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Impact-modified nylon 6/polypropylene blends: 1. Morphology–property relationships

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Two types of elastomers grafted with maleic anhydride (MA), an ethylene–propylene random copolymer 9EPR) and a styrene–ethylene/butylene–styrene triblock copolymer (SEBS) were found to function both as impact modifiers and compatibilizers for nylon 6/polypropylene blends. The maleic anhydride grafted to the rubber reacts with the amine end-groups of the polyamide, forming a rubber–nylon 6 graft copolymer that locates at the interface between nylon 6 and polypropylene (PP) and thus acts as a compatibilizer. The SEBS-*g*-MA material appears to be the most effective compatibilizer. The two rubbers were equally effective for increasing room temperature toughness by dispersing in the nylon 6 phase of the blends. Lower ductile–brittle transition temperatures are obtained when EPR-*g*-MA rubber is used, owing to its lower T_g and lower modulus at low temperatures compared to SEBS-*g*-MA rubber. Blend parameters such as rubber content, nylon 6/PP ratio and molecular weight of the components strongly influence the morphology and toughness of the blends. Low ductile–brittle transition temperatures were obtained for blends in which any combination of the above parameters yielded a morphology where nylon 6 was the matrix phase with polypropylene and rubber finely dispersed in it, provided the component molecular weights were high enough to provide adequate intrinsic ductility.

(Keywords: nylon 6; polypropylene; blends)

INTRODUCTION

In recent years there has been much interest in the development of alloys based on engineering polymers such as polyamides. For example, blends of polyamides with polyolefins, when properly compatibilized, can potentially offer a wide range of desirable characteristics such as good chemical resistance, low water sorption and reduced cost. The mechanical properties depend strongly on the ratio of polyamide to polyolefin; however, a low notched impact strength is a common feature of these blends.

Toughened versions of both nylon 6 and polypropylene (PP) have become important industrial products. Nylon 6 has been successfully toughened by the use of reactive rubbers[1–7] grafted with functional groups that react during melt processing with the end-groups of nylon 6. The nylon–rubber copolymer formed during melt blending increases the interfacial adhesion between the rubber and the polyamide and provides control of the size of the rubber particles, both of which are believed to be essential for promoting toughness. Polypropylene can be toughened either by melt blending with an olefinic rubber[8–15] (usually ethylene-propylene rubber) or by 'copolymerization', where ethylene is introduced into the reactor feed at the end of the main propylene polymerization process[16,17]. Toughened polypropylene materials formed by a reactive scheme similar to the one employed for the polyamides have also been recently reported[18].

Maleated olefinic rubbers are especially effective impact modifiers for nylon 6; therefore, they are a primary choice for impact modification of nylon 6/PP blends. An additional benefit of using these reactive rubbers is the affinity of the olefinic rubber for the PP. Even though PP and the rubber are not miscible, there is a certain affinity that leads to good adhesion between the phases[8,9,19]. Thus, the rubber may serve as a compatibilizer in addition to being an impact modifier. Recent literature has focused on the use of functionalized styrenic block copolymers[20–23] and ethylene–propylene copolymers[20,22,24,25] as modifiers for nylon 6/polypropylene blends. However, fundamental understanding of the requirements to achieve toughness in these blends is still very limited.

This series of papers focuses on the use of two types of maleic anhydride (MA) grafted rubbers as compatibilizers and/or impact modifiers for nylon 6/PP blends, viz. a random copolymer of ethylene and propylene (EPR) and a styrene–ethylene/butylene–styrene triblock copolymer (SEBS). There are many variables that may affect the toughness of nylon 6/PP blends: the ratio of polyamide to polypropylene, the volume fraction of the rubber, the molecular weights of the nylon 6 and polypropylene, the composition and degree of functionality of the rubber

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and the degree of functionality of the polypropylene. The present paper will show how the first three variables affect the morphology and mechanical properties of these blends. A second paper will deal with the changes in properties related to changes in the degree of functionality of the rubber and PP. A third paper will deal with the deformation mechanisms of toughened nylon 6/PP blends.

EXPERIMENTAL

The base polymers used in this study were all commercially available products whose properties are described in *Table 1*. Unless otherwise indicated, the nylon 6 and polypropylene used throughout the present study were Capron 8207F and PP 5520, respectively. The properties of the rubber modifiers used are summarized in *Table 2*. The maleated ethylene–propylene rubber (EPR-*g*-MA) contained 1.14% maleic anhydride by weight. The two block copolymer elastomers used were similar in composition except that the ethylene–butylene midblock of one was maleated (SEBS-*g*-MA), while it was not for the other (SEBS). The commercial version of SEBS-*g*-MA contained 1.84% MA. In order to be able to compare rubbers with the same maleic anhydride contents a blend of SEBS and SEBS-*g*-MA was prepared that matched the MA content of the EPR-*g*-MA rubber. This was done by melt mixing 38% of SEBS and 62% of SEBS-*g*-MA rubber at 200°C and 40 rev min^{-1} to give an MA content of approximately 1.14%, equivalent to that of EPR-*g*-MA rubber. Previous authors[1,26] have successfully used mixtures of SEBS and SEBS-*g*-MA rubbers to modify nylon 6 and nylon 6,6 resins and have shown that the rubber particle size changes proportionally with the SEBS/SEBS-*g*-MA ratio in the blend; based on all evidence, it appears that blends of SEBS and SEBS-*g*-MA form a homogeneous phase that creates one population of rubber particles in such polyamide blends. In the following text this mixture of SEBS and SEBS-*g*-MA rubbers will be referred to simply as SEBS-*g*-MA.

Prior to processing, nylon 6 was dried in a vacuum oven for a period of 16 h at 80°C. The different rubbers and polypropylenes were also dried in a convection oven under the same conditions as for nylon 6. The blends were prepared by simultaneous addition of all components to a Killion single-screw extruder ($L/D = 30$, $D = 2.54$ cm) equipped with a high intensity mixing screw operating at 240°C and 40 rev min^{-1}. The grafting of nylon 6 chains to the maleated elastomers increases the overall melt viscosity, which tends to aid dispersion in these blends. The extruded materials were injection moulded into standard tensile and Izod impact specimens using an Arburg Allrounder injection-moulding machine. 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 location of the notch relative to the gate end of the Izod bar did not significantly affect the impact strength observed. The ductile–brittle transition temperature for each toughened blend was determined from the midpoint of the jump in the notched Izod impact strength as the temperature was varied.

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

Table 1 Materials used

Commercial designation	Composition	Molecular weight	Melt flow rate (g per 10 min)	Brabender torque (m g)	Source
B-5	Nylon 6	$\overline{M}_n = 38\,500$		1980	BASF
Capron 8209	Nylon 6	$\overline{M}_n = 31\,400$		1290	Allied Signal
Capron 8207F	Nylon 6	$\overline{M}_n = 22\,000$		620	Allied Signal
Capron 8202	Nylon 6	$\overline{M}_n = 16\,700$		325	Allied Signal
B-1	Nylon 6	$\overline{M}_n = 14\,000$		280	BASF
PP 5B82H	Polypropylene		0.6	1320	Huntsman
PP5B56N	Polypropylene		1.2	1020	Huntsman
PP 5520	Polypropylene	$\overline{M}_n = 39\,200$ $\overline{M}_w = 347\,000$	5	580	Huntsman
PP 5820	Polypropylene		12	400	Huntsman
PP 5B04Z	Polypropylene		20	260	Huntsman

Table 2 Rubber modifiers

Designation used here	Material (commercial designation)	Composition by weight	Molecular weight	Density (g cm^{-3})	Source
SEBS	Styrene–ethylene/butylene–styrene (Kraton G 1652)	29% styrene	Styrene block = 7000 EB block = 37500	0.91	Shell
SEBS-*g*-MA	(Styrene–ethylene/butylene–styrene)-*g*-maleic anhydride (Kraton G 1901 X)	29% styrene 1.84% MA	Not available	0.91	Shell
EPR-*g*-MA	Ethylene–propylene rubber grafted with maleic anhydride (Exxelor 1803)	43% ethylene 57% propylene 1.14% MA	Not available	0.85	Exxon

Specimens for microscopy were prepared by trimming samples with a mill and a razor blade to form blocks of approximately 5 × 5 × 2 mm. These blocks were further trimmed to the shape of a pyramid with the tip faced off to an area of approximately 0.2 × 0.2 mm. A Reichert–Jung Ultracut E microtome was used to obtain thin sections (20–50 nm thick) from these blocks. Sectioning was performed under cryogenic conditions (−45°C) using a diamond knife. Samples were taken from Izod bars in sections oriented perpendicular to the flow direction. Specimens were viewed with a JEOL 200CX transmission electron microscope operating at 120 kV. Phase contrast between the different components of the blends was achieved by staining with either an aqueous solution (2% by weight) of phosphotungstic acid to stain the polyamide phase or ruthenium tetroxide (RuO_4) to stain the maleated elastomer, as desired.

Saturated rubbers such as ethylene–propylene rubber are difficult to stain by conventional techniques; thus, for blends containing EPR-*g*-MA rubber it was necessary to use a special staining technique to achieve the desired contrast between the polypropylene and the rubber phase. The staining technique used was similar to that reported by Montezinos *et al.*[27] and Tervoort-Engelen and van Gisbergen[28] to stain polyolefins and their blends. A trimmed block was immersed in a solution of RuO_4 for a period of 12 h, then it was rinsed with deionized water and dried in air. After this, the sample was sectioned according to the procedure described above. Problems associated with this staining technique are hardening, shrinkage and etching of the surface of the block. These features made it impossible to obtain good sections from the top 2–5 μm of the block; however, it was possible to obtain sections below this depth, but not deeper than about 10 μm below the original surface, that were useful for transmission electron microscopy (TEM). This is approximately the region of the sample that gets stained by submerging the block in the RuO_4 solution.

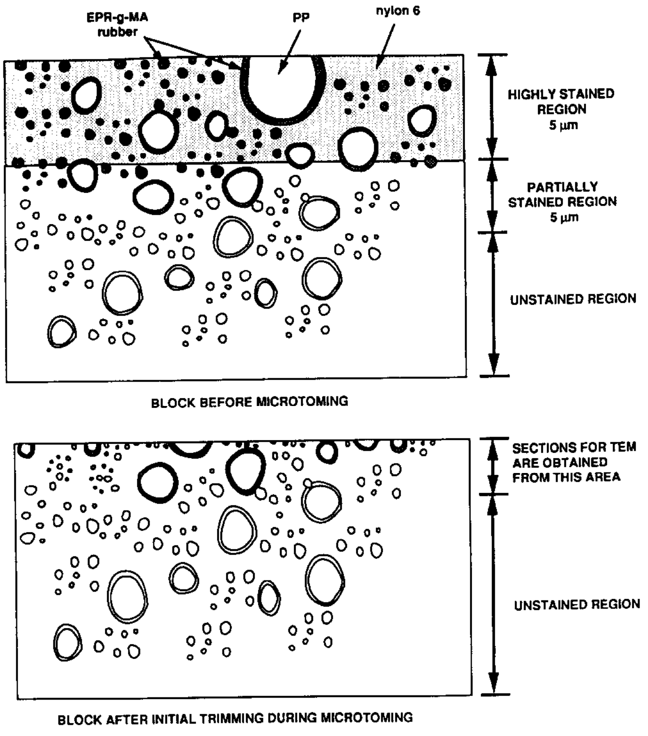


Figure 1 Schematic of a ternary blend sample before and after initial trimming for preparing thin sections for TEM. The sample was stained by submersion in 0.5% aqueous RuO_4 for 12 h

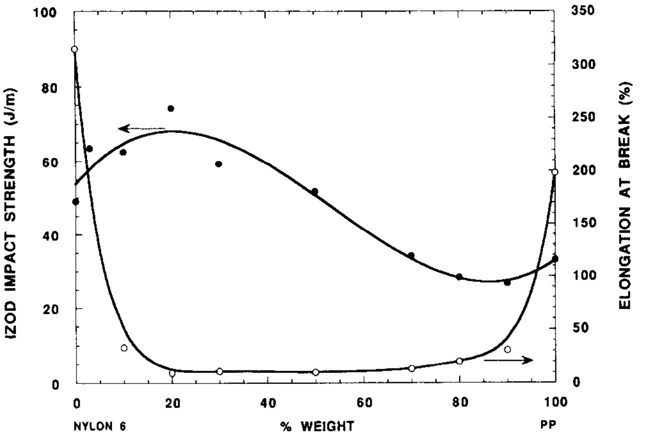


Figure 2 Izod impact strength and elongation at break of unmodified binary blends of nylon 6 and polypropylene

When this staining technique is applied to PP/EPR-*g*-MA binary blends, the EPR-*g*-MA domains are stained. However, for nylon 6/EPR-*g*-MA blends, the nylon phase is stained light grey but none or very few of the EPR-*g*-MA particles are stained dark. This seems to indicate that the RuO_4 cannot diffuse well into the rubber particles when nylon 6 is the matrix and/or that only the rubber particles in the very first micrometres from the surface of the sample get stained. However, as mentioned before, it is very difficult to section this region of the sample, and the sections obtained at greater depths show unstained rubber particles. When the technique is applied to ternary blends of nylon 6, polypropylene and EPR-*g*-MA, a combination of the effects seen in the binary blends is observed. Nylon 6 stains as a light grey phase, the rubber particles dispersed in the nylon 6 do not stain, while the polypropylene and EPR-*g*-MA rubber, around or in the polypropylene phase, stain as light grey and black domains, respectively. Therefore, the TEM photomicrographs will clearly show the location of the rubber around and in the polypropylene domains, but there will be some ambiguity between rubber and polypropylene particles dispersed in the nylon phase since they are not stained. These observations are summarized in *Figure 1* where a schematic of the stained block before and after sectioning are shown.

EFFECT OF MALEATED RUBBER TYPE

Mechanical properties

Figure 2 shows the Izod impact strength and elongation at break of simple binary blends of nylon 6 and polypropylene. The elongation at break 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 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. Compatibilization of these blends with functionalized polypropylenes has a

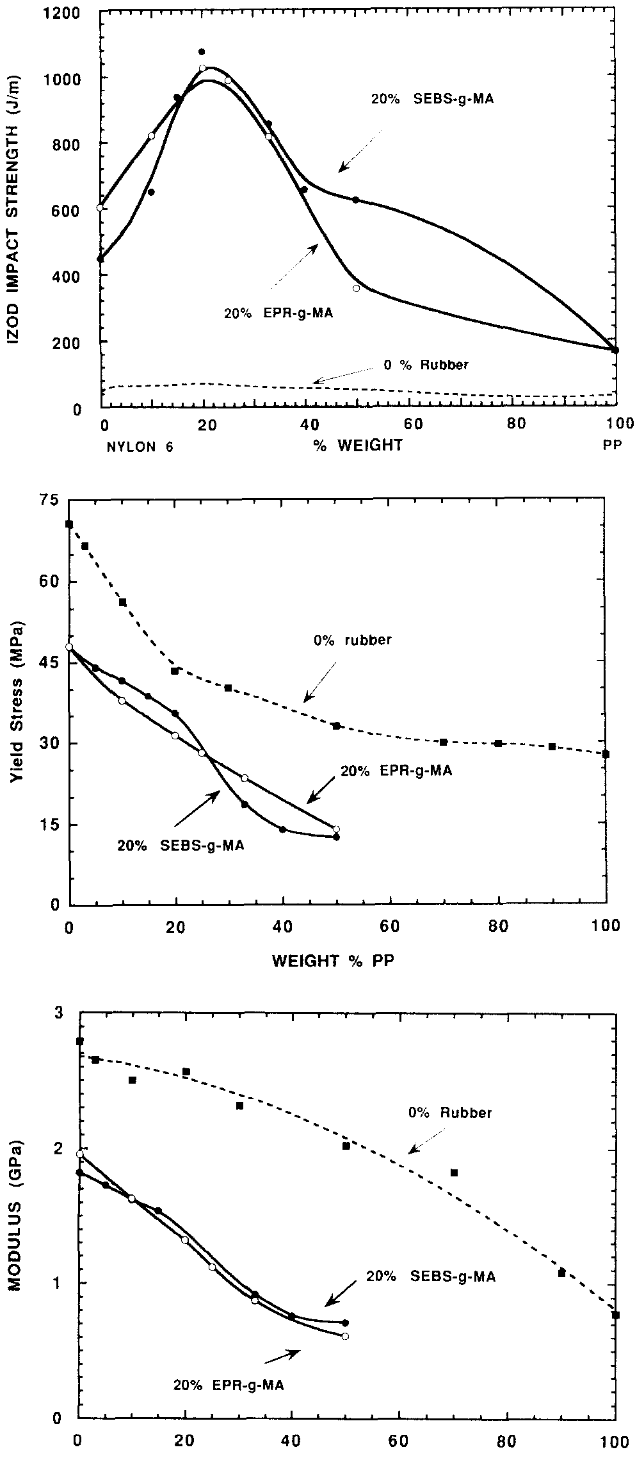


Figure 3 Mechanical properties of nylon 6/polypropylene blends modified with 20% EPR-*g*-MA or SEBS-*g*-MA: (a) Izod impact strength; (b) yield stress; (c) modulus. The composition shown on the abscissa is the percentage of polypropylene relative to nylon 6 in the blend on a rubber-free basis. The dashed lines correspond to the properties of unmodified binary blends

dramatic effect on the morphology and improves the mechanical properties[22,29–31]. However, the impact strength of these blends remains low over all the composition range.

The effect of the two maleated rubbers EPR-*g*-MA and SEBS-*g*-MA, containing equivalent amounts of maleic anhydride, on the mechanical properties of nylon 6/PP blends is shown in *Figure 3*. *Figure 3a* shows that the Izod impact strength is greatly improved by addition of 20% by weight of the maleated rubbers, equivalent to 25.1% and 23.8% by volume of EPR-*g*-MA and SEBS-*g*-MA, respectively. The improvement in impact strength is relatively independent of the type of rubber used. Previous authors[20,22,23] have suggested that EPR-*g*-MA rubbers are not suitable as impact modifiers for nylon 6/polypropylene blends. However, both rubbers appear equally effective in the present case. High impact strengths were obtained in the range 0–50% of polypropylene. Beyond 50% polypropylene, the impact strength is lower; this reduction appears to occur at the point where the polypropylene becomes the continuous phase. The impact strength shows a maximum at about 20–25% polypropylene for both rubbers.

Addition of the maleated rubbers to nylon 6/PP blends reduces both the yield stress and modulus as expected; in addition, *Figures 3b* and *3c* show that both tensile properties decline monotonically as the weight fraction of polypropylene increases. The trend is about the same for both rubbers, although the blends containing SEBS-*g*-MA have a slightly higher yield stress below 25% polypropylene, while above this level blends containing EPR-*g*-MA have higher values. It is interesting to note that there is no maximum or minimum in the yield stress or modulus corresponding to the maximum observed for the Izod impact strength for compositions containing 20–25% polypropylene.

Figure 4 shows Izod impact strength versus temperature for 80/20 nylon 6/PP blends containing 20% EPR-*g*-MA or SEBS-*g*-MA. It is apparent that the ductile–brittle transition temperature is affected by the type of rubber used as the modifier for these blends. The lowest ductile–brittle transition temperature is observed using EPR-*g*-MA rubber; this can be attributed to the differences in rubber structure, glass transition temperature and modulus. The difference in T_g of the rubbers is not large (−45°C for EPR-*g*-MA, −38°C for SEBS-*g*-MA); however, the differences in modulus above the T_g are considerable, as shown in *Figure 5*. The polystyrene microdomains of SEBS-type materials act as physical

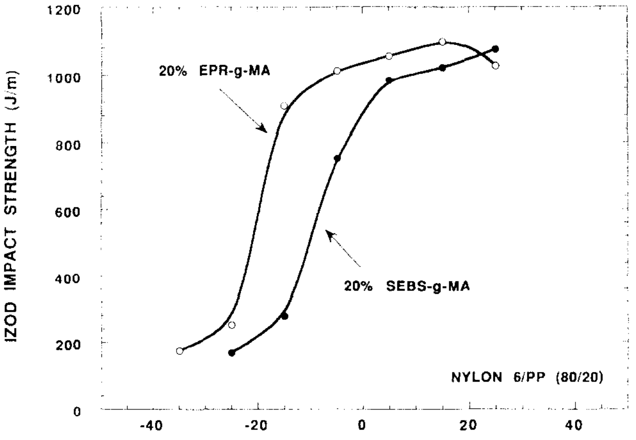


Figure 4 Effect of temperature on the Izod impact strength for blends with fixed nylon 6/PP ratio (80/20) containing 20% EPR-*g*-MA or SEBS-*g*-MA

crosslinks and retain their integrity as a function of temperature up to the T_g of these domains (95°C). In addition, the rigid polystyrene microdomains make up a volume fraction of about 0.26 in these materials, acting as a filler. This is the main reason for the large difference in modulus observed for these two types of rubber. These mechanical differences are no doubt a main reason for the better low temperature toughness of the nylon 6/PP blends containing EPR-*g*-MA relative to similar blends containing SEBS-*g*-MA.

Morphology

Interpretation of TEM photomicrographs showing how the two maleated rubbers affect the morphology of nylon 6/polypropylene blends will be aided by the schematics shown in *Figure 6*. Binary blends of the different components of the rubber-modified blends have similar morphologies: a dispersed phase of one component in a matrix of the remaining component. Which phase is the matrix and the size of the dispersed phase depend on the volume and viscosity ratios of the components. The rubber domains in the nylon 6/maleated rubber blends are usually very small owing to the reaction that takes place between these two polymers during melt processing. In contrast, TEM photomicrographs of ternary blends of nylon 6, polypropylene and the maleated rubbers reveal a quite different type of morphology; some of the rubber tends to be dispersed in the nylon 6 phase, while the remainder tends to locate at the interface between nylon 6 and polypropylene. That is, the rubber seems to act as an impact modifier for the nylon 6 phase and also as an interfacial compatibilizer for the blend. At a fixed weight fraction of rubber, the relative size of the polypropylene domains is a function of both the polypropylene volume fraction and viscosity. It is expected that at a certain composition, phase inversion will take place and the polypropylene will become the continuous phase. However, the location of the rubbery phase does not seem to change with these gross changes of morphology, as will be shown later and as reported in the previous literature for blends compatibilized with SEBS-*g*-MA[20,21].

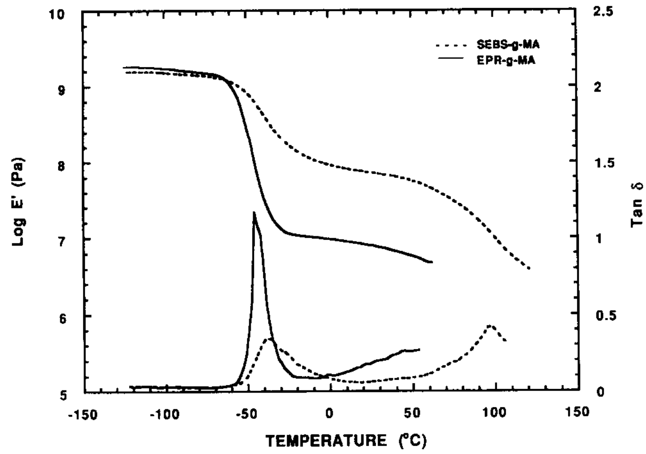


Figure 5 Dynamic mechanical properties of EPR-*g*-MA and SEBS-*g*-MA measured at a frequency of 1 Hz

Figure 7 shows TEM photomicrographs of nylon 6/polypropylene blends containing the two different maleated rubbers. In *Figure 7a* (rubber = SEBS-*g*-MA), the blend is stained with RuO_4 vapour; therefore, the grey phase is the nylon 6 matrix, the dark phase is the rubber and the light phase is the polypropylene. This photomicrograph clearly shows that the SEBS-*g*-MA

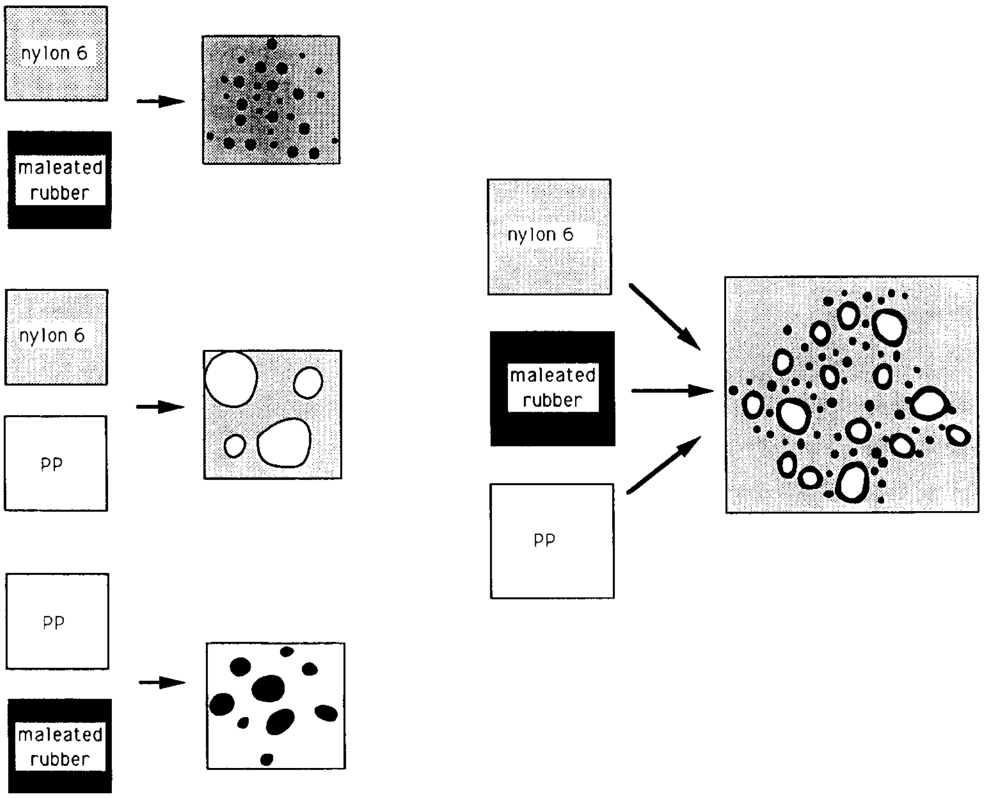


Figure 6 Schematic of the morphology of binary and ternary blends of maleated rubber, nylon 6 and polypropylene

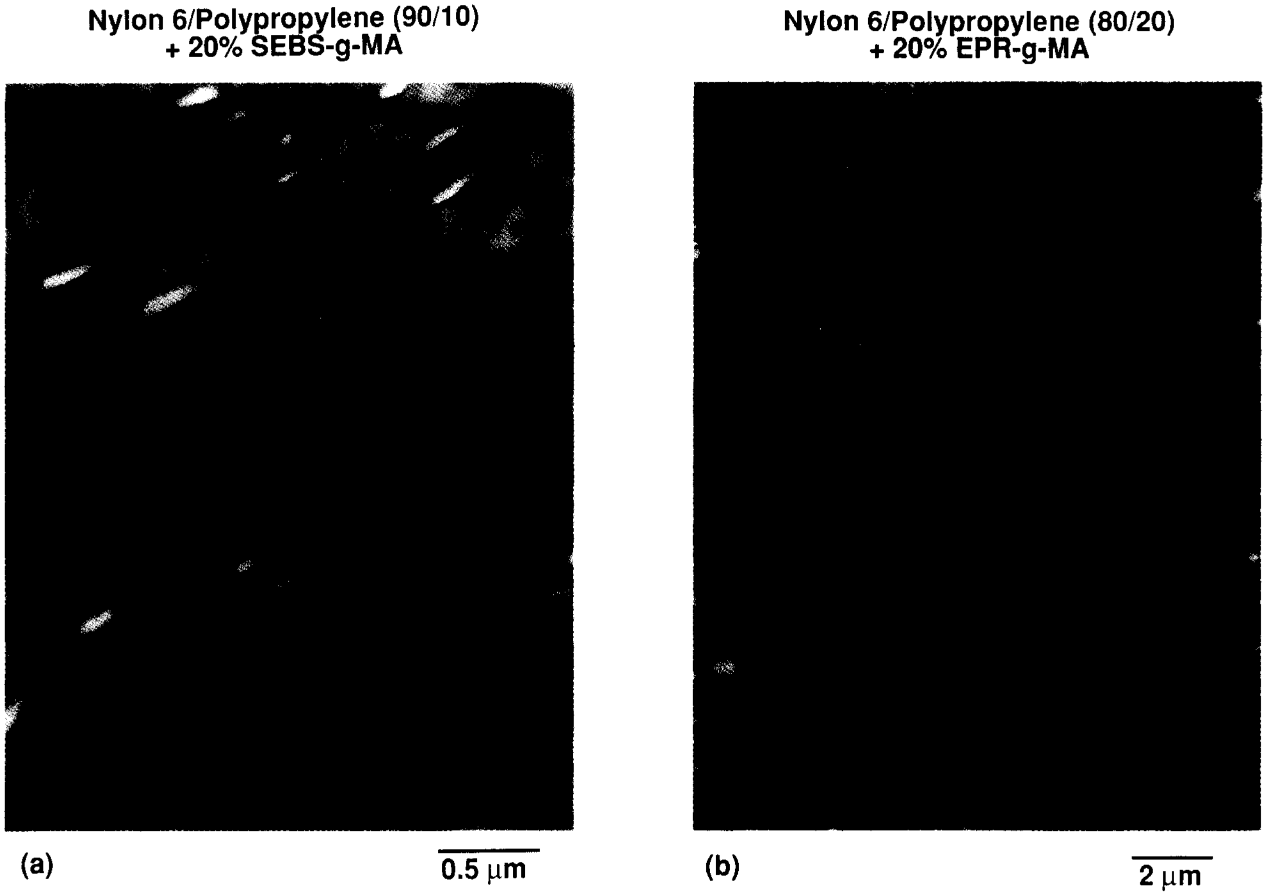


Figure 7 Morphology of (a) a 90/10 nylon 6/PP blend modified with 20% SEBS-*g*-MA and stained with RuO_4 vapour (the rubber is stained dark grey, the light grey background is nylon 6 and the white particles are PP) and (b) an 80/20 nylon 6/PP blend modified with 20% EPR-*g*-MA and stained with RuO_4 solution (the rubber is stained black, the grey background is nylon 6, the dark grey particles are PP and the white particles are unstained rubber and PP particles)

rubber is well distributed in the nylon phase and also surrounds the polypropylene domains, as shown in the schematic of *Figure 6*. In *Figure 7b* (rubber = EPR-*g*-MA), the blend is stained with a solution of RuO_4; thus, the light grey phase is the nylon 6 matrix, the black phase is the rubber, the dark grey dispersed phase is the polypropylene and the white dispersed phase is either rubber or polypropylene that did not stain. As explained earlier, it is very difficult to stain preferentially the EPR-*g*-MA rubber; the technique used stains only some of the rubber located at the interface with polypropylene and very few of the rubber particles dispersed in the nylon phase. However, this photomicrograph confirms the location of the rubber in the blend and its role as both an impact modifier and compatibilizer.

More definitive proof that the rubber is indeed located at the interface between the nylon 6 and PP can be found in the high magnification TEM photomicrographs in *Figure 8*. *Figure 8a* shows a 66/33 nylon 6/PP blend containing 20% SEBS-*g*-MA rubber stained with RuO_4. The fine scale light and dark texture reflects the styrene (which stains dark) and ethylene–butylene (which does not stain) microdomains of the block copolymer. The rubber forms a relatively uniform layer at the interface between the nylon 6 and PP in addition to the particles of rubber dispersed in the nylon 6 phase. *Figure 8b* shows a high magnification view of an 80/20 nylon 6/PP blend containing EPR-*g*-MA which has also been stained with RuO_4. The rubber (dark phase) forms a relatively thick, non-uniform layer around the PP domains. It is also interesting to note that some rubber particles seem to be part of this interfacial layer. Crystalline lamellae of both nylon 6 and PP seem to penetrate the rubber phase, suggesting an intimate interaction with these phases.

The morphologies of nylon 6/PP blends modified with EPR-*g*-MA in the co-continuous region tend to be more complicated than expected from the discussion above. *Figure 9* shows photomicrographs of a 66/33 nylon 6/PP blend modified with EPR-*g*-MA rubber having a co-continuous morphology. In *Figure 9a*, the polyamide is stained with phosphotungstic acid, while the rubber and polypropylene are unstained. Nylon 6 forms a co-continuous phase and also fine particles in the polypropylene phase. The white domains within the dark phase represent particles of rubber and polypropylene dispersed in the nylon 6 phase. Evidently, the surfactant-like character of the nylon–rubber graft copolymer serves to disperse nylon 6 finely in the polypropylene phase and polypropylene and rubber in the nylon 6 phase. *Figure 9b*, where the same blend is stained with RuO_4, verifies that the rubber is also located in the polypropylene phase. The rubber appears as dark domains, while the polypropylene and nylon 6 both appear as light grey phases. The co-continuous nylon 6 phase is somewhat understained and appears to have no particles dispersed in it (the morphology of this phase is better illustrated in *Figure 9a*); the co-continuous polypropylene phase is where all the dark particles are dispersed. The rubber seems to disperse well in the polypropylene phase and to locate at the interface

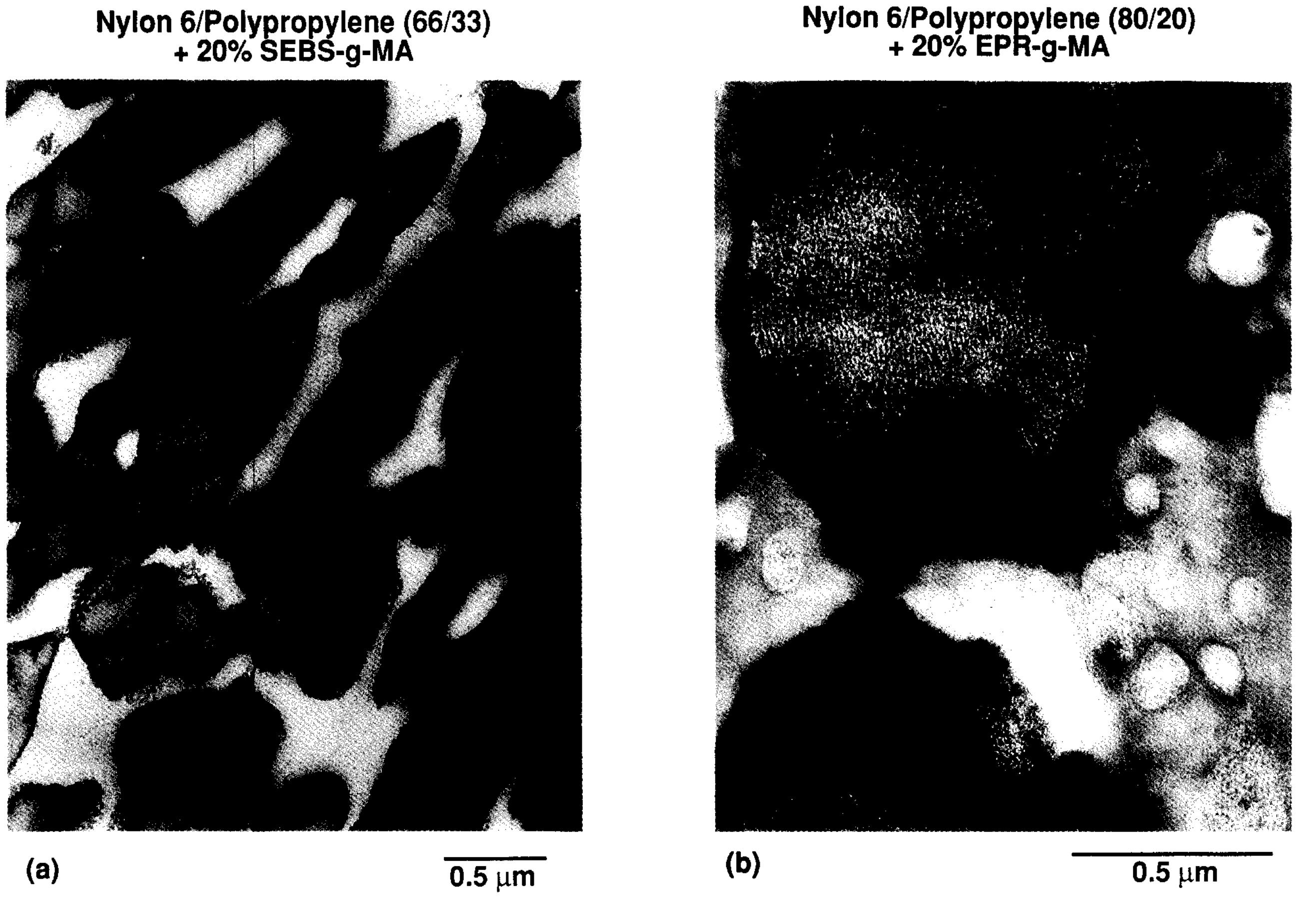


Figure 8 Morphology of (a) a 66/33 nylon 6/PP blend modified with 20% SEBS-*g*-MA and stained with RuO_4 vapour (the rubber is stained dark, the grey background is nylon 6 and the white phase is PP) and (b) an 80/20 nylon 6/PP blend modified with 20% EPR-*g*-MA and stained with RuO_4 solution (the rubber is stained black, the grey background is nylon 6, the grey particles are PP and the white particles are unstained rubber particles

between nylon 6 and polypropylene. Morphologies like this were not observed for blends with SEBS-*g*-MA, where all the rubber seems to locate in the nylon 6 phase and at the nylon 6/PP interface (see *Figure 8a*).

EFFECT OF RUBBER CONTENT IN NYLON 6/PP BLENDS

As suggested above, the maleated rubbers appear to function both as impact modifiers and as compatibilizers for nylon 6/PP blends. In either role, the rubber content in the blend is expected to be a key variable affecting the toughness of nylon 6/PP blends. An increase in the rubber content might be expected to have a two-fold effect. First, it will increase the volume fraction of rubber dispersed in the nylon 6, which greatly affects the toughness of this phase; second, it will promote the generation of more rubber–nylon graft copolymer, which in turn should contribute to an improved dispersion of the polypropylene phase. *Figure 10* shows the response of the impact strength to EPR-*g*-MA content for nylon 6/PP blends containing varying amounts of PP. It is interesting to note that significant impact strength is achieved, even at 10% rubber levels, when there is 10–30% PP in the blend. Blends without any rubber have much lower impact strengths, as shown in *Figure 2*. It appears that 15% EPR-*g*-MA rubber is sufficient to achieve toughness over a wide range of compositions at room temperature. However, the amount of rubber strongly influences the low temperature behaviour of the blends, as shown in *Figure 11*; blends containing 10% EPR-*g*-MA are within the ductile–brittle region at room temperature. The ductile–brittle transition of these blends is dramatically shifted to lower temperatures as more EPR-*g*-MA is added to a blend of fixed nylon 6/PP (80/20) ratio.

The effect of EPR-*g*-MA on the morphology of these blends is shown by the series of TEM photomicrographs in *Figure 12*; the polyamide phase is stained dark with phosphotungstic acid, while the rubber and polypropylene are unstained. It is clear that on average, the size of the polypropylene domains decreases as the amount of EPR-*g*-MA in the blend increases. Similar behaviour was observed for blends modified with SEBS-*g*-MA. These observations confirm that the maleated rubbers change the morphology of these blends, i.e. there is evidence for their role as compatibilizers in addition to being impact modifiers.

EFFECT OF NYLON 6/PP RATIO

The mechanical properties of the nylon 6/polypropylene blends depend strongly on the nylon 6/polypropylene ratio. *Figures 13* and *14* illustrate this by showing how impact strength varies with temperature for blends modified with EPR-*g*-MA and SEBS-*g*-MA rubbers. When EPR-*g*-MA is used (see *Figure 13*), the lowest ductile–brittle transition temperature is achieved when there is no polypropylene, i.e. for a blend of nylon 6 and 20% EPR-*g*-MA. Beginning at this lower limit, the ductile–brittle transition temperature increases as polypropylene is added. A different tendency is observed

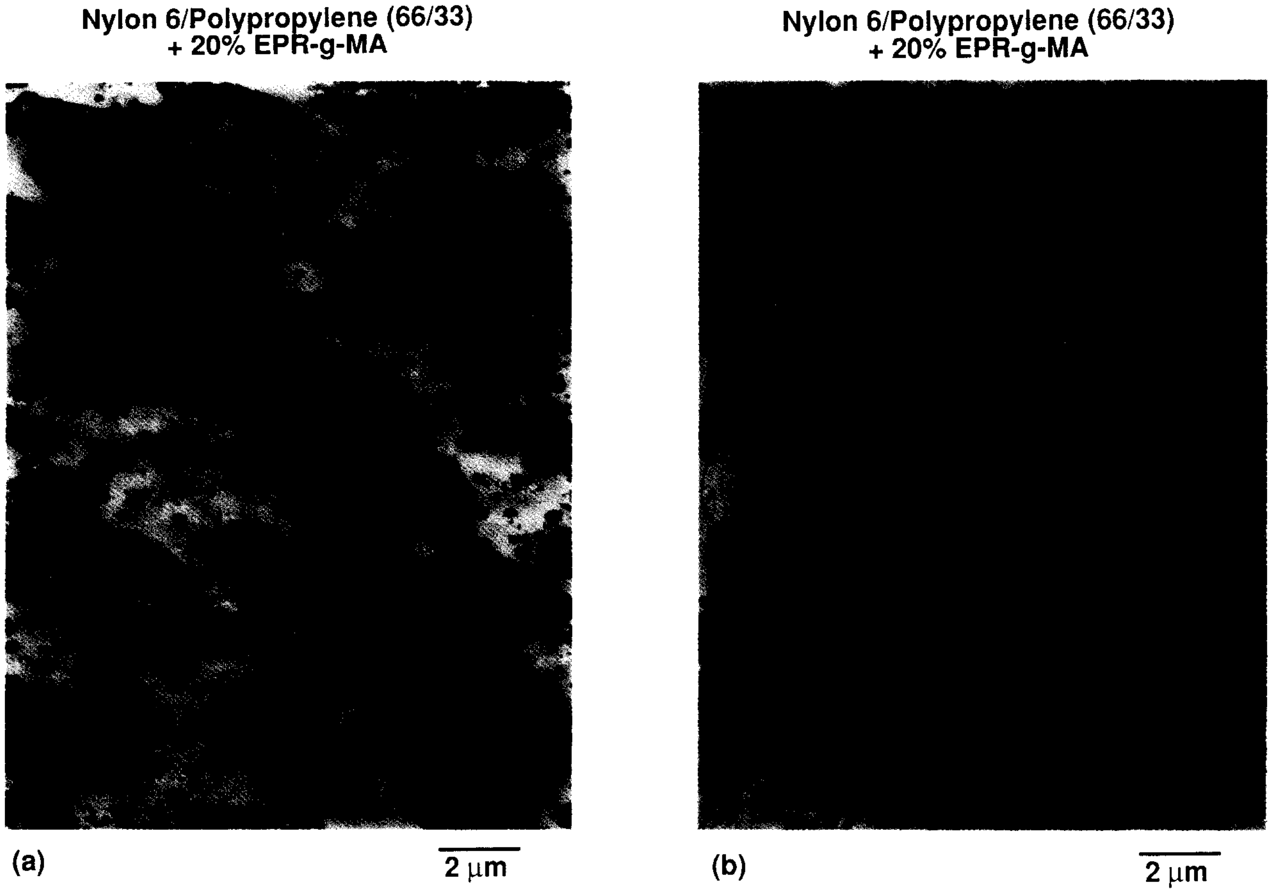


Figure 9 Morphology of a 66/33 nylon 6/PP blend modified with 20% EPR-*g*-MA and stained with (a) phosphotungstic acid (the nylon 6 is stained dark, rubber and PP are unstained) and (b)RuO_4 solution (the rubber is stained dark, nylon 6 is the grey phase and contains rubber and PP particles that are not distinguishable, and PP is the light phase and contains the rubber and nylon 6 particles that are stained)

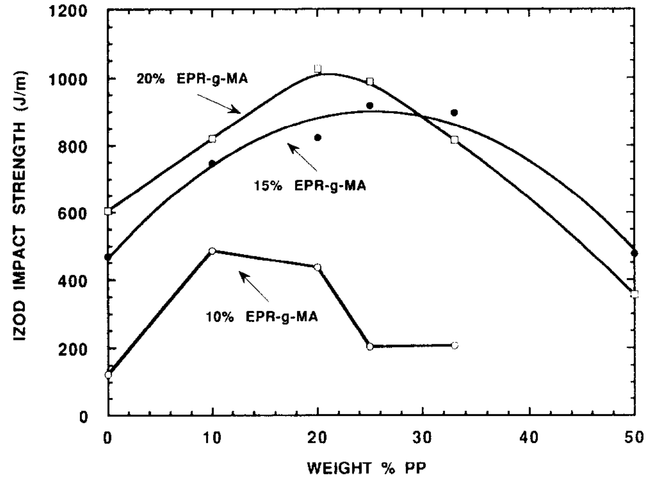


Figure 10 Izod impact strength of nylon 6/PP blends modified with different amounts of EPR-*g*-MA. The composition shown on the abscissa is the percentage of polypropylene relative to nylon 6 in the blend on a rubber-free basis. The rubber content is based on the total mass of the ternary blend

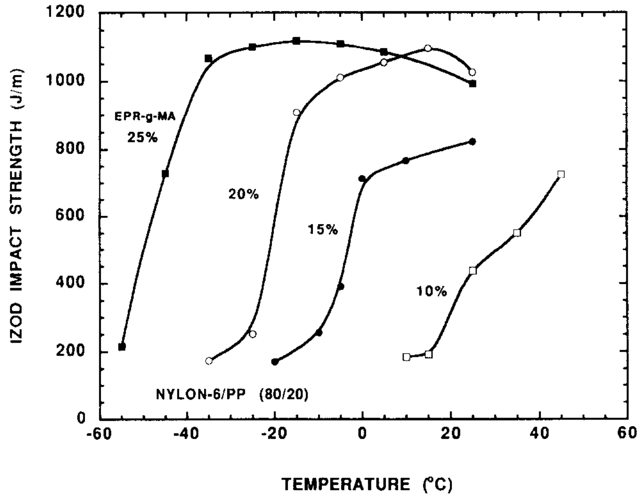


Figure 11 Effect of temperature on the Izod impact strength of 80/20 nylon 6/PP blends modified with different amounts of EPR-*g*-MA

for the blends with SEBS-*g*-MA rubber (see *Figure 14*). In this case, the lowest ductile–brittle transition occurs at a nylon 6/PP ratio of 90/10. The blend with an 80/20 nylon 6/PP ratio shows the same ductile–brittle transition temperature as the blend without polypropylene (80% nylon 6, 20% SEBS-*g*-MA). However, the former shows substantially greater toughness at room temperature. Beyond the 80/20 nylon 6/PP ratio, the ductile–brittle transition temperature increases continuously as polypropylene is added. The blends containing SEBS-*g*-MA rubber have higher ductile–brittle transition temperatures than those containing EPR-*g*-MA.

The morphology of these blends is altered by changes in the nylon 6/PP ratio, as shown by the TEM

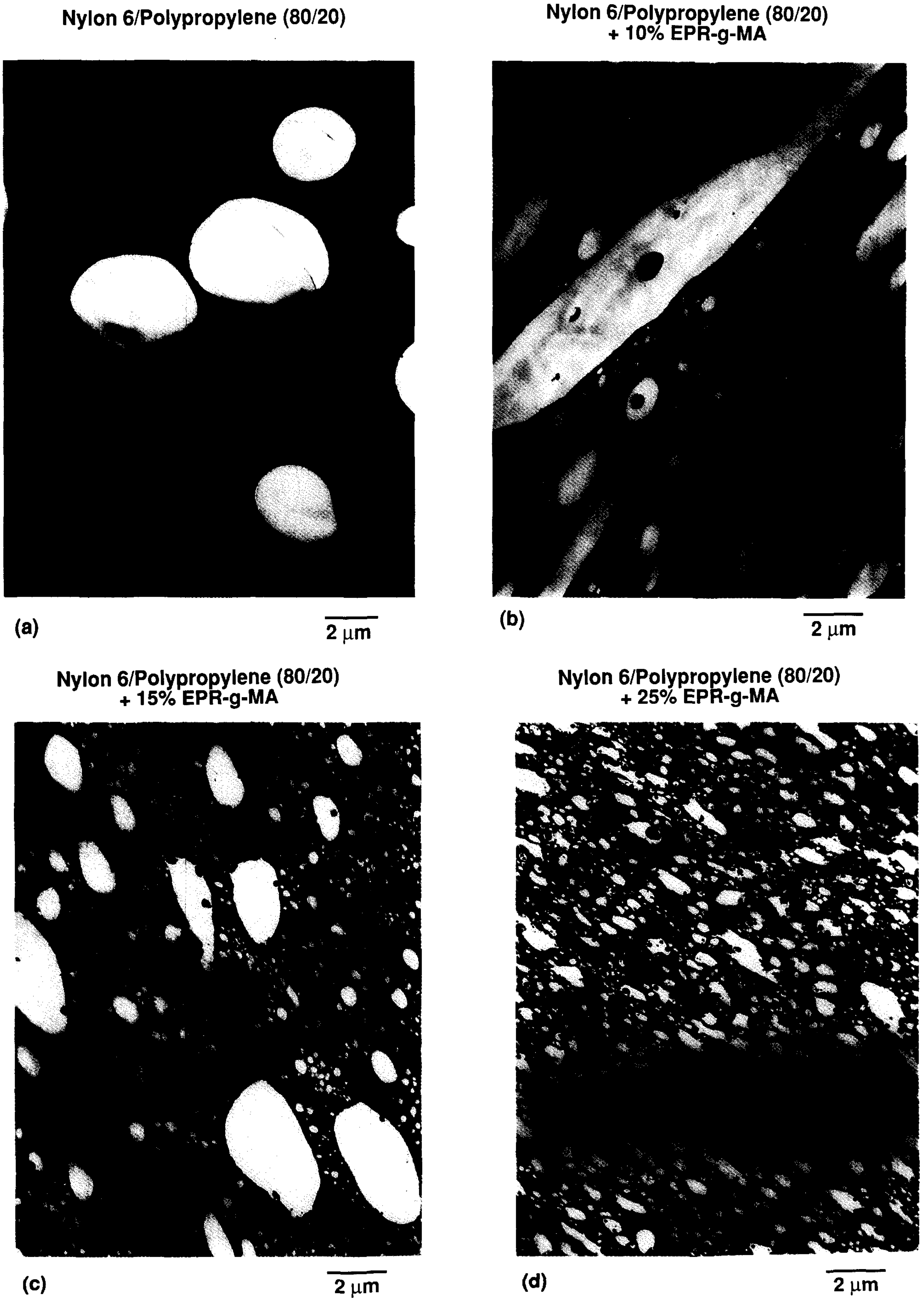


Figure 12 Morphology of 80/20 nylon 6/PP blends modified with (a) 0% EPR-*g*-MA, (b) 10% EPR-*g*-MA, (c) 15% EPR-*g*-MA and (d) 25% EPR-*g*-MA. The nylon 6 phase is stained with phosphotungstic acid

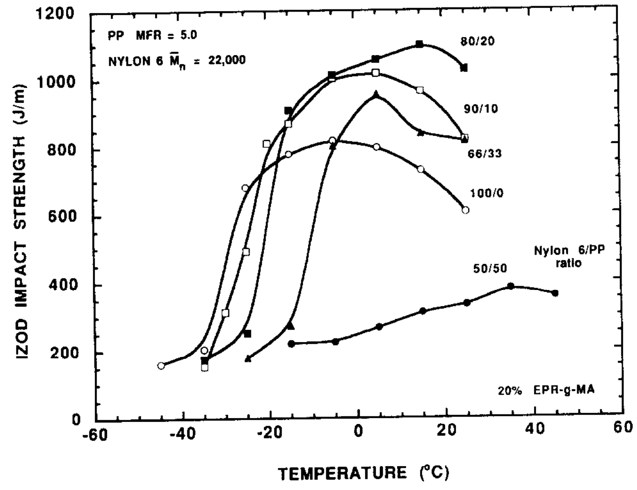


Figure 13 Effect of temperature on the Izod impact strength of blends containing 20% EPR-*g*-MA and differing nylon 6/PP ratios (MFR = melt flow rate)

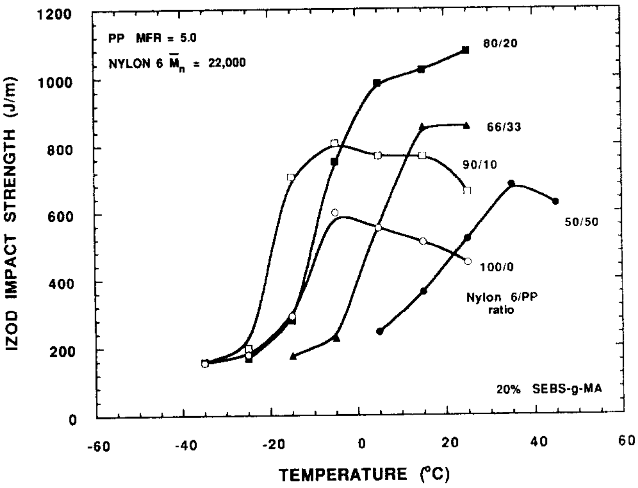


Figure 14 Effect of temperature on the Izod impact strength of blends containing 20% SEBS-*g*-MA and differing nylon 6/PP ratios

photomicrographs in *Figures 15* and *16*. For blends based on either EPR-*g*-MA (*Figure 15*) or SEBS-*g*-MA (*Figure 16*), the morphology changes from a continuous nylon 6 matrix to a co-continuous morphology, and then undergoes phase inversion to a PP continuous phase as the amount of polypropylene is increased. Note that the compositions of the blends in *Figures 15* and *16* are different to illustrate that the change to co-continuity and then phase inversion seems to take place at higher nylon 6/PP ratios for blends with SEBS-*g*-MA rubber. For instance, an 80/20 nylon 6/PP blend with 20% SEBS-*g*-MA rubber (*Figure 16b*) shows a tendency to break up the nylon 6 matrix and form a co-continuous morphology; however, in a similar blend with EPR-*g*-MA (see *Figure 7b*), the polypropylene clearly forms a dispersed phase in a nylon 6 matrix. The changes in morphology observed here correspond well to those reported for binary blends of nylon 6 and polypropylene and for other polymer systems[32–35].

The ductile–brittle behaviour of these blends seems to be closely related to their morphology. Blends with the lowest ductile–brittle transition temperatures have a continuous nylon matrix with rubber and polypropylene phases finely dispersed in it.

The above observations on morphology and ductile–brittle transition behaviour are summarized in *Figure 17*, where the ductile–brittle transition temperature for each blend is plotted *versus* the weight percentage of PP in the blend. The ductile–brittle transition temperature of blends modified with EPR-*g*-MA rubber increases in a continuous manner as polypropylene is added. On the other hand, for blends modified with SEBS-*g*-MA rubber, the ductile–brittle transition temperature first decreases as polypropylene is added, reaching a minimum at about 10% PP, and then increases. As noted above, the co-continuous region is reached at a lower weight percentage of PP when SEBS-*g*-MA rubber is used. It is interesting to note that the dispersed polypropylene particles are smaller for the blends containing SEBS-*g*-MA than for the blends containing EPR-*g*-MA. It appears that the SEBS-*g*-MA rubber is a more effective compatibilizer than EPR-*g*-MA. The lower ductile–brittle transition temperatures for blends containing EPR-*g*-MA follow from the fact[36] that this rubber is the better impact modifier for nylon 6, which, as suggested earlier, no doubt stems from the differences in the modulus *versus* temperature characteristics of the two rubbers (see *Figure 5*).

Low ductile–brittle transition temperatures are obtained in the region where the nylon 6 is the continuous phase, no matter which rubber is used. Departure from this morphology towards co-continuity or phase inversion results in an increased ductile–brittle transition temperature. Thus, in order to achieve toughness in nylon 6/polypropylene blends, it is desirable to have the rubber and the polypropylene separately dispersed in the nylon 6 matrix. This observation agrees well with the relative toughenabilities of nylon 6 and polypropylene. Toughened nylon 6 shows higher impact strength values than toughened polypropylene (Izod impact strength for the former is of the order of 1000 $\mathrm{J\,m^{-1}}$, whereas values of the order of 200 $\mathrm{J\,m^{-1}}$ are typical for the latter). Also, the ductile–brittle transition temperatures of toughened nylon 6[3–5,37,38] are generally much lower than those reported for toughened PP[15]. The difference in toughenability between nylon 6 and polypropylene is related to differences in the chemical structure, molecular dynamics, chain entanglement density and crystalline texture of the neat polymers, in addition to differences in morphology of the rubber-modified blends. Certainly, these factors contribute to the higher impact strengths and lower ductile–brittle transition temperatures observed for blends where nylon 6 is the matrix phase.

The particle size of the polypropylene phase in these blends increases as the nylon 6/PP ratio decreases until the co-continuous region is reached; for example, the weight average particle diameter $\bar{d}_w$ increases from 0.64 to 1.0 μm as the nylon 6/PP ratio goes from 90/10 to 80/20 (see *Figure 17*) for blends modified with EPR-*g*-MA rubber. Similar increases in particle size with concentration are observed in binary blends[32,34,39], and this response is usually attributed to an increased probability of particle coalescence[32,40,41]. It is difficult to ascertain whether the size of the PP particles *per se* has a significant effect on toughness for the blends or not, since many other factors are involved. More dramatic factors may be

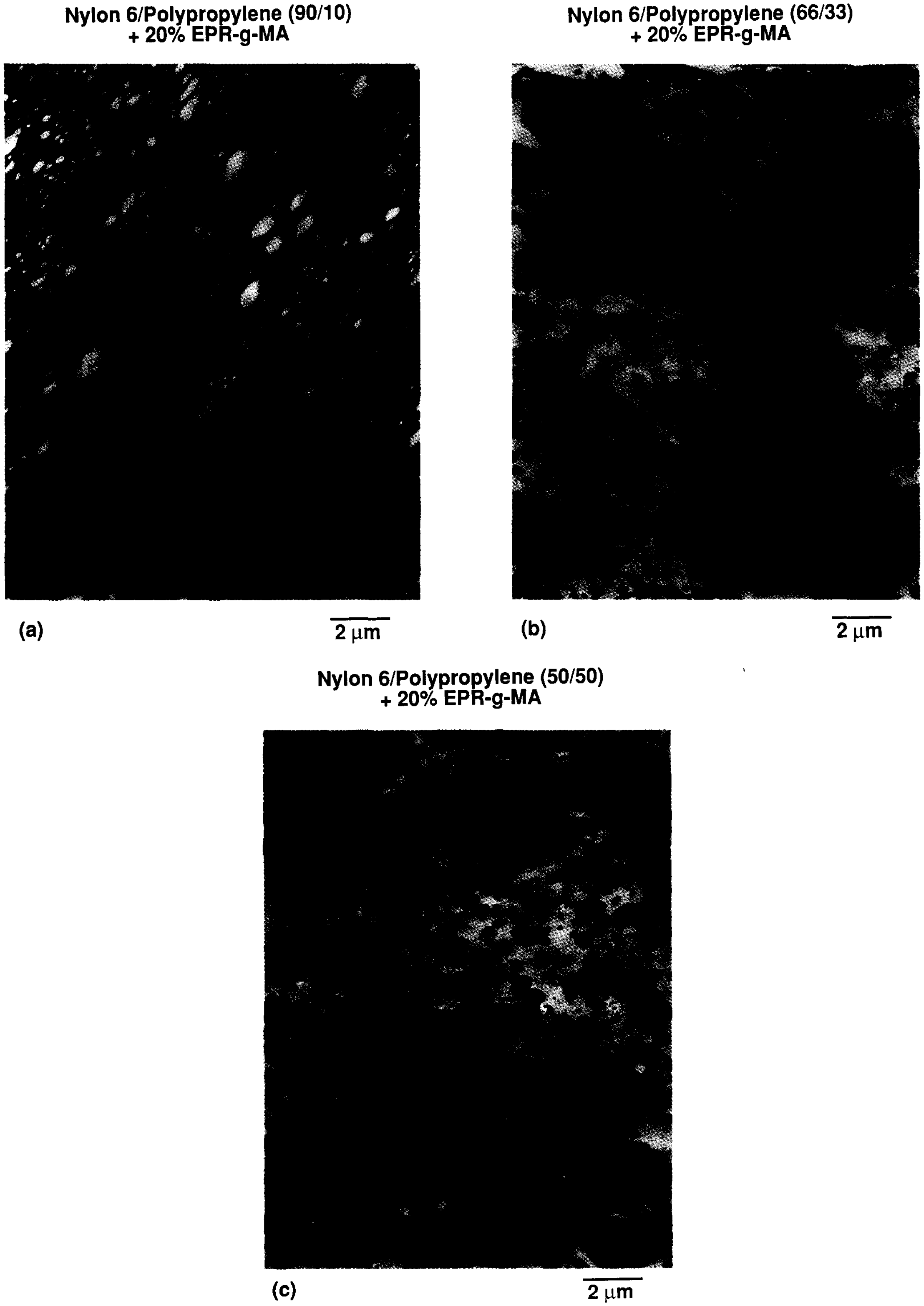
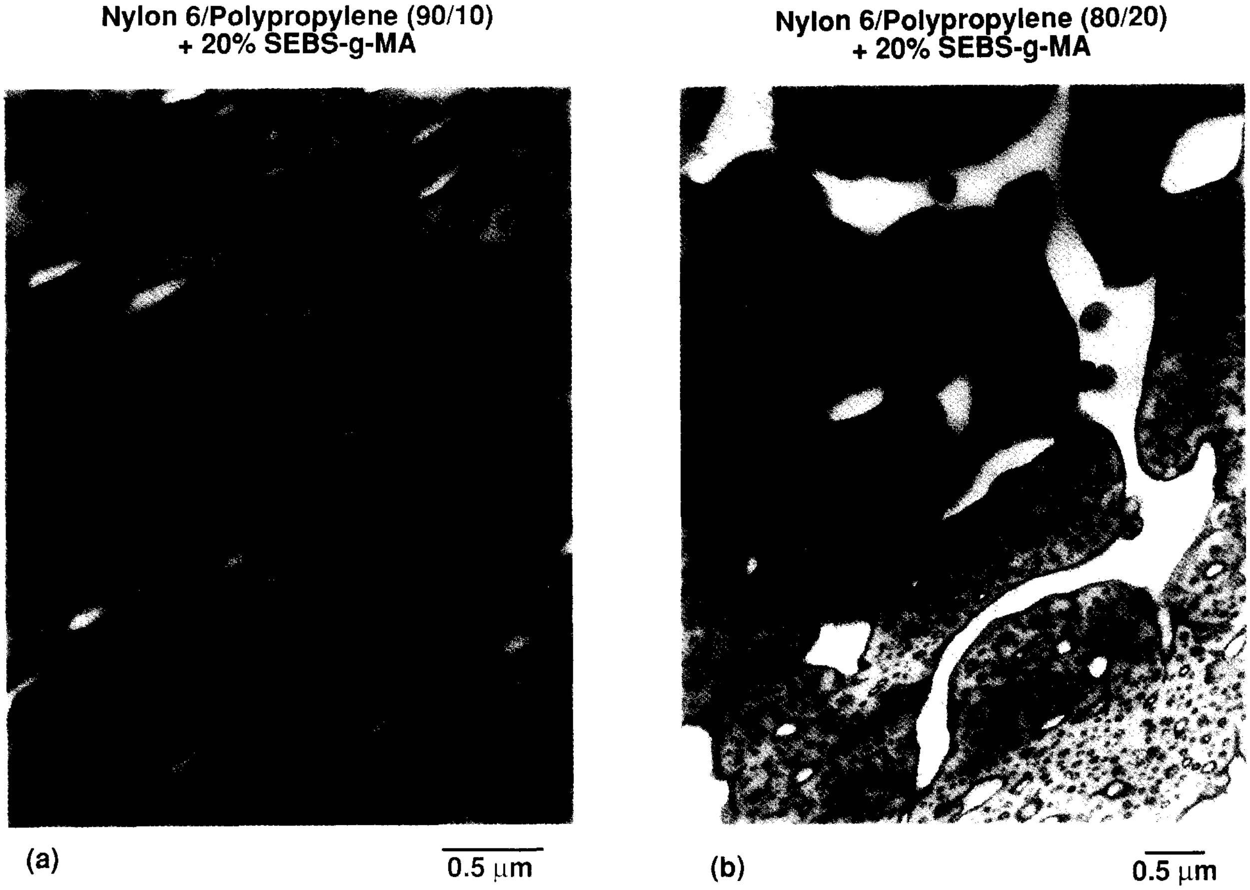


Figure 15 Morphology of nylon 6/PP blends modified with 20% EPR-*g*-MA: (a) 90/10 nylon 6/PP ratio; (b) 66/33 nylon 6/PP ratio; (c) 50/50 nylon 6/PP ratio. The nylon 6 phase is stained with phosphotungstic acid


Nylon 6/Polypropylene (90/10) + 20% SEBS-g-MA

Nylon 6/Polypropylene (80/20) + 20% SEBS-g-MA


Nylon 6/Polypropylene (66/33) + 20% SEBS-g-MA

Figure 16 Morphology of nylon 6/PP blends modified with 20% SEBS-g-MA: (a) 90/10 nylon 6/PP ratio; (b) 80/20 nylon 6/PP ratio; (c) 66/33 nylon 6/PP ratio. The blends are stained with RuO_4 (rubber stains dark, nylon 6 grey and polypropylene remains unstained)

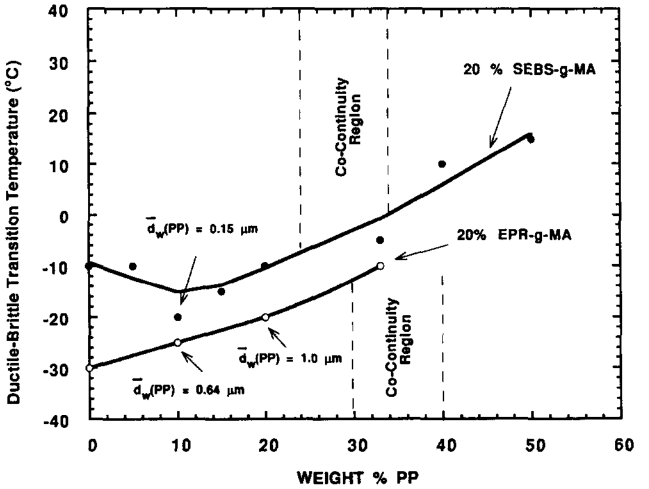


Figure 17 Ductile–brittle transition temperature as a function of the percentage of polypropylene relative to nylon 6 on a rubber-free basis for blends modified with 20% EPR-*g*-MA or SEBS-*g*-MA ($\bar{d}_W$ is the weight average PP particle diameter)

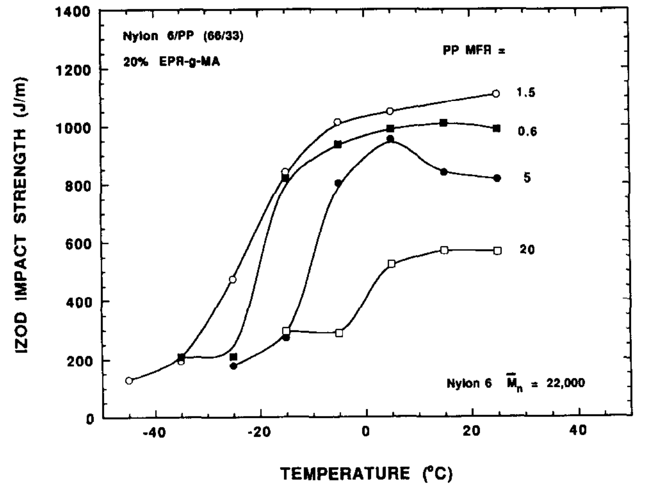


Figure 18 Effect of temperature on the Izod impact strength of 66/33 nylon 6/PP blends modified with 20% EPR-*g*-MA rubber. The melt flow rate (*MFR*), i.e. molecular weight, of the polypropylene is varied

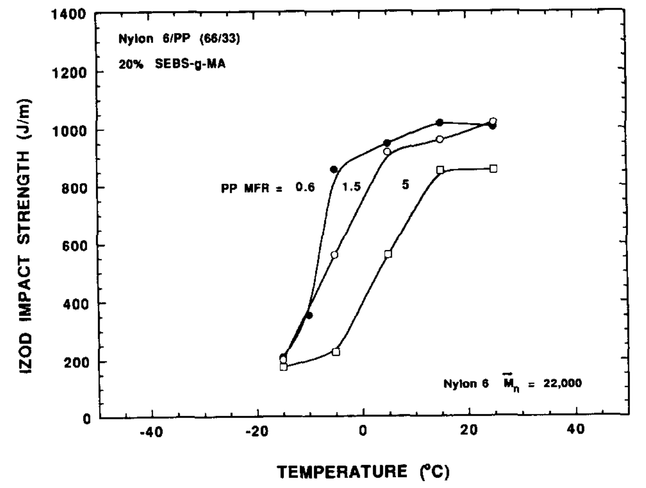


Figure 19 Effect of temperature on the Izod impact strength of 66/33 nylon 6/PP blends modified with 20% SEBS-*g*-MA rubber. The melt flow rate (*MFR*) of the polypropylene is varied.

the actual volume fraction and particle size of rubber in the nylon phase. We expect that as the volume fraction of polypropylene increases, more rubber is required to stabilize (compatibilize) the interface between nylon 6 and polypropylene, and the volume fraction of rubber dispersed in the nylon 6 phase decreases.

Rubber-modified blends with co-continuous nylon 6 and PP phases show good toughness at room temperature but have poorer low temperature toughness than blends with lower amounts of PP in the form of dispersed particles. Blends where PP is the continuous phase are not tough at room temperature. In fact, the 50/50 nylon 6/PP blend containing 20% EPR-*g*-MA does not appear to become tough at any temperature (see *Figure 13*); consequently, no ductile–brittle transition temperature is recorded for this material in *Figure 17*.

EFFECTS OF THE MOLECULAR WEIGHTS OF THE NYLON 6 AND PP COMPONENTS

This section explores the effects of the molecular weights of the nylon 6 and PP components on the mechanical properties and morphologies of the blends.

Figure 18 shows how the molecular weight of the polypropylene, expressed as melt flow rate (*MRF*), for a fixed nylon 6 component affects the low temperature toughness of blends modified with EPR-*g*-MA at a fixed nylon 6/PP ratio. Use of polypropylenes with low melt flow rates (high molecular weights) produces blends with lower ductile–brittle transition temperatures. As the melt flow rate of the PP increases, the ductile–brittle transition temperature of the blend increases and the room temperature impact strength decreases. In addition, the absolute level of toughness above this transition temperature, e.g. room temperature, decreases as the PP molecular weight decreases. Similar, but less dramatic, tendencies are observed for blends modified with SEBS-*g*-MA, as shown in *Figure 19*. These changes in blend toughness are related, at least in part, to changes in blend morphology. *Figure 20* shows TEM photomicrographs of some of the blends from *Figure 18*. In these photomicrographs the nylon 6 is the stained dark phase, whereas, polypropylene and rubber appear as unstained light phases. Decreasing the molecular weight of polypropylene (and hence its melt viscosity) causes a change of morphology similar to that induced by increasing the PP content (see *Figure 15*). The highest molecular weight polypropylene generates a morphology where nylon 6 is the continuous phase (in *Figure 20a*), the medium molecular weight polypropylene leads to a co-continuous morphology and the lowest molecular weight polypropylene gives rise to a PP continuous phase. Once again, the lowest ductile–brittle transition temperature corresponds to the blend where the nylon 6 is the matrix phase.

Large changes in ductile–brittle behaviour and morphology are also observed when the molecular weight of the nylon 6 is varied. *Figure 21* shows the effect of temperature on impact strength for blends of fixed composition and PP molecular weight, but where the nylon 6 molecular weight is varied. In contrast to what was observed on varying the PP molecular weight, in this case the blend with the highest molecular weight nylon 6 is brittle and does not show ductile behaviour even well above room temperature. The blend based on a medium

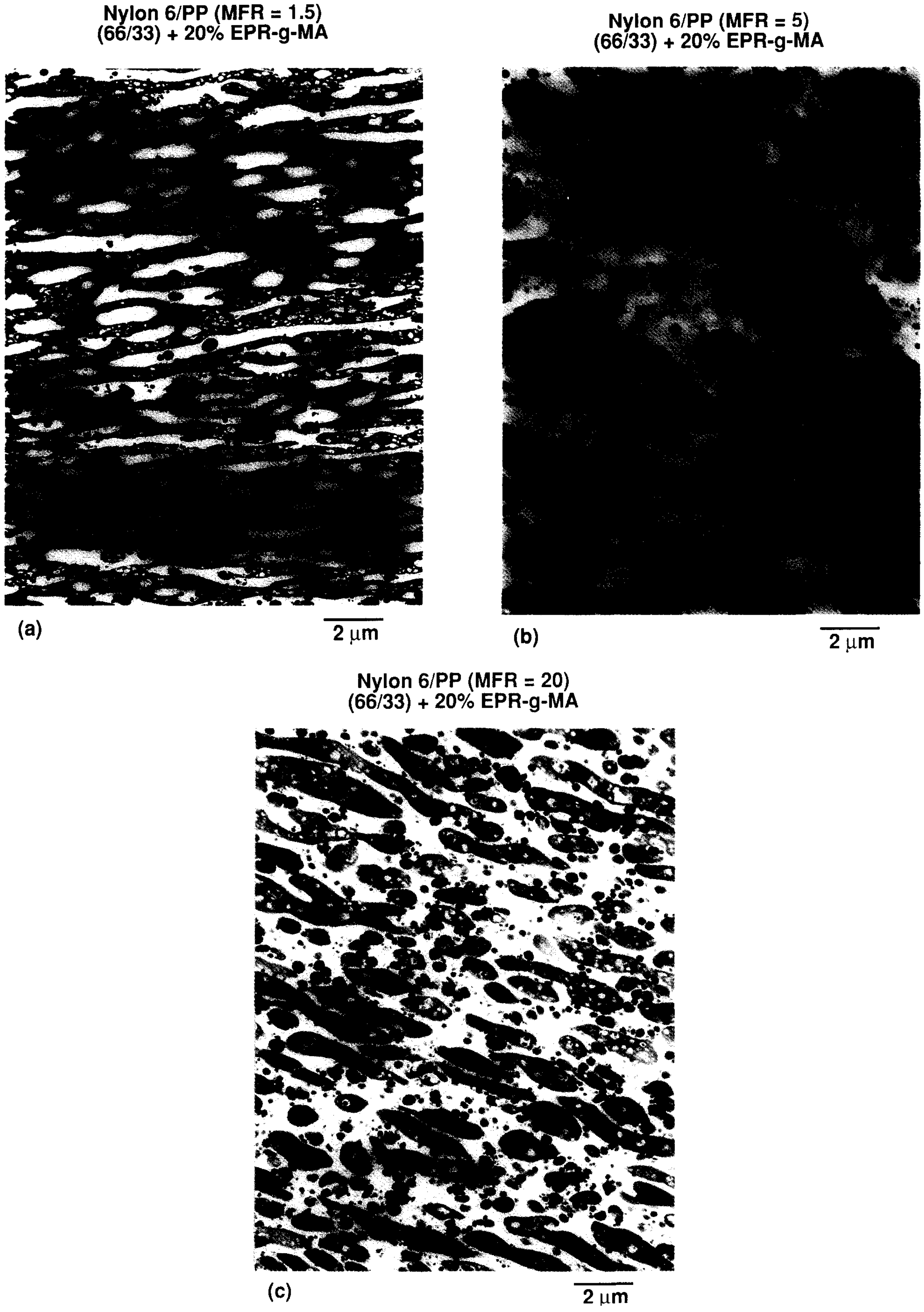


Figure 20 Morphology of a 66/33 nylon 6/PP blend modified with 20% EPR-g-MA rubber as a function of polypropylene melt flow rate: (a) PP *MFR* = 1.5; (b) PP *MFR* = 5; (c) PP *MFR* = 20

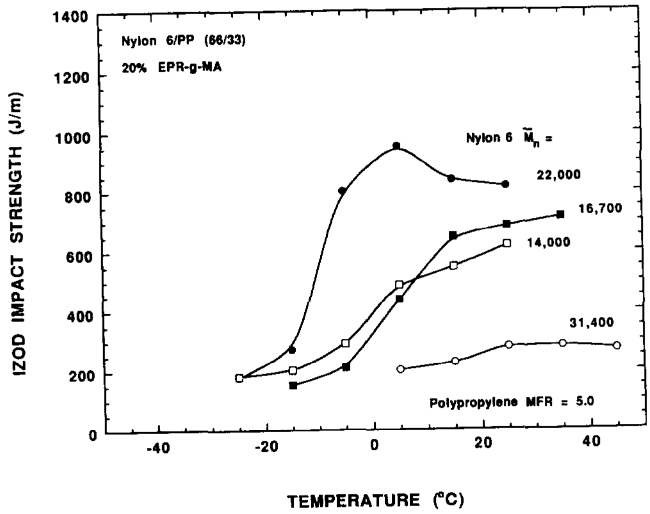


Figure 21 Effect of temperature on the Izod impact strength of 66/33 nylon 6/PP blends modified with 20% EPR-*g*-MA rubber. The molecular weight of the nylon 6 is varied.

molecular weight nylon 6 ($\overline{M}_n = 22\,000$) has a low ductile–brittle transition temperature and shows excellent toughness at room temperature. Use of nylon 6 materials with lower molecular weights gives higher ductile–brittle transition temperatures and lower room temperature toughnesses. It is apparent that changing the molecular weight of the nylon 6 component leads to large changes in blend morphology, as shown in *Figure 22*. The low toughness of the blend based on the highest molecular weight nylon 6 corresponds to a morphology where PP forms the continuous matrix phase. The blend with the lowest ductile–brittle transition temperature (*Figure 22b*) has a co-continuous morphology. The blends based on low molecular weight nylon 6 have large, poorly dispersed domains of nylon 6 and PP, which seems to be the reason for the lower toughness observed for these blends. A similar trend was observed for blends with an 80/20 nylon 6/PP ratio, but in this case the nylon 6 molecular weight at which co-continuity or phase inversion occurred was higher ($\overline{M}_n = 38\,500$).

The response of blend morphology to changes in molecular weight of the components is no doubt related to the corresponding changes in melt viscosity of the phases. It is well known that the morphology of polymer blends is a function of the melt viscosity ratio and volume ratio of the components[32–35,42]. Thus, for a given volume ratio there is a viscosity ratio at which phase inversion will occur. The TEM photomicrographs shown in *Figures 20* and *22* correspond to blends with a fixed nylon 6/PP ratio (66/33 weight ratio, 60/40 volume ratio) modified with 20% of the elastomer. Changes in the molecular weight of either nylon 6 or polypropylene shift the viscosity ratio of the phases, thus generating morphologies that range from a continuous polyamide matrix to a continuous polypropylene matrix. A descriptive quantitative analysis based on viscosity ratios, such as the one proposed by Jordhamo *et al.*[35], cannot be attempted owing to the complexity of the system (a ternary blend where there is a reaction occurring during melt processing and the rubber locates at both the interface and inside the nylon 6 or PP phase). However, the changes in morphology qualitatively correspond to those expected of binary blends where the viscosity ratio of the components changes while the volume ratio is fixed.

Molecular weight can have significant effects on mechanical properties. Impact strength and tensile properties are reported[43] to change with the molecular weight of nylon 6. Also, the ductile–brittle transition temperatures of toughened materials like nylon 6[44] and polycarbonate[45] have been reported to change with the molecular weight of the matrix phase. We can expect that changes in the molecular weight of nylon 6 or PP would affect the final properties of their blends in addition to any changes due to the morphology of the blend. This is illustrated by the tendency to higher ductile–brittle transition temperatures and lower impact strengths showed by blends with low molecular weight nylon 6. To some extent the decrease in room temperature Izod values shown in *Figure 18* as the PP molecular weight decreases may be attributed to this. These intrinsic effects of molecular weight are expected to be more important for the matrix phase of a blend than for the dispersed phase.

Figure 23 shows that nylon 6/PP blends in a 66/33 ratio and modified with 20% EPR-*g*-MA experience large changes in modulus as the molecular weight of either the nylon 6 or PP is varied. The modulus of these blends decreases with increasing nylon 6 molecular weight and with decreasing polypropylene molecular weight (increasing melt flow rate). These results are in part a consequence of the change in blend morphology that occurs as the molecular weights of polypropylene and nylon 6 are varied (see *Figures 20* and *22*). Blends where polypropylene is the continuous or co-continuous phase will undoubtedly show lower moduli than blends where nylon 6 forms the continuous phase, owing to the difference in elastic modulus between these two polymers (2.6 GPa for nylon 6 and 1.42 GPa for polypropylene). It has been reported for nylon 6/PP blends that the crystallization kinetics and the final degree of crystallinity of each component can be affected by the formation of graft copolymers[46,47]. A decreased degree of crystallinity of either the polypropylene or the nylon 6 phase could also be a contributing factor to the decrease in modulus observed for these blends. Such measurements were beyond the scope of the present study, but will be included in future work.

Equivalent experiments with SEBS-*g*-MA rubber were not performed; however, similar trends to those of the blends with EPR-*g*-MA may be expected.

CONCLUSIONS

Maleated rubbers such as EPR-*g*-MA and SEBS-*g*-MA were found to be good impact modifiers and compatibilizers for nylon 6/polypropylene blends. Both rubbers were equally effective for room temperature toughening.

The ductile–brittle transition temperature of these toughened blends depends on the amount and type of rubber used and its degree of dispersion, as well as on the weight fraction and degree of dispersion of the polypropylene phase. EPR-*g*-MA blends have lower ductile–brittle transition temperatures than blends based on SEBS-*g*-MA rubbers, evidently because of the lower modulus of the EPR-*g*-MA material at low temperatures. However, SEBS-*g*-MA seems to be a better compatibilizer than EPR-*g*-MA, as judged by the degrees

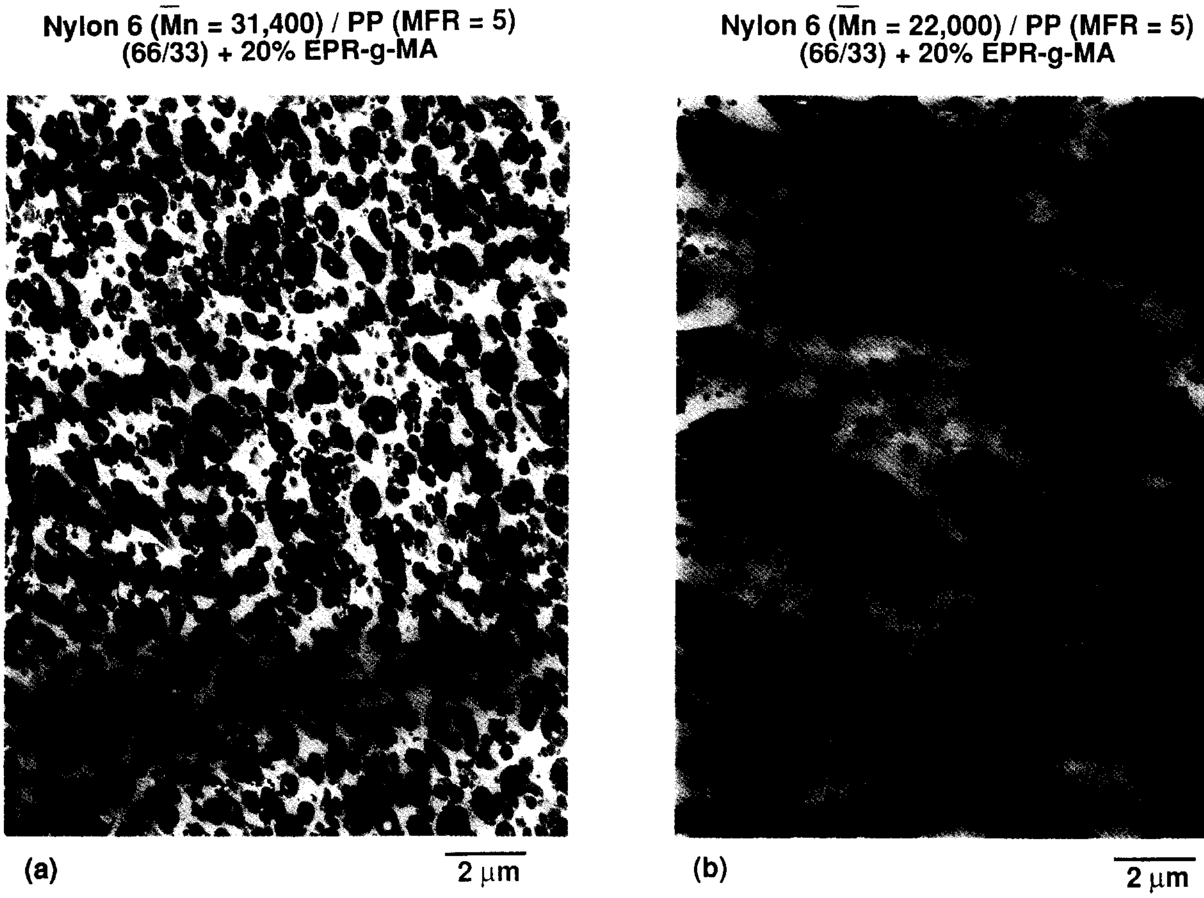


Figure 22 Morphology of a 66/33 nylon 6/PP (*MFR* = 5) blend modified with 20% EPR-*g*-MA as a function of nylon 6 molecular weight: (a) $\overline{M}_n = 31\,400$; (b) $\overline{M}_n = 22\,000$; (c) $\overline{M}_n = 16\,700$

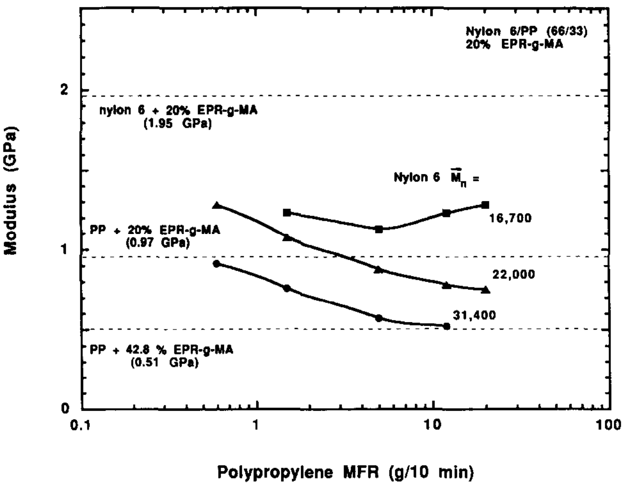


Figure 23 Effect of polypropylene molecular weight (expressed as *MFR*) and nylon 6 molecular weight on the modulus of 66/33 nylon 6/PP blends modified with 20% EPR-*g*-MA. The horizontal lines indicate the moduli for the binary blends nylon 6/EPR-*g*-MA and polypropylene/EPR-*g*-MA

of dispersion of polypropylene and the rubber in the blends. The lowest ductile–brittle transition temperatures for these blends are obtained when the nylon 6 is the continuous phase and the rubber and polypropylene are finely dispersed in it.

The molecular weights of nylon 6 and polypropylene affect the toughness of the blends through changes in morphology in response to the melt viscosity of these components. By simply adjusting component melt viscosities, nylon 6 or polypropylene can be made the continuous phase. Toughness was greatest for blends where the nylon 6 phase was continuous or co-continuous and the rubber was well dispersed in it. Molecular weight also influences the intrinsic ductility of the pure components.

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