

Blends of isotactic polypropylene and nitrile rubber: morphology, mechanical properties and compatibilization

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Morphology and mechanical properties of blends of isotactic polypropylene (PP) and nitrile rubber (NBR) have been investigated with special reference to the effects of blend ratio. Morphological observations of blends showed a two-phase system, in which the rubber phase was dispersed as domains in the continuous PP matrix at lower proportions of NBR ($\leq 50\%$). The 30/70 PP/NBR blend was found to exist as a co-continuous system. Attempts have been made to correlate the changes in morphology with properties. The mechanical properties of blends were found to depend on the blend ratio. Various composite models, such as the series model, the parallel model, the Halpin–Tsai equation and Coran's model, have been used to fit the experimental mechanical properties. The effect of concentration of maleic-modified polypropylene (MA-PP) and phenolic-modified polypropylene (Ph-PP) as compatibilizers on the morphology and mechanical properties of the blend was also investigated. The compatibilizer concentrations used were 1, 5, 10 and 15 wt%. The domain size of the dispersed NBR particles decreased with the addition of a few per cent of the compatibilizer followed by a levelling off at higher concentrations. The levelling off was an indication of interfacial saturation. The mechanical properties of the blends were improved by the addition of the compatibilizer followed by a levelling off at higher concentrations. The levelling off was an indication of interfacial saturation. The mechanical properties of the blends were improved by the addition of the compatibilizers. The experimental results were compared with the current compatibilization theories of Noolandi and Hong.

(Keywords: blends; morphology; compatibilization)

INTRODUCTION

Thermoplastic elastomers (TPEs) possess the excellent processing characteristics of thermoplastic materials at higher temperatures, and the wide range of physical properties of elastomers at service temperature^{1–5}. During the last few years, a large number of studies on thermoplastic elastomeric blends have been reported^{6–12}. A thorough understanding of the blend morphology is important, since the properties of polymer blends are strongly dependent on the blend morphology^{13–17}.

Most of the polymer blends are found to be incompatible. These incompatible blends are characterized by a two-phase morphology, narrow interphase, poor physical and chemical interactions across the phase boundaries and poor mechanical properties. These problems can be alleviated by the addition or *in situ* formation of compatibilizers or interfacial agents^{18,19}. According to Paul and Barlow²⁰, the addition of a suitably selected compatibilizer to binary immiscible blends should (1) reduce the interfacial energy between

the phases, (2) permit a finer dispersion during mixing, (3) provide a measure of stability against gross segregation, and (4) result in improved interfacial adhesion. The effect of addition of block and graft copolymers as compatibilizers in binary polymer blends has been studied in detail^{21–27}. Recently, the reactive compatibilization technique has been used for compatibilizing polyethylene (PE)/polystyrene (PS), polypropylene (PP)/nylon-6, PS/nylon-6, PP/PE, PS/EPDM and NR/PP systems^{28–35}.

Finally, thermodynamic theories concerning the emulsifying effect of block copolymers in polymer blends have been developed by Leibler^{36,37}, and Noolandi and Hong^{38–40}. The theory of Noolandi and Hong^{38–40} states that localization of some of the block copolymer at the interface results in a lowering of the interaction energy between two immiscible homopolymers, broadening of the interphase between homopolymers, and a decrease in free energy, and ultimately limits the amount of copolymer present at the interphase.

Blends of nitrile rubber (NBR) and PP combine the oil-resistant properties of nitrile rubber and the excellent mechanical and processing characteristics of PP. They can be successfully used for high-temperature, oil-

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resistant applications. However, these blends are found to be immiscible and incompatible. They are characterized by a sharp interface, coarse morphology and poor physical and chemical interactions across the phase boundaries. Although some studies have been reported^{41,42} on the thermodynamics, structural properties and compatibilization of NBR/PP blends, detailed investigations relating morphology to the properties and compatibilizing efficiency to the nature and concentration of the copolymer are lacking. The purpose of the present study is to investigate systematically the influence of blend ratio on the morphology and mechanical properties of NBR/PP blends. The effects of concentration of two compatibilizers, maleic-modified PP and phenolic-modified PP, on the morphology and mechanical properties of the blend were investigated quantitatively. The experimental results were applied to test the current compatibilization theories of Noolandi and Hong.

EXPERIMENTAL

Materials

Isotactic PP (Koylenc M3060) with a melt flow index of 3 g/10 min was supplied by IPCL, Vadodara, India. NBR, with 32% acrylonitrile content, was supplied by Synthetics and Chemicals, Bareilly, U.P., India.

Maleic-modified PP (MA-PP) was prepared by melt mixing PP with maleic anhydride (5 parts), benzoquinone (0.75 parts) and dicumyl peroxide (3 parts) in a Brabender Plasticorder at 180°C (ref. 11). Phenolic-modified PP (Ph-PP) was prepared by melt-mixing PP with dimethylol phenolic resin (Sp-1045; 4 parts) and stannous chloride (0.8 parts) at 180°C (ref. 11).

Blend preparation

The blends are referred to as P₀, P₃₀, P₅₀, P₇₀ and P₁₀₀, where the subscripts denote the weight percentage of PP in the blend. These blends were prepared in a Brabender Plasticorder (model PLE-330) at a temperature of 180°C. The rotor speed was 60 rev min⁻¹ and the blending was carried out for 6 min. The compatibilizer concentrations used were 1, 5, 10 and 15 wt%.

Physical testing of the samples

The samples for physical property measurements were prepared by compression-moulding the mixes at 180°C in a hydraulic press into sheets with dimensions 15 cm × 15 cm × 0.15 cm. The tensile property measurements were done on a Zwick Universal Testing machine (model 1474) using dumb-bell shaped specimens at a crosshead speed of 500 mm min⁻¹, in accordance with ASTM D412-81. The tensile impact strength of the samples was measured on a Ceast Impact Tester (model 6545/000) using dumb-bell shaped specimens. The hardness of the samples was measured using shore A and shore D Hardness Durometer. The crystallinity of the samples was measured using a Perkin-Elmer DSC differential scanning calorimeter. The weight percentage crystallinity of PP was determined from the ratio of the heat of fusion of the blend to that of the 100% crystalline PP ($\Delta H_{pp} = 138 \text{ J g}^{-1}$ (ref. 43)).

Morphology studies

The samples for morphology studies were prepared by cryogenically fracturing the samples in liquid nitrogen.

The fractured end of the sample was kept immersed in chloroform for two weeks. The samples were then dried in an oven. For morphology studies, samples (the NBR phase was preferentially extracted) were sputter-coated with gold and photographs were taken in a JEOL scanning electron microscope. The domain size was measured from the scanning electron photomicrographs. Several micrographs were taken for each blend and about 100 domains were taken for number-average domain diameter measurements. The apparent domain diameter was obtained from the measurement of hole diameter obtained as a result of the extraction of the rubber phase.

RESULTS AND DISCUSSION

Processing characteristics

The processing characteristics of the blends have been studied from the Brabender Plastographs. The torque–time and torque–temperature relationships obtained from Brabender plastographs are shown in Figure 1. In all cases, the mixing torque falls rapidly up to 3 min of mixing time and then levels off to give uniform values at the end of the mixing cycle, indicating a good level of mixing. Favis¹⁷ has reported that the final morphology of the blend is strongly influenced by the time of mixing. All the blends show a higher mixing torque than PP, and the torque is found to increase with increase in NBR content. This is due to the higher melt viscosity of NBR as compared to PP. This result clearly indicates that all the blends have higher melt viscosity than PP. It is also seen from Figure 1 that the mixing temperature of the blends increases with increase in NBR content. This is due to the fact that high shear forces are involved as the NBR content increases owing to its higher viscosity as compared to PP.

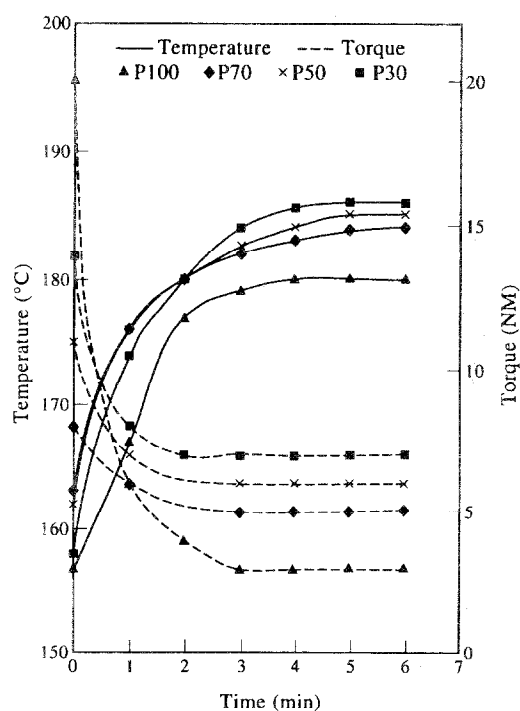


Figure 1 Brabender plastograph showing the variation of mixing torque and temperature with time of mixing

Morphology of the binary blends

The morphology of heterogeneous polymer blends depends on blend composition, viscosity of individual components and processing history. Danesi and Porter¹⁴ have shown that for blends with the same processing history, the morphology is determined by the melt viscosity ratio and composition. Generally, the least viscous component was observed to form the continuous phase over a larger composition range⁴⁴.

The scanning electron micrographs of blends P₇₀, P₅₀ and P₃₀, from which the NBR phase has been extracted, are shown in Figures 2a to c. In the P₇₀ blend, NBR is found to be dispersed as domains in the continuous PP matrix. This is due to the higher melt viscosity and lower content of NBR compared to PP in the blend. As the rubber content in the blend increases from 30 to 50 wt% NBR, the average size of the dispersed NBR phase increases from 5.87 to 17.90 μm . The bigger particle size of the rubber phase with increase in rubber content is attributed to the reagglomeration or coalescence of the dispersed rubber particles. The occurrence of coalescence at higher concentrations of one of the components has been reported by many authors^{45–47}. In the P₃₀ blend, both NBR and PP phases exist as co-continuous phases. This is associated with the higher proportions of NBR and low viscosity of the PP phase.

Mechanical properties

The properties of rubber–plastic blends are determined by (1) material properties of rubber and plastic phases, (2) rubber/plastic proportions, (3) the phase morphology, and (4) the interaction at the interface⁴⁸. The stress–strain curves of the P₁₀₀, P₇₀, P₅₀, P₃₀ and P₀ blends are shown in Figure 3. From the stress–strain curves it is possible to determine the differences in the deformation characteristics of the blends under an applied load. The stress–strain curve of PP is similar to that of a brittle material. It shows very high initial modulus with a definite yield point. The addition of NBR changes the nature of stress–strain curves considerably. The stress–strain curves of PP and blends containing a higher proportion of PP have distinct elastic and inelastic regions. In the inelastic region they undergo yielding. The elastic moduli of the blends are found to be considerably reduced with the increase in rubber concentration. The improved rubbery behaviour of P₃₀ blend compared to P₇₀ and P₅₀ can be explained in terms of the phase inversion of NBR from dispersed to continuous phase on passing from P₅₀ to P₃₀. The stress–strain behaviour of NBR is typical of uncross-linked soft elastomer.

Table 1 and Figure 4 show the variation of mechanical properties as a function of weight percentage of NBR.

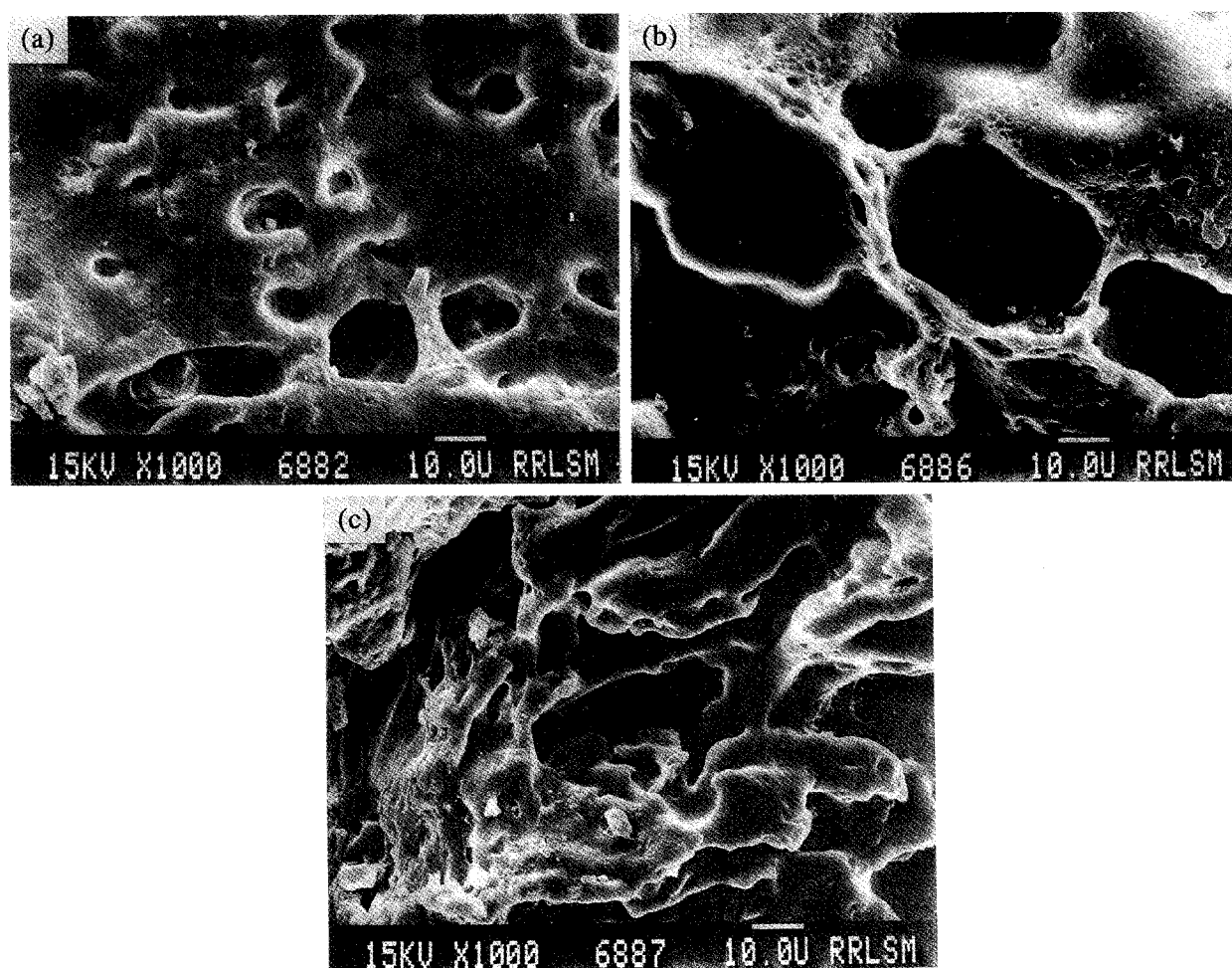


Figure 2 Scanning electron photomicrographs of NBR/PP blends from which NBR was extracted with chloroform. (a) 30/70 NBR/PP blend: NBR is dispersed as domains in the continuous PP matrix. (b) 50/50 NBR/PP blend: NBR is dispersed as domains in the continuous PP matrix. (c) 70/30 NBR/PP blend with co-continuous morphology

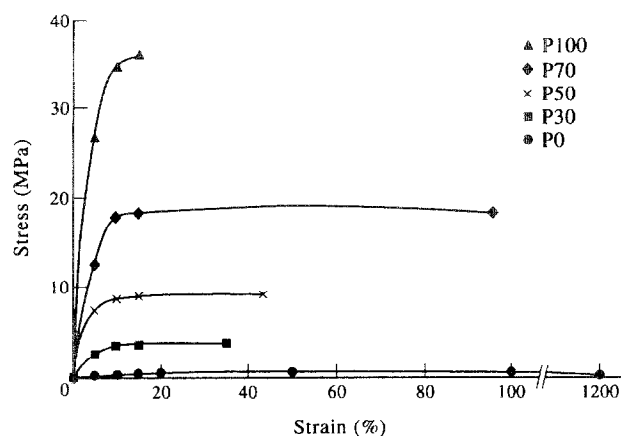


Figure 3 Stress-strain curves of the samples

Pure isotactic PP has the highest tensile strength and Young's modulus. From the table it is seen that with increase in NBR content, the tensile strength and Young's modulus decrease. The strength of NBR/PP blends depends on the strength of the PP phase, which in turn depends on the extent of crystallinity. It has been observed that the crystallinity of the blend was decreased by the incorporation of NBR (Table 2). Martuscelli *et al.*⁴⁹ have shown that the spherulite growth of isotactic PP in blends with rubber is hindered by the presence of the rubber phase. Hence the observed decrease in tensile strength and Young's modulus with increase in NBR content is due to the presence of the soft rubber phase and fall in crystallinity of the PP phase. It can be noticed from Figure 4 that the tensile strength-composition curve shows a negative deviation, i.e. blend properties lie below the additivity line. The observed negative deviation is due to the poor interfacial adhesion between the non-polar PP and polar NBR phases, which causes poor stress transfer between the matrix and the dispersed phase. A clear change in the slope of this tensile strength-composition curve is seen between the composition range 50/50 PP/NBR to 30/70 PP/NBR. The observed change in slope is attributed to phase inversion of NBR from dispersed phase to continuous phase. This type of slope change in a mechanical property-composition curve has been reported by Danesi and Porter for the PP/EPDM system¹⁴.

The elongation at break of the PP/NBR blend is found to increase with the addition of 30 wt% NBR and after that it decreases with increase in rubber content (Table 1). The elongation at break also shows negative deviation. This decrease in elongation at break at

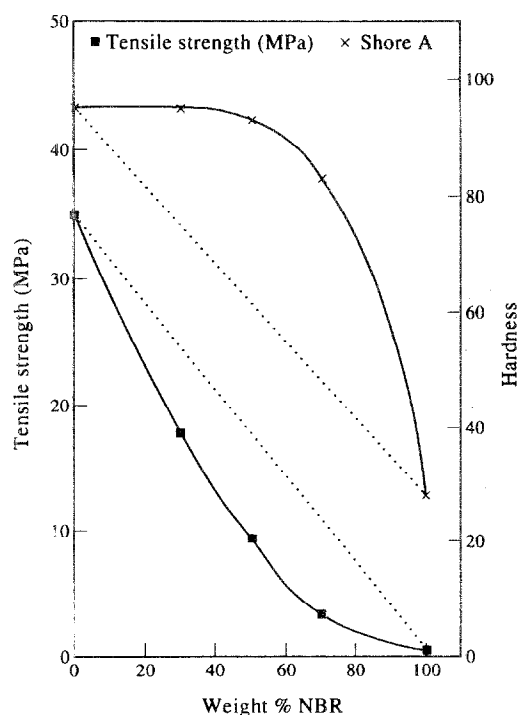


Figure 4 Effect of weight percentage of NBR on tensile strength and shore A hardness of NBR/PP blends

Table 2 Crystallinity of PP/NBR blends

Composition	Crystallinity (%)
P ₁₀₀	55.3
P ₇₀	33.9
P ₅₀	20.9
P ₃₀	13.7

higher rubber content is due to the poor interfacial adhesion between the homopolymers.

From Table 1 it is also seen that the tensile impact strength decreases with the addition of NBR up to 50 wt%. In immiscible blends, the tensile impact strength usually depends on the particle size of the dispersed phase. Smaller and uniformly distributed particles are more effective at initiating crazes and terminating them before they develop into catastrophic sizes. The decrease in tensile impact strength in PP/NBR blends up to 50 wt% NBR content is due to the poor interfacial adhesion and bigger particle size of the dispersed NBR phase, as seen in the scanning electron photographs of P₇₀ and P₅₀ blends. The poor interfacial adhesion causes

Table 1 Variation of mechanical properties with blend composition

Property	Composition				
	P ₁₀₀	P ₇₀	P ₅₀	P ₃₀	P ₀
Tensile strength (MPa)	35	18.30	9.20	3.50	0.475
Young's modulus (MPa)	500	250	135	47	1.5
Elongation at break (%)	15.6	95.58	43.45	38.64	1267
Tensile impact strength (J m ⁻¹)	1110	1008	920	1448	—
Hardness shore A	95	95	93	83	28
Hardness shore D	55	55	45	18	—

premature failure as a result of the usual crack-opening mechanism. Karger-Kocsis *et al.*⁵⁰ have shown that with increase in particle size of the dispersed rubber phase, the tensile impact strength of the PP/EPDM blend decreases. Above 50 wt% NBR content, the tensile impact strength is found to increase sharply. This sharp increase in impact strength may be due to the continuous nature of the NBR phase, which forms a co-continuous structure with the plastic phase (Figure 2). Similar results were reported in the case of the PP/EVA system⁵¹.

From Table 1 it is seen that the addition of 30 wt% NBR does not change the hardness. However, further addition of NBR decreases the hardness. The hardness–composition curve shows a slope change beyond 50 wt% NBR (Figure 4). The reduction in hardness and the slope change in the curve at higher proportions of NBR (>50%) can be explained by the phase inversion of NBR from dispersed to the continuous phase on passing from the 50/50 PP/NBR to the 30/70 PP/NBR blend. It is interesting to see that the hardness values show a positive deviation.

Various composite models, such as the parallel model, the series model, the Halpin–Tsai equation and Coran's equation, have been used to predict the mechanical properties of these blends. The highest-upper-bound

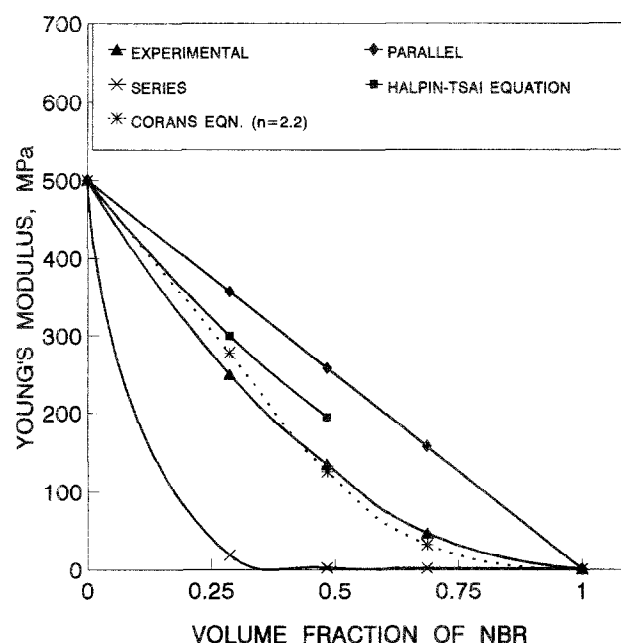


Figure 5 Experimental and theoretical values of Young's modulus as a function of volume fraction of NBR phase

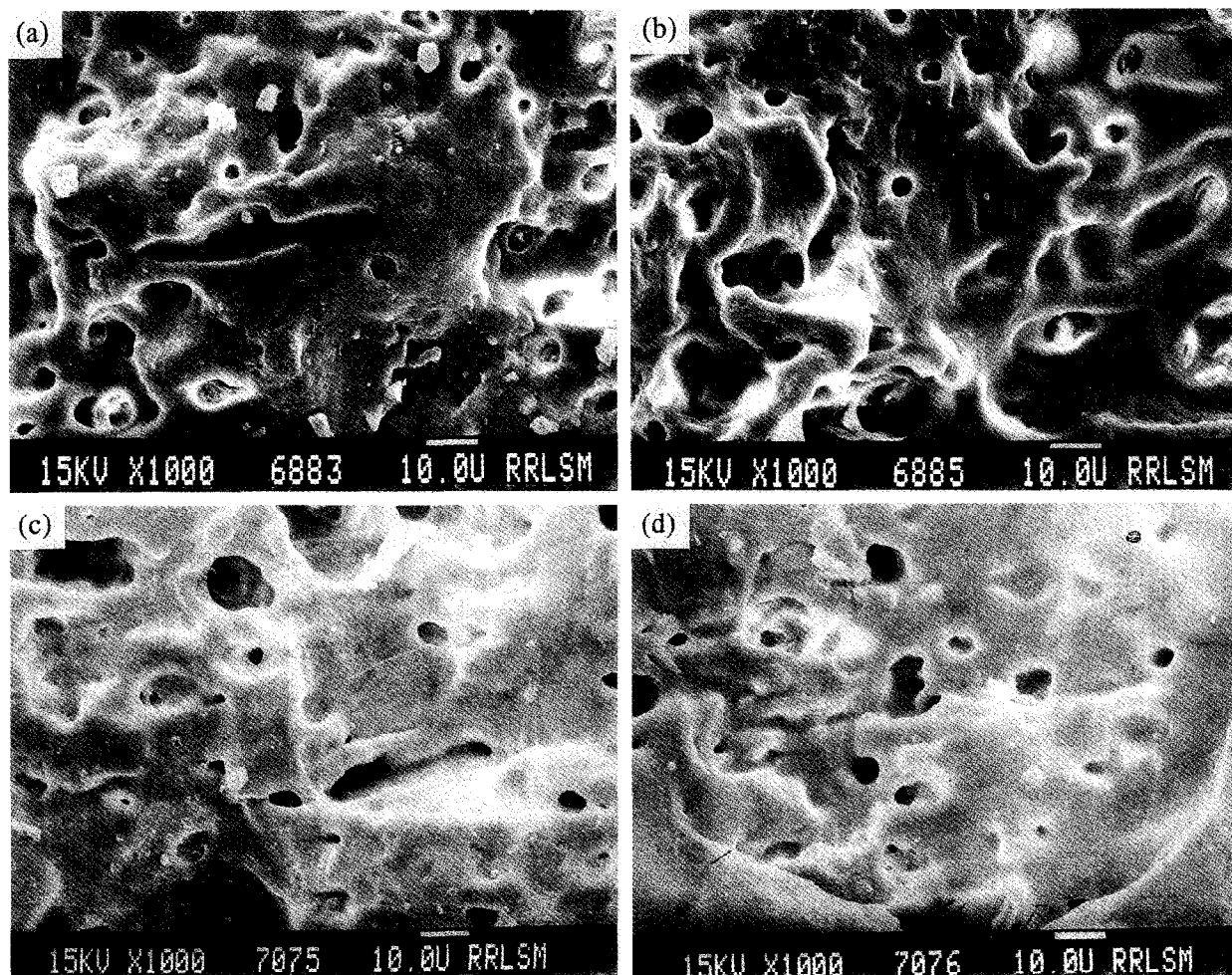


Figure 6 Scanning electron micrographs of 30/70 NBR/PP blend compatibilized with MA-PP: (a) 1% MA-PP; (b) 5% MA-PP; (c) 10% MA-PP; (d) 15% MA-PP

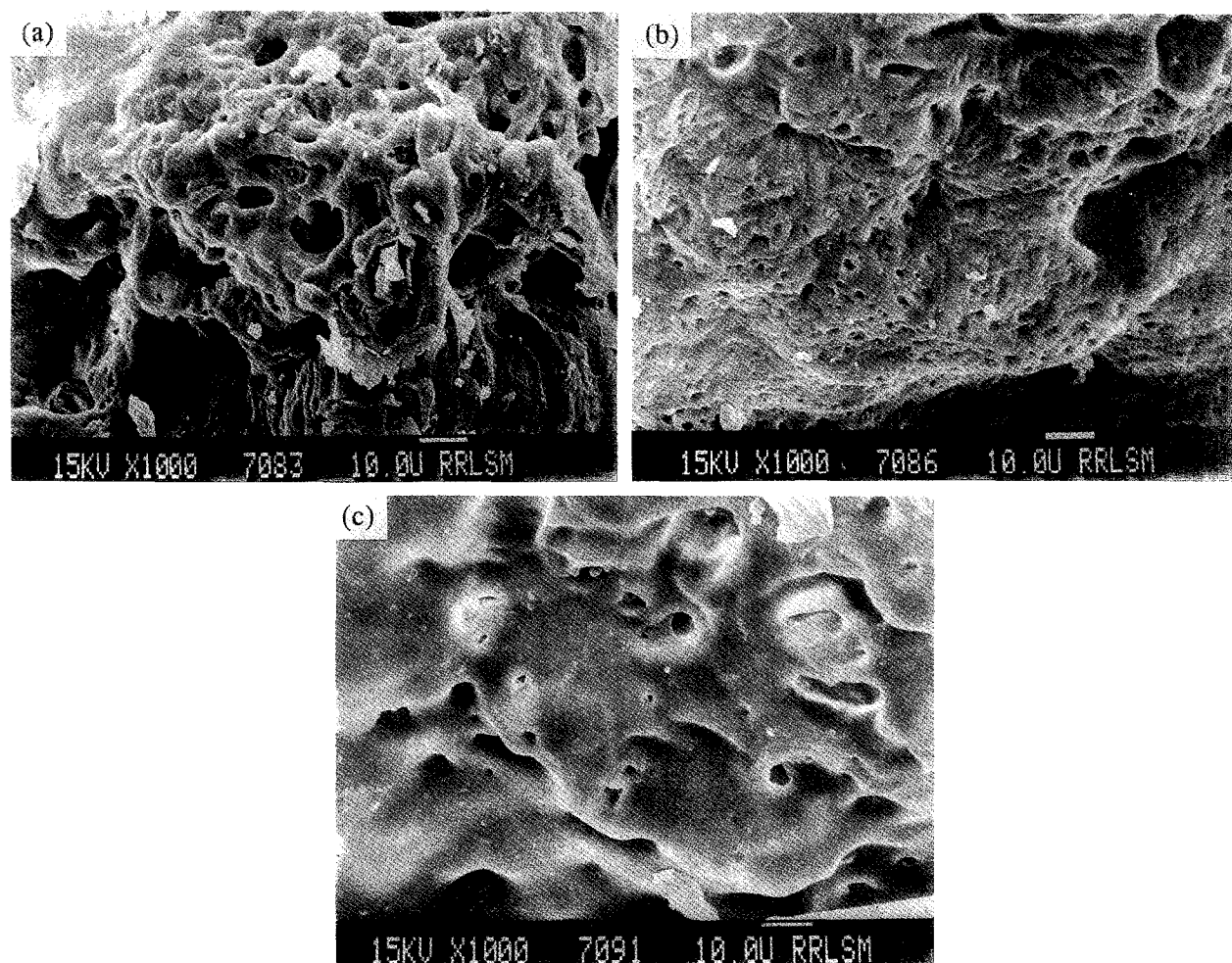


Figure 7 Scanning electron micrographs of 30/70 NBR/PP blend compatibilized with Ph-PP: (a) 1% Ph-PP; (b) 10% Ph-PP; (c) 15% Ph-PP

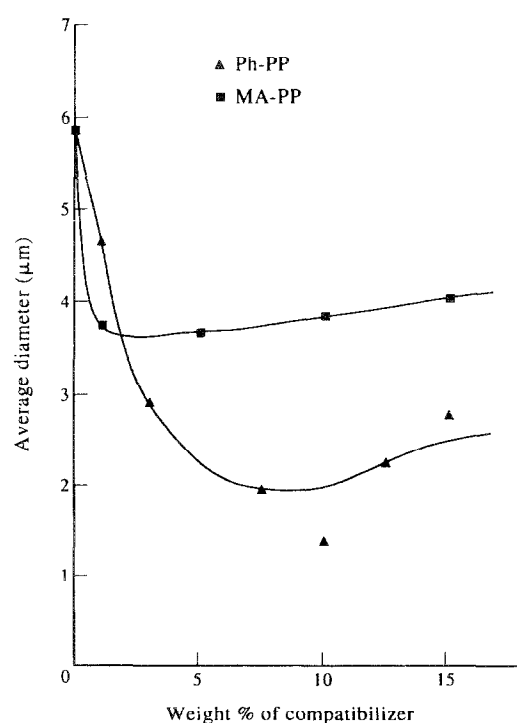


Figure 8 Effect of compatibilizer concentration on the domain size of the dispersed phase of 30/70 NBR/PP blend

parallel model is given by the rule of mixtures:

$$M = M_1\phi_1 + M_2\phi_2 \quad (1)$$

where M is any mechanical property of the composite, M_1 and M_2 are the mechanical properties of components 1 and 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively. This equation holds for models in which the components are arranged parallel to one another so that an applied stress elongates each component by the same amount. The lowest-lower-bound series model is found in models in which the components are arranged in series with the applied stress. The equation for this case is:

$$1/M = \phi_1/M_1 + \phi_2/M_2 \quad (2)$$

According to the Halpin-Tsai equation^{52,53}:

$$M_1/M = (1 + AiBi\phi_2)/(1 - Bi\phi_2) \quad (3)$$

$$Bi = (M_1/M_2 - 1)/(M_1/M_2 + Ai) \quad (4)$$

In the Halpin-Tsai equation, subscripts 1 and 2 refer to the continuous phase and dispersed phase respectively. The constant Ai is defined by the morphology of the system. For elastomer domains dispersed in a continuous hard matrix, $Ai = 0.66$.

For an incompatible blend, mechanical properties are generally between the parallel model upper bound (M_U) and the series model lower bound (M_L). According to

Coran's equation⁴⁸:

$$M = f(M_U - M_L) + M_L \quad (5)$$

where f can vary between zero and unity. The value of f is a function of phase morphology. The value of f is given by:

$$f = V_H^n (nV_S + 1) \quad (6)$$

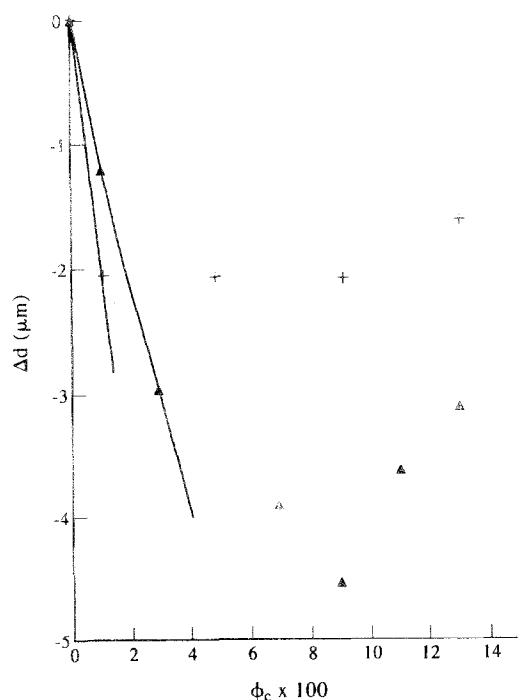


Figure 9 Effect of volume fraction of compatibilizer on the particle size reduction of 30/70 NBR/PP blend

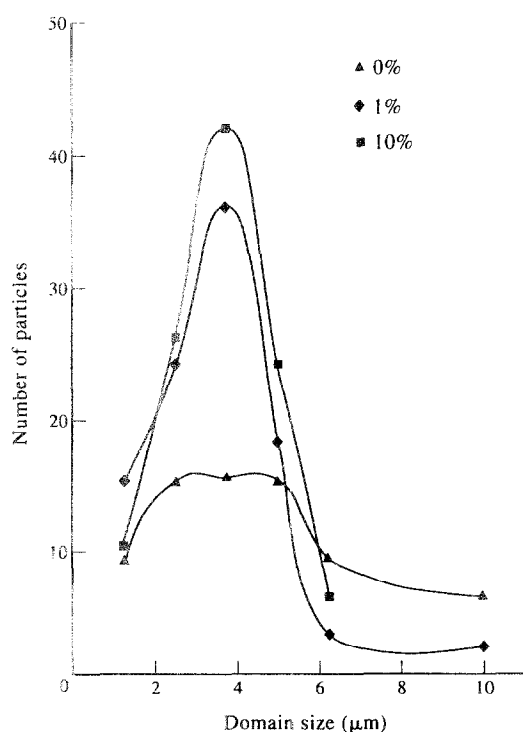


Figure 10 Effect of MA-PP concentration on domain size distribution of 30/70 NBR/PP blend

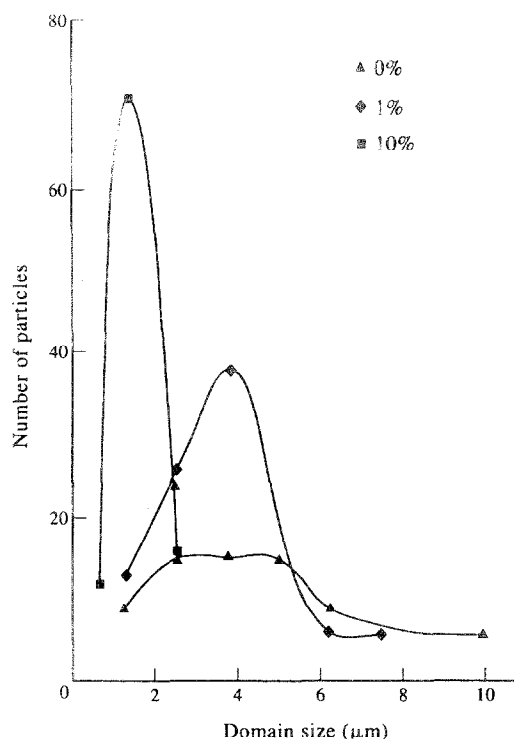


Figure 11 Effect of Ph-PP concentration on domain size distribution of 30/70 NBR/PP blend

where n contains the aspects of phase morphology, and V_H and V_S are the volume fractions of the hard-phase and soft phase, respectively. The change in f with respect to V_H is greatest when $V_H = (n - 1)/n$, thus the value of $(n - 1)/n$ could be considered as the volume fraction of hard-phase material that corresponds to a phase inversion.

Figure 5 shows the experimental and theoretical curves of Young's modulus as a function of soft-phase volume fraction. It can be seen that experimental data are very close to Coran's model, in which $n = 2.2$. The value of $n = 2.2$ corresponds to $V_H = 0.545$, as the hard-phase volume fraction that corresponds to a phase inversion of NBR from dispersed phase to continuous phase. This result is consistent with our experimental results from morphology and mechanical property studies.

COMPATIBILIZATION

Morphology of compatibilized blends

The effect of MA-PP and Ph-PP as compatibilizers on the morphology of the 70/30 PP/NBR blend is shown by the scanning electron micrographs of Figures 6 and 7, respectively. Figures 6a–d show blends containing 1%, 5%, 10% and 15% MA-PP compatibilizer, respectively, and Figures 7a–c show blends containing 1%, 10% and 15% Ph-PP compatibilizer, respectively. The morphology of an uncompatibilized blend has been given in Figure 2a. From the scanning electron micrographs it is seen that the size of the dispersed NBR phase decreases with the addition of modified polymers. This reduction in particle size with the addition of modified polymers is due to the reduction in interfacial tension between the dispersed NBR phase and PP matrix.

The average domain sizes of the compatibilized blends were analysed as a function of compatibilizer concentration (Figure 8). The average domain size of the

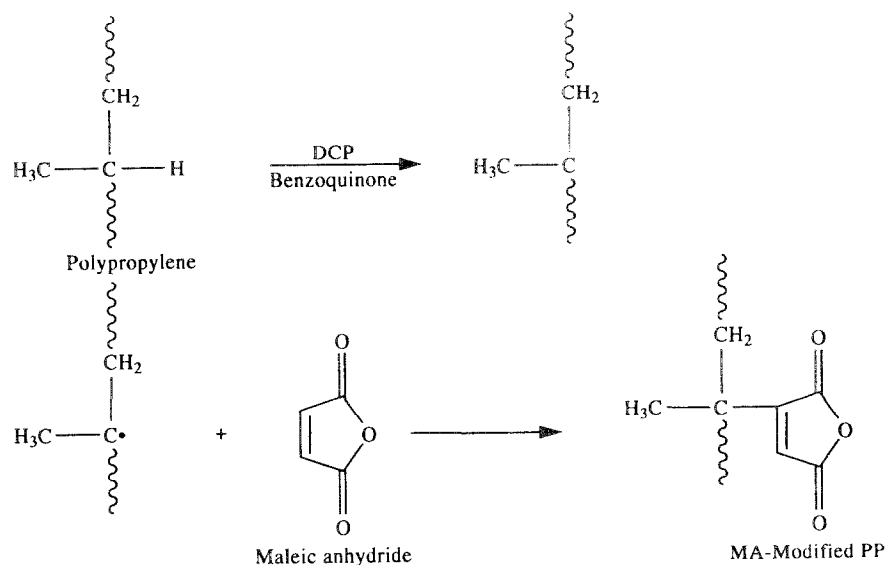


Figure 12 Reaction scheme for the maleic anhydride modification of polypropylene

unmodified blend is $5.87\ \mu\text{m}$. From Figure 8, it is seen that in the case of MA-PP compatibilized blends, addition of 1% MA-PP causes a reduction in domain size of 35%. Further addition of MA-PP does not change the domain size considerably, but a levelling off is observed. In the case of Ph-PP compatibilized blends, the average diameter of the dispersed NBR phase decreases up to the addition of 10 wt% Ph-PP. With 10 wt% Ph-PP, the domain size is reduced by 77% of the domain size of the unmodified blend. However, further addition of compatibilizer increases the domain size. The equilibrium concentration at which the domain size levelled off can be considered as the critical micelle concentration (*CMC*), i.e. the concentration at which micelles are formed. Generally, *CMC* is estimated from the plot of interfacial tension *versus* copolymer concentration. Since the interfacial tension is directly proportional to the domain size, the estimation of *CMC* from the plot of domain size *versus* concentration is warranted⁵⁴. The *CMC* indicates the critical amount of compatibilizer required to saturate unit volume of interface. The increase in domain size above *CMC* may be due to the formation of micelles of compatibilizer at the continuous PP phase. Several authors have reported on the interfacial saturation of binary polymer blends by the addition of compatibilizers^{27,35,55,56}. Thomas and Prud'homme²⁷ reported that in PS/poly(methyl methacrylate) blends at lower concentrations of copolymer, the dispersed phase size decreased linearly with increasing copolymer concentration, whereas at higher concentration, it levelled off. Noolandi and Hong also suggested that there is a critical concentration of block copolymer at which micelles are formed in the homopolymer phases. All the above experimental observations, including the present study and theoretical predictions of Noolandi and Hong, suggest that a critical concentration of compatibilizer is required to saturate the interface of a binary blend. Above this critical concentration the compatibilizer may not modify the interface any more, but forms compatibilizer micelles in the bulk phase.

The interfacial saturation point can be further

explained by Taylor's theory. In Taylor's theory⁵⁷ of particle deformation, the critical Weber number, *We*, is given by the equation:

$$We = \frac{\eta_m dn \dot{\gamma}}{2\tau_{12}} \quad (7)$$

where η_m is the viscosity of the matrix, dn is the number-average diameter of the dispersed phase, $\dot{\gamma}$ is the shear rate and τ_{12} is the interfacial tension. From the equation it is clear that there is a critical value of *We* below which there is no particle deformation and, as a result, a critical particle size. At this point the compatibilizer attains the maximum possible interfacial area and therefore there must be a maximum quantity of compatibilizer required to saturate the interface.

The theories of Noolandi and Hong can be applied to these highly incompatible PP/NBR blends for concentrations less than *CMC*. According to them the interfacial tension is expected to decrease linearly with the addition of compatibilizer below *CMC*, and above the *CMC* a levelling off is expected. The expression for interfacial tension reduction (Δr) in a binary blend A/B upon the addition of divalent copolymer A-b-B is given by⁴⁰:

$$\Delta r = d\phi_c[(1/2\chi + 1/Z_c) - 1/Z_c \exp(Z_c\chi/2)] \quad (8)$$

where d is the width at half-height of the copolymer profile given by the Kuhn statistical segment length, ϕ_c is the bulk volume fraction of the copolymer in the system, χ is the Flory-Huggins interaction parameter between A and B segments of the copolymer, and Z_c is the degree of polymerization of the copolymer. According to this equation, the plot of interfacial tension reduction *versus* ϕ_c should yield a straight line. Although this theory was developed for the action of symmetrical diblock copolymer A-b-B in incompatible binary systems (A/B), this theory can be successfully applied to other systems in which the compatibilizing action is not strictly by the addition of symmetrical block copolymers⁵⁸. Since interfacial tension reduction is directly proportional to the particle size reduction, as suggested by Wu⁵⁴, we can replace the interfacial tension reduction term by the

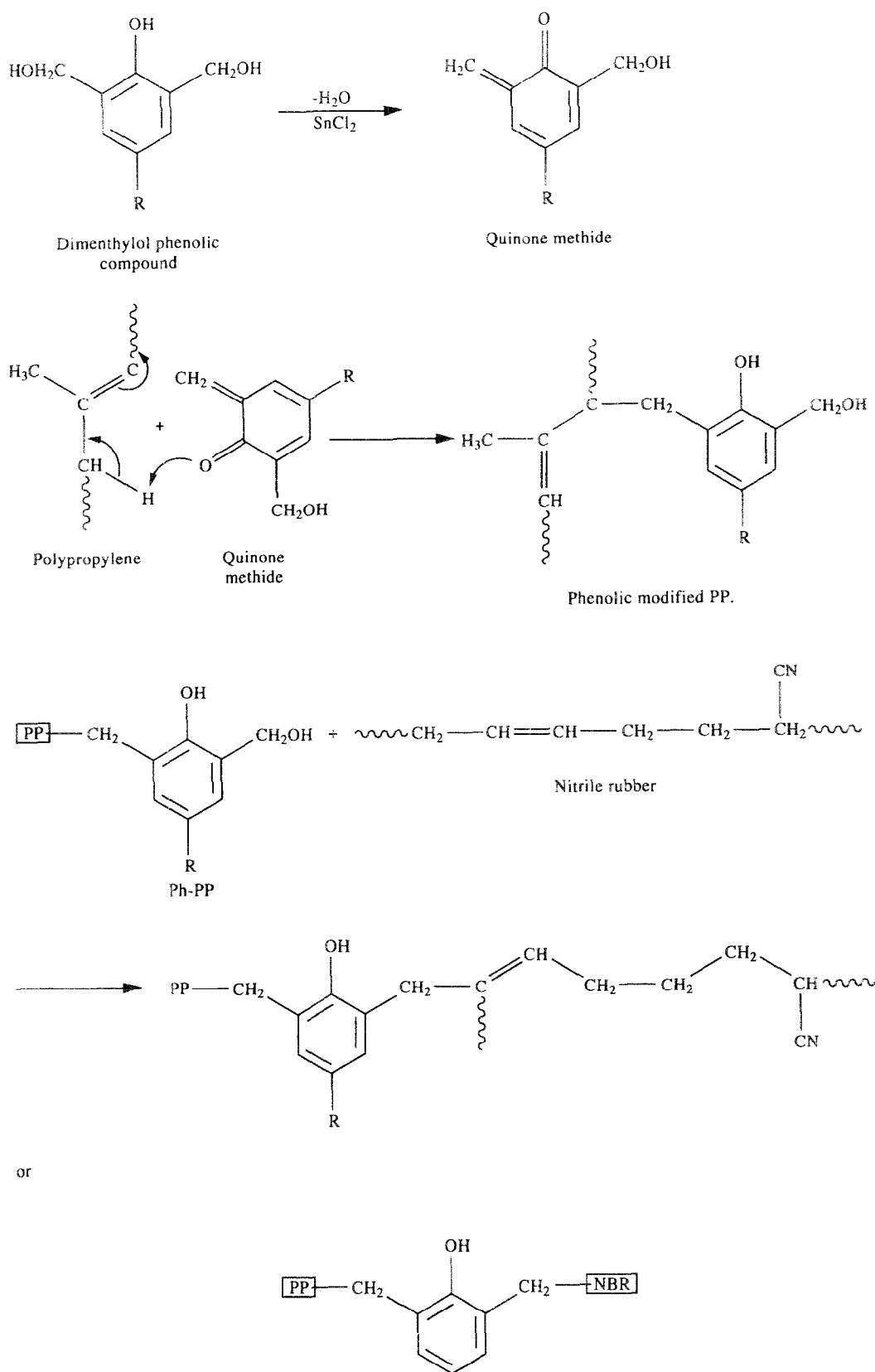


Figure 13 Reaction scheme for the dimethylol phenolic resin modification of polypropylene

particle size reduction (Δd) term in Noolandi and Hong's equation. Therefore:

$$\Delta d = Kd\phi_c[(1/2\chi + 1/Z_c) - 1/Z_c \exp(Z_c\chi/2)] \quad (9)$$

where K is a proportionality constant.

The plot of particle size reduction as a function of the

volume percentage of compatibilizer is shown in Figure 9. It can be seen that at low copolymer concentrations (below the CMC), d decreases linearly with increasing copolymer volume fraction, whereas at higher concentrations (above the CMC) it levels off, in agreement with the theories of Noolandi and Hong.

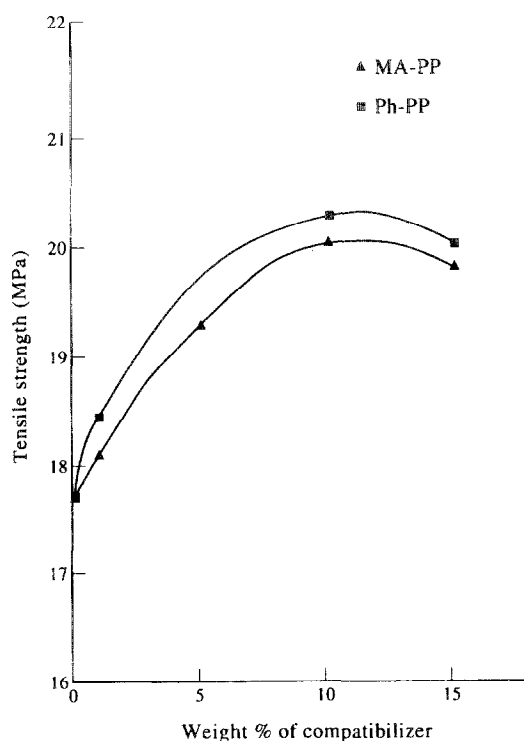


Figure 14 Effect of compatibilizer concentration on the tensile strength of 30/70 NBR/PP blend

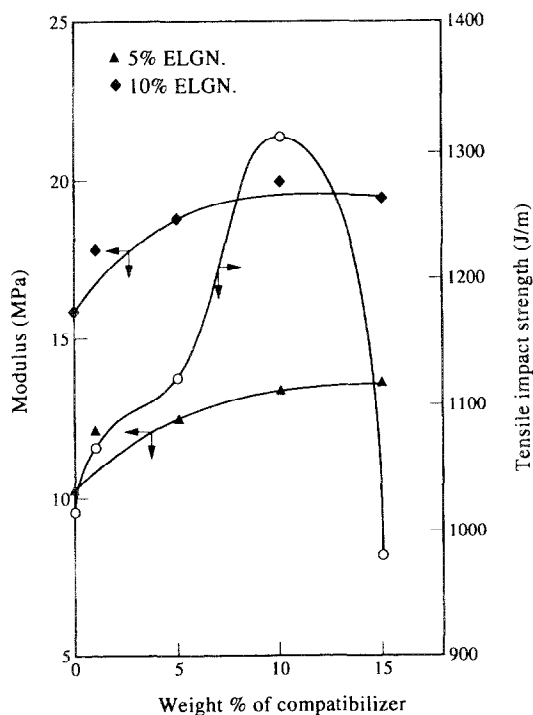


Figure 15 Effect of Ph-PP concentration on the modulus at 5% and 10% elongation and tensile impact strength of 30/70 NBR/PP blend

The domain size distribution curves for the MA-PP and Ph-PP compatibilized blends are shown in Figures 10 and 11, respectively. In the case of the unmodified blend, a high degree of polydispersity is evident by the large width of the distribution curve. With increasing concentration of compatibilizer (Ph-PP and MA-PP), the polydispersity decreases, as evident by the decrease in the

width of the distribution curve. In the case of the Ph-PP compatibilized blend, a very narrow distribution is obtained with the addition of 10% Ph-PP. Willis and Favis³⁵ have also shown that the addition of compatibilizer to polyolefin/polyamide system not only reduces the dimensions of the minor phase, but also results in uniform distribution of the minor phase.

The mechanism of compatibilization and the difference in the behaviour of MA-PP and Ph-PP as compatibilizers in NBR/PP blends can be explained as follows. In the MA-PP, maleic anhydride groups are grafted onto the PP chain backbone¹¹ as shown in Figure 12. The compatibilizing action of MA-PP is due to the dipolar interaction between the maleic anhydride groups of MA-PP and NBR. This causes a reduction in interfacial tension, which reduces the domain size of the dispersed phase. In Ph-PP, dimethylol groups are grafted onto the PP chain, as shown in Figure 13. At low concentration of Ph-PP ($\leq 5\%$), the compatibilizing action is only due to the dipolar interaction between the dimethylol phenolic groups and NBR. But on reaching 10% Ph-PP concentration, there is a possibility of the formation of graft copolymer between Ph-PP and NBR¹¹, as shown in Figure 13. This graft copolymer acts as an emulsifier at the interface and thus reduces the interfacial tension, leading to small and uniform distribution of the NBR phase as seen in the scanning electron micrograph of the 10% Ph-PP compatibilized blend.

Mechanical properties of compatibilized blends

The mechanical properties of immiscible polymer blends are affected by the addition of compatibilizers. Figure 14 shows the variation of tensile strength of the 70/30 PP/NBR blend with weight percentage of two compatibilizers, Ph-PP and MA-PP. With increase in compatibilizer concentration the tensile strength is found to increase up to 10 wt% of compatibilizer and then levels off for both compatibilizers. This increase in tensile strength is due to the increase in interfacial adhesion between PP and NBR phases which is evident from the scanning electron micrographs. The highest tensile strength of the 10 wt% Ph-PP compatibilized blend is due to the lowest particle size of NBR domains in this system. In the case of MA-PP compatibilized blends, the increase in tensile strength is due to the increased dipolar interaction between the MA-PP and NBR phase, which causes an increase in interfacial adhesion between PP and NBR phases, although there is no reduction in particle size with the increase in MA-PP concentration beyond 1%. Similar results have been reported for the Nylon/PP system²⁹.

The variation of tensile modulus at 5% and 10% elongation and tensile impact strength with the Ph-PP concentration is shown in Figure 15. The tensile modulus is found to increase with increase in concentration of Ph-PP up to 10%, and after that it levels off.

From Figure 15 it is seen that the tensile impact strength of the blend increases significantly with the addition of up to 10% Ph-PP, and after that it decreases drastically. This result is consistent with the literature reports on the increase of tensile impact strength with reduction in particle size of the dispersed phase. The reduction in tensile impact strength for the blend containing 15 wt% Ph-PP is due to the formation of

compatibilizer micelles in the homopolymer phases. Similar results have been reported for the low-density polyethylene/polydimethylsiloxane system⁵⁹.

CONCLUSION

The morphology and properties of thermoplastic elastomers from nitrile rubber (NBR) and polypropylene (PP) have been studied, with special reference to the effects of blend ratio and compatibilizing agents. The processability characteristics analysed from the Brabender plastographs show that the viscosity of NBR/PP blends increases with increase in NBR content. The morphology of the blends indicates a two-phase structure in which the rubber phase is dispersed as domains in the continuous PP matrix at lower proportions of NBR, and the size of the domains increases with increase in rubber content. At 70 wt% of NBR, it also forms the continuous phase, resulting in a co-continuous morphology. The mechanical properties of the blends are found to be strongly influenced by the blend ratio. The Young's modulus, tensile strength and hardness of the blends were decreased with increase in NBR content. The tensile impact strength decreases with up to 50 wt% NBR content and after that it shows an increase. In general, all the mechanical property-composition curves show a change in slope after 50 wt% NBR. This is associated with the change in morphology of the blends. A negative deviation from the additive line was observed for all mechanical properties except hardness. Various composite models have been used to fit the experimental mechanical data. The tensile strength and Young's modulus of the blends could be predicted by Coran's equation. The phenolic-modified PP and maleic-modified PP are found to act as compatibilizers in PP/NBR blends. With increase in concentration of compatibilizers, the domain size of the dispersed NBR phase decreases, followed by a levelling off at higher concentrations, which is an indication of interfacial saturation. The theories of Noolandi and Hong predict a linear decrease of interfacial tension with compatibilizer volume fraction for concentrations less than the CMC. Considering the fact that the interfacial tension is directly proportional to the domain size, it is demonstrated that the experimental data are in agreement with these theories. The mechanical properties of the blend are found to increase with the addition of compatibilizers, followed by a levelling off at higher concentration.

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REFERENCES

- Walker, B. M. (Ed.) 'Handbook of Thermoplastic Elastomers', Van Nostrand Reinhold, New York, 1979
- Legge, N. R., Holden, G. and Schoeder, H. E. (Eds) 'Thermoplastic Elastomers - A Comprehensive Review', Hanser Publishers, Munich, 1987
- Bhowmick, A. K. and Stephens, H. L. (Eds) 'Handbook of Elastomers - New Developments and Technology', Marcel Dekker, New York, 1988
- De, S. K. and Bhowmick, A. K. (Eds) 'Thermoplastic Elastomers from Rubber - Plastic Blends', Ellis Horwood, New York, 1990
- Wheelan, A. and Lee, K. S. (Eds) 'Thermoplastic Rubbers in Developments in Rubber Technology', Applied Science Publishers, New York, 1988
- Kresge, E. N. *J. Appl. Polym. Sci. Appl. Polym. Symp.* 1984, **39**, 37
- Campbell, D. S., Elliot, D. J. and Wheelans, M. A. *NR Technol.* 1978, **9**, 21
- Kuriakose, B. and De, S. K. *Polym. Eng. Sci.* 1985, **25**, 630
- Akhtar, S., De, P. P. and De, S. K. *Mater. Chem. Phys.* 1985, **12**, 235
- Coran, A. Y., Patel, R. and Williams, D. *Rubber Chem. Technol.* 1982, **55**, 116
- Coran, A. Y. and Patel, R. *Rubber Chem. Technol.* 1983, **56**, 1045
- Coran, A. Y., Patel, R. and Williams, D. *Rubber Chem. Technol.* 1985, **58**, 1014
- Thomas, S., De, S. K. and Gupta, B. R. *Kautschuk + Gummi Kunststoffe* 1987, **40**(7), 665
- Danesi, S. and Porter, R. S. *Polymer* 1978, **19**, 448
- Stehling, F. C., Huff, T., Speed, C. S. and Wissler, G. J. *J. Appl. Polym. Sci.* 1981, **26**, 2693
- Jancar, J., Di Anselmo, A., Di Benedetto, A. T. and Kucera, J. *Polymer* 1993, **34**, 1684
- Favis, B. D. *J. Appl. Polym. Sci.* 1990, **39**, 285
- Paul, D. R. and Newman, S. (Eds) 'Polymer Blends', Academic Press, New York, 1978
- Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer-Polymer Miscibility', Academic Press, New York, 1978
- Paul, D. R. and Barlow, G. W. *ACS, Adv. Chem. Ser.* 1979, **176**, 315
- Molau, G. E. *J. Polym. Sci.* 1965, **A3**, 4235
- Molau, G. E. and Wittbrodt, W. M. *Macromolecules* 1968, **1**, 260
- Riess, G., Kohler, J., Tournut, C. and Banderet, A. *Makromol. Chem.* 1967, **101**, 58
- Riess, G., Kohler, J., Tournut, C. and Banderet, A. *Eur. Polym. J.* 1968, **4**, 187
- Fayt, R., Jerome, R. and Teyssie, Ph. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 2209
- Fayt, R., Jerome, R. and Teyssie, Ph. *Polym. Eng. Sci.* 1987, **27**, 328
- Thomas, S. and Prud'homme, R. E. *Polymer* 1992, **33**, 4260
- Baker, W. E. and Saleem, M. *Polymer* 1987, **28**, 2057
- Ide, F. and Hasegawa, A. *J. Appl. Polym. Sci.* 1974, **18**, 963
- Choudhury, N. R. and Bhowmick, A. K. *J. Appl. Polym. Sci.* 1989, **38**, 1091
- Cheung, P., Suwanda, D. and Balke, S. T. *Polym. Eng. Sci.* 1990, **30**, 1063
- Mori, E., Pukanszky, B., Kelen, T. and Tudos, F. *Polym. Bull.* 1984, **12**, 157
- Ballegooie, Van P. and Rudin, A. *Polym. Eng. Sci.* 1988, **28**, 21
- Ballegooie, Van P. and Rudin, A. *Macromol. Chem.* 1989, **190**, 3153
- Willis, J. M. and Favis, B. D. *Polym. Eng. Sci.* 1990, **30**, 1073
- Leibler, L. *Makromol. Chem. Macromol. Symp.* 1985, **16**, 17
- Leibler, L. *Macromolecules* 1982, **15**, 1283
- Noolandi, J. *Polym. Eng. Sci.* 1984, **24**, 70
- Noolandi, J. and Hong, K. M. *Macromolecules* 1982, **15**, 482
- Noolandi, J. and Hong, K. M. *Macromolecules* 1984, **17**, 1531
- Liu, N. C., Xie, H. Q. and Baker, W. E. *Polymer* 1993, **34**, 4680
- Frenkel, R., Duchacek, V., Kirillove, T. and Kuzmin, E. *J. Appl. Polym. Sci.* 1987, **34**, 1301
- Boder, G. 'Structural Investigations of Polymers', Ellis Horwood, New York, 1991
- White, J. L. *Polym. Eng. Sci.* 1973, **13**, 46
- Dao, K. C. *Polymer* 1984, **25**, 1527
- Heikens, D. and Barentsen, W. M. *Polymer* 1977, **18**, 69
- Walczak, Z. K. *J. Appl. Polym. Sci.* 1973, **17**, 169
- Coran, A. Y. 'Handbook of Elastomers - New Development and Technology' (Eds A. K. Bhowmick and H. L. Stephens), Marcel Dekker, New York, 1988, p. 249
- Martuscelli, E., Silvestre, C. and Abate, G. *Polymer* 1982, **23**, 229
- Karger-Kocsis, J., Kiss, L. and Kuleznev, V. N. *Int. Polym. Sci. Technol.* 1981, **8**, T/21
- Thomas, S. *Mater. Lett.* 1987, **5**, 360
- Nielsen, N. E. *Rheol. Acta* 1974, **13**, 86
- Halpin, J. C. *J. Compos. Mater.* 1970, **3**, 732
- Wu, S. *Polym. Eng. Sci.* 1987, **27**, 335
- Spiros, H. A., Gancarz, I. and Koberstein, J. T. *Macromolecules* 1989, **22**, 1449

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| <p>56 Fayt, R., Jerome, R. and Teyssie, Ph. <i>Makromol. Chem.</i> 1986, 187, 837</p> <p>57 Willis, J. M. and Favis, B. D. <i>Polym. Eng. Sci.</i> 1988, 28, 1416</p> | <p>58 Oommen, Z., Thomas, S. and Gopinathan Nair, M. R. <i>Polym. Eng. Sci.</i> (in press)</p> <p>59 Santra, R. N., Samantaray, B. K., Bhowmick, A. K. and Nando, G. B. <i>J. Appl. Polym. Sci.</i> 1993, 49, 1145</p> |
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