

Impact Strength and Dynamic Mechanical Properties Correlation in Elastomer-Modified Polypropylene

S. H. JAFARI,* A. K. GUPTA

Centre for Polymer Science and Engineering, Indian Institute of Technology, Hauz Khas, New Delhi-110016, India

Received 19 January 1999; accepted 20 August 1999

ABSTRACT: This article describes the impact and dynamic mechanical properties of rubber-modified binary blends of polypropylene (PP). Two conventional elastomers [viz. ethylene vinyl acetate copolymer (EVA) and ethylene propylene diene terpolymer (EPDM)] were used as an impact modifier for PP. It is clearly indicated by the results that EPDM is better than EVA as an impact modifier of PP. Analysis of data of dynamic mechanical properties and impact properties at various compositions of the blends revealed a direct correlation between impact properties and dynamic mechanical loss tangent. The energy dissipation due to viscoelastic relaxation is therefore suggested as a mechanism of impact toughening of PP, in addition to the other commonly known mechanisms of toughening (viz. shear yielding and crazing induced by deformation of rubber-phase domains). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 962–971, 2000

Key words: polypropylene blend; PP/EVA blend; PP/EPDM blend; impact properties; dynamic mechanical properties

INTRODUCTION

One of the major drawbacks of polypropylene (PP) is its low impact strength, particularly at low temperatures. Hence, impact toughening of PP with various types of elastomers has gained much attention in recent years.^{1–13} Several mechanisms of impact toughening has been proposed for elastomer-modified PP. Shear yielding and crazing is known to be the main mechanisms of impact toughening for PP. However, it is known that mechanical properties at low strain (i.e., before the occurrence of detectable crazing and shear yielding) depend on viscoelastic behavior of individual components of the blends.¹⁴ Viscoelastic energy dissipation may be expected to make a

significant contribution in the impact energy, owing to the fact that the time scale involved in impact deformation is of comparable order of magnitude as the relaxation time of viscoelastic relaxations, (i.e., on the order of milliseconds). Correlation of impact strength with dynamic mechanical properties is indicated by many authors.^{15–22} Gill and Hansel found a correlation between the intensity of loss peak at -110°C and the drop-weight impact strength determined at -29°C for impact-modified PP. In elastomer blends, toughness shows some correlation with the area of the loss peak due to primary or secondary transition of rubbery component. Sacher emphasized the relationship between the impact strength and the dynamic mechanical dissipation factor ($\tan \delta$) determined under the same temperature and frequency conditions. However, Hiltner and Baer²¹ and Ramsteiner²² rejected the possibility of any quantitative correlation between the dynamic mechanical relaxations measured in the region of linear viscoelasticity and the yield and

Correspondence to: A. K. Gupta.

* Present address: Institute of Polymer Research Dresden, Hohe Str. 6, Dresden 01069, Germany.

Journal of Applied Polymer Science, Vol. 78, 962–971 (2000)
© 2000 John Wiley & Sons, Inc.

Table I Characteristics of the Polymers Used

Materials	Trade Name and Grade	Supplier	Characteristics
PP	Koylene S3030	Indian Petrochem. Co. Ltd., India	MFI = 3.0 g/10 min Density = 0.90 g/cm ³
EVA	1802F	Polyolefines India Ltd., India	MFI = 2.0 g/10 min Density = 0.94 g/cm ³ VA = 18
EPDM	Herlene IM-7200	Herdillia Unimers Ltd., India	MFI = 0.9 g/10 min Density = 0.87 g/cm ³ E = 62 wt % P = 34 wt % D (Ethylidenenorbornene) = 4 wt %

fracture energy because of the predominance of nonlinear effects in the latter phenomena.

In this article we report on a study of impact and dynamic mechanical properties of the two rubber-toughened PP systems, the binary blends of PP with ethylene vinyl acetate copolymer (EVA) and ethylene propylene diene terpolymer (EPDM) (viz. PP/EVA and PP/EPDM blends at varying blend compositions). Interesting observations about the correlation of impact and dynamic mechanical relaxation of PP in its glass transition region are reported and discussed.

EXPERIMENTAL

Materials and Blend Preparation

The polymers used and their important characteristics are listed in Table I. Binary blends of PP with EVA and EPDM in the blend composition range of 0–30 wt % of the second component of the blend were prepared by melt–mixing techniques. Melt–mixing was done on a twin-screw extruder (Brabender Plasticorder PLE 651, Germany). All the polymers were dried in a vacuum oven at 70°C for over 24 h to ensure complete removal of moisture. The granules were dry mixed in appropriate ratios and extruded at 200°C and at a screw speed of 10 rpm. The extruded strands were quenched immediately in a water bath at ambient temperature. The extrudates were then chopped into granules and finally dried at 70°C for over 24 h before injection molding into test specimens. The pure polymers were also extruded in the same way so that they would have the same history as the blend samples.

Preparation of Test Specimens

Test specimens for measurement of impact and dynamic mechanical properties were prepared by injection molding on a Windsor SP-1 (Germany) injection molding machine having a reciprocating screw (max. shot 53 mL). Test specimens in the shape of rectangular bars (3 × 10 × 35 mm, thickness × width × length) were cut smoothly from the injection-molded tensile specimens in accordance with ASTM D2236 for dynamic mechanical test and rectangular-shaped bar specimens (4 × 10 × 64 mm, thickness × width × length) were made for the impact test. The processing temperatures used were the same as used in the extrusion process (i.e., 190–200°C in the different zones of the injection molding machine).

Measurements

Izod Impact Testing

The impact test was done by using an FIE Izod impact tester (Model IT 0.42 pendulum-hammer-type). A notch of 2.5-mm depth with an angle of 45° was made on the specimens for impact testing. Impact energy was calculated from the difference of potential energy of the pendulum hammer before and after the impact. The impact strength is expressed in terms of the energy absorbed per meter of notch (J/m). Sample dimensions conformed to ASTM D-256. All measurements were done at ambient temperature. The values reported are average values of at least five samples.

Scanning Electron Microscopy

The SEM micrographs were recorded on a Cambridge Stereoscan 360 scanning electron micro-

Table II Impact Strength of Rubber-Modified Binary Blends of PP

Blends	Blending Ratio	Impact Strength (J/m)
PP/EVA	100/00	18.5
	95/05	19.4
	90/10	25.3
	80/20	31.6
	70/30	36.9
PP/EPDM	100/00	18.5
	95/05	27.2
	90/10	37.4
	80/20	251.0
	70/30	350.9

scope (UK). Impact-fractured surface of the specimens after suitable etching were sputter-coated with silver prior to scanning. Toluene and xylene were used to etch out the EVA and EPDM component of the blends, respectively.

Dynamic Mechanical Properties

Dynamic mechanical properties were measured on a dynamic mechanical thermal analyzer

(DMTA) manufactured by Polymer Laboratories (UK). Experiments were carried out on a single cantilever arrangement in bending mode in the temperature range from -100 to 150°C at a heating rate of $5^{\circ}\text{C}/\text{min}$. In the bending mode, the sample is usually in the form of a rectangular bar clamped rigidly at both ends and with its central point vibrated sinusoidally by the drive clamp.²³ Cooling was achieved by pumping liquid nitrogen through the accessories provided in the instrument. Samples were scanned with imposed frequency of 10 Hz. A plot of storage modulus (E'), loss modulus (E''), and $\tan \delta$ were recorded as a function of temperature. The T_g is taken as the temperature of the maximum in E'' or $\tan \delta$ ($\tan \delta = E''/E'$) plots. Measurements of all the samples were made at identical conditions for a valid and reliable comparison of the results.

RESULTS AND DISCUSSION

Impact Properties

The notched Izod impact strength (called hereafter impact strength) of PP/EVA and PP/EPDM

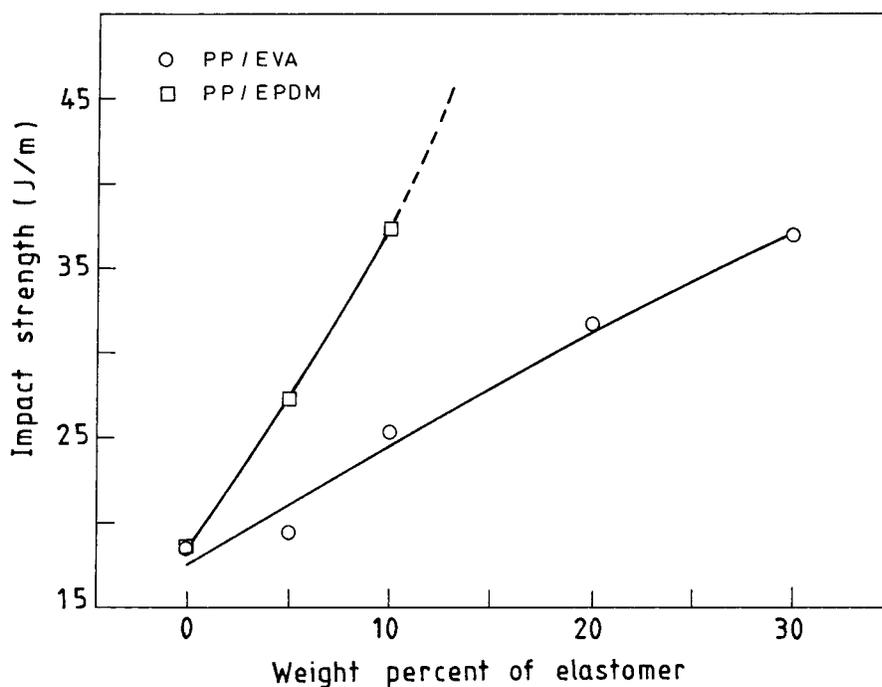


Figure 1 Variations of impact strength as a function of weight percent of elastomer component in the binary blends of PP.

blends are given in Table II. Variations of impact strength with blend composition are shown in Figure 1. In general, impact strength of PP improved by blending with the elastomers. However, the extent of improvement of impact strength varied with the nature of the second component of the blends (i.e., the elastomer). It is seen that blending with EPDM produces greater improvement of impact strength of PP, as compared to the case of PP/EVA blend.

Based on polynomial curve fitting, the following relations were found between the impact strength (IS) and weight fraction (ϕ) of minor component for the studied blends. This relationship is linear in the case of the PP/EVA blend with a zero value of ϕ^2 term, whereas it is slightly nonlinear for the PP/EPDM blend with the occurrence of the ϕ^2 term with a much lower weight (or coefficient) than the ϕ term.

$$(IS)_{PP/EVA} = 0.0\phi^2 + 0.37\phi + 17.06 \quad (R = 0.95) \quad (1)$$

$$(IS)_{PP/EPDM} = 0.21\phi^2 + 6.04\phi - 0.61 \quad (R = 0.96) \quad (2)$$

Values of the coefficient of regression (R) are close to unity for both the blend systems, suggesting good reliability of relationship (1) and (2). The occurrence of the ϕ^2 term only in PP/EPDM blend suggests a faster rise of impact strength with an increase of the elastomer content for the PP/EPDM blend than for the PP/EVA blend. On comparing the coefficient of the linear term [i.e., (ϕ)], one can see that PP/EPDM again shows a higher value for coefficient of ϕ , suggesting a greater efficiency of EPDM than of EVA in impact toughening of PP.

In general, EPDM was found to be the better impact modifier for PP in the entire studied range of blend composition. At 30% EPDM content, the impact strength of the blend was higher than that of pure PP by a factor of 19.0. PP/EVA blend, on the other hand, shows only two times higher impact strength than that of PP at the higher EVA content, (i.e., 30%). The increase of impact strength in PP/EPDM and PP/EVA blends is attributed to the rubbery nature of the minor phase, which absorbs a part of the impact energy and undergoes deformation. This is evident from the SEM micrographs of the impact-fractured surface of the blends. Figure 2a, b shows the SEM pho-

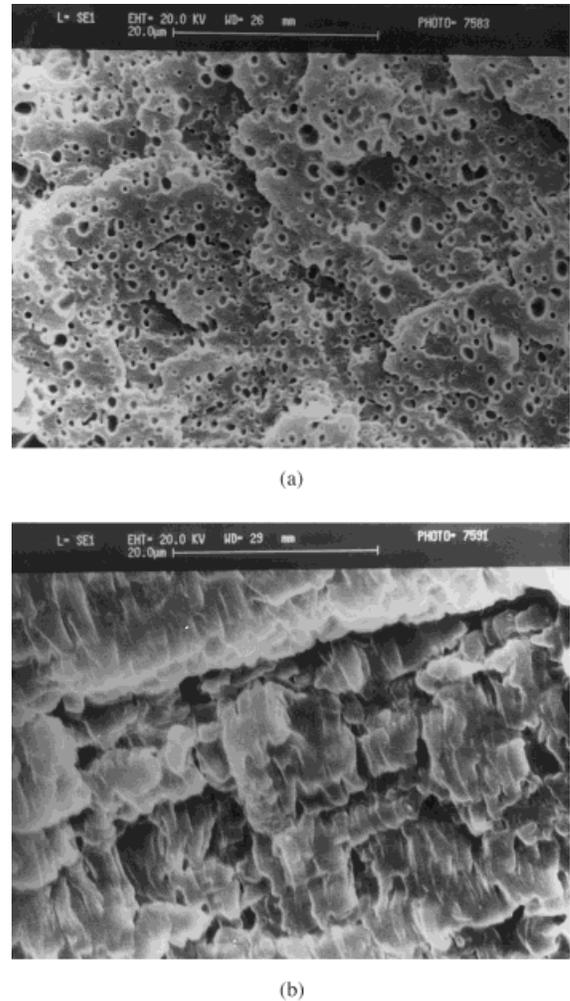


Figure 2 SEM photo micrographs of impact-fractured surface of the PP binary blends: (a) PP/EVA (70/30), (b) PP/EPDM (70/30).

tomicrographs of PP/EVA and PP/EPDM blends at comparable blending ratio [i.e., (70/30), respectively]. The rubber domains are highly deformed particularly in the case of the PP/EPDM blend. These deformed domains causes shear yielding and/or formation of crazes in the surrounding matrix, which further absorb the impact energy. Shear yielding is usually known to be the main mechanism of impact toughening in rubber-modified PP blend at ambient temperature.^{24–26} Shear yielding is more predominant in PP than crazing at temperatures above its T_g ; hence, this may be considered the predominant mechanism of impact toughening of these blends at the test temperatures. Furthermore, because dynamic mechanical

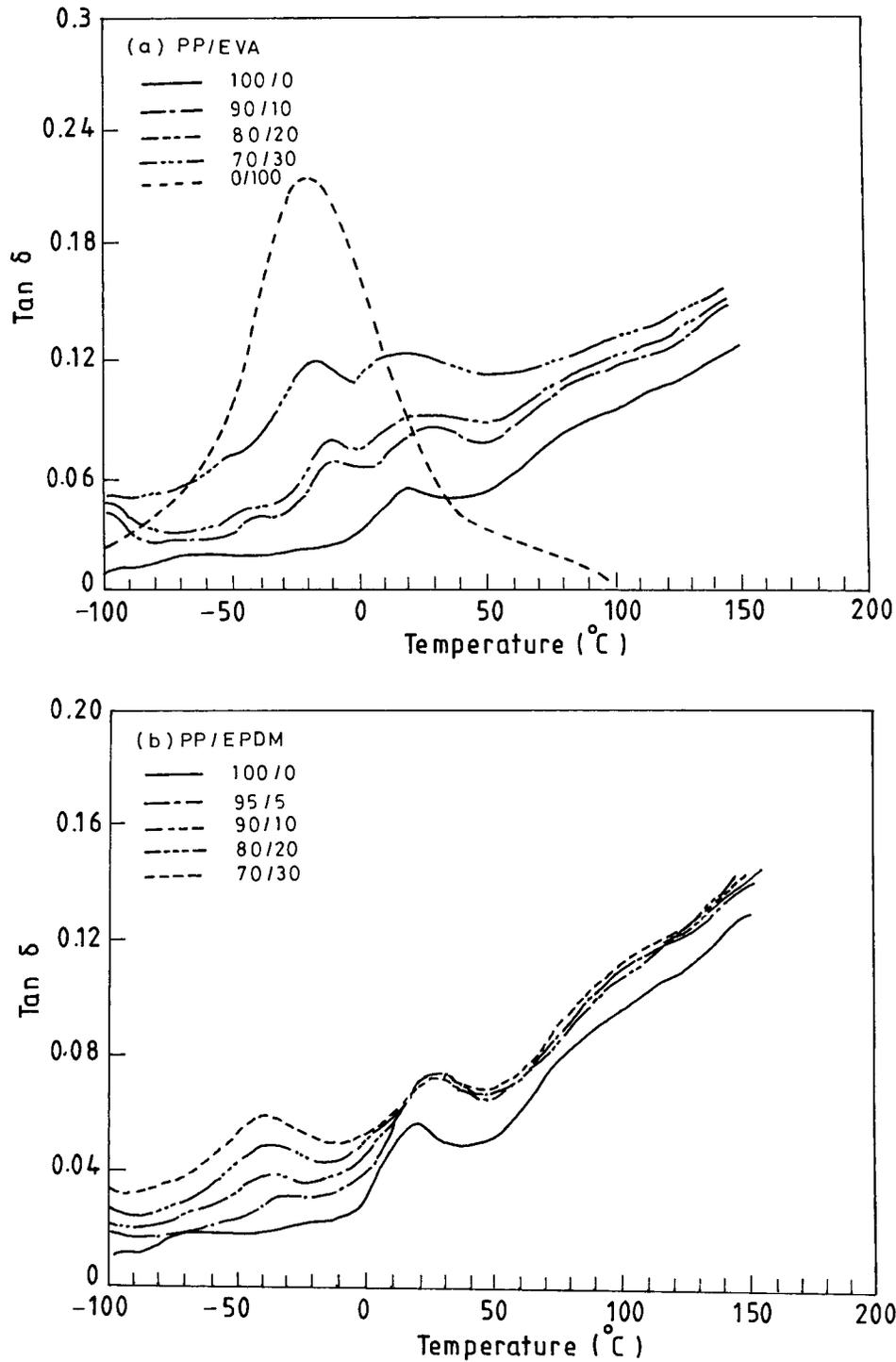


Figure 3 Plots of $\tan \delta$ versus temperature for elastomer-modified PP at various blending ratios: (a) PP/EVA, (b) PP/EPDM.

properties around glass transition relaxation are affected by the shear yielding of the matrix, a contribution of dynamic mechanical energy

dissipation may be expected in the impact toughening of PP, as will be explored in the following section.

Table III Dynamic Mechanical Properties of Rubber-Modified Binary Blends of PP

Blends	Blending Ratio	$\tan \delta$	Loss Peak Area (A_{PP}) (Arb. units)	T_g ($^{\circ}\text{C}$)	BW HH (Arb. units)	Total Loss Peak Area (Arb. units)	E' (MPa)
PP/EVA	100/00	0.058	16.0	17.0	48.0	17.0	2.11E6
	90/10	0.083	16.6	28.0	52.0	24.5	8.47E5
	80/20	0.091	18.1	18.0	54.5	30.6	7.25E5
	70/30	0.123	20.2	12.0	56.0	39.1	4.75E5
PP/EPDM	100/00	0.058	16.0	17.0	48.0	17.0	2.11E6
	95/05	0.078	13.3	24.5	55.0	18.3	2.07E6
	90/10	0.078	12.7	24.0	55.0	21.5	1.89E6
	80/20	0.079	12.3	24.0	55.0	28.5	1.47E6
	70/30	0.078	9.5	24.5	55.0	34.2	1.72E5

Dynamic Mechanical Properties

Damping ($\tan \delta$)

Dynamic mechanical measurements on these binary blends of PP show well-defined separate peaks corresponding to the glass transition relaxations of the individual components of the blends. The plots of $\tan \delta$ as a function of temperature for PP/EVA and PP/EPDM at the various compositions of the blends are presented in Figure 3 a, b, respectively. These separate peaks for the individual components are indicative of incompatible nature of the blends. These dynamic mechanical properties data in quantitative terms are calculated according to the procedure described elsewhere²⁷ and presented in Table III for further comparison and analysis. It is seen that loss maximum ($\tan \delta_{\max}$) of PP component of the blends shifts to higher/lower temperature or remains almost unchanged depending on the type of the elastomer used in these blends. Similarly, the height, area under the loss peak (loss peak area), and band-width-at-half-height (BW HH) corresponding to PP component of the blends change depending on the nature of the elastomer component of the blends. The increase in height and area of the loss peak is representative of, respectively, the maximum and total energy dissipated because of viscoelastic relaxation of the PP component of these blends. However, the increase in width may represent the presence of an increase in the range of the order or crystallinity of the PP component as a result of blending.²⁸

In general it is seen that $\tan \delta_{\max}$ and loss peak area and BW HH of PP increase on blending it with EVA and decreases or remains unchanged

on blending PP with EPDM. This may be attributed to the crystallizable nature of the second component of the blend. The PP/EPDM blend contains a noncrystallizable second component, whereas, in the PP/EVA blend, the second component (viz. EVA) is a crystallizable polymer.

Furthermore, the data in Table III shows that in the case of PP/EVA blend, the increase in $\tan \delta_{\max}$ and the loss peak area are more pronounced at higher EVA content, whereas BW HH shows an almost continuous increase by increasing EVA content of the blend. This indicates that the energy dissipation due to glass transition relaxation of PP increases with increasing EVA content of the blend more prominently at higher EVA content. However, the $\tan \delta$ peak temperature (T_g) first increases to higher temperature on initial addition of 10% EVA, and thereafter it decreases rapidly up to 30% EVA content. In the case of PP/EPDM blend, on the other hand, the increase in $\tan \delta_{\max}$, T_g , and BW HH are more pronounced on initial addition of 5% EPDM, whereas these remain almost unchanged at higher EPDM content. The observed increase of T_g of PP on initial addition of EPDM may be attributed to the effect of EPDM domains on the segmental mobility of PP. It seems that EPDM owing to its superior interfacial adhesion with PP than EVA produces greater restrictions on segmental mobility of PP chains. Better interfacial adhesion of EPDM with PP, than EVA with PP, is expected due to the affinity of olefinic groups of EPDM with PP. It is also known from our studies of crystallization behavior of these blends, reported elsewhere,^{29,30} that the increase of crystallinity of PP is more in the PP/EPDM blend than in PP/EVA blend at

identical blending ratios. Increase in crystallinity affects the segmental mobility or the glass transition temperature of PP. Therefore, in PP/EPDM blend the relaxation corresponding to glass transition of PP occurs at higher temperatures. On the other hand, at higher EVA content, the rubbery nature of EVA or more specifically the amorphous region of EVA, seems to be more effective than its role in increasing the crystallinity of the PP and it lowers the T_g of the matrix polymer. In the case of PP/EPDM, it seems that the effect of crystallinity is more pronounced as loss peak area decreases and T_g increases as a result of the blending. Comparison of the DSC crystallinity of the PP component in these two blends suggests that EPDM is more effective than EVA in enhancing the crystallinity of PP in the blend.^{29,30} This may be due to the difference of interfacial effects produced by EPDM than EVA on PP crystallization.

Stiffness (Storage Modulus)

Stiffness is an important end-use property for impact-modified PP. The glass transition-like behavior for the blend may be visualized at a temperature at which the blend (on cooling) goes from a flexible, more rubberlike form, to a more rigid inflexible form. This may be mainly governed by the glass transition temperature of the matrix (i.e., the major component of the blend), although affected by the presence of the second component. The stiffness of the blend, which is a critical parameter in determining the suitability of the blend for specific applications, therefore, depends on the glass transition of the matrix component in the impact-modified PP blend. It also is affected by structure, morphology, degree of crystallinity, and interfacial adhesion between the component polymers. DMTA is a versatile instrument to monitor stiffness under dynamic loading of the blends over a wide temperature range, to provide quantitative and qualitative information about the performance of such materials. The plots of storage modulus (E') as a function of temperature for PP/EVA and PP/EPDM blends, at the entire range of compositions studied, are shown in Figure 4 a, b. In general, the storage modulus decreased as temperature increased. However, in the region corresponding to the maxima in $\tan \delta$ plots, the decrease of storage modulus is more rapid. Storage-modulus values at a tem-

perature corresponding to T_g of PP in the blend at the various compositions are presented in Table III for these binary blends of PP. Elastomers with their low modulus are known to decrease the stiffness of PP; however, because both the elastomers used in this work (viz. EVA and EPDM) enhanced the crystallinity of the PP^{29,30}; the fall in modulus values up to certain level of blending ratio were not appreciable, especially for PP/EPDM blends which retain the stiffness up to 20% EPDM content.

Correlation of Impact Strength with Dynamic Mechanical Properties

Plots of impact strength versus area under loss peaks and $\tan \delta_{\max}$ for the PP/EVA and PP/EPDM blends are shown in Figures 5 a, b and 6a, b, respectively. Because the impact tests were performed at ambient temperature that was above the T_g of PP, only the area of the loss peaks below this ambient temperature were taken into account.²⁷

From Figure 5a, b, it is seen that as the area under the loss peak increases the impact strength also increases. The rate of increase of impact strength varies with the nature of the polymers used as a second component of the PP binary blend. There is a linear relationship between impact strength and loss peak area in PP/EVA blend. This suggests that the viscoelastic energy dissipation is quite significant in impact toughening of this blend. However, the PP/EPDM blend shows two slopes in impact strength versus dynamic loss peak area curves, one at lower blending ratio indicating slow rise of impact strength with increase of loss peak area, and the second slope at higher blending ratios, where impact strength increases rapidly as the loss peak area increases. This indicates that for this blend, energy dissipation due to viscoelasticity of the component polymers plays a significant role in impact toughening of PP only at a low weight fraction of the elastomer component in the blend (i.e., up to 10 wt %), whereas, at higher elastomer content, mechanisms other than this might be operative so as to account for such rapid rise of impact strength. It was already mentioned that the shear yielding, crazing, plastic deformation, and/or large deformation of dispersed-phase domains were the main mechanisms of impact toughening for this blend at higher blending ratios.

We have also attempted to examine the correlation of impact strength with the value of

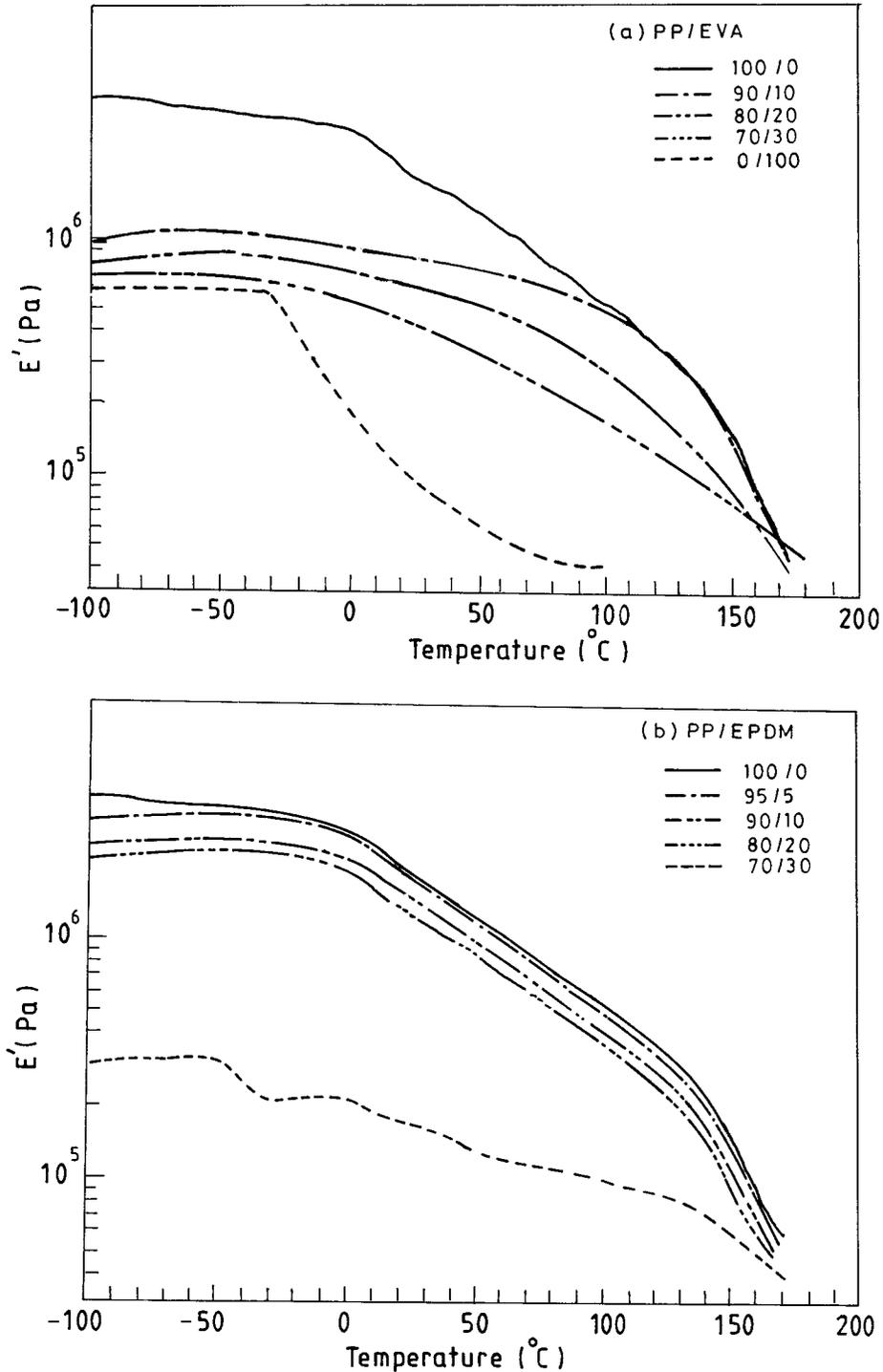


Figure 4 Plots of storage modulus versus temperature for elastomer-modified PP at various blending ratios: (a) PP/EVA, (b) PP/EPDM.

glass transition relaxation peak height of PP in the blends, [i.e., $(\tan \delta_{\max})$]. The results are shown in Figure 6 a, b. It is seen that, with the

increase of intensity of $\tan \delta$ peak, the impact strength of the blends increases, suggesting that the increase of relaxation intensity or of

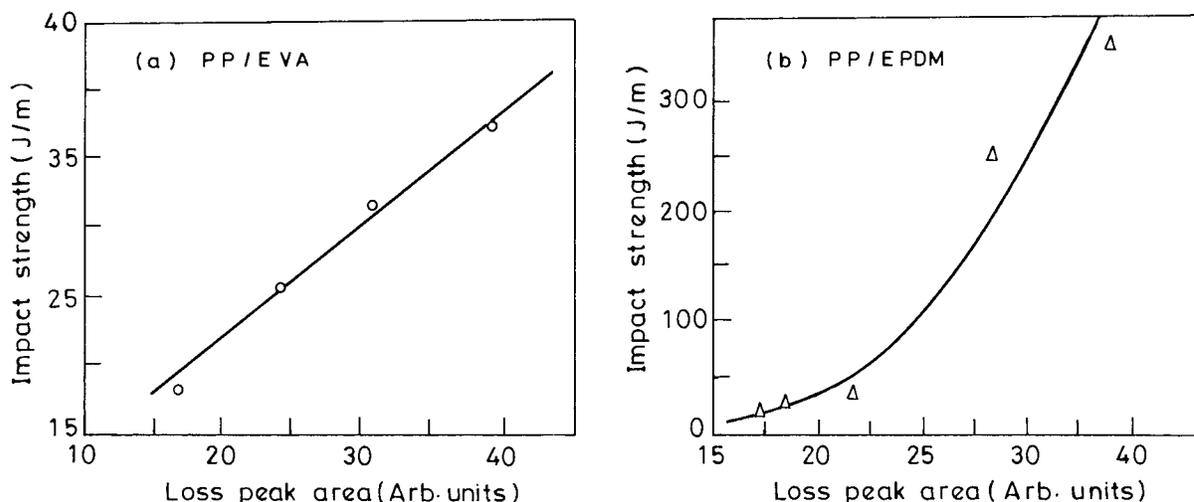


Figure 5 Correlation of impact strength and dynamic mechanical loss peak area for elastomer-modified PP: (a) PP/EVA blend, (b) PP/EPDM blend.

viscoelastic energy dissipation of the blends, is accompanied by an increase of impact strength of these blends. However, in the case of PP/EPDM, it seems the energy dissipated because of the viscoelastic relaxation of the EPDM component of the blend is more operative in enhancing the impact strength of the blend than the energy dissipated because of the relaxation of the PP component of the blend, or it may be the simultaneous effect of the relaxation of both the components of the blend.

Thus, from these observations it may be stated that in addition to crazing, shear yielding, and deformation of dispersed domains and plastic deformation of the matrix polymer, viscoelastic energy dissipation also contributes to the impact toughening of PP binary blends.

CONCLUSION

EPDM and EVA were used for impact improvement of PP. EPDM is found to be a better impact modifier for PP by increasing the impact strength of PP by a factor of up to about 20, whereas the EVA showed only two times the improvement in impact properties of PP. The analysis of dynamic mechanical properties revealed that there is a direct correlation between impact strength and loss peak area, the impact strength of blend increased with the increase of the loss factor. This suggested that the energy of dissipation due to viscoelasticity of the blend is an important mechanism of impact toughening of PP/EVA blend. However, PP/EPDM showed a nonlinear correlation between loss peak area and impact strength,

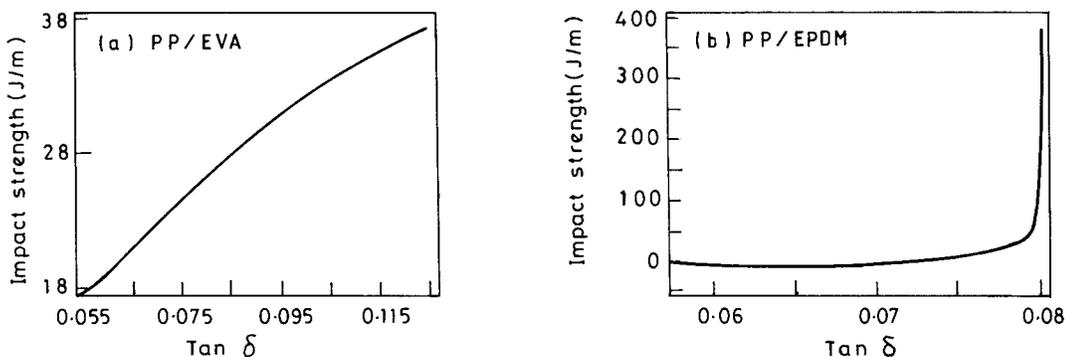


Figure 6 Correlation of impact strength and dynamic mechanical $\tan \delta_{\max}$ for elastomer-modified PP: (a) PP/EVA blend, (b) PP/EPDM blend.

suggesting the importance of this mechanism of impact toughening due to viscoelasticity of the blend only at lower rubber content. At higher EPDM content, the fast rise of impact strength with increasing EPDM content is due to the involvement of other mechanisms such as shear yielding and deformation of rubber particles due to absorbance of impact energy. Thus, in addition to commonly known mechanisms of impact toughening, the energy dissipation due to viscoelasticity should be taken into account for designing rubber-toughened polymers.

REFERENCES

1. Ho, W. J.; Salovev, R. *Polym Eng Sci* 1981, 21, 839.
2. Orazio, L. D.; Greco, R.; Martuscelli, E.; Ragosta, G. *Polym Eng Sci* 1983, 23, 489.
3. Gupta, A. K.; Srinivasan, K. R.; Krishna Kumar, P. *J Appl Polym Sci* 1991, 44, 4415.
4. Gupta, A. K.; Ratnam, B. K.; Srinivasan, K. R. *J Appl Polym Sci* 1992, 45, 1303.
5. Kim, Y.; Cho, W. J.; Ha, C. S. *Polym Eng Sci* 1995, 35, 1592.
6. Wang, C. L.; Wang, S. J.; Qi, Z. N. *J Polym Sci, Part B: Polym. Phys.* 1996, 34, 193.
7. Inoue, T.; Suzuki, T. *J Appl Polym Sci* 1996, 59, 1443.
8. Mouzakis, D. E.; Gahleitner, M.; Karger-Kocsis, J. *J Appl Polym Sci* 1998, 70, 837.
9. Sengupta, A.; Konar, B. B. *J Appl Polym Sci* 1998, 70, 2155.
10. Vander Wall, A.; Mighof, R.; Gaymans, R. J. *Polymer* 1999, 40, 6045.
11. Vander Wall, A.; Mighof, R.; Gaymans, R. J. *Polymer* 1999, 40, 6057.
12. Vander Wall, A.; Mighof, R.; Gaymans, R. J. *Polymer* 1999, 40, 6087.
13. Gaymans, R. J.; Vander Wall, A. ANTEC99, Society of Plastic Engineers, USA, Paper no. 84 (1999).
14. Oberst, H. *Kunststoffe* 1963, 53, 541.
15. Boyer, R. F. *Polym Eng Sci* 1968, 8, 161.
16. Heijboer, J. J. *J Polym Sci, Part C: Polym Phys* 1967, 16, 3755.
17. Wagner, E. R.; Robeson, I. M. *Rubber Chem Technol* 1970, 43, 1129.
18. Gill, P. S.; Hassel, K. L. DuPont Instruments Thermal Analysis Application Brief, No. TA76.
19. Keskkula, H.; Turley, S. G.; Boyer, R. F. *J Appl Polym Sci* 1971, 15, 151.
20. Sacher, E. J. *J Appl Polym Sci* 1975, 19, 1421.
21. Hiltner, A.; Baer, E. *Polymer* 1974, 15, 1405.
22. Ramsteiner, A.; *Polymer* 1979, 20, 819.
23. Operators' Manual; Dynamic Mechanical Thermal Analysis; MK 11, Polymer Laboratories, UK.
24. Newman, S. *Polym Plast Technol Eng* 1973, 2, 67.
25. Sultan, J. N.; Liable, R. C.; Magarry, F. J. *J Appl Polym Symp* 1971, 16, 127.
26. Petrich, R. P. *Polym Eng Sci* 1977, 12, 757.
27. Gupta, A. K.; Purwar, S. N. *J Appl Polym Sci* 1986, 31, 535.
28. Mark, J. A.; Bikales, N. M.; Overberger, C. G.; Mengis, G., Eds., in *Encyclopedia of Polymer Science and Engineering*, Vol. 13, 1988, p 468.
29. Jafari, S. H. Ph.D. Thesis, IIT, Delhi, India, 1998.
30. Jafari, S. H.; Gupta, A. K. in *Proceeding of National Seminar on Polymer Research in Academy, Industry and R&D Organization*, University of Calcutta, India, 1998, p 120.