

Effect of Addition of Polyethylene on Properties of Polypropylene/Ethylene-Propylene Rubber Blends

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SYNOPSIS

Toughening of polypropylene was carried out by adding two types of ethylene-propylene rubber (EPR) having different ethylene content, and three commercial types of EPR containing high density polyethylene (PE). The concentration of EPR was varied from 0–30%. Globular morphology of the dispersed phase was observed at all concentrations. Average particle size of the dispersed phase (EPR) was about 2–4 μm with about 10% within the 0.5–1 μm range. Although most of the properties were not affected by the presence of polyethylene, high notched Izod impact strength was achieved only with samples containing PE. Melt flow rate, yield strength and modulus were found to decrease almost linearly with increasing elastomer concentration in the blend. Elongation at break was enhanced by the addition of EPR, particularly those containing PE. The contribution of PE to the properties was explained by the specific EPR/PE particle morphology (core-shell or interpenetrating) but the exact mechanism of toughening of PP with EPR in the presence of PE is not clear.

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INTRODUCTION

Neat polymers may have a number of unsatisfactory properties that limit their applications. Modification of properties can be obtained by blending them with other polymers. Properties of blends depend not only on properties of starting components, their concentration, and component miscibility, but also on the morphology of the blend, that is, the size and the shape of the dispersed phase. In the case of miscible polymers the properties of the blend are usually averages of properties of the components; in immiscible blends qualitatively new properties may be obtained. For example, polypropylene (PP) is a material with a relatively low impact strength that can be significantly improved by the addition of a rubbery component. According to Bucknall,¹ to prepare a blend with good impact strength, several conditions should be fulfilled: a two phase system with the rubbery phase being dispersed in the hard phase; strong

bonding should exist at the phase interface; viscoelastic properties of the melts of both components should be taken into account by adjusting viscosity ratios. It is also necessary to know the effect of the particles of the dispersed phase on specific deformation processes. For the proper activity of the dispersed phase, the particle size should be below 2 μm .

Of course, such broad statements are not sufficient when designing new materials and careful analysis and research is required when applied to particular systems. In the case of PP modification, intuitively one would select ethylene-propylene rubber (EPR) or modified EPR with a small amount of diene monomer (EPDM) as an impact resistance additive. First, the similarity in chemical composition would help interphase bonding (due to the low interaction parameter) and second, the material is readily available at a very acceptable price. However, excellent impact strength may be obtained easier with the addition of a third component, as it will be shown here. Addition of an elastomer as an impact strength modifier is based on the fact that it separates as a dispersed phase, changing and modifying the mechanism of craze formation and propagation.

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The accepted explanation of impact strength improvement from the addition of elastomer to the glassy polymer is that it acts as a stress concentrator that stops the crack propagation by generating a large number of crazes. These, in turn, consume impact energy and convert it to heat. The mechanism of deformation in a semicrystalline polymer, like PP, above glass transition may involve shear yielding. Newman² listed six different mechanisms of toughening including those previously mentioned. Speri and Patrick³ suggested that rubber particles cause a decrease in crystallite size in semicrystalline polymers thus increasing the impact strength. They also showed that the addition of polyethylene (PE) to the rubbery phase considerably improved notched impact strength. Stehling et al.⁴ studied the effect of EPR on and EPR/PE addition to PP on properties of composites. They found that PE as a ternary component has a detrimental effect on impact strength when the concentration of PE in the PE/EPR particles is greater than 50%. They attributed that finding to the specific particle morphology, whereby above that limit the PE phase is not completely covered, causing poor adhesion between the PE phase and the PP matrix. Generally, they found that partial replacement of EPR by PE decreases impact strength at -29°C , although the decrease was relatively small when the PE content in the PE/EPR phase was less than 50%. The optimum size of dispersed particles in the blend falls as the ductility of the matrix increases. PP is a ductile material at room temperature that deforms by shear yielding. As a conclusion Stehling et al.⁴ suggested that premixing of PE with EPR gives an interpenetrating structure, but which of the two morphologies (interpenetrating or shell/core) prevail has little effect on impact strength. It has been suggested that improvement in impact properties with the addition of HDPE (high-density PE) comes from the improved dispersion and homogeneity of the ternary blends.⁵ Karger-Kocsis and Csikai⁶ suggested that multiple crazing and shear yielding are responsible for the impact energy dissipation. Above the glass transition temperature (T_g) of PP shear yielding is favored by very fine and narrow dispersion of the impact modifier. With particle size below $0.6\ \mu\text{m}$, crazing and shear yielding simultaneously take place without disturbing each other. Coarser particles were found to lead to moderate impact strength because shear bands stop the craze propagation. Details of the toughening mechanism in systems that deform by shear yielding, such as the sequence of events like cavitation and shear yielding, were discussed by

Yee and coworkers.⁷⁻⁹ A number of authors found that partial replacement of EPR with PE in the dispersed phase raises the impact strength of the blend.^{3,10,11} Fortelny et al.¹² suggested that depending on the conditions of mixing and on the rheological properties of components, substituting one part of EPDM elastomer with PE may lead to an increase or decrease in impact strength of the final product. These variations that reflected quality of mixing were relatively modest, however. Nomura et al.¹³ studied the toughening mechanism of PP/EPR composites for automotive applications. They found that the blends with less than 30% EPR had a PP matrix-domain structure, whereas those with more than 40% EPR exhibited interpenetrating cocontinuous morphology.

Judging by the considerable recent attention to the subject, PP/EPR blends have significant industrial importance, such as, use in molding impact resistant car bumpers. A number of articles have been published on various aspects of structure,¹⁴⁻¹⁸ properties,¹⁹⁻²⁴ and processing^{12,25,26} of PP/elastomer blends.

In this study we compare the effect of two types of EPR impact modifiers, neat EPR and EPR containing PE, on impact resistance and other properties. We have selected two different neat EPRs from DSM-Holland, Keltan 740 P and Keltan 778 P, having different ethylene content, and three commercial EPR impact modifiers containing PE. EPR/PE compounds came from three different companies: Keltan 9200 from DSM, Vestopren 10000 from Hüls, and Nordel NDG 4167 from Du Pont. The aim of this research was to compare different impact modifiers and resolve some contradictions existing in published studies about the effect of the PE phase in the EPR on impact resistance and other properties. We selected commercial grades because we feel that their structure is optimized to get the best properties, although we are deprived of some structural information due to the fact that the preparation of the impact resistance modifiers for PP containing PE are proprietary secrets. All samples in our study were prepared in the same manner and, while approximately the same morphology was obtained upon mixing, the properties were different.

EXPERIMENTAL

Materials

Isotactic PP Hipolen MA3, produced by HIPOL (Odžaci, Yugoslavia), melt flow rate (MFR) of 11

g/10 min, was used as the matrix material. Keltan 740 P, supplied by DSM (Holland), was specified as pure EPR (or EPDM) having MFR of 0.1 g/10 min, measured at 230°C under a load of 50 N. The content of ethylene in the copolymer is 60%. Keltan 778 P, supplied by DSM, is an EPDM copolymer having ethylene content of 65% and no PE. The MFR was 0.1 g/10 min. Keltan 9200 P (DSM) is a master batch consisting of 72% EPR and 28% HDPE. MFR was 3 dg/min. Vestopren 10000 is a master batch of EPDM in PE, having a MFR of 1.1 g/10 min (at 190°C under load of 49 N) and hardness of 75 U of shore A. Nordel NDG 4167, supplied by Du Pont, is a blend of EPDM and HDPE, having MFR of 0.5–1.2 g/10 min. Blends of PP with impact modifiers were prepared in concentrations listed in Table I.

Methods

Blends were prepared by mixing Hipolen MA-3 with impact modifiers at 180°C for 5 min in a Haake Rheomix mixer. Samples were then compression molded to obtain plates 0.5 and 3 mm thick. Compression molding was carried out using the following conditions: preheating for 2 min at low pressure, compression for 2 min at 6.8 MPa at 230°C, and then cooling in the mold for 2 min at 107 MPa. Specimens for mechanical tests were cut from the plates.

MFR were measured at 230°C under a load of 19.62 N. A Du Pont differential scanning calorimeter (DSC), model 951, was used for measurements of thermal transitions (T_g and melting points). A heating rate of 10°C/min was used. A thermomechanical analyzer (TMA), Du Pont model 945, was utilized to obtain coefficients of expansion and thermal transitions. A heating rate was 5°C/min and the sample thickness was 3 mm.

Tensile properties were measured on an Instron 1122 Tensile Tester at the extension rate of 100 mm/min. Specimens were 50 mm long, 10 mm wide, and 0.5 mm thick. Flexural moduli were measured on samples 3 mm thick, 25 mm wide, and 40 mm long at the rate of 1 mm/min. Izod impact strengths were measured on notched samples according to ASTM D 256, on a CEAST impact tester model 6545/000. A JEOL JSM-35 scanning electron microscope (SEM) was used to observe blend morphology. Samples were prepared by brittle fracturing under liquid nitrogen or by dissolving the rubber phase in xylene. Wide angle X-ray diffraction (WAXD) was carried out on a Philips diffractometer on 0.5 mm

Table I Weight Concentrations of Various Impact Modifiers in PP/EPR Blends

Type of EPR	Concentration (wt %)				
Keltans	5	10	15	20	30
Vestopren	7	10	15	20	—
Nordel	—	15	20	25	30

thick samples. A polarizing microscope (Amplival POL-d, Zeis, Germany) was used to observe coarse morphology.

RESULTS AND DISCUSSION

Processing neat PP in a mixer at the stated conditions was carried out to establish if any degradation occurred during the mixing process. It was found that MFR increased by one or two units indicating that some degradation does occur. MFR is an inverse function of viscosity and could be used to qualitatively assess the interaction between the phases. Because the viscosity of EPR is much higher than that of the matrix (MFR of the elastomer could not be measured under standard conditions), and PP and EPR are not miscible in the melt,²⁷ the blend melt could be treated as a suspension of solid particles in a fluid. Einstein's equation for the case of suspensions relates the relative viscosity with the volume fraction (ϕ) of the dispersed phase ($\eta/\eta_0 = 1 + 2.5\phi$). This equation is valid for spherical particles in the absence of interactions between the dispersed phase and the matrix. In the presence of interactions, the effective size of the particle, and thus volume fraction, is increased due to the formation of a boundary layer around the particle. This causes a higher increase in relative viscosity than Einstein's equation predicted, which was observed in our case. Figure 1 shows the decrease of MFR with the increase of elastomer concentration. Differences in MFR among different PP/EPR samples reflect differences in composition, molecular weight of elastomer, and morphology (particle shape and size). Generally, a decrease in MFR could be approximated with a linear function in the concentration range used in this work. At a 30% concentration, MFR fell to approximately one-half of the original value (according to Einstein's equation $\eta_0/\eta = 0.57$ for $\phi = 0.3$). DSC measurements showed no significant effect of elastomer addition on the melting point of PP. Also, the glass transition of elastomers

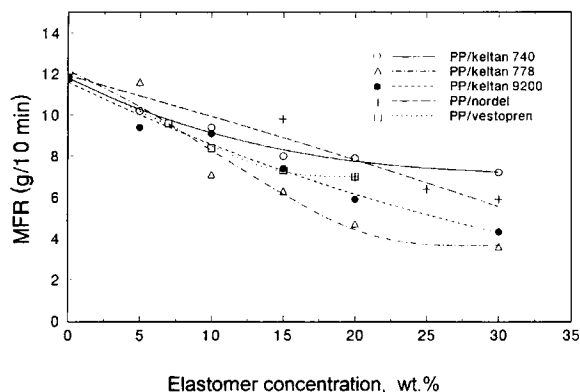


Figure 1 Dependence of MFR on elastomer concentration in PP/elastomer blends.

varied within limits of error with the change of elastomer concentration in the blend, indicating a very low degree of mixing of the components. Table II displays the variation of glass transition of elastomers with the addition of 20% elastomer, as measured by DSC. DSC registered the melting peaks for PE in addition to those of PP in blends containing the former component. The presence of PE in Keltan 9200, Nordel, and Vestopren was detected by WAXD, but additional components were detected in Vestopren, which could arise from some low molecular additives such as nucleating agents.

Linear coefficients of expansion were measured from the slopes of TMA curves below the glass transition of PP (at -20°C) and the results are shown in Figure 2. The values of linear coefficients of expansion can be related to the interaction of components.^{28,29} The scatter of the results makes interaction analysis unreliable and merely reflects the complex multiphase nature of the system (crystalline and amorphous PP, amorphous elastomer, and presence of PE). Results above the glass transition of PP (20°C) show the same trend except the scatter is greater, and absolute values may reach $120 \times 10^{-6} \text{ K}^{-1}$ at 30% elastomer.

X-ray and optical microscopy results showed that the addition of elastomers did not significantly affect the crystallinity of the PP matrix. The total crystallinity of the sample decreased with increasing concentration of elastomer; but adjusted for the PP fraction in the blend, it was essentially constant at about 60% (determined by the Weidinger and Hermans method³⁰). Hlavata et al.²⁴ also found that crystallinity of isotactic PP was only slightly influenced by the copolymer (hydrogenated isoprene/styrene and butadiene/styrene) presence. Others¹⁸ found the opposite. In all cases

Table II Glass Transition ($^{\circ}\text{C}$) of Neat Elastomers and Elastomers in 20% EPR Blend

	740 Keltan				
	740	778	9200	Nordel	Vestopren
Neat elastomer	-60	-47	-54	-60	-61
PP/elastomer	-55	-48	-50	-60	-65

but one, the α modification of isotactic PP was the only species present. In the case of PP/Keltan 740 (15%), the β modification was registered also. Published data suggest that the presence of the EPR dispersed phase decreases the crystallite size³ and spherulite size.^{6,31-33} An increase in spherulite size of PP upon the addition of an elastomer has also been reported.¹⁸ In addition it has been shown that the EPR particles are located in interlamellar spaces within spherulites as well as in the spherulitic boundary layer.^{18,34} In our case the cooling period during sample preparation was fairly short so that spherulite size is expected to be small even in the neat PP. The fact that the melting points did not vary with elastomer content suggests that crystallite sizes were comparable in all samples.

Analysis of fractured surfaces of the blend samples using SEM showed good dispersion of the rubbery phase. The average size of elastomer particles, depending on concentration, was about $2-3 \mu\text{m}$ for blends containing up to 15% elastomer and about $4-5 \mu\text{m}$ for higher concentrations of elastomer. The characteristics of the morphology of all samples, except that of Keltan 778 P, are presented in Figures 3(a-m). Every sample is shown at the high magnification of $\times 20,000$ and two micrographs at low

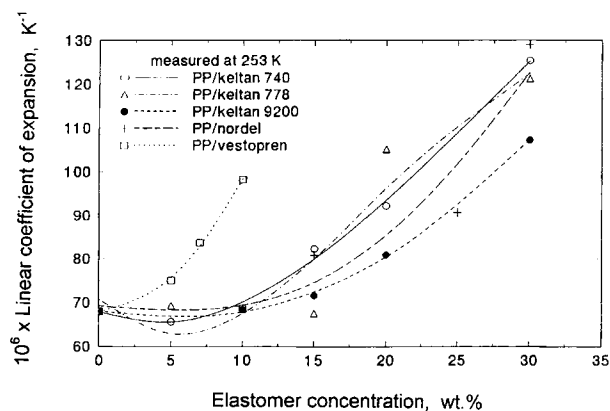
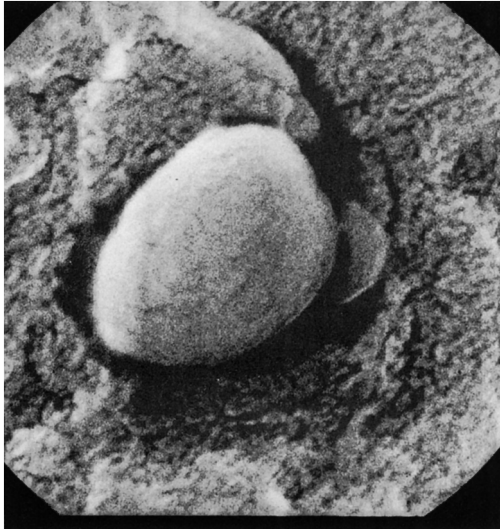
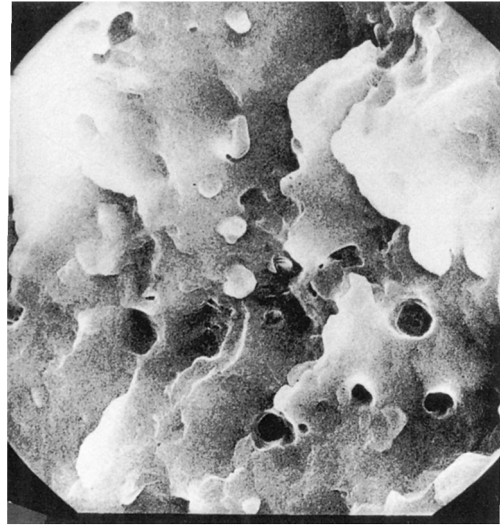


Figure 2 The effect of elastomer concentration on linear expansion coefficient of PP/elastomer blends at -20°C .



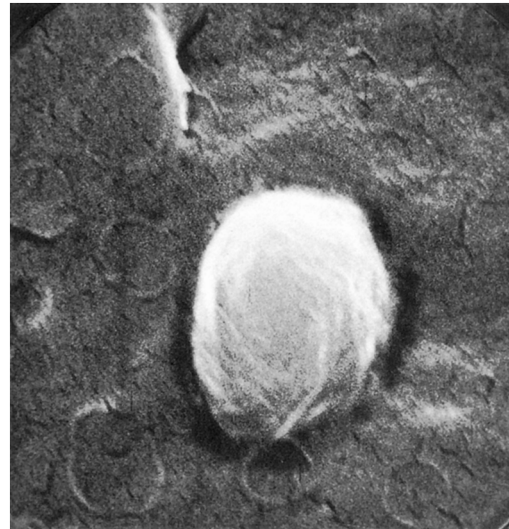
a



b

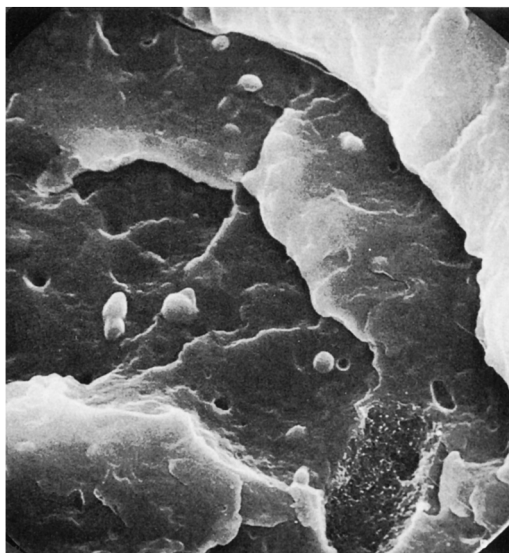


c



d

Figure 3 Morphology of PP/elastomer blends. (a-c) Keltan 740 at magnification $\times 20,000$, 2000, and 2000; (d-f) Keltan 9200 at mag. $\times 20,000$, 2000, and 2000; (g-i) Vestopren at mag. $\times 20,000$, 2000, and 2000; (j-l) Nordel (15%) at mag. $\times 20,000$, 2000, and 2000; (m) contact of PE core with the PP matrix in a sample with removed EPR (mag. $\times 20,000$). Samples (c), (f), (i), and (l) were prepared by removing EPR phase with xylene. All samples contain 15% elastomer except (a-c), which have 30%.



e



f



g

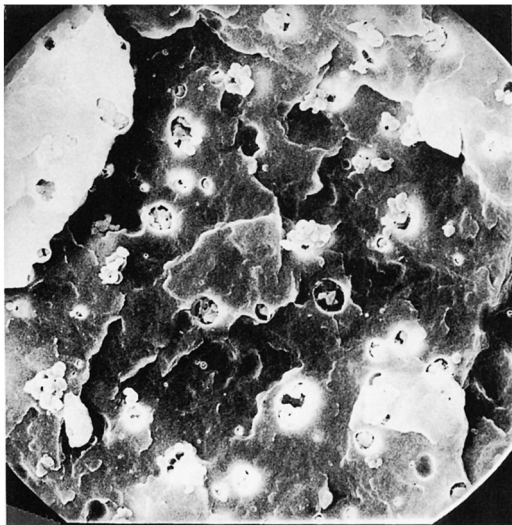


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Figure 3 (Continued from the previous page)

magnification of 2000, one with and the other without the elastomer phase, which was removed with xylene. While high magnification reveals the details at the particle–matrix interface, micrographs at low magnification show the quality of dispersion and the size and shape of the dispersed particles. Micro-

graphs of the samples with the removed elastomer phase reveal the shape of the PE phase in the dispersed particles. The elastomer concentration in all samples was 15% except in Figures 3(a–c) where it was 30%. Figures 3(a–m) illustrate the more or less round shape of the elastomer particles in the PP



i



j



k

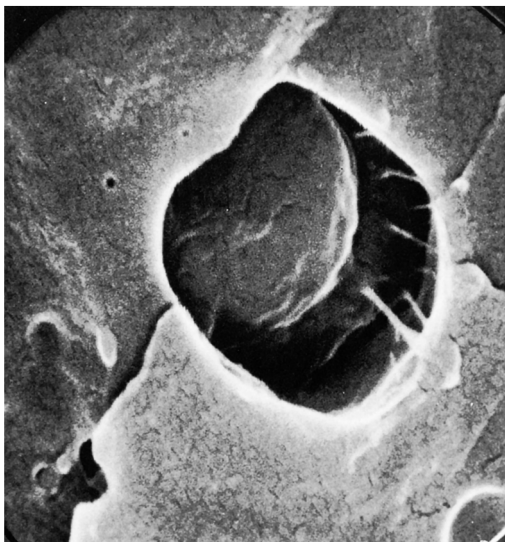


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matrix. It is interesting that the elastomer master batches (Vestopren, Nordel, and Keltan 9200) were dispersed in the PP matrix in much the same way, producing a similar blend morphology. They also displayed a specific characteristic particle morphology: PE seems to form a core surrounded by and

protruding occasionally through the elastomer, which forms a shell in contact with the PP matrix [Figs. 3(f,i,l)]. Such morphology is clearly seen in samples where the elastomer phase was washed out by xylene. At higher magnification it could be observed that some elastomeric particles were not in



m

Figure 3 (Continued from the previous page)

contact with the PP matrix over their entire surface. This may be the result of higher shrinkage of the elastomer below the crystallization temperature of the PP. Fibrils stretching from the matrix to the center are observed in elastomers containing PE, [Fig. 3(m)]. The PE core in samples with Nordel and Keltan 9200 are ellipsoidal and compact; in Vestopren they may be agglomerates of several globules. As will be shown later, such a morphology has a profound effect on the impact strength of the blends with master batches.

Tensile properties were characterized by measuring stress at break, σ_k , yield stress, σ_p , and cor-

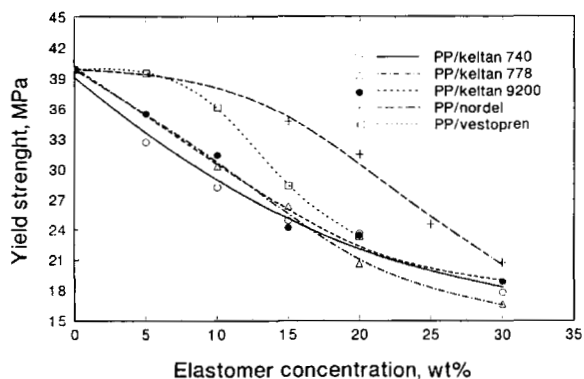


Figure 4 Effect of elastomer concentration on yield strength of PP/EPR blends.

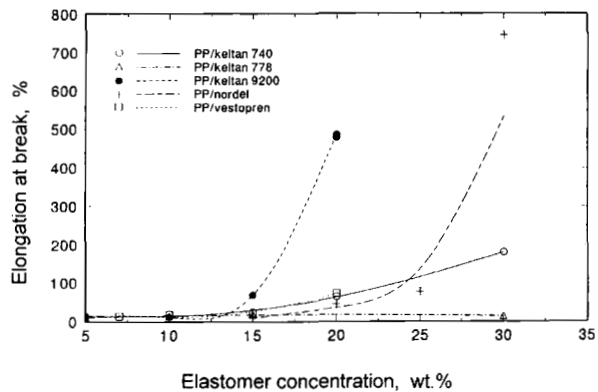


Figure 5 Effect of elastomer content on elongation at break of PP/EPR blends.

responding elongations. Because breakage usually occurred at low elongations just above the yield point where stress began to decrease, σ_p was usually higher than σ_k and decreased with increasing elastomer concentration. For example, by increasing the elastomer concentration from 5 to 30% the yield stress decreased from 30 to 15 MPa. As seen in Figure 4, at low concentrations of elastomer, σ_p decayed more slowly with Nordel and Vestopren than with the Keltan types. Elongation at break of the neat PP when measured on thin (0.5 mm) and wide strips was very low. The same material when 3 mm thick, showed changes in elongation of several hundred percent. However, all comparisons here are made under the same conditions on thin strips. Figure 5 demonstrates the effect of elastomer concentration on the elongation at break. At concentrations above 15% the materials displayed higher elongation including necking and orientation, indicating that the elastomer seems to flexibilize the matrix and somehow change the mechanism of failure. Especially

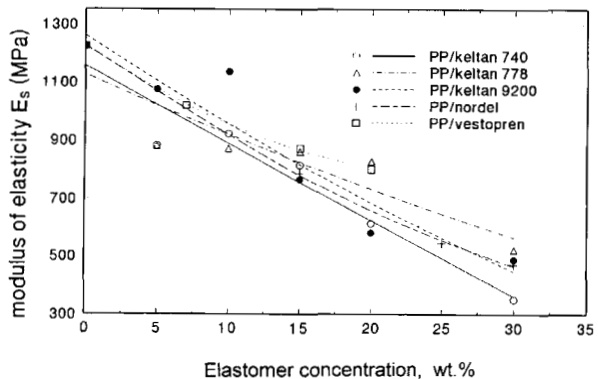


Figure 6 Effect of elastomer content on flexural modulus of PP/EPR blends.

significant are the effects of the two PE containing elastomers.

The flexural modulus of a composite is a complex function of the moduli of the components and the composition. Experimental values for moduli are shown in Figure 6, and they are generally lower than those calculated using the Kerner model.²⁸

A PE presence in the EPR is expected to increase the modulus of the PP/EPR composites compared to those without PE. However, it seems that the concentration of PE in EPR was fairly low and that effect was not pronounced.

The decrease in modulus with increasing concentration of elastomer is almost linear in the range of concentrations used, with small variations among the various types of elastomer. The most important mechanical property for the application of this type of blends, impact strength, is displayed as a function of elastomer content in Figure 7. It is evident that the three PE containing elastomers gave dramatically better notched impact strength compared to the two types of EPR without PE. At the concentration of 30%, Nordel gave virtually unbreakable material; with Keltan 9200 only some samples could not be broken, and the result presented is an average value of the broken samples (unbroken were not counted). This result would suggest that in our case, the addition of PE is essential for good impact strength of PP/EPR blends. The effect of PE in EPR on impact strength has not been adequately clarified in published studies. It has been suggested that PE may facilitate dispersion of EPR even at mild mixing conditions. The PE might also more easily produce the right particle size, but in our case the particle size of pure EPR was in the same range. The particle size in all samples was comparable, and an increased notched impact strength can be attributed solely to the presence of PE. It should be emphasized that other factors include good dispersion and perhaps core/shell or interpenetrating morphology of the two phases. This was achieved already in the supplied material so that mixing only served to dilute the master batch preserving the form of PE particles. Although this morphology is favorable for obtaining high impact strength, it is still unclear what is the precise toughening mechanism in the presence of the PE phase.

CONCLUSION

A series of EPR compounds were used as additives to improve the impact strength of PP. It was shown

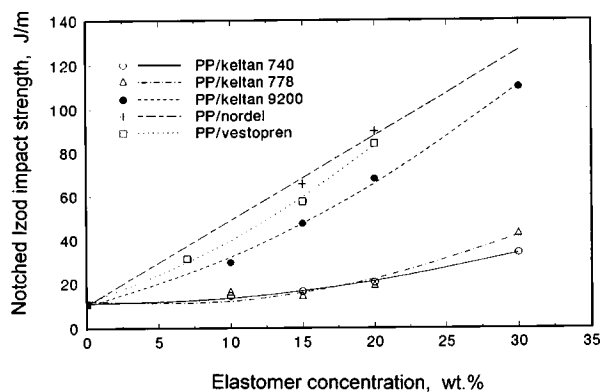


Figure 7 Effect of elastomer concentration on notched Izod impact strength of PP/EPR blends.

that the EPR containing PE was much more efficient in improving impact strength of PP/EPR blends than neat EPR. This was attributed to the specific morphology of dispersed rubber particles. The addition of PE had a significant effect on the elongation at break, but had no effect on other mechanical or rheological properties.

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