout was PP 5520 from Huntsman. Three different maleated polypropylenes were used: two medium molecular weight grades (PB 3001 and PB 3002 from BP) containing 0.2 and 0.4% by weight of maleic anhydride, respectively, and a highly grafted PP-*g*-MA (3.1% MA from Himont) of low molecular weight. Information on the rubber modifiers can be found in *Table 2*. Two commercial maleic anhydride grafted elastomers were used: an ethylene–propylene random copolymer (EPR-*g*-MA) containing 1.14% MA and a styrene–ethylene/butylene–styrene triblock copolymer (SEBS-*g*-MA) containing 1.84% MA. This latter rubber was used to prepare materials with different levels of functionality by blending it down with the unfunctionalized SEBS rubber. Blends of these rubbers were prepared in a single-screw extruder at 200°C and 40 rev min^{-1}. Oshinski *et al.*[17,18] have reported that a single population of rubber particles is observed when such mixtures of SEBS and SEBS-*g*-MA are used as impact modifiers for nylon 6 and nylon 6,6. These results suggest that blends of SEBS and SEBS-*g*-MA form a homogeneous rubber phase, and validate the blending of functionalized and unfunctionalized SEBS rubbers as a means of adjusting the MA content of these materials.

Mixtures of polypropylene and a maleated polypropylene (PP-*g*-MA) were prepared by melt blending 87.1% of polypropylene and 12.9% of the highly grafted PP-*g*-MA (HG-201 from Himont) in a single-screw extruder, equipped with a high intensity mixing screw, at 200°C and 40 rev min^{-1}. These mixtures had a total maleic anhydride content of 0.4% by weight, equivalent to that of a commercially available maleated polypropylene (e.g. PP 3002). The melt viscosity of the final mixture was tailored by using different polypropylenes for each mixture.

Prior to melt processing, nylon 6 was dried at 80°C for 16 h in a vacuum oven; all other materials were dried in a convection oven under similar conditions. Blends were prepared in a Killion single-screw extruder ($L/D = 30$, $D = 2.54$ cm) equipped with a high intensity mixing screw and operating at 240°C and 40 rev min^{-1}. Tensile and Izod impact specimens were moulded in an Arburg Allrounder injection-moulding machine. The specimens were tested dry as moulded (after a conditioning period of 24 h in a vacuum desiccator) according to tensile (ASTM D638) and Izod (ASTM D256) standards. The ductile–brittle transition temperature for each

Table 1 Materials used

Commercial designation	Chemical description used here	MA content by weight (%)	M_n	M_w^a	M_z^a	Melt flow rate (g per 10 min)	Brabender torque^b(m g)	Source
HG-201	PP-*g*-MA	3.1	18 900	90 700	316 000		80	Himont
PB 3001	PP-*g*-MA	0.2					470	BP
PB 3002	PP-*g*-MA	0.4	53 800	291 000	887 000		550	BP
PB 5520	PP	0	39 200	347 000	1 197 000	5.0	580	Huntsman
PP 5B56N	PP	0				1.2	1020	Huntsman
Capron 8207F	Nylon 6		22 000				620	Allied Signal

^{a} Determined by gel permeation chromotography
^{b} Measured by torque rheometry at 240°C and 60 rev min^{-1}

Table 2 Rubber Modifiers

Designation used here	Material (commercial designation)	Composition by weight	Molecular weight	Density (g cm^{-3})	Brabender torque^a (m g)	Source
SEBS	Styrene–ethylene/butylene–styrene (Kraton G 1652)	29% styrene	Styrene block = 7000 Ethylene/butylene block = 37 500	0.91	1075	Shell
SEBS-*g*-MA	(Styrene–ethylene/butylene–styrene)-*g*-maleic anhydride (Kraton G 1901 X)	29% styrene 1.84% MA	Not available	0.91	650	Shell
EPR	Ethylene/propylene rubber	43% ethylene 57% propylene	$M_n = 54\,000$ $M_w/M_n = 2$	0.85	1480	Exxon
EPR-*g*-MA	Ethylene/propylene rubber grafted with maleic anhydride (Exxelor 1803)	43% ethylene 57% propylene 1.14% MA	Not available	0.85	990	Exxon

^{a} Measured by torque rheometry at 240°C and 60 rev min^{-1}

toughened blend was determined from the midpoint of the jump in the notched Izod impact strength as the temperature was varied.

The melt viscosities of the different polypropylenes and their blends with maleated polypropylenes were characterized by torque measurements in a Brabender Plasticorder at a fixed speed of 60 rev min^{-1} and 240°C.

The glass transition temperatures (T_g) and storage moduli of the maleated polypropylenes were determined by dynamic mechanical analysis at a frequency of 1 Hz.

For morphological characterization, thin sections were prepared using a Reichert–Jung Ultracut E microtome equipped with a diamond knife and operated under cryogenic conditions (−45°C). Samples were taken from Izod bars in sections oriented perpendicular to the flow direction. Microscopy was carried out using a JEOL 200CX transmission electronic microscope operating at 120 kV. Phase contrast between the different components of the blend was achieved by staining with either a 2% aqueous solution of phosphotungstic acid to stain the polyamide phase or ruthenium tetroxide (RuO_4) to stain the maleated elastomer, as desired. EPR-*g*-MA rubber was stained using a 0.5% aqueous RuO_4 solution following a procedure similar to that of Montezinos *et al.*[19] and Tervoort-Engelen and van Gisbergen[20]. This procedure permits preferential staining of the rubber in and around the polypropylene domains, leaving the rubber particles dispersed in the nylon 6 phase unstained. Further details on the staining technique can be found in the first paper of this series[12].

Transmission electron microscopy (TEM) was also used to establish the degree of homogeneity of blends of PP and PP-*g*-MA along with a special staining technique. This technique was based on the reaction of the maleic anhydride of the PP-*g*-MA with a diamine suitable for staining with RuO_4, such as *m*-xylenediamine. If a separate PP-*g*-MA phase exists, the diamine will locate there owing to the reaction with the anhydride units, and after exposure to RuO_4 vapour this phase will appear dark in the TEM photomicrograph. More detailed information on this technique can be found in a previous paper and elsewhere[5,21].

EFFECT OF RUBBER FUNCTIONALITY

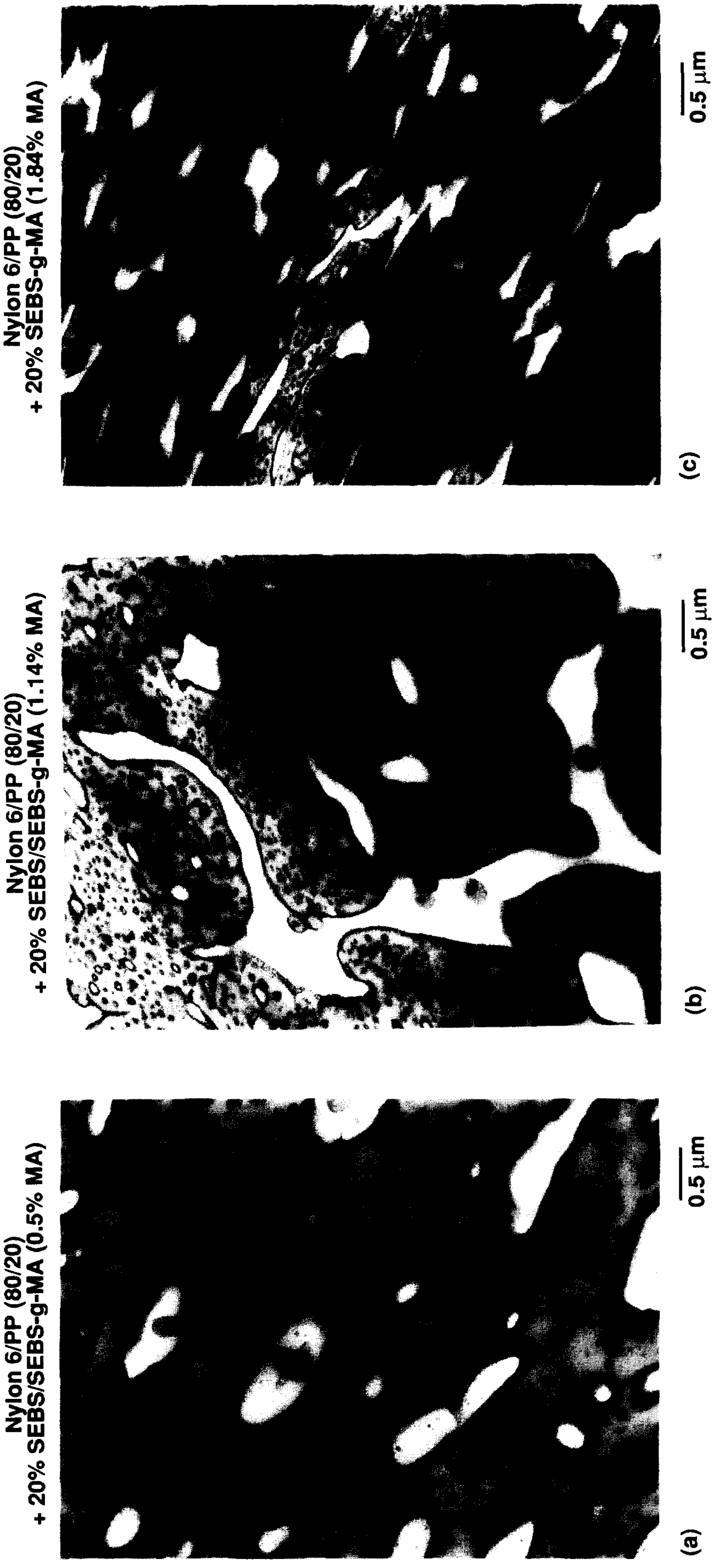
The extent of maleation of the rubber added to nylon 6/PP blends is expected to have an important effect on the morphology and mechanical properties of these materials, and this issue is examined here. As explained earlier, the maleic anhydride content of the block copolymer elastomers can be varied from 0 to 1.84% using appropriate mixtures of the SEBS and SEBS-*g*-MA materials described in *Table 2*. Analogous experiments were not carried out with EPR rubbers, but similar trends can be expected.

Figure 1 shows TEM photomicrographs of 80/20 nylon 6/PP blends modified with 20% SEBS/SEBS-*g*-MA rubbers. The samples were stained with RuO_4, so the rubber appears dark, the nylon 6 appears grey and the polypropylene is unstained. When the rubber contains 0.5% MA (*Figure 1a*), nylon 6 forms the continuous phase, while the rubber forms both small particles dispersed in the nylon phase and a relatively thick layer encapsulating rather large polypropylene particles. If the MA level in the rubber is increased to 1.14% (see *Figure 1b*), the polypropylene domains become elongated and tend to interconnect, while the nylon phase tends to break up. The rubber continues to remain as small particles in the nylon 6 phase and at the nylon 6/PP interface. When pure SEBS-*g*-MA (1.84% MA) is used, the blend is clearly co-continuous even though polypropylene is the minor component, i.e. the nylon 6/PP ratio is fixed at 80/20. The rubber remains dispersed in the nylon 6 and at the interface; however, the rubber layer at the interface seems to be thinner than when the rubber contains 0.5% MA

Similar changes in morphology were previously reported for ternary blends of nylon 6, PP and PP-*g*-MA as the ratio of PP to PP-*g*-MA, or the total maleic anhydride content of the polypropylene phase, was varied[5]. It was observed that as the MA content increased, the blend morphology changed from one where nylon 6 formed the continuous phase to a co-continuous structure, and then to one where polypropylene formed the continuous phase, similar to what is observed here. One factor that contributes to these profound changes in morphology is the increase in melt viscosity of the nylon 6 phase due to the reaction of its amine chain-ends with the maleic anhydride grafted to the rubber (or polypropylene in the former case). The morphology of binary polymer blends of fixed composition has been found to change depending on the viscosity ratio of components[22–25]. Changes in the viscosity ratio of the components can lead to co-continuity or phase inversion at constant composition. The higher the maleic anhydride content of the rubber, the larger is the increase in melt viscosity of the nylon 6 phase. In addition to the viscosity effect, there is an increase in the amount of graft copolymer formed as a result of higher maleic anhydride levels, which can change the nylon 6/PP interfacial characteristics. This may be a factor in the tendency for the nylon 6 phase to break up and form discrete particles as the MA content of the rubber increases.

Figure 2 shows the modulus and notched Izod impact strength for the same blends described in *Figure 1* as a function of the MA level in the rubber. Blends where nylon 6 is the continuous phase (*Figures 1a* and *1b*) show essentially the same modulus; however, as polypropylene tends to form a co-continuous phase (*Figure 1c*), the modulus declines as expected. Room temperature Izod impact strengths are about the same for all these blends. *Figure 3* shows how the Izod impact strength of these blends changes with temperature. The ductile–brittle transition temperatures are nearly the same for all these blends; however, the blend where the rubber contains 1.14% MA appears to have a slightly lower value. It seems that, at least at this particular composition (80/20 nylon 6/PP), the ductile–brittle transition temperature is relatively insensitive to large changes in morphology.

As the nylon 6/PP ratio is changed from 80/20 to 66/33, a more dramatic effect of the maleic anhydride content on blend properties becomes apparent (see *Figure 4*). The ductile–brittle transition temperature of the blend modified with rubber containing 1.14% MA is 10–20°C lower than that observed for blends based on rubber containing 0.5 or 1.84% MA. At room temperature, the Izod impact strengths are about the same for blends where the rubber contains 0.5 or 1.14% MA, while the Izod impact strength is much lower in the case of 1.84% MA. These trends, while more exaggerated, are



(a) Nylon 6/PP (80/20) + 20% SEBS/SEBS-g-MA (0.5% MA)

(b) Nylon 6/PP (80/20) + 20% SEBS/SEBS-g-MA (1.14% MA)

(c) Nylon 6/PP (80/20) + 20% SEBS-g-MA (1.84% MA)

Figure 1 Morphologies of 80/20 nylon 6/PP blends modified with 20% by weight of mixtures of SEBS and SEBS-*g*-MA in the ratios (a) 14.6/5.4 (0.5% MA), (b) 7.6/12.4 (1.14% MA) and (c) 0/100 (1.84% MA)

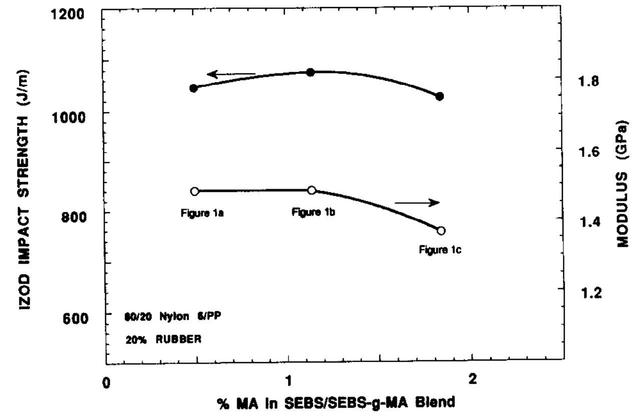


Figure 2 Room temperature Izod impact strength and modulus for 80/20 nylon 6/PP blends modified with 20% SEBS/SEBS-*g*-MA containing different levels of maleic anhydride

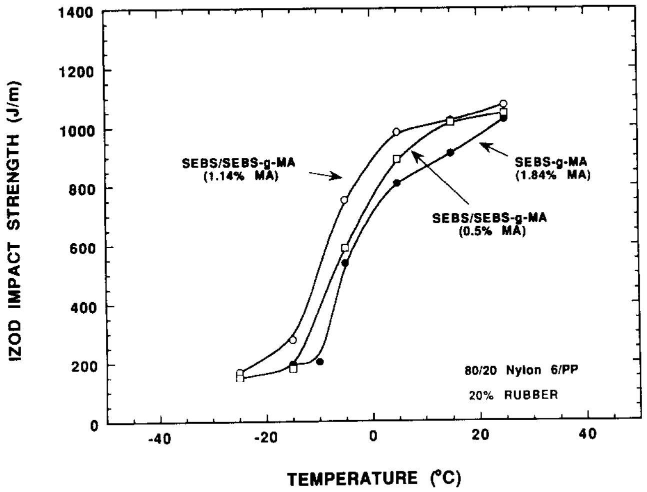


Figure 3 Effect of temperature on the Izod impact strength of 80/20 nylon 6/PP blends modified with 20% SEBS/SEBS-*g*-MA containing different levels of maleic anhydride

similar to those observed in *Figure 3*; there seems to be an optimum level of functionality in the rubber at which the best low temperature toughness is achieved. A similar trend has been observed for nylon 6 containing 20% SEBS-*g*-MA materials with MA contents equivalent to those used in the blends of *Figures 3* and *4*[26]. These changes in properties relate, at least partly, to the morphology of the blends, as shown in the photomicrographs in *Figure 5*. These blends were stained with RuO_4, so the nylon 6 shows as grey domains, the polypropylene is unstained and the fine dark structure corresponds to the stained polystyrene microdomains of the SEBS copolymer. At 1.14% MA (*Figure 5a*), nylon 6 and polypropylene form co-continuous phases, the rubber being exclusively dispersed in the nylon phase and at the interface. For pure SEBS-*g*-MA (1.84% MA) (*Figure 5b*), the polyamide tends to break up into well-defined domains that agglomerate together, while the polypropylene becomes the continuous phase. As the polypropylene becomes the continuous phase, the toughness of the blend decreases. This trend was also observed in a previous paper[12] for nylon 6/PP blends modified with EPR-*g*-MA rubber, but in that case the morphology changes were due to variations in the volume ratio of the components.

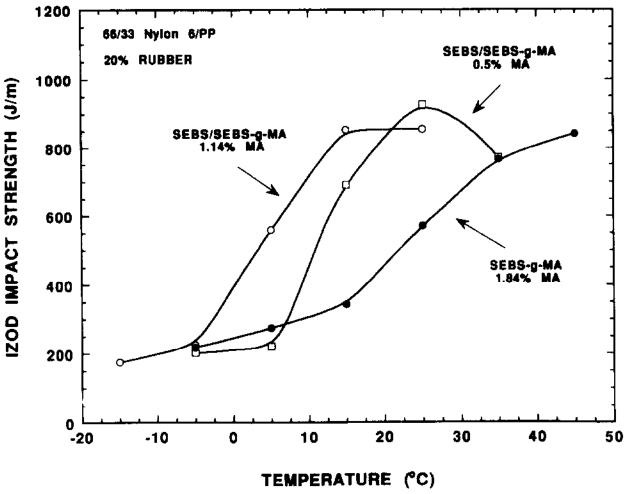


Figure 4 Effect of temperature on the Izod impact strength of 66/33 nylon 6/PP blends modified with 20% SEBS/SEBS-*g*-MA containing different levels of maleic anhydride

EFFECT OF POLYPROPYLENE AND RUBBER FUNCTIONALITY

The results shown above and elsewhere[12,21] indicate the maleated elastomers based on either EPR or SEBS improve the levels of phase dispersion in nylon 6/PP blends through graft reactions that increase the melt viscosity and form interfacial compatibilizers; in addition EPR and SEBS serve as impact modifiers. In the following sections, blends containing polypropylene functionalized with maleic anhydride are explored. First, it is useful to compare the mechanical properties of binary blends of nylon 6 and maleic anhydride grafted polypropylene with those of blends containing unfunctionalized polypropylene. Then the morphology and properties of ternary blends where polypropylene, rubber or both rubber and polypropylene are maleated are examined. Finally, the effect of phase heterogeneity of PP/PP-*g*-MA blends on the morphology and properties of rubber-modified blends is considered.

Binary blends of nylon 6 with PP and with PP-g-MA

As mentioned before, maleated polypropylenes are well-known compatibilizers for nylon 6/PP blends[1–5]. *Figure 6* shows the Izod impact strength and elongation at break of blends of nylon 6 with non-maleated and maleated polypropylene (PB 3002 from BP). The elongation at break for the uncompatibilized blends (dashed line) is considerably depressed over the whole composition range relative to the values of the pure components, while the impact strength shows a more additive but complex response that reflects the differences in the regions where the polyamide or the polypropylene forms the continuous phase. The low values of elongation at break reflect the delamination that occurs during tensile deformation because of poor interfacial adhesion. Replacement of the polypropylene in these blends by a maleated polypropylene containing 0.4% MA has a dramatic effect on the morphology[5] and improves the mechanical properties. These compatibilized blends

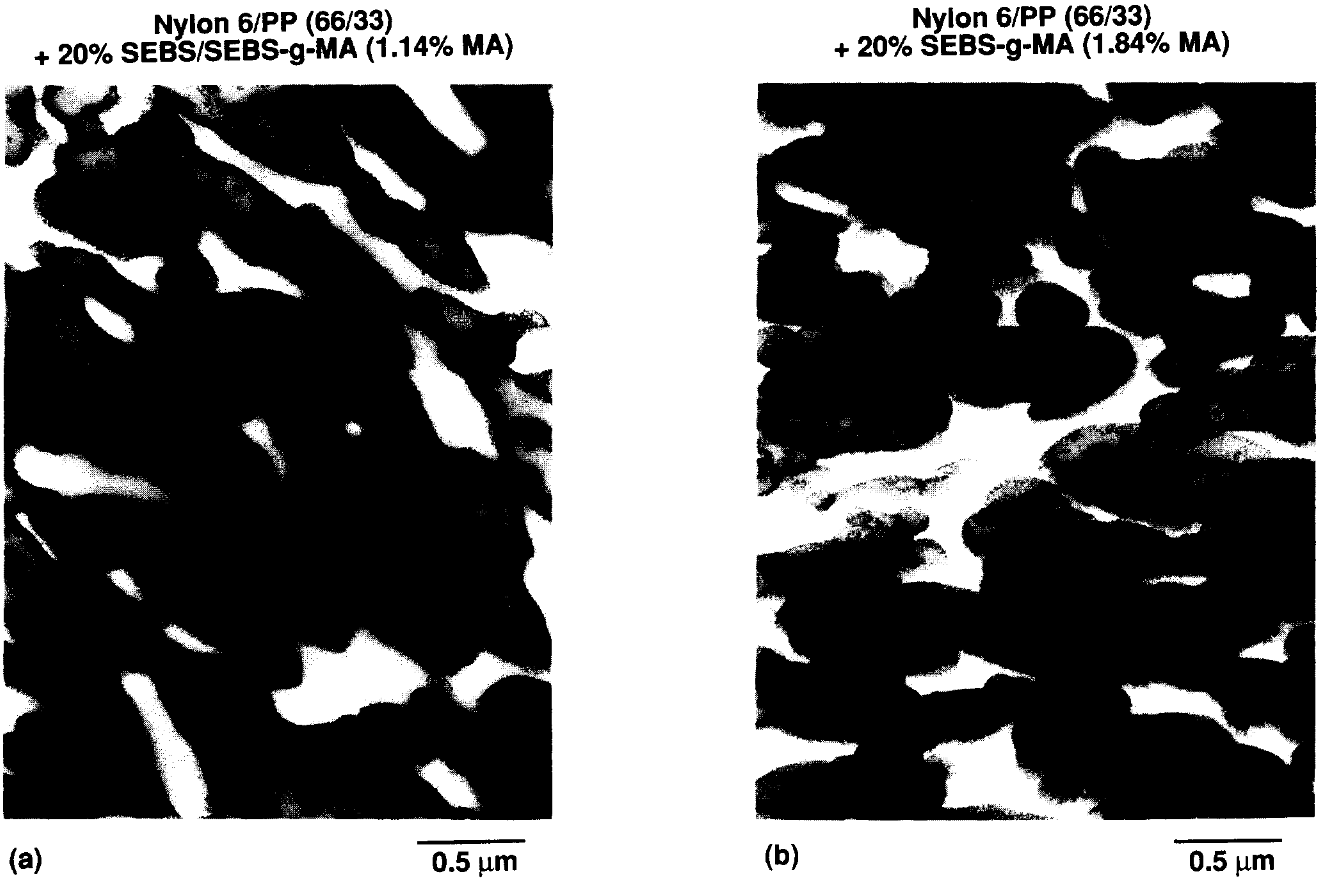


Figure 5 Morphologies of 66/33 nylon 6/PP blends modified with (a) 20% SEBS/SEBS-*g*-MA (1.14% MA) and (b) 20% SEBS-*g*-MA (1.84% MA). The blends are stained with RuO_4 (rubber appears dark, nylon 6 grey and polypropylene white)

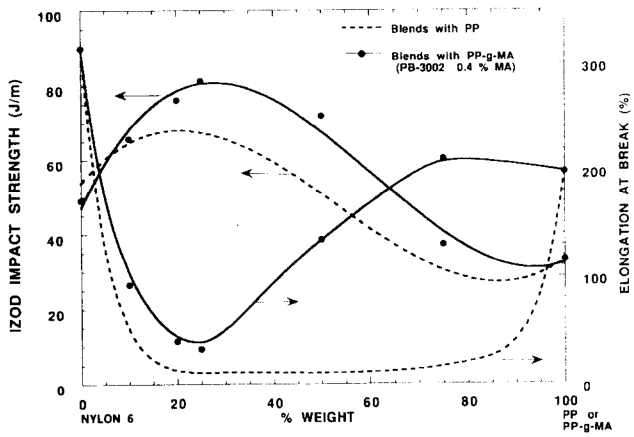


Figure 6 Room temperature Izod impact strength and elongation at break for binary blends of nylon 6 and polypropylene (dashed line) or maleated polypropylene (solid line)

show higher elongation at break, and all compositions exhibit ductile fracture in the tensile test, even those in the region of the minimum elongation at break. This confirms that interfacial adhesion is enhanced by the reaction of the polyamide with the maleic anhydride units. Use of PP-*g*-MA instead of PP leads only to marginal improvements in Izod impact strength. To make a dramatic improvement in toughness it is necessary to incorporate a rubber phase into these blends, as shown previously[12].

Ternary blends where either the polypropylene or the rubber is maleated

Unfunctionalized olefinic rubbers are commonly used to toughen polypropylene[27], but are not effective in polyamides. Their effectiveness for toughening nylon 6/PP-*g*-MA blends is examined here. The TEM photomicrographs in *Figure 7* shows the morphologies of 66/33 nylon 6/PP-*g*-MA blends modified with EPR and SEBS rubbers. In *Figure 7a*, the nylon 6 phase is stained with phosphotungstic acid, while the rubber and polypropylene are not stained. The photomicrograph shows that the polyamide forms a continuous phase in which polypropylene and EPR rubber are dispersed. The location of the rubber is verified by staining with a RuO_4 solution (see *Figure 7b*). In this case the EPR rubber appears as a dark phase, while the polypropylene and nylon 6 appears as light grey phases. The rubber locates preferentially in the polypropylene phase in the form of elongated domains. The morphology of an equivalent blend containing SEBS rubber is shown in *Figures 7c* and *7d*. *Figure 7c* shows again a nylon 6 matrix (stained with phosphotungstic acid) in which polypropylene and rubber (unstained phase) are dispersed. The location of the rubber is confirmed by staining with RuO_4 (see *Figure 7d*). The rubber (dark phase) is located within the polypropylene domains (white phase) dispersed in the nylon 6 matrix (grey phase). From these photomicrographs it is clear that nylon 6/PP-*g*-MA blends modified with unfunctionalized rubbers (either EPR or SEBS) have very similar morphologies.

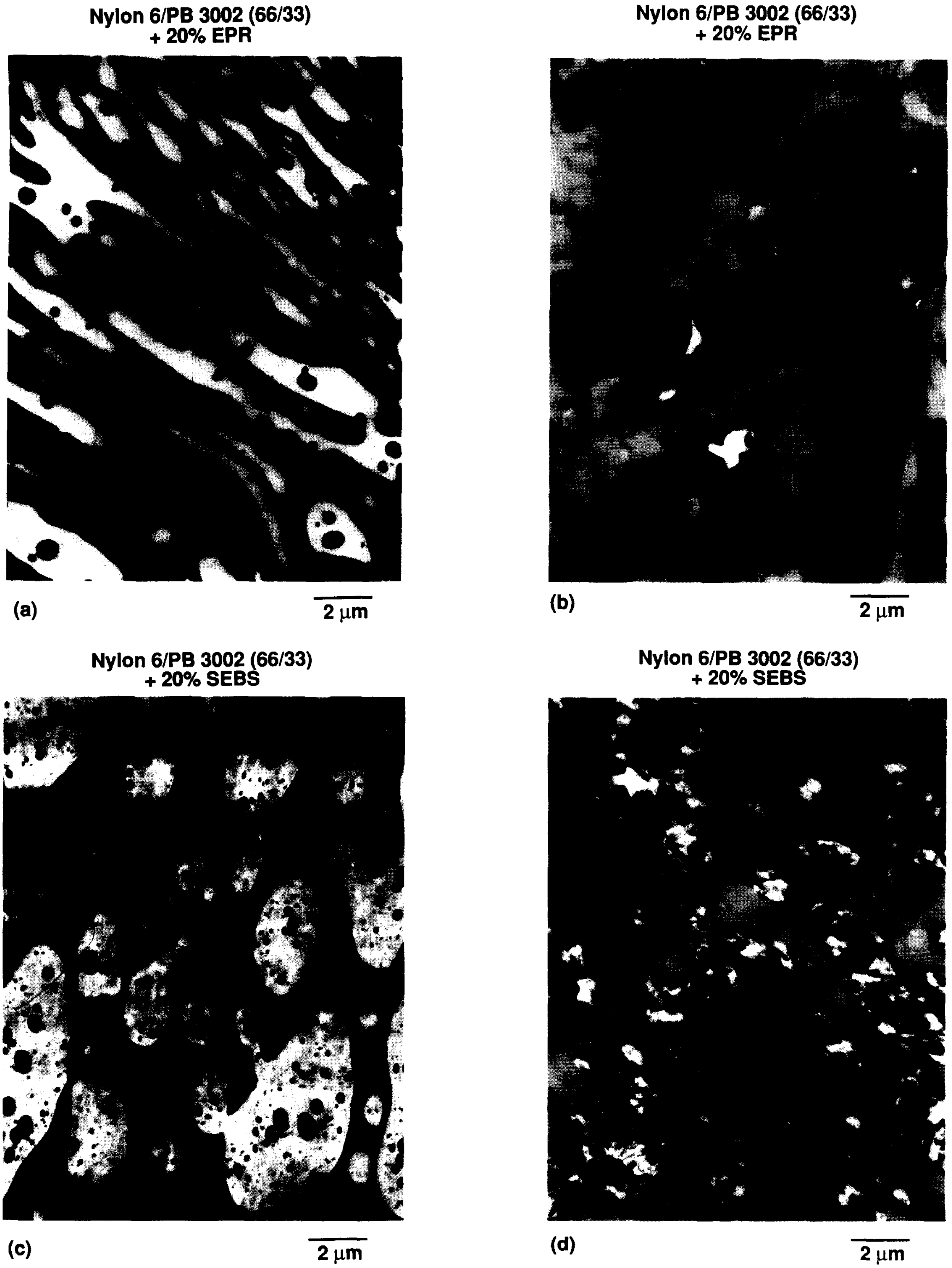


Figure 7 Morphologies of 66/33 nylon 6/PB 3002 (PP-*g*-MA, 0.4% MA) blends modified with 20% by weight of (a) EPR rubber (nylon 6 phase stained with phosphotungstic acid), (b) EPR rubber, blend stained with RuO_4 solution (EPR rubber appears dark, nylon 6 and PP light grey), (c) SEBS rubber (nylon 6 stained with phosphotungstic acid) and (d) SEBS rubber, blend stained with RuO_4 vapour (SEBS rubber stains dark, nylon 6 grey, PP is unstained)

On the other hand, when the rubber has a reactive functionality instead of the polypropylene, a very different morphology results, as shown in *Figure 8a* for EPR-*g*-MA rubber and *Figure 8b* for SEBS-*g*-MA rubber. In *Figure 8a*, the polyamide phase is stained with phosphotungstic acid, while the rubber and polypropylene remain unstained. In *Figure 8b*, the sample is stained with RuO_4; therefore, the rubber stains dark, the nylon 6 grey and the polypropylene is unstained. Both show co-continuous phases of nylon 6 and polypropylene with the rubber particles well dispersed in the nylon 6 phase. The rubber has also been shown to locate at the interface with the polypropylene[8,10,12]. The dramatic differences in morphology observed between *Figures 7* and *8* relate to the type of grafted copolymer that forms during melt processing of the blends. The amine end-groups of nylon 6 react with the maleic anhydride grafted to either the polypropylene or rubber to form a graft copolymer that remains at the interface of nylon 6 with either polypropylene or rubber, whichever is maleated. This graft copolymer acts as a compatibilizer and reduces the phase dimensions by reducing the rate of domain coalescence during melt processing. The graft copolymer acts as a compatibilizer for both the PP and rubber phases, although it will preferentially compatibilize the maleated component. In blends where the rubber is maleated, some of the PP is well dispersed in the nylon 6 domains (*Figure 8*); however, in blends where the PP is maleated, the rubber does not disperse in the nylon 6 matrix but locates in the PP phase (*Figure 7*). In other words, the rubber–nylon 6 graft copolymer is a better compatibilizer for PP than the PP-nylon 6 graft copolymer is for the rubber. Several factors may contribute to this tendency; two are mentioned next. The maleic anhydride content of the PP-*g*-MA used (0.4% MA) is well below that in the maleated rubbers (either EPR-*g*-MA or SEBS-*g*-MA) used (1.14% MA). This difference will directly affect the amount of graft copolymer or compatibilizer formed, and in turn will reflect on the degrees of dispersion of polypropylene and rubber. Rheological differences may also be partly responsible. The unfunctionalized rubbers have higher melt viscosities than the functionalized ones (see *Table 2*), and are 1.5–2.5 times more viscous than nylon 6 or polypropylene. Thus, it is more difficult to disperse unfunctionalized rubber in nylon 6 than unfunctionalized polypropylene. It should be noted that the types of morphologies shown in *Figure 8* are preferred since it appears necessary to have the rubber well dispersed in the nylon phase to achieve toughness in rubber-modified nylon 6/PP blends[8,10,12].

Ternary blends where both the polypropylene and the rubber are maleated

Figure 9 shows the notched Izod impact strength as a function of temperature for the blends described in *Figures 7* and *8* and for blends where both the polypropylene and the rubber are maleated. The nylon 6/PP-*g*-MA blend containing unfunctionalized EPR shows low impact strength at room temperature and a

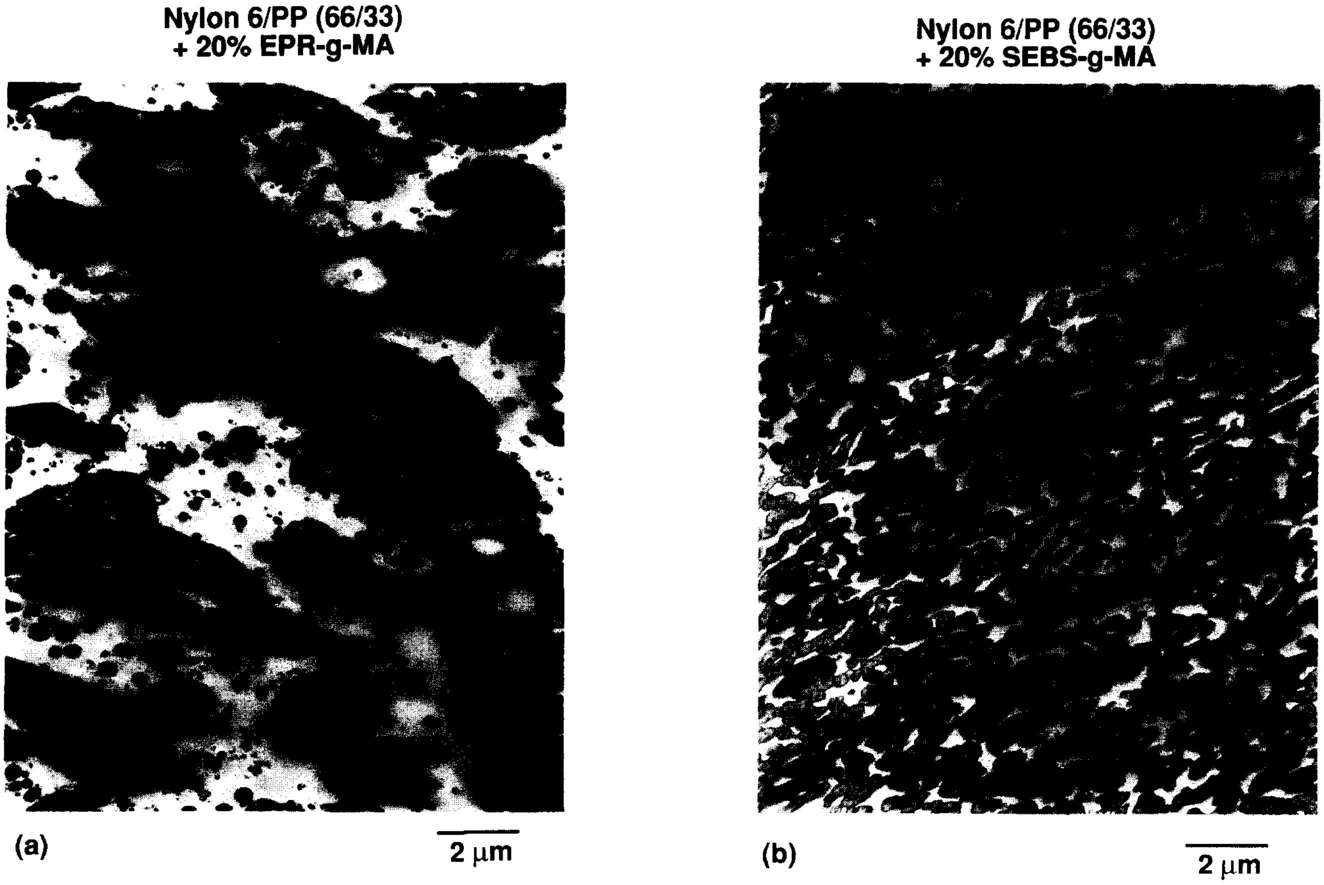


Figure 8 Morphologies of 66/33 nylon 6/PP blends modified with (a) 20% EPR-*g*-MA (nylon 6 phase stained with phosphotungstic acid) and (b) 20% SEBS/SEBS-*g*-MA (1.14% MA), blend stained with RuO_4 vapour (the rubber stains dark, nylon 6 grey and PP remains unstained)

high ductile–brittle transition temperature. A significant improvement in impact strength and ductile–brittle transition temperature is observed when the rubber is grafted with maleic anhydride. Even higher room temperature impact strengths and lower ductile–brittle transition temperatures are achieved when both the rubber and the polypropylene are maleated. A similar tendency is observed for blends modified with SEBS (see *Figure 10*), but the differences in ductile–brittle behaviour are more exaggerated. Comparison of *Figures 9* and *10* reveals that the blends based on the EPR-*g*-MA rubbers have lower ductile–brittle transition temperatures than those based on SEBS/SEBS-*g*-MA, even when the maleated polypropylene is used. These differences in ductile–brittle behaviour have been noted before[12] and are related to the differences in the structures and the resulting thermomechanical characteristics of the two rubbers.

Figure 11 summarizes the response of the ductile–brittle transition temperature of blends containing 20% EPR-*g*-MA (1.14% MA) to the percentage PP-*g*-MA in the blend. The solid lines indicate blends based on PP-*g*-MA materials, while the dashed line is for blends based on unmaleated PP. Up to 16% PP-*g*-MA, the ductile–brittle transition temperature remains at the same low value (−30°C) of impact-modified nylon 6 without any polypropylene; thereafter it increases. The ductile–brittle transition temperatures of these blends are independent of the MA content (0.2 and 0.4% MA) until the point of

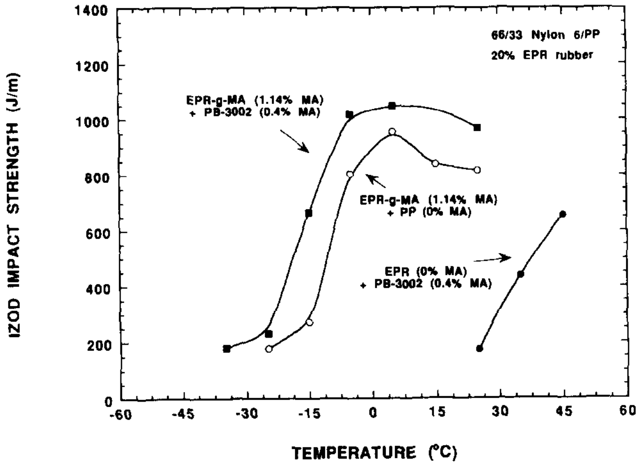


Figure 9 Effect of temperature on the Izod impact strength of 66/33 nylon 6/PP blends modified with 20% EPR rubber, where either the polypropylene, the rubber or both are maleated

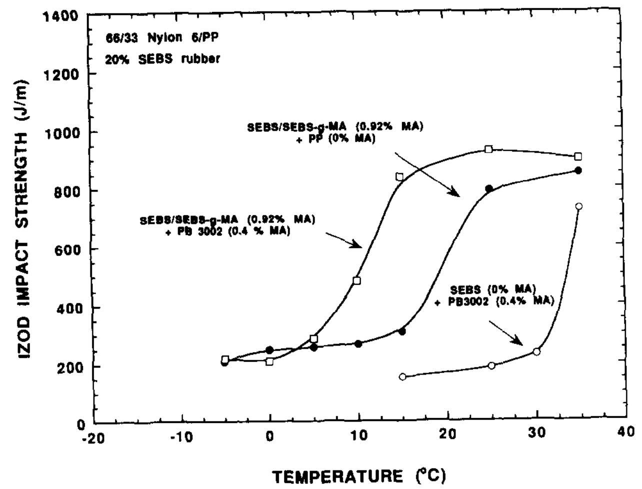


Figure 10 Effect of temperature on the Izod impact strength of 66/33 nylon 6/PP blends modified with 20% SEBS rubber, where either the polypropylene, the rubber or both are maleated

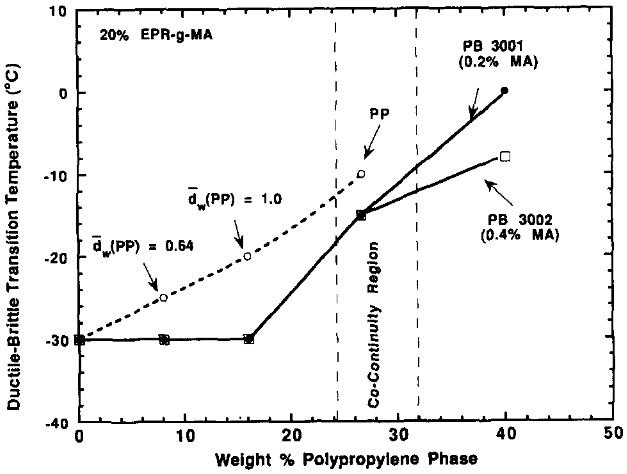


Figure 11 Ductile–brittle transition temperature as a function of the percentage of polypropylene or maleated polypropylene in ternary blends with nylon 6 and 20% EPR-*g*-MA ($\bar{d}_w$ is the weight average particle diameter)

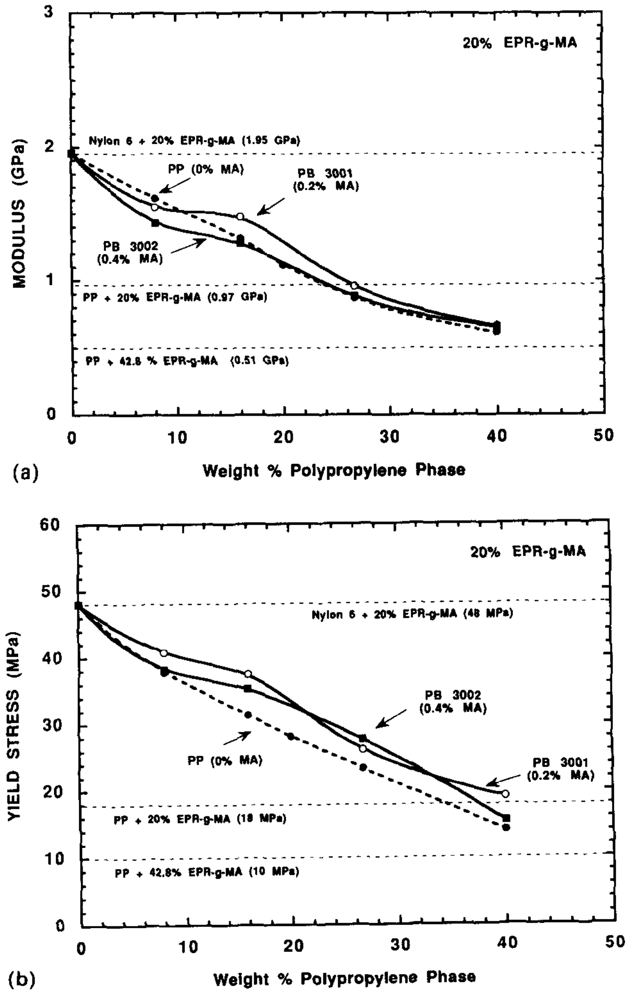


Figure 12 Mechanical properties of nylon 6/PP-*g*-MA and nylon 6/PP blends modified with 20% EPR-*g*-MA: (a) modulus; (b) yield stress. The composition shown on the abscissa represents the percentage of polypropylene in the ternary blend

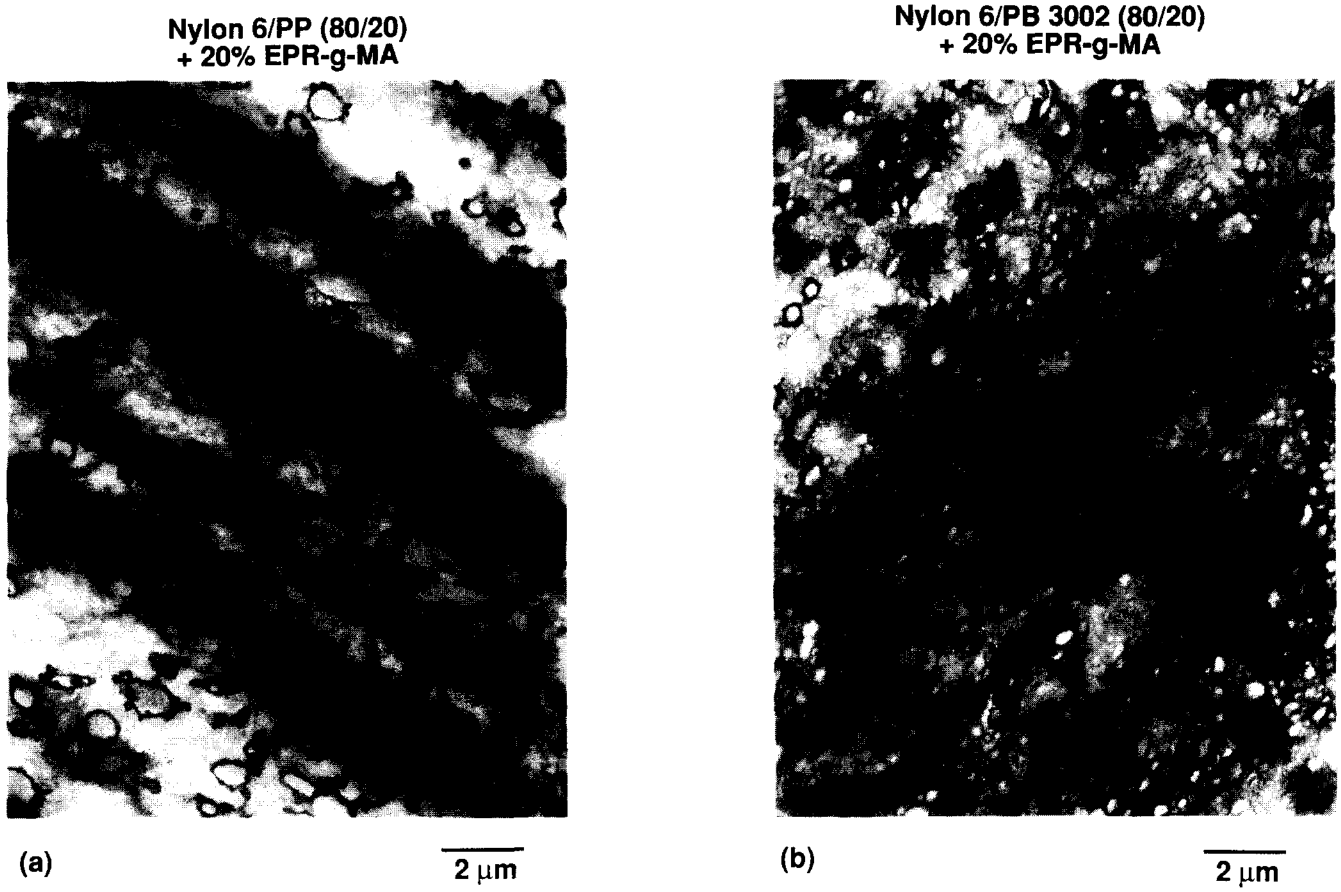


Figure 13 Morphologies of (a) 80/20 nylon 6/PP and (b) 80/20 nylon 6/PB 3002 (PP-*g*-MA, 0.4% MA) blends modified with 20% ERP-*g*-MA. The blends are stained with RuO_4 solution, so that the rubber around the polypropylene particles stains dark, the nylon 6 stains grey and PP is unstained

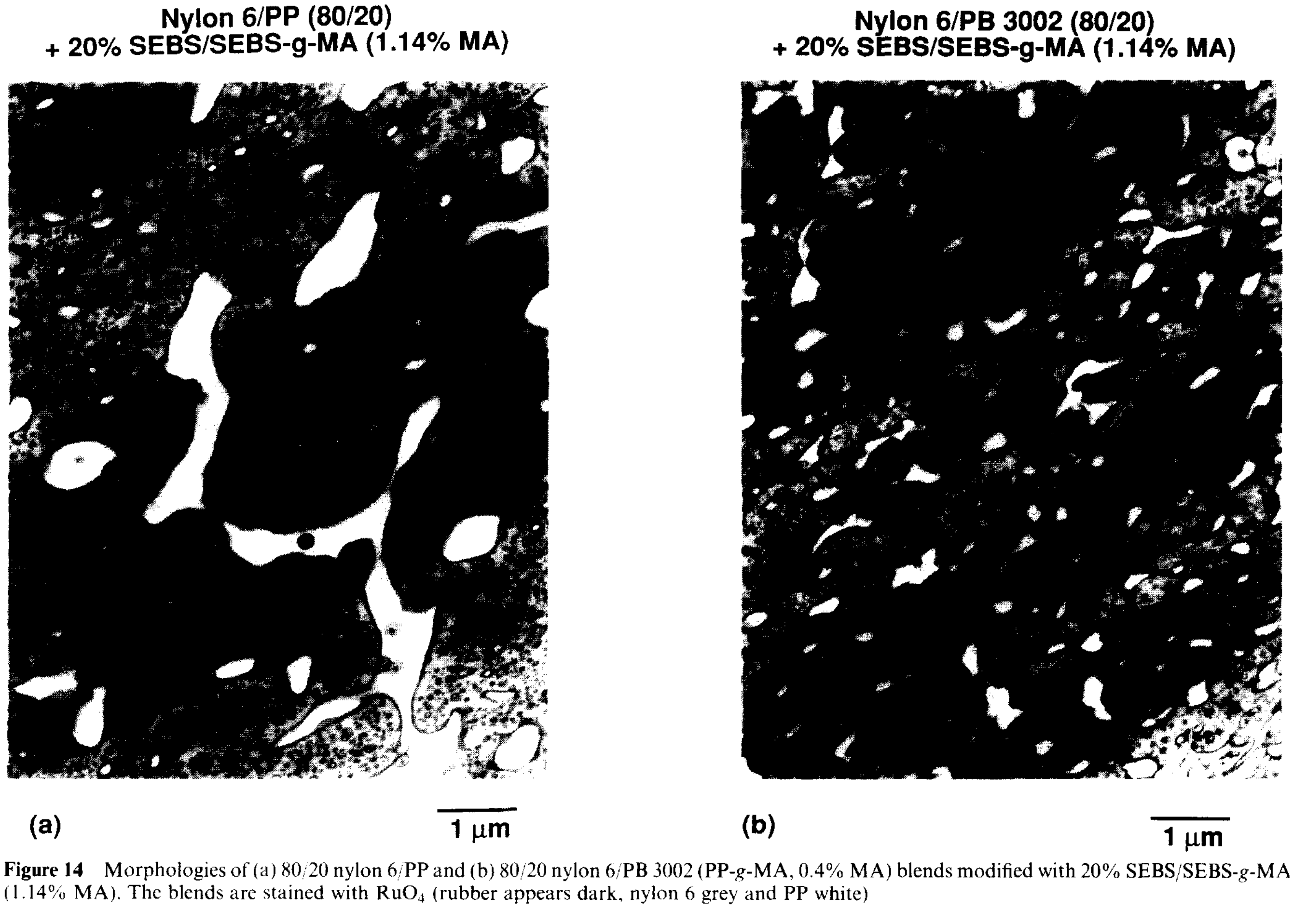


Figure 14 Morphologies of (a) 80/20 nylon 6/PP and (b) 80/20 nylon 6/PB 3002 (PP-*g*-MA, 0.4% MA) blends modified with 20% SEBS/SEBS-*g*-MA (1.14% MA). The blends are stained with RuO_4 (rubber appears dark, nylon 6 grey and PP white)

phase inversion is reached; beyond this, blends based on PP-*g*-MA with 0.4% MA show a lower ductile–brittle transition temperature. The ductile–brittle transition temperatures are lower than those of blends based on unfunctionalized polypropylene (dashed line).

From these data it is clear that using a maleic anhydride grafted polypropylene leads to significant improvements in the low temperature toughness of these blends. The tensile moduli of these blends are shown in *Figure 12a* as a function of polypropylene content. In every case, stiffness decreases as the proportion of polypropylene relative to nylon 6 increases. This trend is understandable because the modulus of polypropylene is lower than that of nylon 6. Also, as noted in the first paper of this series[12], a decrease in the degree of crystallinity of the PP or nylon 6 phase could also contribute to the observed decrease in modulus. Any effect of maleation level is at best subtle and varies with composition. The tensile yield stress of these materials shows similar trends, as shown in *Figure 12b*.

The effect of the maleation level of the polypropylene on the morphology of typical blends is shown in *Figure 13*. In these TEM photomicrographs, the EPR-*g*-MA rubber located at the interface between nylon 6 and PP is preferentially stained, so the dispersed particles surrounded by a dark layer are polypropylene, while the grey matrix is nylon 6 containing dispersed rubber and PP particles that are unstained. A finer degree of dispersion of the polypropylene domains is observed in blends where the polypropylene contains grafted maleic anhydride. The weight average particle diameter $\bar{d}_w$ of the polypropylene domains is 1 μm for the blend with unfunctionalized polypropylene (*Figure 13a*), while $\bar{d}_w = 0.63\,\mu$m for the blend with the maleated polypropylene containing 0.4% MA (*Figure 13b*).

Similar trends are observed for nylon 6/PP blends modified with 20% SEBS/SEBS-*g*-MA rubber having the same amount of MA (1.14%) as the EPR-*g*-MA material. When the polypropylene is not maleated (*Figure 14a*), it forms elongated domains (white phase) in the nylon 6 matrix. The rubber (dark phase) is located in the nylon 6 (grey phase) and at the interface between nylon 6 and PP. In contrast, when the polypropylene is grafted with 0.4% MA (PB 3002), there is a finer dispersion of this phase in the nylon 6 matrix (see *Figure 14b*). This reduction in size is no doubt related to the presence of the PP–nylon 6 graft copolymer generated during melt processing. These grafted chains locate at the nylon 6/PP interface, in addition to the rubber–nylon 6 graft copolymer, and probably act to reduce the particle size by preventing coalescence of the polypropylene domains. To some degree, both types of graft copolymer, strengthen the interface between nylon 6 and polypropylene. The changes in both the morphology and the interfacial character caused by these graft reactions contribute in some way to the lower ductile–brittle transition temperatures observed for these blends relative to those of similar compositions based on unfunctionalized polypropylene (*Figure 11*).

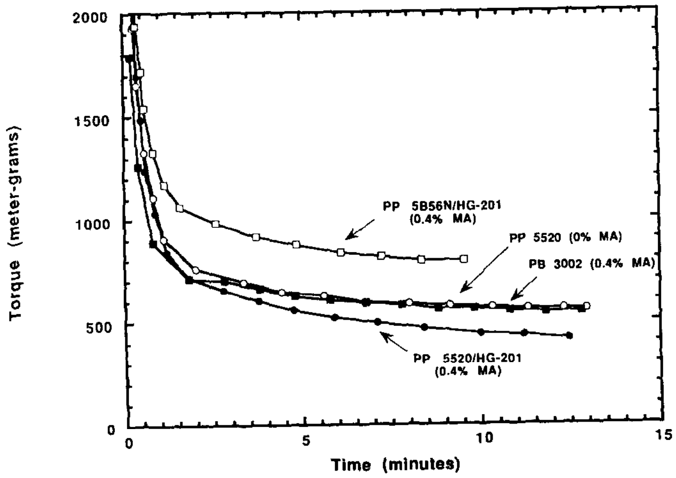


Figure 15 Torque rheometry results for polypropylene and PP/PP-*g*-MA mixtures measured in a Brabender Plasticorder at 240°C and 60 rev min^{-1}

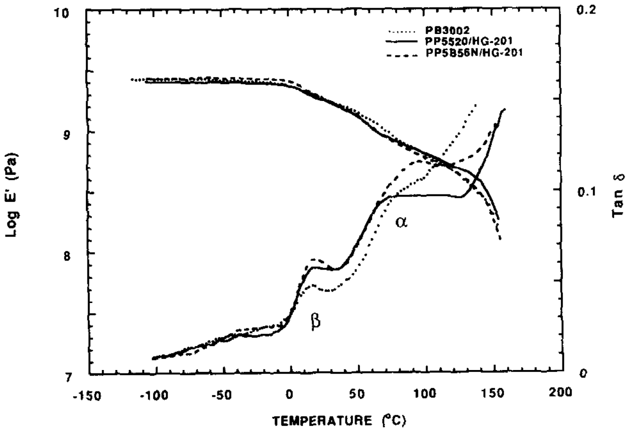


Figure 16 Dynamic mechanical properties of PP/PP-*g*-MA materials measured at a frequency of 1 Hz

Table 3 Properties of PP/PP-*g*-MA mixtures

Material	MA content by weight (%)	Yield stress (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Brabender torque[a] (m g)
PB 3002	0.4	30.8	1.37	323	550
PP 5520/HG-201 (87.1/12.9)	0.4	28	1.32	135	400
PP 5B56N/HG-201 (87.1/12.9)	0.4	28.6	1.41	88	800
PP 5520	0	28.6	1.43	198	550

[a] Measured by torque rheometry at 240°C and 60 rev min^{-1}

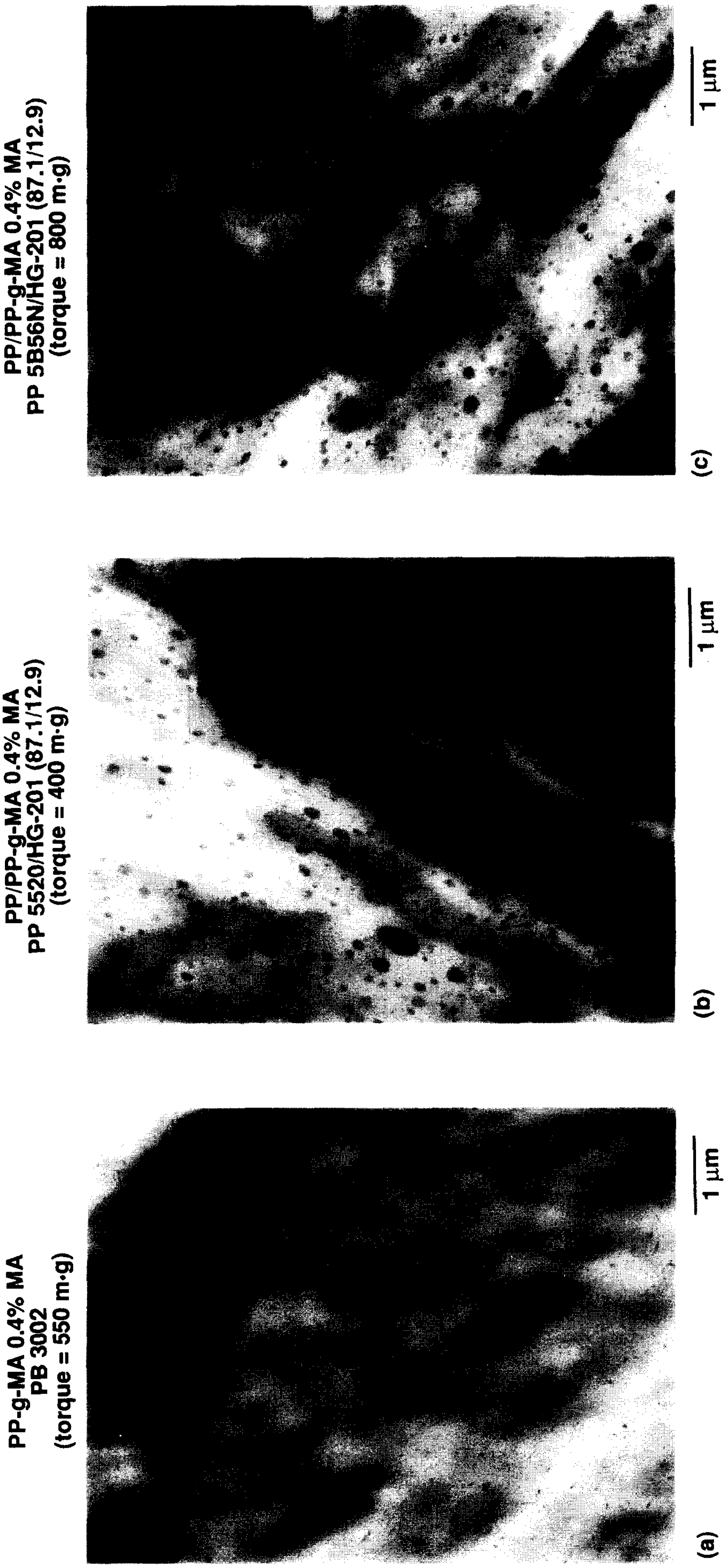


Figure 17 TEM photomicrographs of (a) PP-*g*-MA (PB 3002), (b) a blend of 87.1% polypropylene (PP 5520) and 12.9% PP-*g*-MA (HG-201, 3.1% MA), and (c) a blend of 87.1% polypropylene (PP 5B56N) and 12.9% PP-*g*-MA (HG-201, 3.1% MA). All samples were first reacted with *m*-xylenediamine and then stained with RuO_4

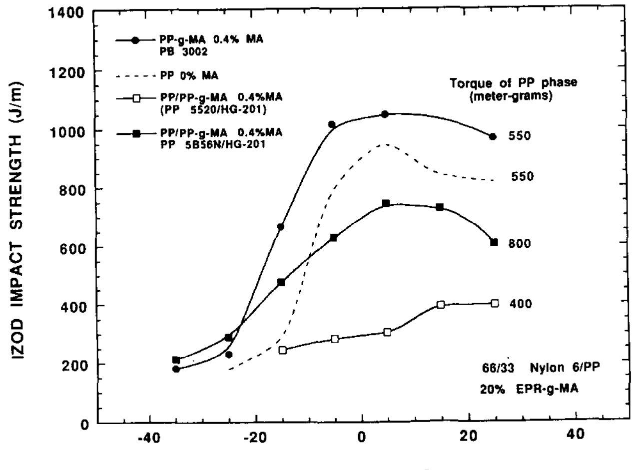


Figure 18 Effect of temperature on the Izod impact strength of 66/33 blends of nylon 6 and polypropylene or PP/PP-*g*-MA mixtures, modified with 20% EPR-*g*-MA

*Effect of the phase heterogeneity of PP/PP-*g*-MA mixtures*

It has been suggested[5] that the commercial PP-*g*-MA material (PB 3002) used in this study is a mixture of a highly grafted polypropylene and neat polypropylene, and that the degree of heterogeneity of such PP/PP-*g*-MA mixtures affects the morphology and properties of their blends with nylon 6. Here we attempt to assess the effect of this physical nature of the PP/PP-*g*-MA mixture on the properties of toughened nylon 6/PP blends.

As stated earlier the miscibility of PP/PP-*g*-MA mixtures is affected by the maleic anhydride level of the PP-*g*-MA. Maleated polypropylenes with low MA content lead to homogeneous blends with PP, while highly grafted PP-*g*-MA materials generate heterogeneous mixtures. An ideal way to determine whether this issue influences the morphology and properties of toughened nylon 6/polypropylene materials would be to compare the use of a PP/PP-*g*-MA mixture that is miscible (low MA content of PP-*g*-MA) with the use of one that is not (high MA content of PP-*g*-MA), prepared in such a way that these mixtures have the same MA contents and the same melt viscosities, since both are important factors. Because of the severe reduction in molecular weight that accompanies MA grafting of polypropylene, a comparison between miscible and immiscible mixtures with the same levels of maleic anhydride and equivalent melt viscosities was not possible, at least with the materials available to us. However, a comparison between PP/PP-*g*-MA mixtures with similar melt viscosities and maleic anhydride contents but different degrees of phase heterogeneity was possible. This was done by preparing a mixture of unmaleated PP and a highly grafted PP-*g*-MA (HG-201 from Himont) that matched the MA content and viscosity of the commercially available PP-*g*-MA (PB 3002). The PP/PP-*g*-MA mixtures prepared here have a different degree of heterogeneity from the PB 3002, as will be shown later. Also, PP/PP-*g*-MA mixtures with similar degrees of heterogeneity and MA contents but different melt viscosities were prepared by changing the molecular weight of the non-maleated polypropylene in the mixture. The effect of this degree heterogeneity on the morphology and final properties of toughened nylon 6/PP blends is described next.

Figure 15 shows torque rheometry results for the PP/PP-*g*-MA mixtures prepared here, the PB 3002 material and a virgin polypropylene resin. Note that PB 3002 and the unmaleated polypropylene (PP 5520) have similar melt viscosities. The mixture of the maleated polypropylene (HG-201) with PP 5520 has a lower viscosity, while this maleated polypropylene mixed with PP 5B56N gives a higher melt viscosity. The tensile properties of these four materials are shown in *Table 3*; all have similar mechanical properties except that the mixtures generated here have lower elongation at break. The dynamic mechanical spectra of the maleic anhydride grafted materials are shown in *Figure 16*. The change in storage modulus with temperature is very similar and the location for the β transition, or T_g, is essentially the same for all the materials. The only appreciable difference between these materials is in the α transition, which is related to the crystallinity of the polypropylene. This transition can be shifted and broadened by changes in the crystallization conditions[28].

The photomicrographs in *Figure 17* show the degrees of heterogeneity of most of the materials identified in *Table 3*. The PP-*g*-MA domains were stained by the diamine technique described earlier; the polypropylene matrix remains basically unstained, showing just a slight texture due to some excess of the diamine. The PB 3002 material contains very small stained domains (PP-*g*-MA) well dispersed in a polypropylene matrix (see *Figure 17a*). This is in contrast with the PP/PP-*g*-MA mixtures generated here (*Figures 7b* and *17c*), where the stained PP-*g*-MA domains are larger and show a broader distribution of sizes. The morphologies of the last two PP/PP-*g*-MA mixtures appear to be very similar, in spite of the difference in viscosity of the base polypropylenes used to prepare them (see *Table 1*). It is not possible to explain exactly why the PB 3002 material has a different morphology, since the details of how this commercial material is prepared have not been revealed.

Figure 18 shows the Izod impact strength as a function of temperature for 66/33 blends of nylon 6 and these PP/PP-*g*-MA materials modified with 20% EPR-*g*-MA. Large differences in room temperature toughness and ductile–brittle behaviour are apparent. Blends based on PB 3002 show the highest impact strength and the lowest ductile–brittle transition temperature, whereas a PP/PP-*g*-MA blend of slightly lower melt viscosity but equivalent MA content is brittle and does not show a ductile–brittle transition. When a PP/PP-*g*-MA mixture of higher melt viscosity is used an improvement in the impact strength is observed; however, the toughness characteristics are still below those obtained with PB 3002. The blend based on unfunctionalized polypropylene has a lower impact strength and higher ductile–brittle transition temperature than the blend based on PB 3002; however, it shows better toughness than the blends based on the two PP/PP-*g*-MA mixtures. These results suggest that the degree of heterogeneity of the PP/PP-*g*-MA mixture, which may be driven by the distribution of the maleation level between PP chains, affects the toughness of the blends because of the clear difference between the PP/PP-*g*-MA mixtures and the commercial blend (PB 3002) in this regard; however, more subtle

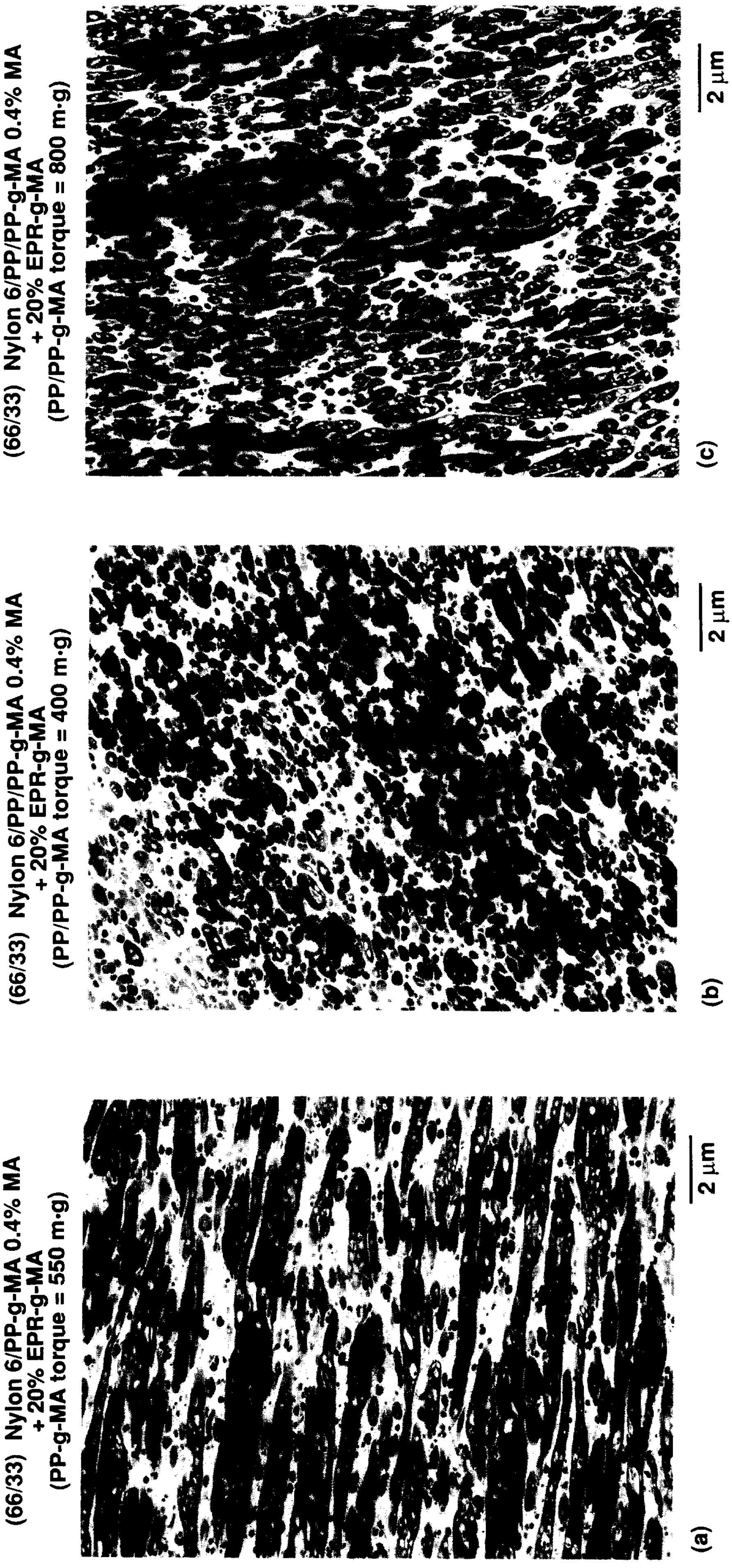


Figure 19 TEM photomicrographs of 66/33 blends of nylon 6 with (a) PP-*g*-MA (PB 3002), (b) PP/PP-*g*-MA (PP 5520/HG-201) and (c) PP/PP-*g*-MA (PP5B56N/HG-201), modified with 20% EPR-*g*-MA. The nylon 6 phase is stained with phosphotungstic acid

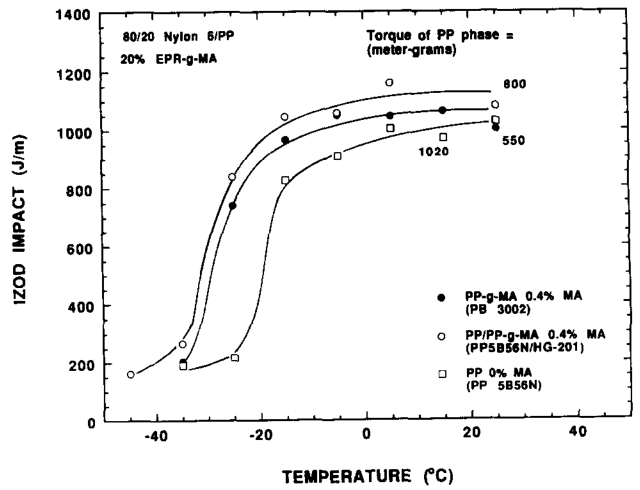


Figure 20 Effect of temperature on the Izod impact strength of 80/20 blends of nylon 6 and polypropylene or PP/PP-*g*-MA mixtures, modified with 20% EPR-*g*-MA

issues relating to the molecular weight distribution of the polypropylene phase have not been considered here.

Figure 19 shows the morphologies of blends corresponding to those whose impact properties are shown in *Figure 18*. Blends based on the PP/PP-*g*-MA mixtures (*Figures 19b* and *19c*) have a finer dispersion of the polyamide phase than the equivalent blend based on the commercial PP-*g*-MA (*Figure 19a*). When PB 3002 is used, nylon 6 and PP form co-continuous phases, while for the mixtures the polypropylene phase is continuous. The PP/PP-*g*-MA mixture with the lower melt viscosity seems to lead to a more finely dispersed and less elongated polyamide phase than does the higher viscosity PP/PP-*g*-MA mixture. This confirms the trend observed in a previous paper[12], in which polypropylenes of high melt viscosity, i.e. high molecular weight, drove the morphology of blends of equivalent composition towards a continuous nylon 6 matrix phase. The above results also confirm the general observation that rubber-modified nylon 6/PP blends show lower toughness when the polypropylene phase is continuous than when the nylon 6 is the matrix phase.

The blends in *Figures 18* and *19* have a 66/33 ratio of nylon 6 to PP. Blends with this composition have morphologies and properties that change drastically with the molecular weights of nylon 6 and polypropylene[12]. Therefore, it is interesting to evaluate the effect of the heterogeneity of PP/PP-*g*-MA mixtures in blends where molecular weight and melt viscosity effects are less pronounced. *Figure 20* shows the Izod impact strength for 80/20 blends of nylon 6 with various PP/PP-*g*-MA materials, modified with 20% EPR-*g*-MA, as a function of temperature. The ductile–brittle transition temperatures for blends based on PB 3002 and the PP/PP-*g*-MA mixture are very similar; both blends show improved low temperature toughness relative to the blends based on unfunctionalized polypropylene. At this particular composition the polypropylene is dispersed in a nylon 6 matrix (see *Figures 13a* and *13b*); thus, it seems that when the polypropylene is the dispersed phase, the level of functionality of the polypropylene has a greater effect than the degree of heterogeneity or melt viscosity of this phase. This is reasonable, since here the polypropylene is acting as a filler and its properties and degree of heterogeneity might not affect the final toughness of the blends as much as when it forms a co-continuous or continuous phase.

CONCLUSIONS

The morphology of nylon 6/PP blends is affected by changes in the functionality of the maleated rubbers used for toughening (and compatibilization). For example, by judicious variation of the level of functionality of SEBS rubbers, it is possible to change the degree of dispersion of the olefinic phase in the nylon 6 matrix and to produce co-continuous morphologies even at reactively high nylon 6/PP ratios; similar trends are expected in EPR-based systems. The low temperature toughness of nylon 6/PP blends modified with SEBS rubbers of different levels of functionality depends both on the nylon 6/polypropylene ratio and on the morphology. The optimum maleic anhydride content is about 1%, where the lowest ductile–brittle transition temperature is observed for these blends.

Unfunctionalized rubbers, such as EPR and SEBS, were found to have limited use as impact modifiers for nylon 6/PP-*g*-MA blends. The use of maleated polypropylene does not help to disperse either of these non-reactive rubbers in the nylon 6 phase; therefore, the rubber was found to locate within the polypropylene domains. Such a morphology leads to blends with low toughness at room temperature and high ductile–brittle transition temperatures.

Use of maleic anhydride grafted polypropylene (PP-*g*-MA) in nylon 6/PP blends modified with maleated rubbers improves the degree of dispersion of the PP phase and strengthens the nylon 6/PP interface, i.e. PP-*g*-MA serves as a compatibilizer. The ductile–brittle transition temperatures of toughened blends containing PP-*g*-MA were found to be lower than those of blends with unfunctionalized polypropylene for any given nylon 6/PP ratio. Blends with nylon 6/PP-*g*-MA ratios above 80/20 showed ductile–brittle transition temperatures equivalent to toughened nylon 6 without any polypropylene.

Mixtures of functionalized (PP-*g*-MA) and unfunctionalized polypropylene (PP) can have varying degrees of heterogeneity. The degree of heterogeneity affects the low temperature toughness of rubber-modified nylon 6/PP blends where the polypropylene phase is co-continuous or continuous. A fine degree of dispersion of the PP-*g*-MA in the PP/PP-*g*-MA mixture improves the low temperature toughness, while mixtures with a larger or broader distribution of PP-*g*-MA domain sizes lead to blends with poor impact strength. The degree of heterogeneity of PP/PP-*g*-MA mixtures does not seem to be a critical parameter in blends when the polypropylene is the dispersed phase.

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REFERENCES

1 Ide, F. and Hasagawa, A. *J. Appl. Polym. Sci.* 1974, **18**, 963

2 Nishio, T., Sukuki, Y., Kojima, K. and Kakugo, M. in 'Proceedings of the IUPAC International Symposium on Speciality Polymers', Hütig and Wepf, Basel, 1991, p. 51

3 Dagli, S. S., Xanthos, M. and Biesenberger, J. A. *Soc. Plast. Eng., ANTEC* 1990, **36**, 1924

4 Hölsti-Miettinen, R. and Seppälä, *J. Polym. Eng Sci.* 1992, **32**, 868

5 González-Montiel, A., Keskkula, H. and Paul, D. R. *J. Polym. Sci., Poly. Phys. Edn* 1995, **33**, 1751

6 Gelles, R., Lutz, R. G. and Gergen, W. P. (Shell) *Eur. Pat. Appl. 0 261 748* 1987

7 Nishio, T., Yokoi, T., Nomura, T., Ueno, K., Akagawa, T., Sakai, I. and Takaski, Y. (Toyoto) *US Pat. 4 988 764* 1990

8 Modic, M. J. and Pottick, L. A. *Plast. Eng.* 1991, **47**, 37

9 Modic, M. J. and Pottick, L. A. *Soc. Plast. Eng., ANTEC* 1991, 1907

10 Modic, M. J. *Soc. Plast. Eng., ANTEC* 1993, 205

11 Rösch, J. and Mülhaupt, R. *Makromol. Chem., Rapid Commun.* 1993, **14**, 503

12 González-Montiel, A., Keskkula, H. and Paul, D. R. *Polymer* 1995, in press

13 Minouri, Y., Ueda, M., Mizunuma, S. and Oba, M. *J. Appl. Polym. Sci.* 1969, **13**, 1625

14 Gaylord, N. G. and Mishra, M. K. *J. Polym. Sci., Polym. Lett. Edn* 1983, **21**, 23

15 Callais, P. A. and Kazmierczak, R. T. *Soc. Plast. Eng., ANTEC* 1990, 1921

16 Duvall, J., Sellitti, C., Myers, G., Hiltner, A. and Baer, E. *J. Appl. Polym. Sci.* 1994, **52**, 207

17 Oshinski, A. J., Keskkula, H. and Paul, D. R. *Polymer* 1992, **33**, 268

18 Oshinski, A. J., Keskkula, H. and Paul, D. R. *Polymer* 1992, **33**, 284

19 Montezinos, D., Wells, B. G. and Burns, J. L. *J. Polym. Sci., Polym. Lett. Edn* 1985, **23**, 421

20 Tervoort-Engelen, Y. and van Gisbergen, *J. Polym. Commun.* 1991, **32**, 261

21 González-Montiel, A. PhD Dissertation, The University of Texas at Austin, 1994

22 Jordhamo, G. M., Manson, J. A. and Sperling, L. H. *Polym. Eng. Sci.* 1986, **26**, 517

23 Favis, B. D. and Chalifoux, J. P. *Polym. Eng. Sci.* 1987, **27**, 1591

24 Favis, B. D. and Willis, J. M. *J. Polym. Sci. B* 1990, **28**, 2259

25 Favis, B. D., Chalifoux, J. P. and Gheluwe, P. V. *Soc. Plast. Eng., ANTEC* 1987, 169

26 Kayano, Y. personal communication, 1994

27 Bucknall, C. B. 'Toughened Plastics', Applied Science, London, 1977

28 Varlet, J. PhD Dissertation, Institute National des Sciences Appliquées de Lyon, 1990