

Toughened Mica-Filled Polypropylene Systems*

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Synopsis

A family of rubber-toughened, mica-filled polypropylene materials was developed. The rubber modifier used was an ethylene-propylene-diene monomer (EPDM) compound. A unique feature of this rubber-modified system is that it can be directly molded from a dry blend. This simplifies processing by eliminating the need for melt compounding which, in turn, contributes to greater flexural moduli since attrition of the mica platelets is reduced. In addition, impact measurements were conducted as a function of temperature for EPDM/polypropylene and EPDM/poly(propylene-ethylene) copolymer blends. The low temperature impact resistance was improved for both systems; however, the modified copolymer system maintained ductile behavior to a far lower temperature than the corresponding homopolymer system.

INTRODUCTION

Mica, a low cost platy filler, is often added to polypropylene for increased stiffness and improved dimensional stability at elevated temperatures. However, a major drawback in the use of mica-filled polypropylene is its low impact resistance.¹ Although the use of coupling agents moderately improves the tensile strength of mica-filled polypropylene, impact properties are reduced further.^{2,3}

Stamhuis⁴ has recognized that the general problem associated with impact strength improvement of polypropylene systems is that other mechanical properties may suffer—especially the flexural modulus. These two properties are intimately related and are often critical for service applications. Coupled with these requirements are the economic advantages that accrue from using filled systems. Consequently, there is a clear need to develop filled polypropylene systems that balance impact resistance and stiffness while maintaining cost-effectiveness.

It is well established that the impact properties of unfilled polypropylene may be improved substantially by blending with ethylene-propylene-diene monomer (EPDM) rubber.⁵ Dao and Hatem have demonstrated that the impact resistance of talc-filled polypropylene can also be improved by compounding with EPDM using a twin-screw extruder.⁶ Recently, Chu et al. have shown that the impact properties of mica-filled polypropylene can be increased by blending with polyethylene and minor quantities of EPDM.⁷ The systems described by these authors were all precompounded prior to molding. In the latter case, compounding was achieved using a high intensity mixer that generated sufficient shear to delaminate the mica platelets.

The work reported here relates to that of Chu et al.⁷ in that an EPDM compound is used to improve the impact properties of mica-filled polypropylene. Whereas the system described by Chu and colleagues was compounded using a high intensity shear mixer, a goal of the work reported in this paper

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was to develop a toughened mica-filled polypropylene system that could be processed with little or no precompounding (i.e., by dry blending). Finally, the effects of EPDM on the low temperature impact properties of polypropylene and a poly(propylene-ethylene) copolymer are described.

EXPERIMENTAL

Materials

Mica. Sixty-mesh coupled and uncoupled phlogopite mica were used in this investigation. The coupling agent was a silane sulfonyl azide.

Resins. The matrix materials were obtained in powder form. They were a polypropylene homopolymer, and two poly(propylene-ethylene) copolymers. One of the copolymers contained a premixed coupling agent system. However, both unfilled copolymers exhibited nearly the same impact behavior which was superior to that of the homopolymer. The copolymer systems will be referred to interchangeably throughout the text. The matrix materials had a nominal melt flow index of 4.0 g/10 min (ASTM method D1238). Ethylene-propylene-diene monomer (EPDM) rubber, in pellet form, was used as a toughener. Analysis performed on the EPDM sample revealed that it contained polyethylene, present either as a blend component or as a block copolymer. Also a small amount of acrylic comonomer was detected. The nominal melt flow index of the EPDM was 1 g/10 min (ASTM method D1238).

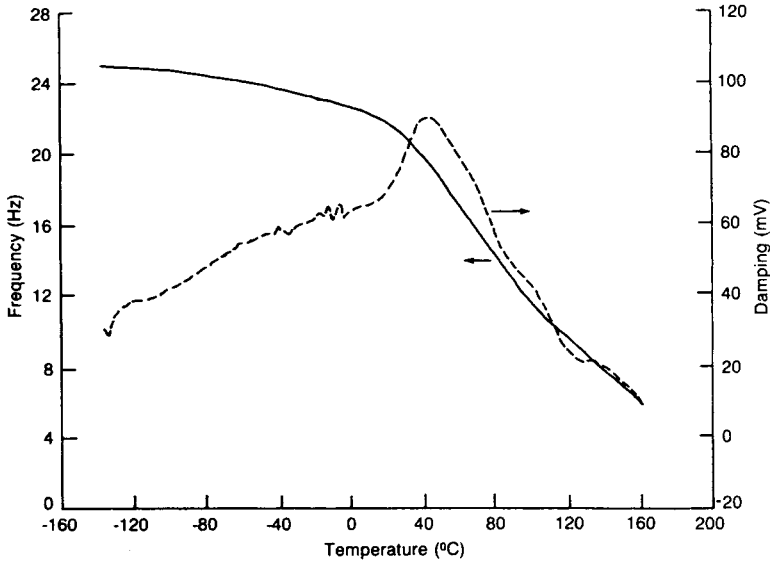
Compounding and Sample Preparation

The components were tumble-blended together in a 4-liter metal container equipped with lateral blades or baffles to aid in mixing. Tumbling took place for 2 hours on a roll mill at room temperature. For the dry-blended system this mixture was directly injection-molded into specimens. To obtain the extrusion-mixed system, the same procedure was followed as for dry blending except the final mixture was subsequently extruded into rods at 180°C. A single-screw Brabender Plasticorder normally employed for blending elastomers with plastics was used for this purpose. The extruded rods were pelletized, dried under a vacuum for 2 h at 100°C, and stored in a desiccator until injection-molded. The difference in compounding for the two cases is that the extrusion-blended compound has an additional melt mixing step. Tensile and flexural bars conforming to ASTM methods D638 (Type I) and D790, respectively, were prepared using a Newbury injection-molding machine. Notched Izod impact samples were prepared from the center portion of the tensile bars.

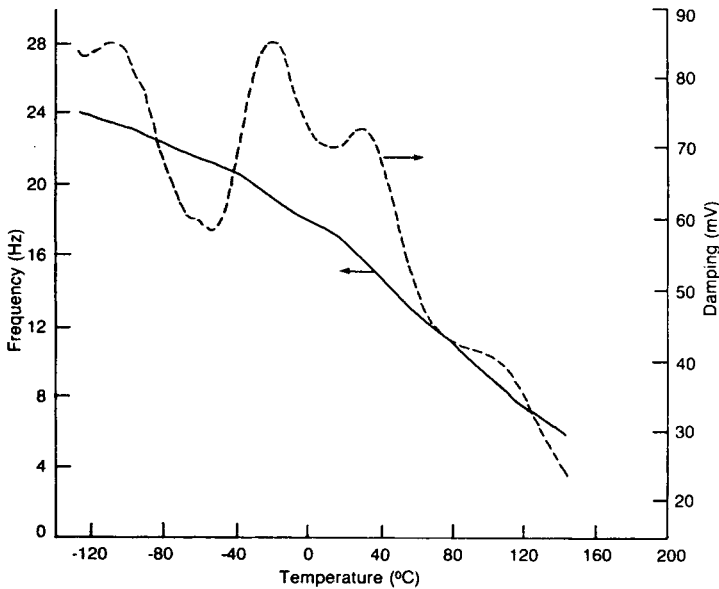
Mechanical Property Determinations

Since impact strength and flexural modulus were identified as key properties to optimize for the material development aspect of this project, the mechanical property determinations were confined to these two. ASTM methods D790 and D256 were followed for determining the flexural modulus and impact values, respectively. All results are averages of 4 to 6 samples.

Measurements for flexural modulus determinations were made at 25°C. Notched Izod impact properties were determined over a range of temperatures. Basically, the notched samples were placed in an environmental chamber at the desired temperature and allowed to thermally equilibrate. The samples were individually removed from the chamber and tested as required.



(a)



(b)

Fig. 1. (a) Dynamic mechanical properties of polypropylene. (b) Dynamic mechanical properties of a poly(propylene-ethylene) copolymer.

Material Characterization

Differential scanning calorimetry (DSC) was used in an effort to identify any low temperature transitions of the resins that could be useful in developing low temperature impact properties. Unfortunately, due to the low magnitude of the change in specific heats, it was difficult to define sharp transitions in the resins—particularly for the matrix materials. However, a glass transition (T_g) temperature of -55°C was detected for the EPDM using this method.

Consequently, dynamic mechanical relaxation spectra were determined using a Du Pont dynamic mechanical analyzer (DMA) to characterize the matrix materials. The Du Pont DMA is a modular unit and was used with a Du Pont 1090 thermal mechanical analyzer console. In essence, a sample was mounted between two pivot arms of the instrument and subjected to cyclic deformation at an operator-defined amplitude. The sample was forced to oscillate at its natural or resonance frequency which is related to the modulus; and, the incremental electrical power added to the system in order to maintain a constant amplitude is related to the mechanical loss or damping.⁸ Both the frequency and the damping were recorded as a function of temperature. In Figures 1(a) and (b) mechanical relaxation spectra for polypropylene and the poly(propylene-ethylene) copolymer are shown, respectively. For polypropylene there is a broad peak near 45°C that is attributed to the T_g . For the poly(propylene-ethylene) copolymer there are three major peaks near or below room temperature. The relative positions of these three peaks agree with those reported by Yeh et al.⁹ for a mechanical relaxation spectrum of a poly(propylene-ethylene) copolymer: the small peak at -105°C is due to amorphous polyethylene; the peak at -20°C is related to the ethylene-propylene rubber; and the peak at 35°C is associated with polypropylene.

RESULTS

Material Properties as a Function of Mica and EPDM Content

In Figure 2 the effects of mica content on the notched Izod impact strength and flexural modulus of polypropylene are shown. The flexural modulus increases monotonically and nonlinearly with increasing mica content. The notched Izod impact properties are low and change very little with mica content.

In Figure 3 the effects of EPDM on the notched Izod impact properties and flexural modulus of polypropylene are shown. Here a dramatic increase in the notched Izod values is evidenced for the rubber-modified systems even at relatively low amounts of EPDM. Over this same compositional range there is only a minor decrease in the flexural modulus. Taken together, the data presented in Figures 2 and 3 provide a reasonable basis for blending EPDM with mica and polypropylene and expecting to achieve a system with improved impact resistance and yet maintain acceptable flexural modulus.

With this framework, a family of compounds was prepared using these components. In Figure 4 the flexural modulus dependence on EPDM and mica contents for the compounds is presented on three-dimensional coordinates in order to detail the effect. The relative flexural moduli, defined as the ratio of

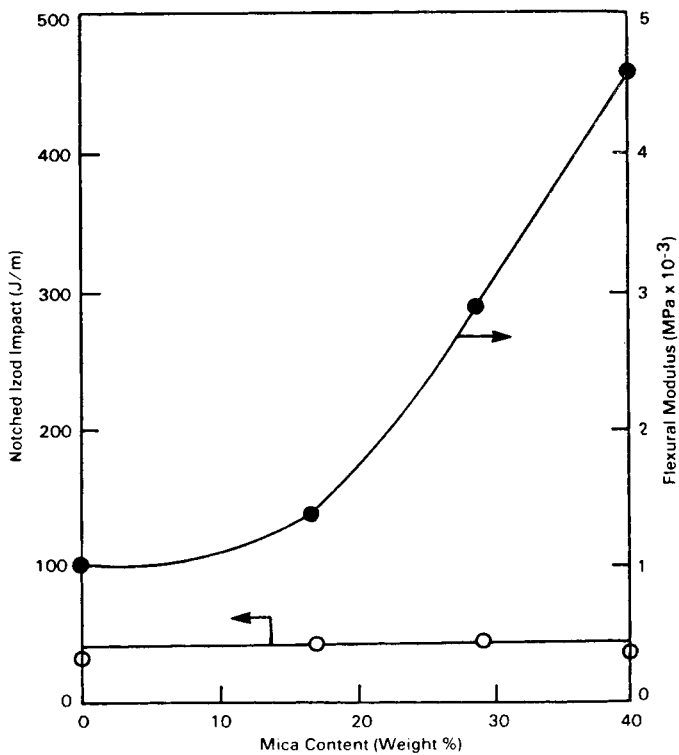


Fig. 2. Effects of mica content on the notched Izod impact and flexural modulus of polypropylene.

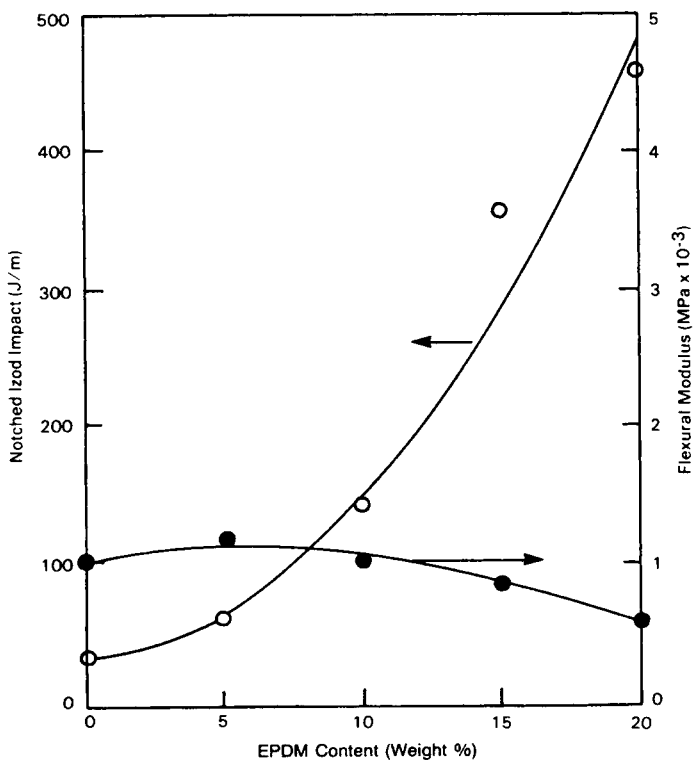


Fig. 3. Effects of EPDM content on the notched Izod impact and flexural modulus of polypropylene.

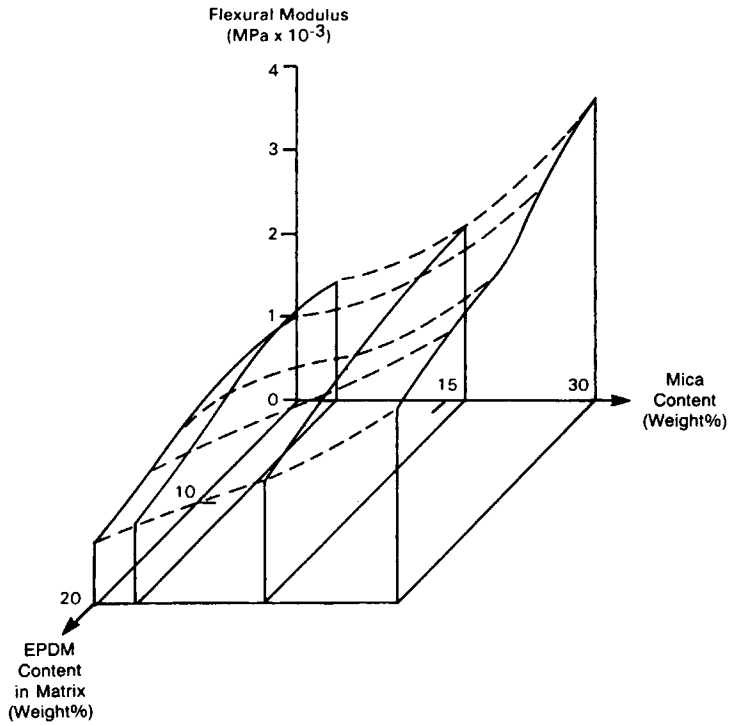


Fig. 4. Three-dimensional plot showing effects of mica and EPDM contents on the flexural modulus.

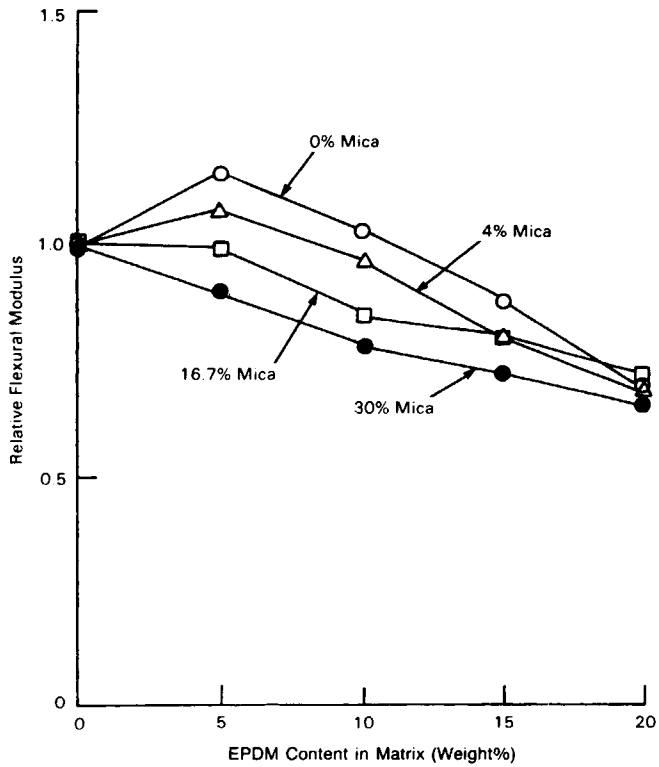


Fig. 5. Effects of EPDM content on the relative flexural modulus of mica-filled polypropylene. (○) 0%; (Δ) 4%; (□) 16.7%; (●) 30% mica.

the flexural modulus of the EPDM-modified system to the flexural modulus of the unmodified system, were determined using the data from Figure 4. The relative flexural modulus is plotted as a function of EPDM content in Figure 5 for the compounds with various mica contents. If no change occurred in the flexural modulus upon addition of modifier to the system, then the relative flexural modulus would be unity. It is interesting to note that for the unfilled system at the 5% modifier level, the flexural modulus is about 15% greater than for the base polypropylene. While surprising, the magnitude of the difference, and the fact that for the system containing 4% mica there is also a relative flexural modulus greater than one, precludes the dismissal of these data as spurious points. Generally, however, these results show that over most of the compositional range the relative flexural modulus decreases systematically with increasing mica content.

In Figure 6 notched Izod impact values are plotted against percent EPDM content in the matrix and percent mica on three-dimensional coordinates.

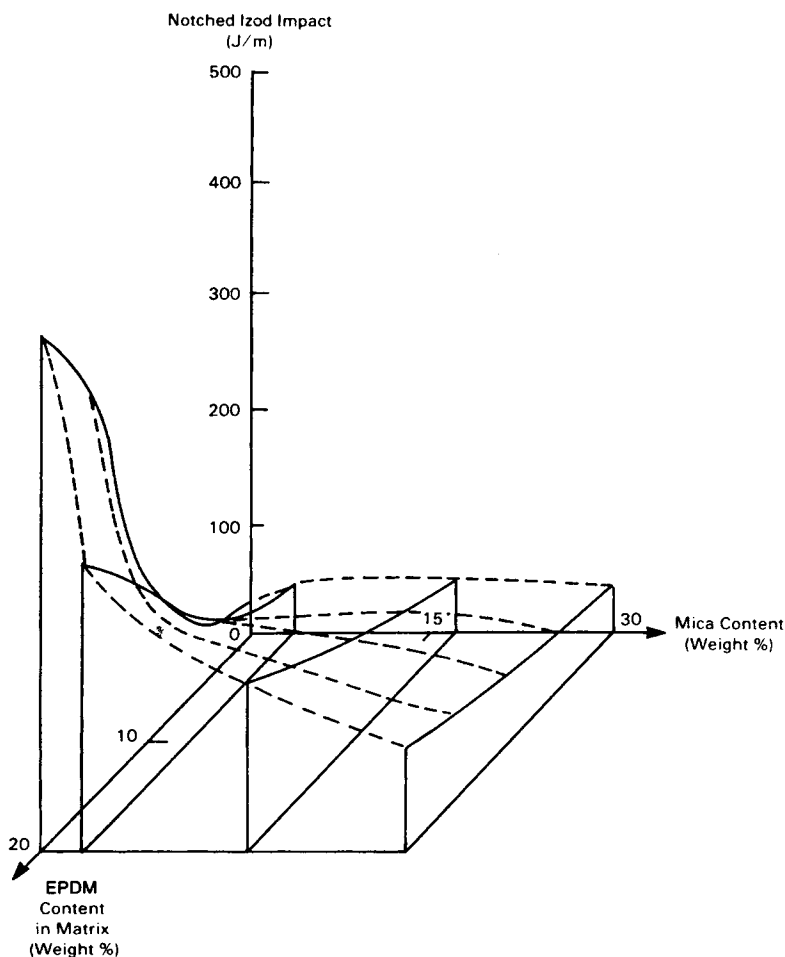


Fig. 6. Three-dimensional plot showing effects of mica and EPDM contents on notched Izod impacts.

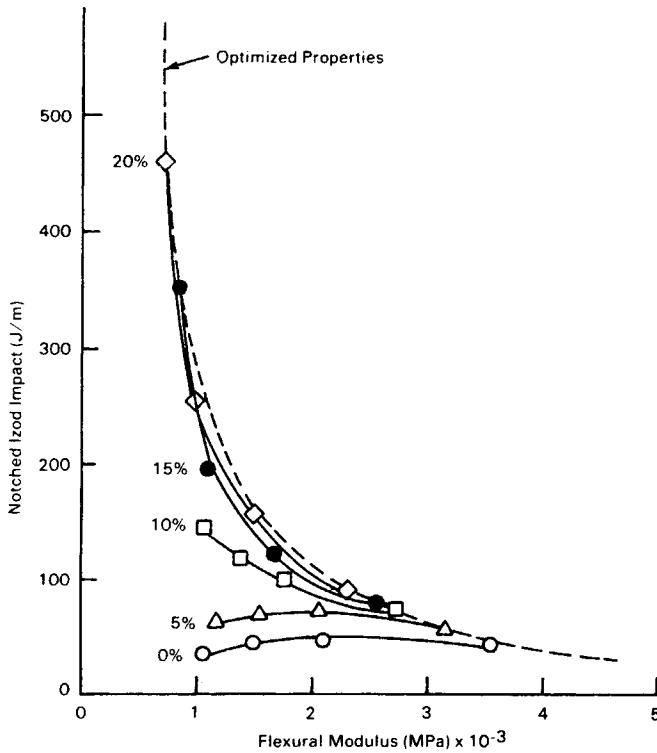


Fig. 7. Notched Izod impact plotted against flexural modulus of EPDM-modified mica-filled polypropylene. (\diamond) 20%; (\bullet) 15%; (\square) 10%; (Δ) 5%; (\circ) 0% EPDM.

Highest impact properties are achieved at lower mica loadings and higher modifier contents.

Notched Izod impact is plotted against flexural modulus in Figure 7 for the family of EPDM-modified mica-filled materials. The mica content is not explicitly stated but increases orderly from 0 to 30% by total weight from left to right along the x axis. Close scrutiny of Figure 7 shows that for a wide range of compositions the data become "compressed" with increasing flexural modulus. The outer limit of these data seems to define a hyperbola as represented by the dashed line. Clearly, for the compositional range covered here this hyperbola defines the maximum Izod impact value attainable for a given flexural modulus using our processing method.

Material Properties as a Function of Compounding Procedure

In Figure 8, a comparison is shown on a bar graph of notched Izod impact values for several polypropylene systems prepared by dry blending and extrusion mixing. Basically, for unfilled polypropylene, there is not much difference in the properties for samples prepared by dry blending and extrusion mixing. The apparent improvement in the notched Izod impacts is not significant considering the level of scatter associated with such low notched impact values of polypropylene. Moreover, these data suggest that the additional extrusion step does not adversely affect the impact properties;

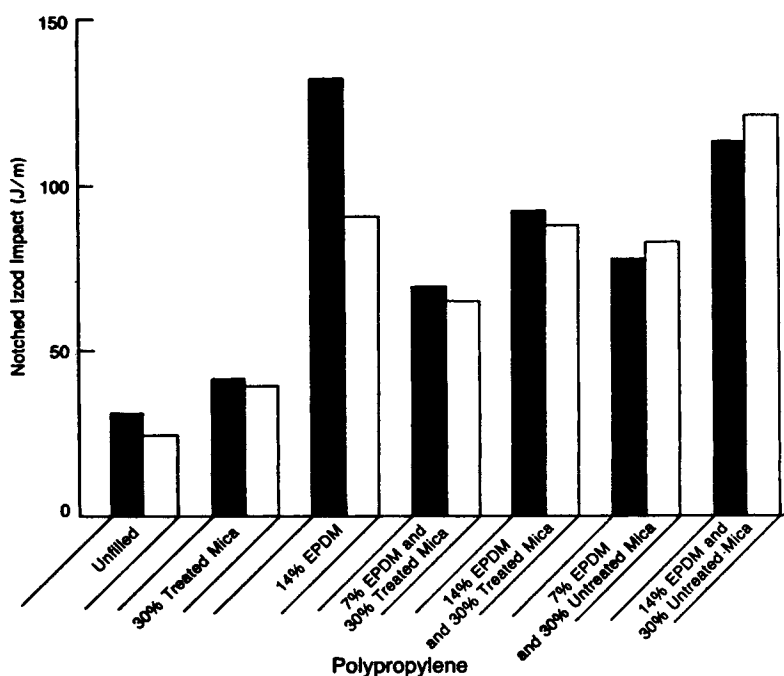


Fig. 8. The effect of compounding procedure on the notched Izod impact of several polypropylene systems. (□) Dry blended; (■) extrusion mixed.

consequently, any significant increase in polymer degradation through extrusion blending is unlikely. Similarly, there is very little change in the impact values for unmodified polypropylene containing mica.

In comparing dry blending with extrusion mixing for polypropylene containing 14% EPDM there is a significant increase in the impact values from 90.2 to 132.4 J/m. Presumably, this is due to the added efficiency of melt extrusion in dispersing the rubber particles.

In the next two columns in the bar graph, for polypropylene containing 30% treated mica with 7% and 14% EPDM, respectively, there are slightly higher impact properties for the extrusion-mixed material. More interesting, however, are the effects of compounding procedure for EPDM-modified systems containing 30% untreated mica. In the final two columns of Figure 8 it is shown that the notched Izod impact values are higher for the dry-blended sample than for the extrusion-mixed system.

In Figure 9 the flexural moduli for the systems described in Figure 8 are shown for the two compounding procedures. For unfilled polypropylene and for polypropylene containing only EPDM there is very little difference for the two compounding methods. However, for the compounds containing mica, the flexural modulus is higher for dry-blended formulations in all cases. According to Lusiš et al.,¹⁰ the flexural modulus decreases with decreasing mica aspect ratio, which they define as the average flake diameter divided by the average thickness. Presumably, for the results presented here, extrusion mixing led to greater reductions in the mica aspect ratios and consequent lower flexural moduli than were observed for the corresponding dry-blended compounds. In

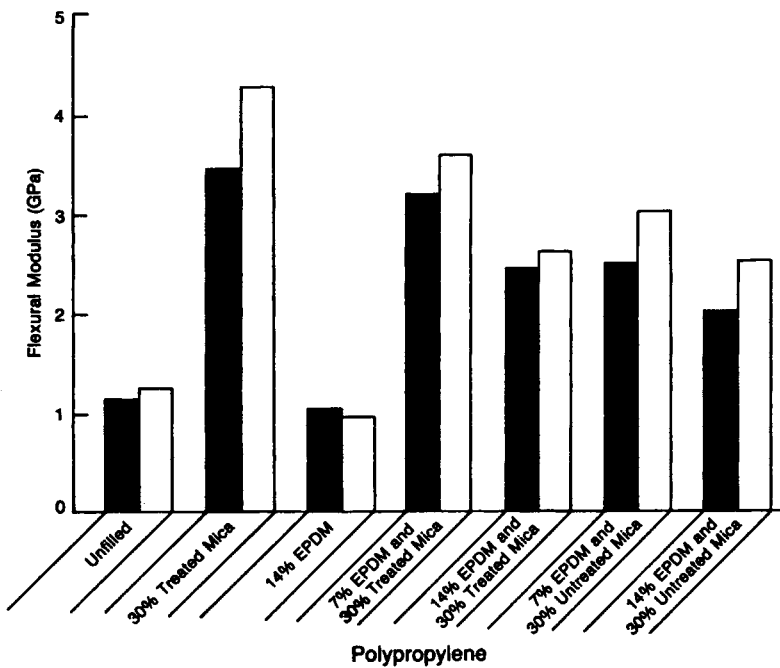


Fig. 9. The effect of compounding procedure on the flexural modulus of several polypropylene systems. (□) Dry blended; (■) extrusion mixed.

fact, larger mica particle sizes, such as the 60 mesh size used in this study, are even more prone to breakup than the smaller sizes.¹¹

Effect of EPDM Content on the Low Temperature Impact Properties of Polypropylene and Poly(propylene-Ethylene) Copolymer Systems

Shown in Figure 10 are data for notched Izod impact strength of EPDM/polypropylene blends as a function of temperature. Increasing the EPDM content for the polypropylene system did not add any significant improvement in impact resistance for samples tested at -10°C and below. These results are consistent with those reported by Jang et al.¹² who noted significant increases in impact values for polypropylene modified with 15% EPDM above 0°C but not below. Other researchers have also reported that the ductile-brittle transition temperature for EPDM-modified polypropylene is a function of rubber content.^{13,14}

According to Jang et al.,¹⁵ the mechanism responsible for the ductile-brittle transition of rubber-modified polypropylene is a change in the deformation mode from shear yielding to crazing. The craze initiation stress is presumed to be less temperature dependent than the shear band initiation stress so that at low temperatures craze formation dominates.¹⁵ Ultimately, the crazes break down to form cracks.

In Figure 11, for the copolymer system, it is noted that increasing the EPDM content leads to tougher materials well below -25°C . Collectively, these results suggest that it is more efficient to select the copolymer system

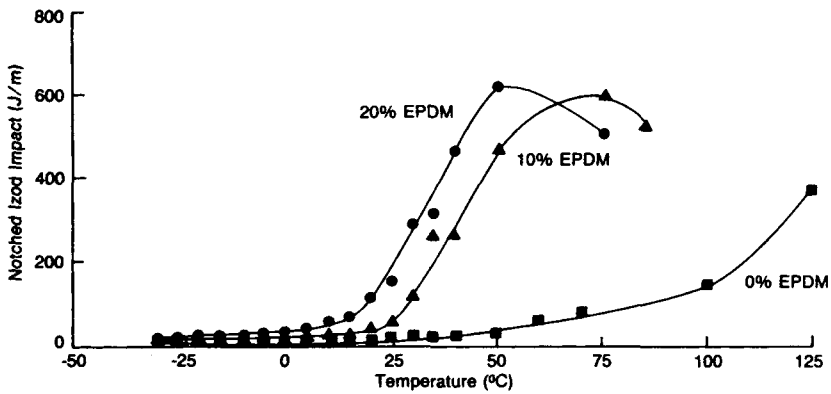


Fig. 10. The effect of temperature on the notched Izod impact of EPDM/polypropylene blends. (●) 20% EPDM; (▲) 10% EPDM; (■) 0% EPDM.

than to further increase the EPDM content in the homopolymer system. This is especially true for impact property improvements at temperatures lower than 0°C.

In comparing Figure 10 with Figure 11, it is seen that the ductile-brittle transition temperature is lowered nearly 70°C by blending 10% EPDM with the homopolymer, in contrast to only 25°C for the same amount of rubber in the copolymer system. However, by further increasing the EPDM content to 20%, the ductile-brittle transition temperature is lowered an additional 15°C in the homopolymer system; in the copolymer system the same EPDM increase lowers the ductile-brittle an additional 25°C. The reason for the

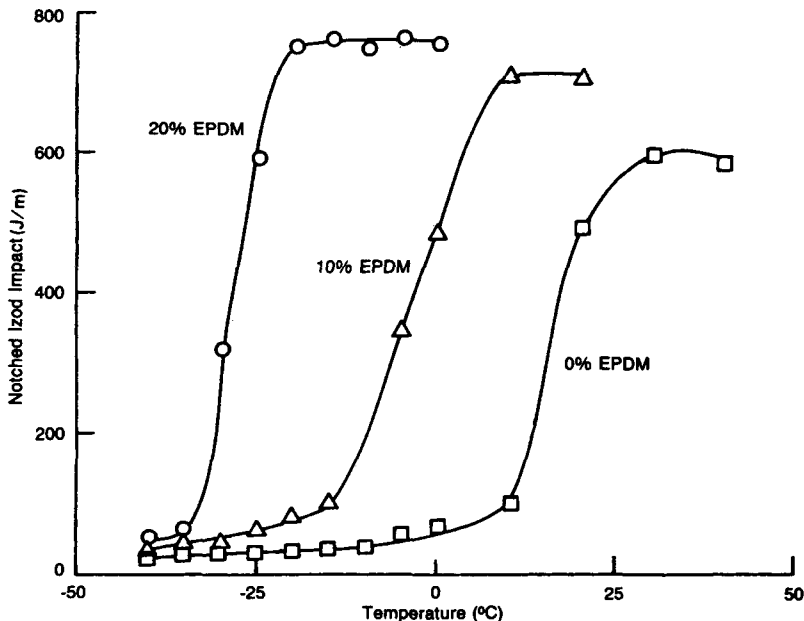


Fig. 11. The effect of temperature on the notched Izod impact of EPDM/poly(propylene-ethylene) copolymer blends. (○) 20% EPDM; (△) 10% EPDM; (□) 0% EPDM.

TABLE I
Notched Izod Impact and Flexural Modulus Data for
Mica-Filled Polypropylene Homopolymer and Copolymer Systems

Composition	Notched Izod impact @ 25°C (J/m)	Notched Izod impact @ -30°C (J/m)	Flexural modulus @ 25°C (GPa)
1. 63% Polypropylene 7% EPDM 30% Mica	81.7 ± 2.6	26.3 ± 3.2	3.00 ± 0.14
2. 63% Poly(propylene-ethylene) copolymer 7% EPDM 30% Mica	129.7 ± 21.6	53.8 ± 6.6	2.22 ± 0.19
3. 70% Poly(propylene-ethylene) copolymer 30% Mica	103.2 ± 11.1	43.9 ± 4.9	2.08 ± 0.18

difference in compositional-dependent behavior is unclear at present. Dao¹⁴ has reported similar observations for his EPDM-modified polypropylene system for impact measurements using an instrumented driven dart test. Specifically, he observed dramatic decreases in the ductile-brittle transition temperature for EPDM up to 10%, but only marginal decreases beyond 10%.

The effect of adding a relatively small amount of EPDM (7%) to minimize modulus decreases was also examined. The impact properties of mica-filled systems at 25°C and -30°C and the flexural moduli at 25°C are listed in Table I. These results show that a substantial increase in the low temperature impact properties occurred when the copolymer was used with untreated mica (43.9 J/m) compared to the EPDM-modified homopolymer system (26.3 J/m). This impact improvement was only slightly enhanced at -30°C by incorporating EPDM rubber into the copolymer matrix, though a more significant increase in the notched Izod impact occurred at 25°C. There was also a sacrifice in the room temperature flexural modulus with both copolymer systems; surprisingly, of the two copolymer systems, however, the EPDM-toughened material was found to have a slightly higher flexural modulus.

DISCUSSION

The foregoing results demonstrate that the Izod impact properties of mica-filled polypropylene can be improved significantly by the blending of ethylene-propylene-diene monomer (EPDM) rubber with only a modest reduction in flexural modulus. For example, the incorporation of 20% EPDM into the matrix of polypropylene containing 30% azidosilane-coupled mica reduced the flexural modulus by only a third but more than doubled the notched Izod impact value. A family of these materials was developed that allows the selection of compounds optimized to give the best balance of impact and flexural modulus.

In examining the effect of compounding procedure on this system, it was determined that dry blending is preferred over conventional extrusion mixing. Even though the extrusion mixing aids in the dispersal of the rubbery phase in the matrix, apparently this advantage is offset by attrition of the mica

platelets that occurred during the additional extrusion step. This mica attrition leads to reduced flexural moduli. While this study was confined to conventional extrusion mixing on a single-screw extruder, it may be possible to achieve better properties if the mica were fed in further downstream from the EPDM feed zone. This should minimize the shear history and subsequent attrition of the mica platelets.

Finally, the low temperature impact properties of this and a related poly(propylene-ethylene) copolymer system were investigated. Mechanical relaxation spectra were obtained for the matrix materials to detect any transitions below the T_g that may be related to their low temperature impact properties. Polypropylene exhibited no significant transition below T_g (near room temperature), but the copolymer exhibited two transitions below room temperature. As expected, based on the relaxation spectra, the copolymer has better low temperature impact resistance. Furthermore, the ductile-brittle transition temperatures of these materials were lowered to different degrees by blending with EPDM rubber. Based on the extent of lowering of the ductile-brittle transition temperature for the two systems, it is concluded that the use of the copolymer matrix is the more efficient route to achieve high impact properties at low temperatures, while the EPDM-modified homopolymer has excellent room temperature impact properties.

CONCLUDING REMARKS

A family of EPDM-toughened mica-filled polypropylene compounds was developed which can be processed by dry blending. Elimination of any melt-compounding procedure not only simplifies the processing, but also leads to increased flexural moduli.

Impact property measurements as a function of temperature revealed well-defined ductile-brittle transition temperatures for both an EPDM-modified polypropylene homopolymer and a poly(propylene-ethylene) copolymer. The ductile-brittle transition temperature was lowered by increasing the EPDM content for both systems. However, the modified copolymer system maintained ductility to far lower temperatures than the corresponding homopolymer system.

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References

1. B. P. N. Ko, *Canadian Plastics*, 40 (1980).
2. T. Vu-Khanh, B. Sanschgrin, and B. Fisa, *Poly. Compos.*, 6, 249 (1985).
3. C. Busigin, R. Lahtinen, G. M. Martinez, G. Thomas, and R. T. Woodhams, *Polym. Eng. Sci.*, 24, 169 (1984).
4. J. E. Stamhuis, *Poly. Compos.* 5, 202 (1984).
5. J. Karger-Kocsis, A. Kallo, and V. N. Kuleznev, *Polymer*, 25, 279 (1984).
6. K. C. Dao and R. A. Hatem, *42nd Annu. Tech. Conf., Preprints*, Soc. Plast. Eng., 198 (1984).
7. K. C. Chu, A. N. Wright, and R. T. Woodhams, *INTEC 85*, Polymer Modifiers and Additives Division, Soc. Plast. Eng. (November 1985).
8. R. L. Blaine and L. Woo, *Am. Chem. Soc., Polymer Preprints*, 17, 1 (1976).

9. P. L. Yeh, A. W. Birley, and D. A. Hemsley, *Polymer*, **26**, 115 (1985).
10. J. Lúsis, R. T. Woodhams, and M. Xanthos, *Polym. Eng. Sci.*, **13**, 139 (1973).
11. M. Xanthos, G. C. Hawley, and J. Antonacci, *35th Annu. Tech. Conf., Preprints*, Soc. Plast. Eng., 352 (April 1977).
12. B. Z. Jang, D. R. Uhlmann and J. B. Vander Sande, *J. Appl. Polym. Sci.*, **30**, 2485 (1985).
13. J. Karger-Kocsis and V. N. Kuleznev, *Polymer*, **23**, 699 (1982).
14. K. C. Dao, *J. Elastomers Plastics*, **15**, 227 (1983).
15. B. Z. Jang, D. R. Uhlmann, and J. B. Vander Sande, *J. Appl. Polym. Sci.*, **29**, 3409 (1984).

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