

Mechanical and Morphological Properties of Elastomer-Modified Polypropylene/Polyamide-6 Blends

JOACHIM RÖSCH and ROLF MÜLHAUPT*

Freiburger Materialforschungszentrum and Institut für Makromolekulare Chemie, Stefan-Meier-str. 31, D-79104 Freiburg i. Br., Germany

SYNOPSIS

Polypropylene/polyamide-6 (70:30) blends, containing dispersed discrete polyamide-6 microphases as matrix reinforcement, represent attractive materials for engineering applications. In order to enhance impact resistance, ethene/propene (EPM) was incorporated as a second separately dispersed microphase using reactive blending technology. Blend morphologies were controlled by adding maleic-anhydride-grafted-polypropylene (PP-*g*-MA) as compatibilizer during melt processing, thus enhancing dispersion and interfacial adhesion of the polyamide-6 phase. With PP-*g*-MA volume fractions increasing from 2.5 to 10 vol %, much finer dispersions of discrete polyamide-6 with average domain sizes decreasing from 8 to 0.8 μm were obtained. When polyamide-6 and ethene/propene (EPM)-rubber are dispersed simultaneously in the polypropylene matrix, impact resistance was improved. The influence of PP-*g*-MA volume fraction and blend morphologies on mechanical properties such as Young's modulus, yield stress, notched Charpy impact resistance was investigated. The ternary polypropylene/polyamide-6/EPM blend properties were compared with those of binary polypropylene blends containing the equivalent volume fraction of EPM. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene, which is produced in economically and ecologically attractive modern processes, is the only commodity resin that can meet the demands of typical high-value in-use engineering resin applications. To qualify for such applications, stiffness, strength, and toughness of polypropylene must be improved simultaneously. This challenge can be met when separate rigid and rubbery microphases are dispersed in the polypropylene matrix. In the case of stiff isotropic or anisotropic dispersed phases, efficient stress transfer between the dispersed phases leads to matrix reinforcement, as expressed by higher Young's modulus. Frequently, such matrix reinforcement is accompanied by substantially lower resistance to crack propagation due to delamination, crack initiation, and propagation at the interfaces.

Therefore, regardless of the chemical nature of the reinforcing microphases, good interfacial adhesion is one of the primary concerns in the development of new polypropylene blends. In reactive blending technologies, a wide range of adhesion promoters, better known as blend compatibilizers, were added to form covalent bonds between matrix and dispersed phase during melt processing. Although fillers are widely applied as reinforcements, recently dispersions of stiff organic polymers have attracted much attention. In principle, it was conceived that polypropylene/polyamide-6 blend formation could lead to unusual blend synergisms, such as higher stiffness and strength combined with improved toughness, high heat distortion temperature, dyeability, heat sealing, adhesion to metals and coatings, low water uptake, and reduced hydrocarbon permeabilities.¹⁻⁵ Investigations of mechanical, rheological, and morphological properties revealed that the nature and volume fraction of the compatibilizer played an important role. In a recent investigation, the influence of blend compatibilizer

* To whom correspondence should be addressed.

molecular architectures, especially stereoregularities and molecular weights, was identified for polypropylene/polyamide-6 blends compatibilized with succinic-anhydride-terminated and maleic-anhydride-*grafted*-polypropylenes.⁶ In spite of excellent interfacial adhesion, most binary polypropylene/polyamide-6 blends compatibilized with maleic-anhydride-*grafted*-polypropylene (PP-*g*-MA) failed to afford markedly higher impact strength. Better results were found when using special blend compatibilizers such as maleic-anhydride-*grafted*-polystyrene-*block*-poly(ethene-*co*-but-1-ene)-*block*-polystyrene,^{2,7} which accumulates at the interfaces between continuous polypropylene matrix and dispersed polyamide-6 microphases.

In order to improve polypropylene/polyamide-6 blends, it is important to explore the potential of rubber modification. For toughening of the polypropylene matrix, several approaches are reported in the literature. In contrast to flexibilizing polypropylene by randomly incorporating ethene into the polypropylene chain, dispersing discrete ethene/propene (EPM) microphases of less than 10 μm average diameter is the method of choice to improve toughness without sacrificing stiffness. This can be accomplished either by copolymerization processes or by melt blending. In EPM-modified polypropylene, the EPM microphases are efficient stress concentrators, which contribute effectively to dissipating impact energy at the crack tip, e.g., by initiating multiple crazing or shear yielding.⁸⁻¹⁰ The purpose of our research was to investigate ternary blends of polypropylene/polyamide-6/EPM where stiff polyamide-6 and rubbery EPM microphases were simultaneously dispersed in the polypropylene matrix. Emphasis was placed on the influence of the PP-*g*-MA compatibilizers and the presence of two different types of stress concentrating microphases on mechanical properties.

EXPERIMENTAL

Materials

All polymers were commercially available and used without further purification. Polypropylene (Hostalen[®] PPN 1060, $M_n = 63,000$ g/mol, $M_w = 182,700$ g/mol, as determined by SEC in 1,2,4-trichlorobenzene at 135°C using polystyrene standard, MFI (230/2,16) = 2 dg/min, $T_m = 165^\circ\text{C}$) was purchased from Hoechst AG. Maleic-anhydride-*grafted*-polypropylene (Exxelor[®] PO2011, 0.031

mol anhydride/kg polypropylene, MFI (230/2,16) = 125 dg/min) was supplied by Exxon Chemicals. Polyamide-6 (Sniamid ASN27, 0.03 mol amine end groups/kg polyamide, $T_m = 222^\circ\text{C}$) was obtained from Snia.

Reactive Blending and Characterization

The polyamide-6 was dried for 6 h at 80°C under oil pump vacuum prior to use. Melt blending was performed using a Haake Rheomix 90 equipped with a 60 mL mixing chamber and online temperature and torque recording. After preheating the mixing chamber at 240°C, 40 g of the blend composed of polypropylene, polyamide-6, maleic-anhydride-*grafted*-polypropylene, and 0.2 g stabilizer mixture (80 wt % Irganox[®] 1010 (20 wt % Irgafos[®] 168) were charged. Blending was performed for 4 min at 240°C. This includes the 2 min required for melting the components. Afterwards, the blend was quickly recovered and quenched to room temperature. The blend compositions of PP/PA, PP/EPM, and PP/PA/EPM blends are listed in Table I.

For testing, sheets of 1.5 mm thickness were prepared by compression molding as follows: the samples were annealed 10 min at 260°C in a heated press (Schwabenthan Polystat 100) and then quenched between water-cooled metal plates. For tensile testing, dumbbell-shaped tensile bars were cut and machined as described by DIN 53544. Stress-strain measurements to determine Young's modulus and yield stress were performed at 10 mm/min crosshead speed on an Instron 4204 at 23°C. Notched Charpy impact strength was determined on five test specimen according to standard procedures by DIN 53453 using a Zwick 5102 pendulum impact test equipped with 2J pendulum. Morphological studies used the Zeiss CEM 902 transmission electron microscope (TEM). Thin sections, suitable for TEM analysis, were cut after staining and hardening the samples in ruthenium tetroxide vapors for 6 h. Microtoming of the samples into sections of 80 to 100 nm thickness was performed using a Reichert Jung Ultracut E device equipped with diamond knives.

RESULTS AND DISCUSSION

For evaluation of morphology and mechanical properties, three families of multiphase polypropylenes were prepared by melt blending at 240°C: first, as

Table I Blends of Polypropylene (PP) with Ethene/Propene (EPM) and Polyamide-6 (PA)

PP (vol %)	EPM (vol %)	PA (vol %)	PP-g-MA ^a (vol %)	PA Domain Size (μm)	EPM Domain Size (μm)	Young's Modulus (MPa)	Yield Stress (MPa)	Notched Charpy Impact Strength (kJm ²)
67.5	—	—	—	—	—	1150	32	6
65.0	2.5	—	—	—	0.5	1050	29	16
62.5	5.0	—	—	—	0.8	920	26	25
57.5	10.0	—	—	—	3.0	720	24	40
47.5	15.0	—	—	—	irr. ^b	640	17	100
67.5	—	30	2.5	8	—	1450	35	5
65.0	2.5	30	2.5	8	0.5	1240	29	6
62.5	5.0	30	2.5	8	0.7	1150	26	7.5
57.5	10.0	30	2.5	8	3.0	940	20	10
52.5	15.0	30	2.5	8	irr. ^b	730	15	15
47.5	20.0	30	2.5	8	irr. ^b	570	10	25
65.0	—	30	5.0	2.5	—	1450	35	8
62.5	2.5	30	5.0	2.5	0.3	1240	33	10
60.0	5.0	30	5.0	2.5	0.7	1170	28	12
55.0	10.0	30	5.0	2.5	2.0	850	21	16
50.0	15.0	30	5.0	2.5	irr. ^b	690	15	28
45.0	20.0	30	5.0	2.5	irr. ^b	500	8	40
60.0	—	30	10.0	0.8	—	1450	35	10
57.5	2.5	30	10.0	0.8	0.5	1140	30	14
55.0	5.0	30	10.0	0.8	1.0	1050	28	15
50.0	10.0	30	10.0	0.8	2.0	980	20	22
45.0	15.0	30	10.0	0.8	irr. ^b	720	15	38
40.0	20.0	30	10.0	0.8	irr. ^b	540	11	60

^a PP-g-MA: maleic-anhydride grafted polypropylene.

^b Irregular ramified shape.

reference blends of elastomer-modified polypropylene, polypropylene (PP) was blended together with ethene/propene (EPM) rubber at different EPM volume fractions; second, in the binary blend 30 vol % polyamide-6 (PA) was blended together with 70 vol % PP, which was partially substituted by 2.5, 5, and 10 vol % of the compatibilizer consisting of polypropylene grafted with maleic anhydride (PP-g-MA); third, the ternary blend system comprised polypropylene/polyamide-6 (70 : 30 vol %), where part of polypropylene was again substituted by EPM and PP-g-MA. During reactive blending, the succinic anhydride groups of PP-g-MA react with amine end groups of polyamide to form polypropylene-*block*-polyamide, which are efficient compatibilizers reducing surface tension and improving both PA dispersion and interfacial adhesion between PA and PP. As was reported in more detail in a previous communication,⁶ the PP-g-MA volume fractions gave excellent control of the average PA domain size, which decreases with increasing compatibilizer con-

tent from 30 μm to less than 0.8 μm . Because transmission electron microscopic (TEM) revealed that PP-g-MA addition did not affect the EPM domain size, which was primarily controlled by the EPM volume fraction, it was possible to vary the average sizes of simultaneously dispersed PA and EPM independently by changing the PP-g-MA and EPM volume fractions. From Table I it is apparent that the EPM domain size increases with EPM volume fraction from 0.3 μm to values > 5 μm . As apparent from transmission electron microscopic image of PP/PA/EPM (50 : 30 : 20), RuO₄ staining improves contrast of the EPM microphase vs. PA. At EPM content of 5 vol % (cf. Fig. 1, top), both grayish PA and dark EPM were simultaneously dispersed as separate spherical microphases in the PP matrix. Above 10 vol %, EPM content (cf. Fig. 1, bottom) EPM microphases were much larger and irregularly shaped, while PA microphases size and shape were not affected by EPM volume fraction. At high EPM content, subinclusions, which most likely consisted

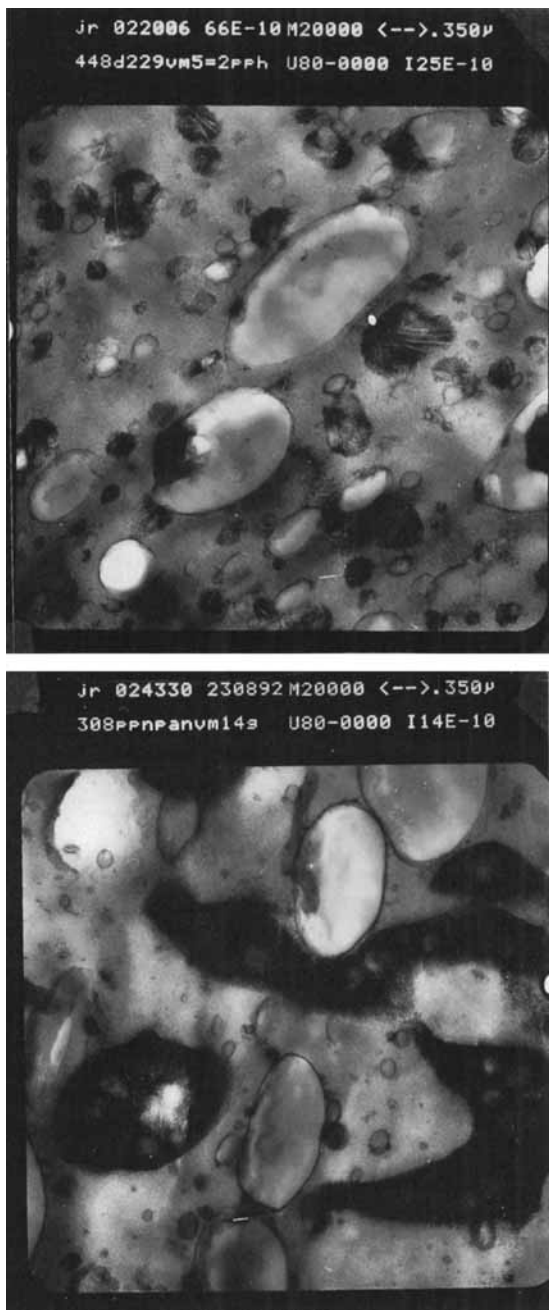


Figure 1 TEM images of RuO₄-stained blends. Top: PP/EPM/PA/ (65 : 30 : 5); bottom: PP/EPM/PA (50 : 30 : 20).

of polypropylene, were detected within the EPM microphase.

For evaluation of basic structure-property relationships, morphology and mechanical properties of compression-molded sheets were determined as a function of EPM and PP-*g*-MA volume fraction. In PP/PA/EPM and PP/EPM blends

the Young's modulus proved to be very sensitive to EPM addition. When the relative Young's moduli, taking into account the ratio of the measured Young's moduli and those of the PP matrix of 1150 MPa or the PP/PA (70 : 30) matrix of 1350 MPa, respectively, were plotted against the EPM volume fraction in Figure 2, very similar decays were found with increasing volume fractions. On the basis of Kerner's model¹¹ and his eq. (1), it is possible to calculate Young's modulus as a function of the EPM volume fraction. Although experimental values were used for PP and PP/PA (70 : 30) matrix, the EPM modulus was determined to be 4 MPa, and the Poisson's ratio μ_1 was assumed to be 0.39 in analogy to other similar blend systems known in literature.

$$\frac{G_b}{G_M} = \frac{\phi_1 G_1 + (\alpha + \phi_2) G_2}{(1 + \alpha \phi_2) G_1 + \alpha \phi_2 G_2} \quad (1)$$

- G_c = shear modulus of blend
- G_1 = shear modulus of matrix (PP or PP/PA, respectively)
- G_2 = shear modulus of dispersed EPM phase
- ϕ_1 = volume fraction of matrix
- ϕ_2 = volume fraction of dispersed EPM phase
- μ_1 = Poisson's ratio of matrix
- Young's modulus $E = 2G(1 + \mu)$
- $\alpha = 2(4 - 5 \mu_1)/(7 - 5 \mu_1)$

In Figure 2, the calculated relative moduli were much higher than those measured for the individual blend systems. This could be attributed to the presence of the large irregularly shaped, ramified EPM microphases. As schematically shown in

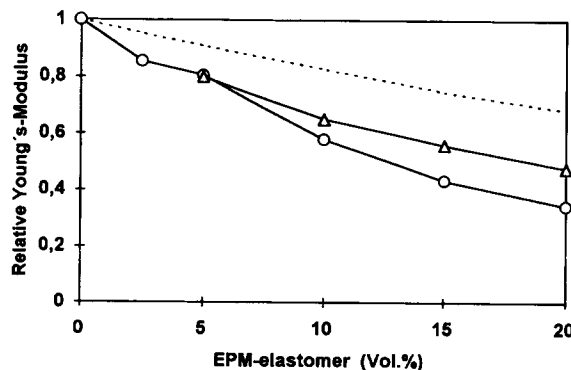


Figure 2 Relative Young's moduli (E_{blend}/E_{matrix}) as a function of the EPM volume fraction for PP/PA/EPM (○), PP/EPM (□) and for theoretical two-phase systems calculated according to the Kerner model (----).

Figure 3, this irregularly shaped EPM dispersed microphases may occupy a much larger volume than expected for spherical EPM microphases at equivalent EPM volume fractions. Yet another explanation could take into account the apparent decrease of the PP matrix crystallinity, which is proportional to the increasing volume fraction of the elastomer.

Similar to the influence of EPM volume fractions on Young's moduli, also the yield stresses of both PP/EPM and PP/PA/EPM blends decrease drastically with increasing EPM volume fractions. Theoretical values of yield stresses were calculated using the effective cross-section model¹² and the corresponding eq. (2). In contrast to the Young's moduli dependence on EPM volume fraction, yield stress of the PP/PA/EPM blend are markedly smaller than those of the PP/EPM blend. Moreover, as apparent from Figure 4, in both blend systems the slope of the relative yield stress decays are much steeper in comparison to those predicted on the basis of the effective cross-section model. Although the origin of this unusual behavior is not fully understood, the irregular shape of the dispersed EPM could be responsible for such deviations encountered at high EPM volume fractions. Most likely, the presence of dispersed PA microphases could favor irregularity of EPM microphases. In accord with earlier observations,⁶ however, at > 5 vol % PP-*g*-MA content PP-*g*-MA compatibilizer volume fraction, which controls the size of the dispersed PA microphase, did not alter yield stresses.

$$\frac{\sigma_b}{\sigma_m} = 1 - 1.21\phi_2^{2/3} \quad (2)$$

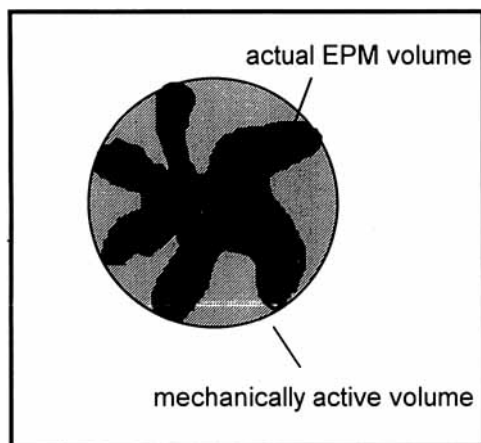


Figure 3 Morphology of the dispersed EPM microphases and evaluation of effective volume fraction.

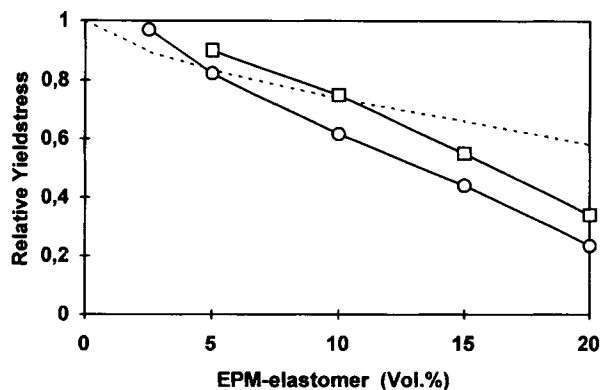


Figure 4 Relative yield stresses ($\sigma_{\text{blend}}/\sigma_{\text{matrix}}$) as a function of the EPM volume fraction for PPPPA/EPM (○), PP/EPM (□) and for theoretical two-phase systems calculated according to the effective cross-section model (----).

- σ_b = yield stress of blend
- σ_m = yield stress of matrix (PP or PP/PA, respectively)
- ϕ_2 = volume fraction of the dispersed EPM phase

One of the primary objectives of this study was to explore the potential of enhancing impact strength of PP/PA blends by simultaneously dispersing EPM microphases. Because PA domain sizes were controlled by the PP-*g*-MA volume fraction and EPM domain sizes by the EPM volume fraction, it was possible to vary both domain sizes independently and to examine the influence of PA domain sizes on notched Charpy impact resistance at 0, 5, 10, 15, and 20 vol % EPM. In Figure 5, the notched Charpy impact resistance is plotted against the EPM volume fraction. Clearly, when the average PA domain size was reduced from 8 to 0.8 μm at identical EPM content, PP/PA/EPM blends containing the smaller PA domains gave up to threefold impact resistance. This effect was more pronounced at higher EPM content. Interestingly, over the entire EPM volume fraction range Young's moduli and yield stresses were only marginally affected by the PA domain sizes.

In spite of the increased impact resistance with decreased PA domain sizes, the impact performance of the PP/PA/EPM blend systems did not match that of the EPM-modified polypropylene. Figure 6 shows the influence of EPM volume fraction on the notched Charpy impact resistance of PP/EPM vs. PP/PA/EPM. In the case of the EPM-modified PP matrix, the impact resistance is much higher than

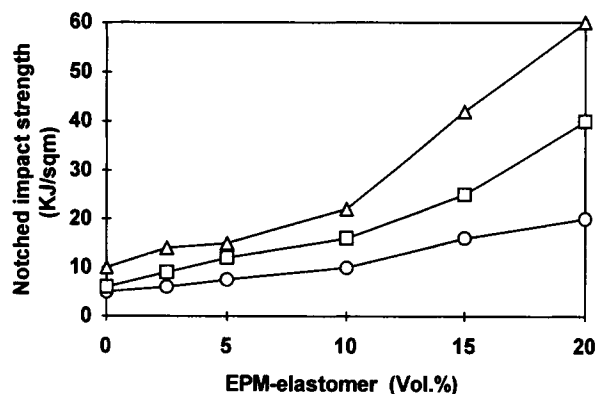


Figure 5 PP/PA/EPM blends: influence of the PA domain size ranging from 8 μm (○) to 2.5 μm (□) and 0.8 μm (Δ) on notched Charpy impact strength plotted against EPM volume fraction.

that of the corresponding PP/PA modified with the equivalent amount of EPM. For example, at 15 vol % EPM, the binary PP/EPM blend gave 100 kJm^{-2} notched Charpy impact strength in comparison to 38 kJm^{-2} measured for the ternary PP/PA/EPM blend at the same EPM volume fraction. Obviously, the presence of a second different type of stress-concentrating microphase adversely affects the energy dissipating capability of the dispersed EPM microphases.

The ultimate goal of enhancing both impact resistance and stiffness by dispersing stiff, reinforcing PA microphases into the EPM-elastomer-modified polypropylene matrix was not achieved. When notched Charpy impact resistance is plotted against Young's modulus in Figure 7, it is apparent that EPM incorporation into the PA-reinforced PP matrix accounts for substantially reduced stiffness. In fact, stiffness losses are not accompanied by significant gains in impact resistance. At EPM volume fractions exceeding 10 vol %, the PA reinforcement is completely sacrificed, and Young's moduli of PP/EPM and PP/PA/EPM blends are almost equivalent. At high EPM content, EPM-modified polypropylene gives much better impact strength/stiffness balance in comparison to the EPM-modified PP/PA blends.

SUMMARY

In conclusion, we have demonstrated that the simultaneous incorporation of rigid polyamide-6 and rubbery EPM microphases into the polypropylene matrix did not lead to synergisms of substantially

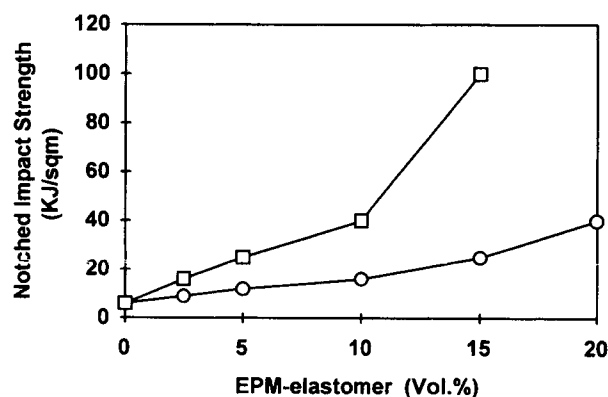


Figure 6 Modulus/impact resistance balance for EPM-modified PP/PA (70:30) (○) vs. EPM-modified PP (□).

higher impact resistance combined with high stiffness. In spite of good interfacial adhesion and efficient morphology control, i.e., simultaneous dispersion of two different microphases, EPM modification failed to improve both impact resistance and stiffness. In PP/PA/EPM ternary blends, impact resistance was enhanced at the expense of unacceptable losses in stiffness. At higher EPM volume fractions, there was no benefit associated with the addition of the PA blend component to the PP/EPM binary blend. As a consequence, overlapping stress concentrations at the interfaces of rigid and rubbery microphases adversely affected energy dissipation at the crack tip as well as stress transfer between rigid dispersed microphases. Therefore, this blend architecture was not suited to overcome stiffness/toughness limitations of conventional binary PP/EPM blends. Other blend architectures, e.g., encapsulating rigid organic or inorganic dispersed

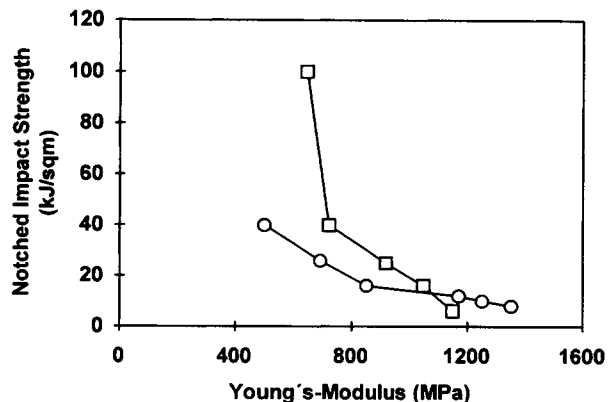


Figure 7 Comparison of PP/EPM (□) and PP/PA/EPM (○) blends: notched Charpy impact strength as a function of PA volume fraction.

microparticles in a rubbery shell, appear to be much more suitable to generate unusual blend synergisms of high toughness combined with high stiffness.

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