

# Effect of Dynamic Crosslinking on Tensile Yield Behavior of Polypropylene/Ethylene-Propylene-Diene Rubber Blends

NEERAJ K. GUPTA,<sup>1</sup> ANIL K. JAIN,<sup>1</sup> R. SINGHAL,<sup>2</sup> A. K. NAGPAL<sup>2</sup>

<sup>1</sup> Department of Material Science, Shriram Institute for Industrial Research, 19, University Road, Delhi—110 007

<sup>2</sup> Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur—208002

Received 8 July 1999; accepted 27 March 2000

**ABSTRACT:** Tensile yield behavior of the blends of polypropylene (PP) with ethylene-propylene-diene rubber (EPDM) is studied in blend composition range 0–40 wt % EPDM rubber. These blends were prepared in a laboratory internal mixer by simultaneous blending and dynamic vulcanization. Vulcanization was performed with dimethylol phenolic resin. For comparison, unvulcanized PP/EPDM blends were also prepared. In comparison to the unvulcanized blends, dynamically vulcanized blends showed higher yield stress and modulus. The increase of interfacial adhesion caused by production of three-dimensional network is considered to be the most important factor in the improvement. It permits the interaction of the stress concentrate zone developed at the rubber particles and causes shear yielding of the PP matrix. Systematic changes with varying blend composition were found in stress-strain behavior in the yield region, viz., in yield stress, yield strain, width of yield peak, and work of yield. Analysis of yield stress data on the basis of the various expressions of first power and two-thirds power laws of blend compositions dependence and the porosity model led to consistent results from all expression about the variation of stress concentration effect in both unvulcanized and vulcanized blend systems. Shapes and sizes of dispersed rubber phase (EPDM) domains at various blend compositions were studied by scanning electron microscopy. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2104–2121, 2000

**Key words:** mechanical properties; cross-linking level; dynamic cross-linking; phase morphology

## INTRODUCTION

Tensile properties for blends of polyolefin materials and rubbers are of considerable importance for engineering applications. Various rubbers such as ethylene-propylene-diene rubber (EPDM) were widely used for improving the mechanical brittleness of isotactic polypropylene (iPP) materials. The mechanism of the improvement by blending rubber, however, is not well elucidated on the molecular and structural change basis. The main

reason for this is due to lack of systematic studies on the relationship between morphology and mechanical properties.

Blends of iPP with EPDM are widely used as engineering polymeric materials. Blends with a high content of polypropylene (PP) are utilized as a high-impact PP, whereas blends with a high content of EPDM can be used as thermoplastic elastomers. It was shown that dynamic cross-linking of EPDM during its melt mixing with PP can improve some properties of high-impact PP.<sup>1–4</sup> Dynamically cross-linked PP/EPDM blends show much better performance than un-cross-linked ones.<sup>2,5,6</sup> Among other mechanical properties, tensile properties determine the use of

---

Correspondence to: A. K. Nagpal.

*Journal of Applied Polymer Science*, Vol. 78, 2104–2121 (2000)  
© 2000 John Wiley & Sons, Inc.

**Table I** Materials and Characteristics

Material	Properties	Source
Isotactic polypropylene (iPP)	MFI = 10 g/10 min; Specific gravity = 0.9 g/c.c.; $M_w = 5,30,000$ ; $M_n = 1,06,000$ ; Degree of crystallinity <sup>a</sup> = 41.63%	Grade Koylene M0030 (Indian Petrochemical Corporation Ltd., India)
Ethylene-propylene-diene rubber (EPDM)	E/P weight ratio = 74/26; ENB = 5 wt %; Mooney Viscosity ML1 + 4 at the rate of 125°C = 65 min., = 80 max.; Specific gravity = 0.87 g/c.c	Grade Herlene 539, (Herdillia Unimer Ltd., Mumbai, India)
Dimethylol phenolic resin	Pale yellow lumps, Methylol content = 8–12%; Softening points = 80–100°C; Specific gravity = 1.02–1.06	Hylax HR 6415 (Bakelite Hylam Ltd., India)

<sup>a</sup> Degree of crystallinity of the virgin PP was calculated by differential scanning calorimetry (DSC) method.

these materials because they decide the applicability of various processing technologies. Blends performance depends 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 shape of the dispersed phase. Danesi and Porter<sup>7</sup> have shown that for blends with the same processing history, the melt viscosity ratio and composition determine the morphology. The least viscous component was observed to form the continuous phase over a larger composition range.<sup>8</sup>

In this paper we present research of tensile properties of unvulcanized and dynamically vulcanized blends of PP/EPDM. To study the effects of blend ratio and dynamic cross-linking of EPDM rubber phase on the final property profiles of the above blends have been carried out. Scanning electron microscopy (SEM) was used to study the stage of dispersion and change in morphology of the dispersed phase droplets with blend composition. Analysis of tensile data in terms of various theoretical models is presented to reveal the variation of interfacial adhesion and stress concentration effect with blend composition in both unvulcanized and dynamic vulcanized blend systems.

## EXPERIMENTAL

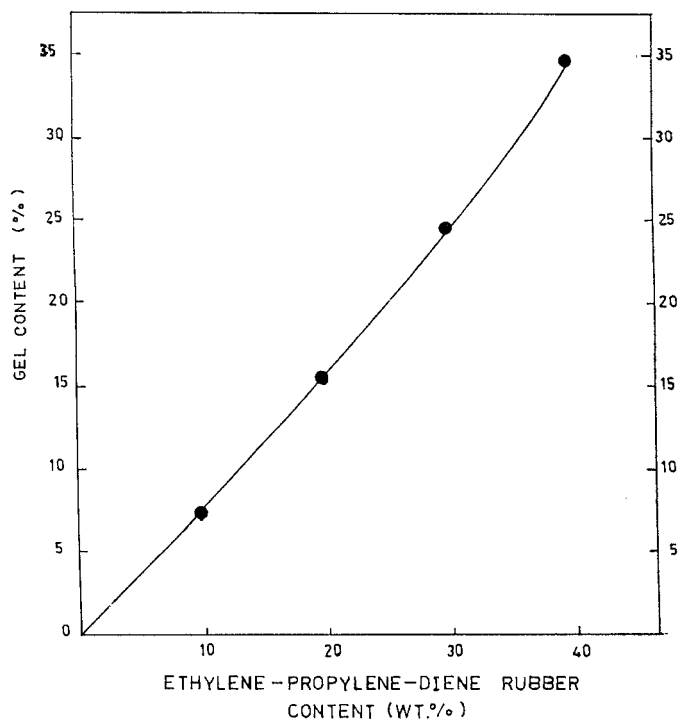
### Materials

The polymers used in this study are listed in Table I. The iPP and the EPDM with ethylidene 2-norbornene (ENB) as a termonomer were all

commercially available grades. The polymers were vulcanized with RESOLE type dimethylol phenolic resin. Stannous chloride used as accelerator was obtained from BDH (India) Limited.

### Blend Formulations

The unvulcanized PP/EPDM blends of compositions 10, 20, 30, and 40 wt % EPDM rubber content were prepared by melt mixing at 190°C for 10 min at 80 rpm in the internal mixer of a torque rheometer, Haake Rheocord RC-90 using two removable roller rotors. The sample size in the mixing chamber is approximately 185 g/batch. The vulcanized blends were prepared under identical conditions. At the onstart of the fifth minute of blending cycle, the curing agent (10 wt % based on EPDM rubber) and accelerator (2 wt % based on EPDM rubber) was introduced into the blend and the vulcanization of EP(D)M rubber component was monitored online till torque stabilization. The in situ rubber curing process took 6 min. The resultant blends were then discharged from the internal mixer in the form of lumps. The cooled lumps were shred in heavy-duty grinder, which were compression molded in a laboratory press at 200°C and 30 MPa pressure. The compression-molded sheets were cut into desired sample sizes for detailed characterizations. The unvulcanized blends were designated as PP<sub>100</sub>, PP<sub>90</sub>EL<sub>10</sub>, PP<sub>80</sub>EL<sub>20</sub>, PP<sub>70</sub>EL<sub>30</sub>, and PP<sub>60</sub>EL<sub>40</sub> and vulcanized blends were designated as PP<sub>90</sub>EB<sub>10</sub>, PP<sub>80</sub>EB<sub>20</sub>, PP<sub>70</sub>EB<sub>30</sub>, and PP<sub>60</sub>EB<sub>40</sub> where the subscripts indicate the amount of PP and EPDM, respectively, in the blend.



**Figure 1** Gel content of various dynamic vulcanized PP/EPDM blends.

## Polymer Characterization

### Gel Content

Gel content of the samples were determined in accordance to ASTM D-2765, wherein about 0.3 g ground was extracted through a 120-mesh stainless steel pouch in boiled cyclohexane for 24 hours.

### Tensile Measurements

Tensile properties were measured on an Instron Universal Tester (model 4302) at  $27^{\circ}\text{C} \pm 2^{\circ}\text{C}$  temperature using dumb-bell shaped specimens at a crosshead speed of 5 mm/min at yield stress and then 50 mm/min up to break in accordance to ASTM D-638, Type IV, with an initial gauge length of 25 mm.

### Morphology Observation

The blend morphology was studied by using a SEM (JEOL JSM-840) after sputter coating the samples with gold on a Fine Coat ion sputter (JEOL JSM-1100). The surface analysis was studied by using cryogenically fractured etched samples in cyclohexane.

## RESULTS AND DISCUSSION

### Gel Content

From Figure 1, it is observed that gel content increases linearly as the concentration of EPDM content, i.e., cross-link density, increases from 0 to 40 wt %. Dynamic vulcanization process causes cross-linking of norbornene (diene part) of the EPDM particles, which is marked by decrease in extractable and increases the gel content. HYLAX HR-6415 used is a heat-reactive modified phenolic resin based on alkyl phenol. It has two independent o-hydroxymethyl groups. The first step is dehydration in the presence of Lewis acid ( $\text{SnCl}_2$ ), induced by heat to produce an o-methylene quinone intermediate. This is then added to unsaturated rubber (or any alkene) via 1, 4 cycloaddition to give a product cross-link with a chroman structure. At the same time PP may react with the second o-hydroxymethyl group to enhance the functionality of PP and produce modified phenolic PP structure (not confirmed in this study). Continuation of this process via addition of a second molecule or rubber (or alkene) gives a cross-link with a bischroman structure.

Lattimer et al.<sup>9</sup> gives a good survey of results of studies for the resol curing of rubber. They con-

**Table II Mechanism and Reaction Products of the Phenolic Resin Vulcanization of Rubber**

Intermediate	Reaction Product	
	Chroman	Chroman/methylene Methylene
Methylene quinone	Hultzschi <sup>10,11</sup> Cunneen <sup>12</sup> Schwarz <sup>13</sup> Fitch <sup>14</sup> Lattimer et al. <sup>9</sup>	Ginsburg et al. <sup>15</sup>      Vander Meer <sup>16,17</sup>
Benzyl cation		Giller <sup>18-20</sup>

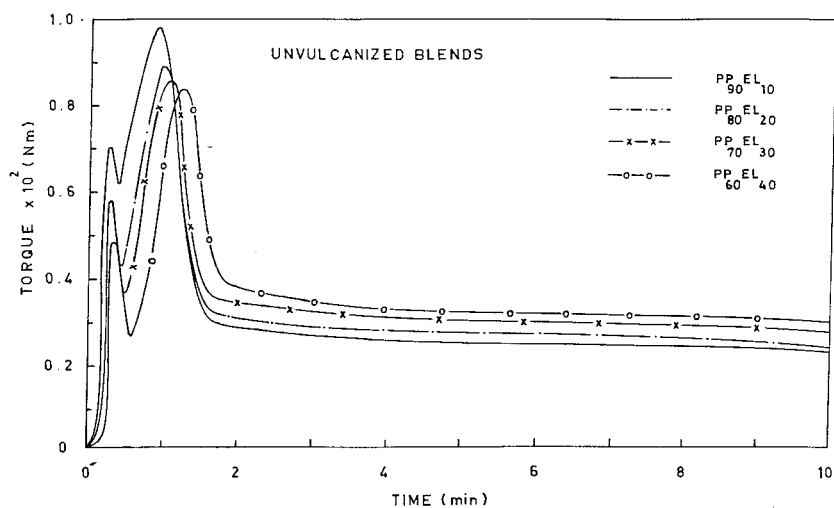
clude that (i) the cross-links obtained by resole curing consist of bisphenol moieties and (ii) only chroman structures, whereas methylene cross-links are not demonstrated. The product structures of resole cured elastomers as suggested by Hultzschi,<sup>10,11</sup> Cunneen et al.,<sup>12</sup> and Schwarz and Kamenskii<sup>13</sup> are, therefore, confirmed. However, other structures have been proposed in combinations with quite a variety of resole curing mechanism (Table II).

#### Mixing Torque Behavior: Prediction of the Critical Blend Ratio and Dynamic Cross-Linking Effect

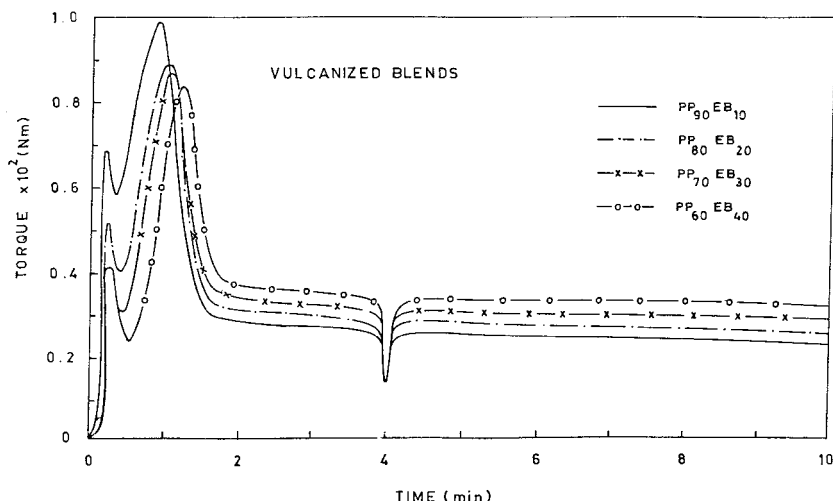
When PP is charged into the mixer, there is sharp increase in torque to maxima of 109.3 Nm. This sudden rise in torque is due to cold polymer being charged into the mixer. The torque maxima reflect simultaneous loading and fusion after which a sharp decrease in torque is obtained. It is during this decrease that the polymer bulk melts.

The torque then gradually approaches semiequilibrium state for the remaining period of mixing. A slight decrease in torque is due to reduction of melt viscosity because torque is an indirect indication of viscosity. It is known that PP undergoes thermo-oxidative degradation if it is not properly stabilized during processing. Thermo-oxidative degradation occurs due to the formation of labile tertiary hydrogen atoms in the chains leading to chain scission. As a result of chain scission the molecular weight reduces, hence a reduction in melt viscosity. The insignificant decrease in torque from 18.64 Nm to 17.52 Nm indicates that the polymer is well stabilized; unstabilized PP undergoes significant reduction in viscosity due to thermoxidative degradation of the melt.

The torque vs. time curves for unvulcanized control blend systems are shown in Figure 2. It can be seen that as PP and EPDM rubber as charged together into the mixer, a shoulder-load-



**Figure 2** Comparison plots of torque development during formation of unvulcanized PP/EPDM blends.



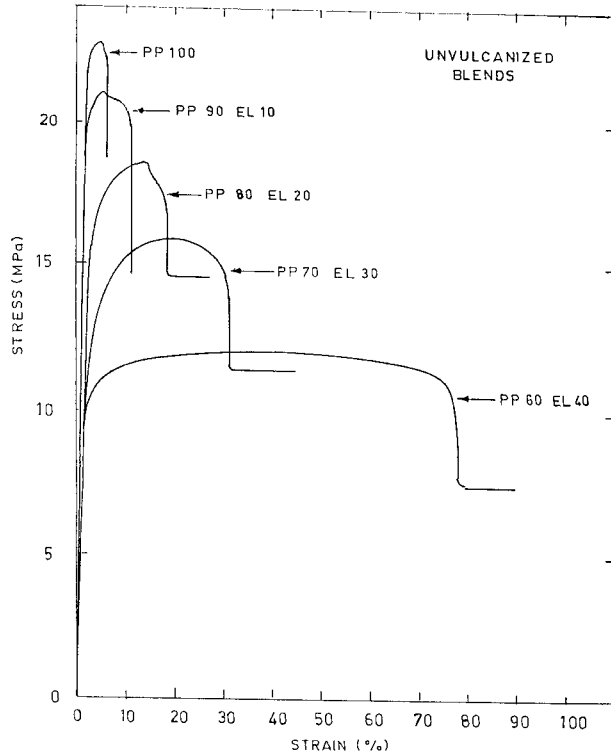
**Figure 3** Comparison plots of torque development during formation of vulcanized PP/EPDM blends.

ing peak to the main loading/fusion peak is formed. This is due to the presence of rubber. At the time of charging both PP and EPDM are cold. Whereas rubber undergoes shear thinning, PP undergoes softening before fusion and finally melting. The rubber also acts as a plasticizer for the rigid matrix of PP. The torque maxima of rubber loading and the loading/fusion of PP show a decrease with rubber loading and is in accordance to expectation based on the above. After melting the torque reaches equilibrium, but is higher than that of PP alone. The torque minima increase with increasing rubber content. The melt viscosity of PP is low due to homogeneous melting of the PP whereas EPDM on the other hand does not undergo melting. It undergoes only viscous flow under shear. The blends exhibit a situation wherein the viscosity of the dispersed rubber is higher than that of the continuous phase, i.e., PP. The higher the rubber contents the higher the viscosity of the blends. These observations are in accordance with classical polymer-rubber mixture.

In vulcanized blend systems, the mixing data at loading/fusion will be the same as that of unvulcanized blends as all the conditions of mixing is the same (Fig. 3). Onstart of fifth minutes of mixing, there is an abrupt fall in torque. This dilation effect is due to the melting of the phenolic curative, which was added after 4 min of blending, i.e., when the initial mixing torque leveled off and is short lived. This short span dilation effect is attributed to internal lubrication of blend system. The effect is more pronounced in blends with

higher EPDM loading, since more phenolic curative is required. Once all the curative melts and the dilation effect reach maxima, cross-linking of EPDM is effected immediately. The final torque development is also higher than the torque development before addition of the phenolic curative. This increased torque remains more or less constant and insignificant at low rubber loading and becomes prominent at its higher concentrations till the end of the melt blending sequence.

A single maxima in torque curve at loading/fusion is observed in all the blend samples and plain PP indicates all samples enter into the molten state simultaneously. There is an ease of fusion of the blends with increasing EPDM rubber content, which is indicated by the decreasing value of torque at loading/fusion. There is also an additional increase in torque in vulcanized blends due to cross-linking of the EPDM rubber phase. This increase is enhanced with increasing rubber content and remains more or less constant throughout mixing cycle. Steady-state torque, which are indirectly indicative of melt viscosity at that temperature increase with increasing EPDM rubber content in both the blend systems and in this increase, is more conspicuous in vulcanized blends. Its viscosity in turn is reflected in increasing values of work energies involved for blend formation, i.e., 685 J/g to 806.5 J/g for unvulcanized blends and 691.5 J/g to 815.6 J/g for vulcanized blends, respectively, and reduced melt flow indices from 9.1 g/10 min to 4.2 g/10 min for unvulcanized blends and 7.5 g/10 min to 0.3 g/10 min for vulcanized blends, respectively, as EPDM



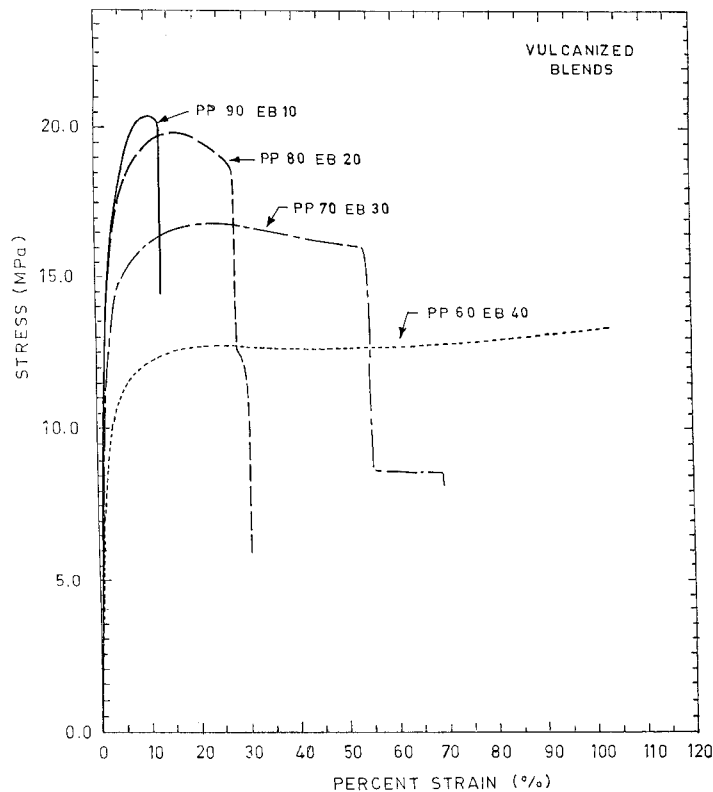
**Figure 4** Change in shape of the stress-strain curves for unvulcanized PP/EPDM blends.

rubber content increases from 10 to 40 wt % in the blend. The enhanced work energies in vulcanized blend systems indicate an increasing degree of cross-linking with increasing EPDM content. The same has also been shown from our findings of the gel contents of the systems.

### Tensile Properties

The stress-strain curves of PP and its blends with EPDM are depicted in Figures 4 and 5. The results of various tensile testing are given in Table III. The stress-strain curves of PP showed that the polymer behaves like a brittle material with a well defined yield peak. With rubber loading reduction in yield stress was accompanied by peak broadening. This reflects reduction in rigidity and an increase in the elastomeric nature of the blends. Yielding is a permanent deformation process that is affected by the molecular slippage past each other and is restrained by rubber inclusions that reduce intermolecular forces between PP molecules and thereby decrease yield strength (Fig. 6).

From stress-strain curves it is observed that rubbery behavior of vulcanized blend higher at

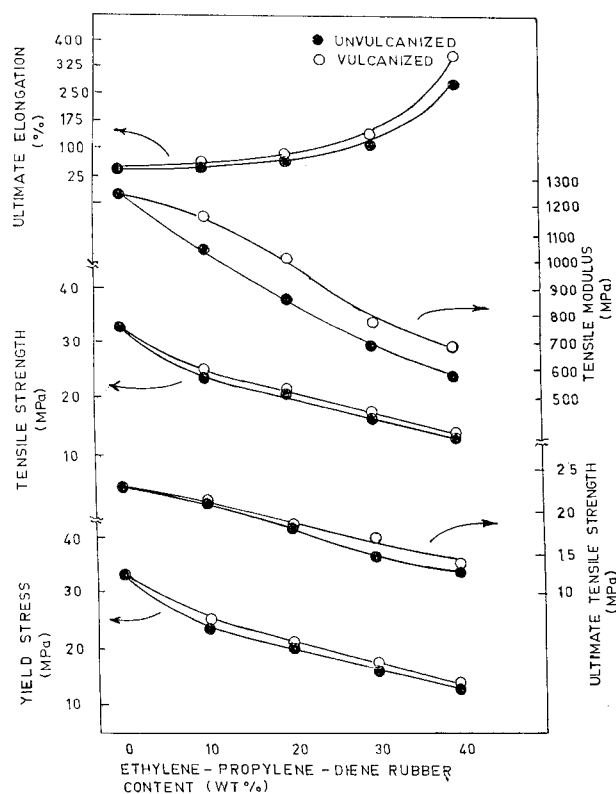


**Figure 5** Change in shape of the stress-strain curves for unvulcanized PP/EPDM blends.

**Table III** Values of Tensile Parameters for Polypropylene (PP)/Ethylene-Propylene-Diene Rubber (EPDM) Blends

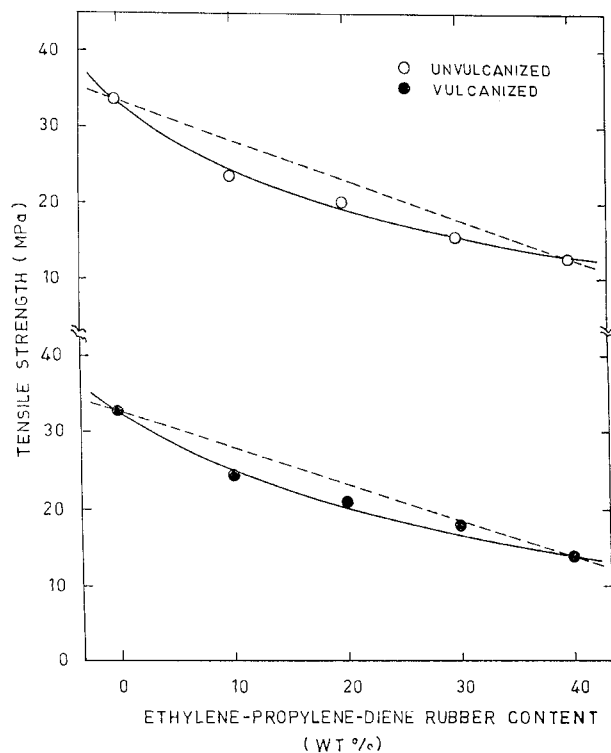
Blend Systems	Sample Notation	Wt % EPDM Rubber	Tensile Stress at Yield (MPa), (YTS)		Tensile Strength at Max. Stress (MPa)		Tensile Strength at Break (MPa)		Tensile Modulus (Young's) (MPa)		Ultimate Elongation (%) (UEL)	Area Under Yield Peak (Arb. Unit)
			Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged		
Unvulcanized control blends												
	PP <sub>100</sub>	00	33.25	35.00	33.25	35.00	23.95	24.62	1240	1320	44	18
	PP <sub>90</sub> EL <sub>10</sub>	10	23.50	24.95	23.50	24.95	20.85	21.35	1050	1125	52	20
	PP <sub>80</sub> EL <sub>20</sub>	20	20.45	23.00	20.45	23.00	18.25	20.06	858	924	66	33
	PP <sub>70</sub> EL <sub>30</sub>	30	16.20	18.02	16.20	18.02	14.60	17.25	695	740	122	49
	PP <sub>60</sub> EL <sub>40</sub>	40	13.00	14.15	13.00	14.15	12.45	13.60	576	622	285	100
Vulcanized blends												
	PP <sub>90</sub> EB <sub>10</sub>	10	24.65	25.00	24.65	25.00	21.15	22.00	1164	1195	56	24
	PP <sub>80</sub> EB <sub>20</sub>	20	20.75	21.60	20.75	21.60	18.30	19.40	1008	1082	76	56
	PP <sub>70</sub> EB <sub>30</sub>	30	17.80	18.00	17.84	18.00	16.80	18.00	787	802	140	99
	PP <sub>60</sub> EB <sub>40</sub>	40	13.94	14.50	13.90	14.50	13.40	13.40	690	680	350	143

low rubber content. This can be best explained in terms of co-continuous phase of EPDM in the continuous PP matrix and resulting in enhanced

**Figure 6** Comparison curves of various tensile properties with blend composition for PP/EPDM blends.

interfacial adhesion. At the temperature of processing, PP may react readily with oxygen forming peroxides and hydroperoxides.<sup>21</sup> Peroxy radicals can react with phenolic resin to stabilize the PP matrix by increasing the functionality of the polypropylene, because phenolic compounds and hindered phenols are the most commonly used stabilizers in polyolefin stabilization. It is believed but not confirmed that an increase in interfacial adhesion in vulcanized blends is caused by the graft copolymer of PP and EPDM at the interface. It is quite possible that coupling of EPDM radicals and PP radicals or with participation of dimethylol phenolic resin radicals under dynamic cross-linking conditions. It is recognized that the interfacial adhesion in a multiphase structure blend is increased by the presence of graft or block polymer of the blend components. This indicates that rubbery nature can be achieved at a lower concentration of EPDM in vulcanized blends as compared with that. The observed behavior of vulcanized blends in having higher tensile stress at yield and higher tensile strength than the corresponding unvulcanized blends is also well documented.<sup>22-25</sup>

The tensile strength versus blend composition curve given in Figure 7 shows a negative deviation, i.e. blend properties lie below, the additivity line. The observed negative deviation in unvulcanized blends is due to poor interfacial adhesion between the nonpolar PP and uncross-linked EPDM phases, which causes poor stress transfer



**Figure 7** Effect of weight percentage of rubber on tensile strength of PP/EPDM blends.

between matrix and dispersed phase and consequently a bigger effect of stress concentration. Comparison with vulcanized systems, which is very close to the additivity line, indicates an increase in interfacial adhesion because of three-dimensional network structure and possibility of the formation of a small amount of graft copolymer with dimethylol phenolic resin.

The vulcanized blends display higher values for yield stress, tensile strength, and elongation at break compared with unvulcanized control blends. These increases are attributed to increased chain entanglements caused by increasing degree of cross-linking and reduced intermolecular forces. Higher degree of chain entanglement results in yielding occurring at higher stresses. Under stress the rubber phases are subjected to large tensile strains, giving rise to a craze-like situation. These craze fibrils are stabilized by the chain entanglements and the rubber network structure. These fibrils can sustain high stresses for longer periods of applied strain. Hence, the observed values are higher. In the unvulcanized control blends the chain entanglements are unstable to prevent flow and fracture in response to applied stresses. Similar behavior is also reported in the literature.<sup>26</sup>

Decrease in Young's moduli in both blend systems is the direct effect of rubber and low modulus of EPDM. Higher values of Young's moduli are expected in a vulcanized blend system due to the increase in the total area under stress-strain curve after the reaction demonstrated that energy absorbed by the specimen before fracture increased. The total area under the stress-strain curve from origin to tip of the yield peak is a measure of the total energy required for the deformation in yield region, or, in other words, "work of yield." As apparent from the values, blending of PP with EPDM increases the work of yield over the total studied range of blend composition. The increase in work of yield with increasing concentration of rubber content is apparently due to the broadening of the yield peak and increase in percent elongation. The simultaneous occurrence of lowering of the yield stress and increase in work of yield indicates that thorough blending causes yielding to occur at a lower stress, the process of yielding requiring greater energy. It was also observed that in the cross-section of tensile specimens of vulcanized PP/EPDM blends, neck formation is facilitated over a wider region as the deformation increases. This behavior change may be explained by the increase of interfacial adhesion and by the increased interaction between the stress concentrate zones in the PP matrix, both of which are caused by the formation of a three-dimensional network structure.

The increase of interfacial adhesion suppresses production of voids or flaws in the PP matrix, which might grow into cracks and shear yielding and can be promoted by the interaction between the stress concentrate zones. At onset of yielding, the increased interfacial adhesion enables the deformation to occur easily in the cross-section and facilitates shear yielding.

### Shear Bands

There is a significant difference in appearance of shear bands in different blend compositions during tensile stretching. These observations are made at a slow rate of deformation viz., 5 mm/min, for convenience of observation of gradual changes in shear bands. During the course of stretching small white streaks appeared with their first appearance, depending on the extent of stretching. The higher the EPDM content, the lower the stretching is required for the first appearance of these streaks. On further stretching the streaks developed into lateral shear bands;



the number and width of the shear bands increases with increasing stretching of the sample. Gradually the overlapping of the bands and formation of wider bands occurs, and finally one of these wide bands develops into the necking zone. The number and surface density of the shear bands increases with an increase of EPDM content in the blend, whereas in the PP sample only one band developed into the neck.

The increasing degree of shear bands with increasing EPDM content indicates that EPDM inclusions give rise to regions of strain inhomogeneities or stress concentration in these blends. The shear bands developed propagates along the lines of zero strain rate at an angle different from 90° with direction of stretching supporting a shear yielding mechanism rather than crazing.

### Analysis of Blend Composition Dependence

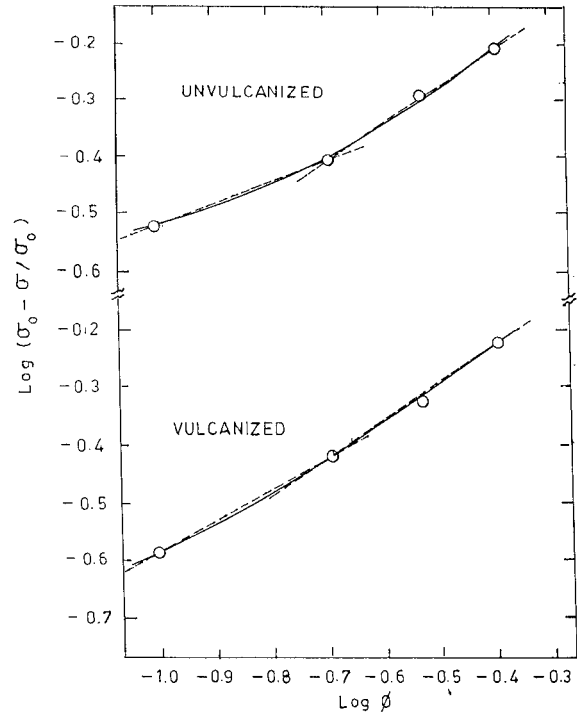
The mechanical properties of material depend on the efficiency of stress-transfer in them, which becomes discontinuous in multicomponent systems at the inter-phase boundaries. The stress transfer in this system depends on the adhesion at the inter-phases and on properties such as size, shape, crystallinity, composition, and so on, of the individual phases. Analysis of these yield stress data as a function of blend composition on the basis of some existing theoretical models, and permits not only the characterization of discontinuity in the structure but also reveals some important differences between the various samples.

The most common expressions of composition dependence of mechanical properties of two-phase blends are based on the first power (eq. 1) and two-thirds power (eq. 2) laws, expressed as:

$$\sigma = \sigma_0(1 - \phi) \quad (1)$$

$$\sigma = \sigma_0(1 - \phi^{2/3}) \quad (2)$$

where  $\sigma$  and  $\sigma_0$  denote the yield stress of the blends and the continuous PP matrix, respectively.  $\phi$  is the volume fraction of the dispersed phase. These power laws originate from the relationship of area fraction and volume fraction of the inclusions.<sup>27,28</sup> For a completely random distribution of the dispersed phase, the first power relationship of area fraction to volume fraction in any randomly chosen plane of fracture is derived on simple mathematical considerations. On the other hand, for the case of spherical inclusions, the two-thirds power law with appropriate

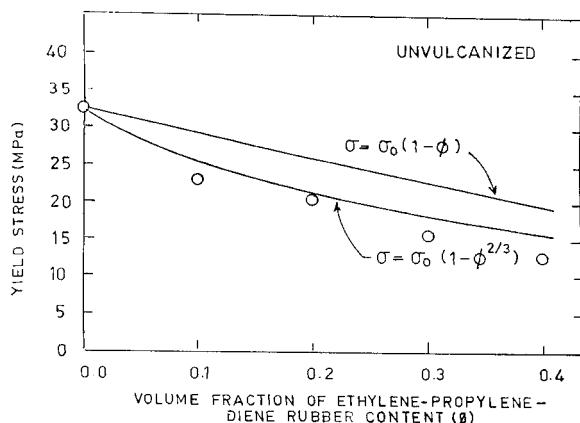


**Figure 8** Variation of  $\log(\sigma_0 - \sigma)/\sigma_0$  as a function of  $\log \phi$  for PP/EPDM blends.

weightage factor is derived for any randomly chosen plane. It is, however, difficult to decide which of these laws do really hold for a given system. Kunori and Geil<sup>27</sup> showed the validity of both first power and two-thirds power relationships of area fraction and volume fraction for the same blend depending on the composition and the shape of the inclusions based on the image analysis of SEM pictures of fracture surface of the specimens of two phase blends.

In order to explore the applicability of first power or two-thirds power law to the present blends system plots of  $\log \{(\sigma_0 - \sigma)/\sigma_0\}$  vs.  $\log \phi$  from these yield stress data are shown in Figure 8 for PP/EPDM blends show a curvature for the blend systems implying a change of slope with blends composition. The slope of this plot gives the values of the power law exponent according to eqs. (1) and (2), respectively.

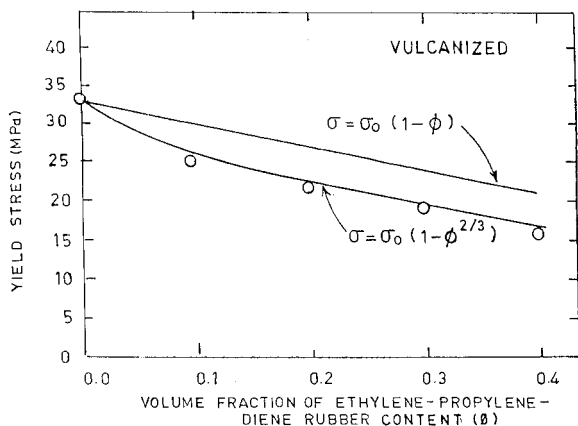
In Figure 8, values of slopes correspond to the two linear portions, shown by broken lines, of each of these curves. For unvulcanized blends the value of slope is 0.40 at low volume fractions and 0.71 at higher volume fraction, whereas for vulcanized blends the slope value is 0.57 at lower volume fraction and 0.62 at high volume fraction. This shows that for both the blends systems the



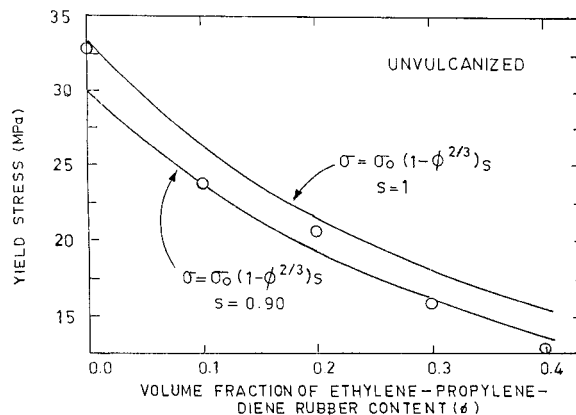
**Figure 9** Comparison of the experimental data with various theoretical relationships according to eq. (1) and eq. (2) for unvulcanized PP/EPDM blends dependence of yield stress.

power law exponent is closer to two-thirds than unity at all the studied range of compositions and at high volume fractions the slopes in all these cases are quite consistent and closer with the two-thirds power law.

Comparisons of theoretical curves according to eqs. (1) and (2) with experimental data presented are in Figures 9 and 10. The curves show that the experimental data points for both the blend systems are closer to the curve representing two-thirds power law at all the studied range of composition. Since according to Piggott and Leidner,<sup>28</sup> the two-thirds power law holds for spherical inclusions, the above analysis suggest morphology with spherical EPDM droplets.



**Figure 10** Comparison of the experimental data with various theoretical relationships according to eq. (1) and eq. (2) for vulcanized PP/EPDM blends dependence of yield stress.



**Figure 11** Comparison of the experimental data with various theoretical relationships according to eq. (3) for unvulcanized PP/EPDM blends dependence of yield stress.

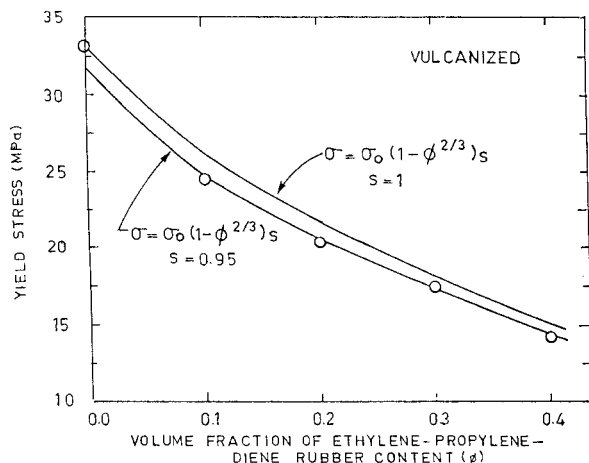
### Stress Concentration Parameters

The realistic features of deformation and fracture, such as the stress concentrations have not been taken into account at the narrow portions of the matrix at the inclusion-matrix interface in the above analysis. In the two-thirds power law Nielsen<sup>29</sup> suggested the use of a parameter  $S$ , eq. (3):

$$\sigma = \sigma_0(1 - \phi^{2/3})S \quad (3)$$

According to Nielsen's definition, the maximum value of parameter  $S$  is unity for the "no stress concentration effect" (or perfect adhesion) case, and the lower the value of  $S$ , the greater the stress concentration effect (or poorer the adhesion).

Comparisons of theoretical curves according to eq. (3) data are presented in Figures 11 and 12 for unvulcanized and vulcanized blend systems respectively. The experimental yield stress data points of unvulcanized blends at higher volume fraction ( $\phi > 0.20$ ) of EPDM are in perfect agreement with theoretical curves according to Nielsen's eq. (3) with  $S = 0.90$  in Figure 11, and deviates upward systematically towards the curve with  $S = 1$  (no stress concentration) as the volume fraction of inclusion decreases. Similar behavior is observed in vulcanized blends as shown in Figure 12. However, here the experimental data points at higher volume fraction ( $\phi > 0.1$ ) lie very close to the theoretical curve according to Nielsen's eq. (3) with  $S = 0.95$ . This indicate that in both systems the stress concen-



**Figure 12** Comparison of the experimental data with various theoretical relationships according to eq. (3) for vulcanized PP/EPDM blends dependence of yield stress.

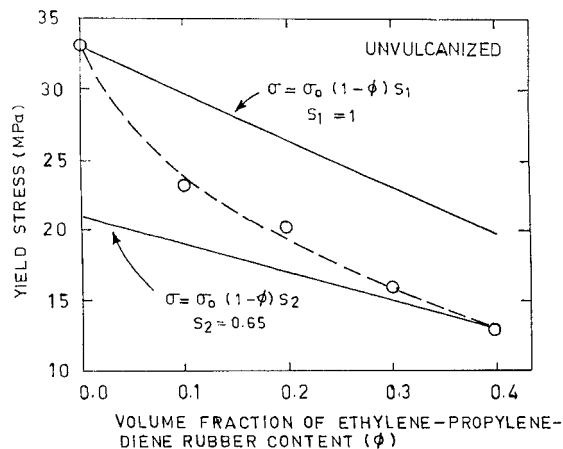
tration effect is predominant at higher volume fraction of EPDM and comparison of the stress concentration effect is less in cases of vulcanized blends than in unvulcanized blends.

A similar modification of first power law has been proposed by Gupta and Purwar<sup>30</sup> by incorporating a stress concentration factor  $S$ , where in the case of  $S = 1$  "no stress concentration" effect and  $S < 1$  where there is an occurrence of stress concentration, and is given by eq. (4):

$$\sigma = \sigma_0(1 - \phi)S \quad (4)$$

Comparison of experimental data with two theoretical lines according to eq. (4) are shown in Figures 13 and 14 for unvulcanized and vulcanized blends respectively. In unvulcanized blends, the experimental data points fall between the two extremes of theoretical curves corresponding to  $S_1 = 1$  and  $S_2 = 0.65$  with a sigmoidal variation and lie close to the theoretical curve with  $S = 1$  at low volume fraction and  $S = 0.65$  at higher volume fraction of EPDM. Similar behavior is observed in vulcanized blends with experimental data points falling between the two extremes of the theoretical curves corresponding to  $S_1 = 1$  and  $S_2 = 0.70$  with a sigmoidal variation.

The above observations indicate that in both blends systems there is sigmoidal transition from a state of low stress concentration to a state of high stress concentration with increasing volume fraction of EPDM in the blend. Comparison of



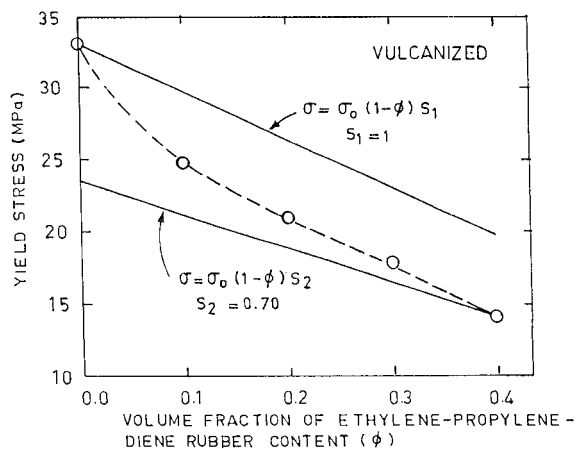
**Figure 13** Comparison of the experimental data with various theoretical relationships according to eq. (4) for unvulcanized PP/EPDM blends dependence of yield stress.

stress concentration parameter  $S$  values of the blend systems also indicate that stress concentration effect is less in case of vulcanized blends than corresponding unvulcanized blends.

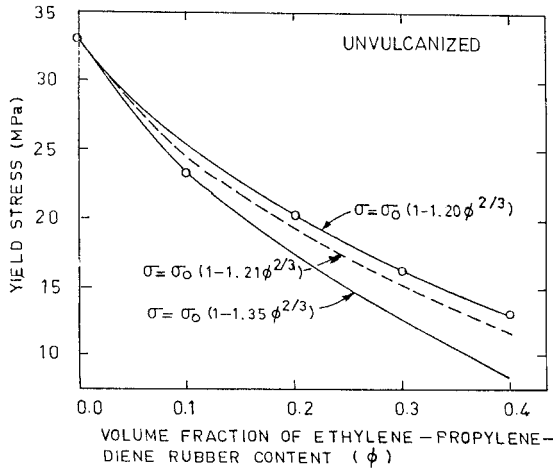
Nicolais and Narkis<sup>31</sup> modified the two-thirds power law by the use of a weightage factor 1.21 given by eq. (5), which takes into account the stress concentration effect.

$$\sigma = \sigma_0(1 - 1.21\phi^{2/3}) \quad (5)$$

The parameter 1.21 in eq. (5) is equivalent to the stress concentration parameter  $S$  of Nielsen and



**Figure 14** Comparison of the experimental data with various theoretical relationships according to eq. (4) for vulcanized PP/EPDM blends dependence of yield stress.



**Figure 15** Comparison of the experimental data with various theoretical relationships according to eq. (5) for unvulcanized PP/EPDM blends dependence of yield stress.

has been shown by Piggott and Leidner<sup>32</sup> to be the outcome of the spherical shape of the inclusions. The Nicolais and Narkis<sup>31</sup> equation (eq. 5), in order to determine the weightage factors, shows some disagreement with these experimental data as shown in Figures 15 and 16, respectively. It is noted that an alternative choice for the parameter 1.21 in this expression does not lead to any desirable agreement, as illustrated in Figures 15 and 16 by the choice of two values 1.35 and 1.20 for unvulcanized blends and values 1.20 and 1.07 for vulcanized blends in place of 1.21. At low volume fraction of EPDM in unvulcanized blends, i.e.,  $\phi$  ( $\leq 0.15$ ), the experimental data points higher than the theoretical curves with weightage factor 1.35, and in vulcanized blends the experimental data point falls close to theoretical curves with weightage factor 1.20. At higher volume fraction of EPDM, i.e.,  $\phi \geq 0.20$ , the experimental data point falls to the theoretical curves with the weightage factor 1.20 for unvulcanized blends and 1.07 for vulcanized blends, respectively. Analysis of the above trends suggest that in both the blend systems there is a lesser stress concentration effect than what is accommodated by Nicolais and Narkis<sup>31</sup> and is an effective analog to reinforcements.

Nicolais and Narkis<sup>31</sup> also described the engineering yield strength of the blend as a function of rubber concentration using the following eq. (6).

$$\sigma = \sigma_0(1 - 1.21\phi^{2/3})S \quad (6)$$

Where  $S = 1$  is a stress reduction factor. For the case of a ductile matrix  $S = 1$  and the effects of local stress concentration are not important because they do not cause the instantaneous failure of the materials.

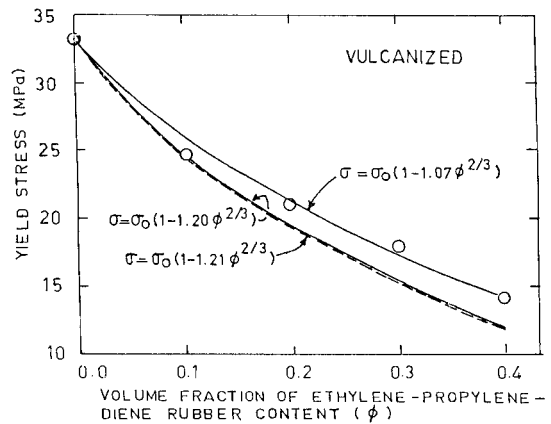
At low EPDM content, the microzone of plastically deformed material around adjacent inclusions are not connected. The material behaves in a brittle manner and the effect of a stress reduction factor has to be utilized ( $S < 1$  in eq. 6). At higher EPDM volume fractions, the probability of connecting yielded microzones around adjacent particles increases and the effect of stress concentration is not detrimental and material fails in a ductile manners.

From Table IV, it is observed that at 0.1 volume fraction of EPDM,  $S = 1$  and experimental data are in good agreement with the prediction using  $S = 1$  (Fig. 17). A further increase of the EPDM volume fraction leads to the decrease of microcracks due to intensive interactions of yielded microzones.

#### Porosity Model

The porosity model representing the behavior of a poor adhesion type blend is to consider the two-phase system as a matrix with pores or voids. Neilsen (Eq. 7) has suggested the applicability of this porosity concept to polymer matrix with voids or holes, and its use for polymer blend.

According to the theory, the specific change  $d\sigma/\sigma$  in a property if the system is directly proportional to the porosity  $P$ , or



**Figure 16** Comparison of the experimental data with various theoretical relationships according to eq. (5) for vulcanized PP/EPDM blends dependence of yield stress.

**Table IV Determination of Stress Reduction Factor of Various Polypropylene (PP)/Ethylene-Propylene-Diene Rubber (EPDM) Blends, According to Eq. 6**

Volume Fraction EPDM Rubber	Yield Stress (MPa)				
	Theoretical Value	Experimental Value		Stress Reduction Factor (S)	
		Unvulcanized	Vulcanized	Unvulcanized	Vulcanized
0.1	24.60	23.50	24.65	0.96	1.00
0.2	19.40	20.45	20.75	1.05	1.07
0.3	15.22	16.20	17.80	1.06	1.17
0.4	11.40	13.00	13.90	1.14	1.22

$$-d\sigma/\sigma = aP \tag{7}$$

Where *a* is proportionality constant, and negative sign implies the decrease of property with increase of porosity. Replacing the total porosity with volume fraction  $\phi$  of the inclusion leads to the following eq. (8) for the two-phase system:

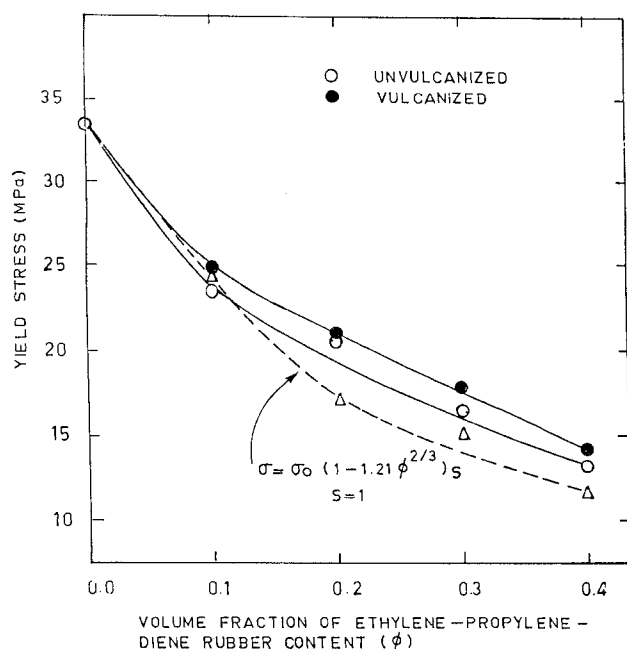
$$\sigma = \sigma_0 \exp(-a\phi) \tag{8}$$

Kunori and Geil<sup>27</sup> has suggested that parameter *a* is related to the stress concentration effect in a manner such that the higher the value of *a* the

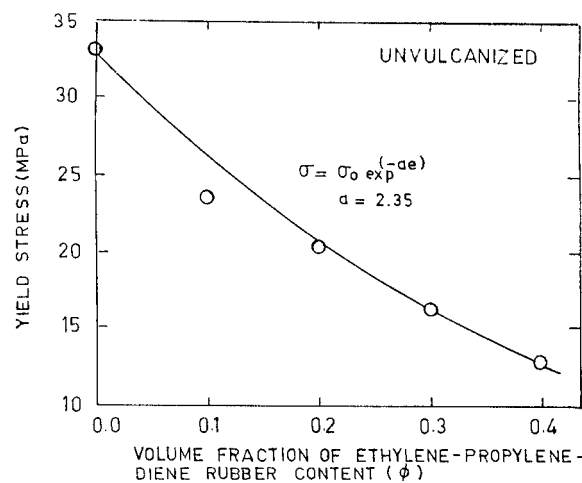
higher is the stress concentration and poorer is interfacial adhesion.

The expression of porosity model (eq. 8) seems to fit quite satisfactorily with these data as shown in Figures 18 and 19 respectively with the single values of the parameter *a* = 2.35 for unvulcanized blend systems and *a* = 2.17 for vulcanized blend systems. The agreement is quite good in the entire range of blend composition studied. Lower values of *a* indicates a higher interfacial adhesion or lower stress concentration effect in vulcanized blends than in the corresponding unvulcanized blends.

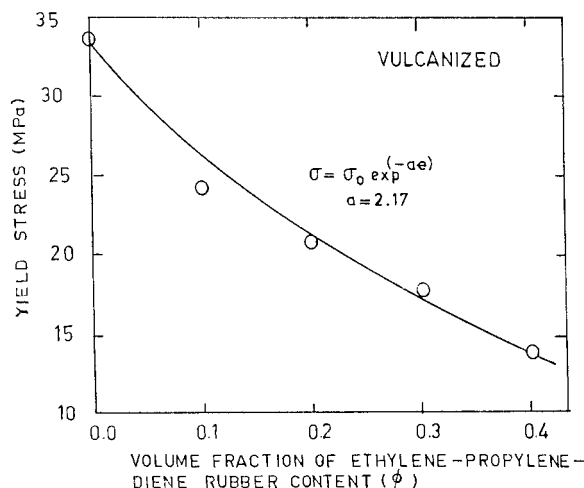
The analysis based on the various theoretical models leads to identical conclusions and strengthens their validity.



**Figure 17** Comparison curves of various blend compositions for PP/EPDM blends according to eq. (6).



**Figure 18** Comparison of the experimental data with various theoretical relationships according to eq. (8) for unvulcanized PP/EPDM blends dependence of yield stress.

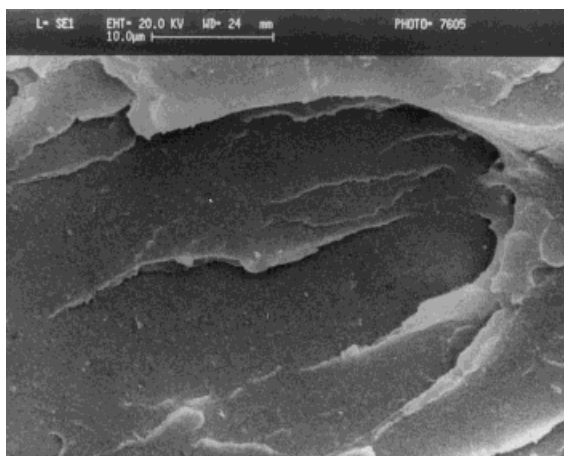


**Figure 19** Comparison of the experimental data with various theoretical relationships according to eq. (8) for vulcanized PP/EPDM blends dependence of yield stress.

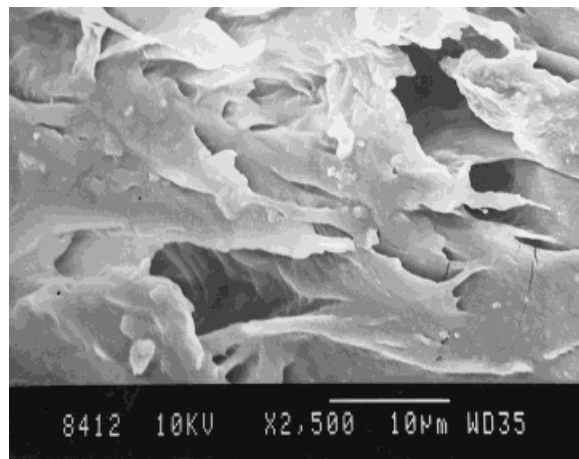
### Scanning Electron Microscopy

The PP fractured sample end shows as expected a clear-cut coarse fibrillar morphology as shown in Figure 20. The roughness of fractured surface increases in both blend systems indicating an increase in ductility with increasing EPDM content. It was also observed at the time of tensile yield behavior study where the necking tendency characteristics of blend disappear and rubbery behavior is exhibited.

SEM photomicrographs of cryogenically fractured etched samples of unvulcanized blend systems from which the EPDM phase has been ex-

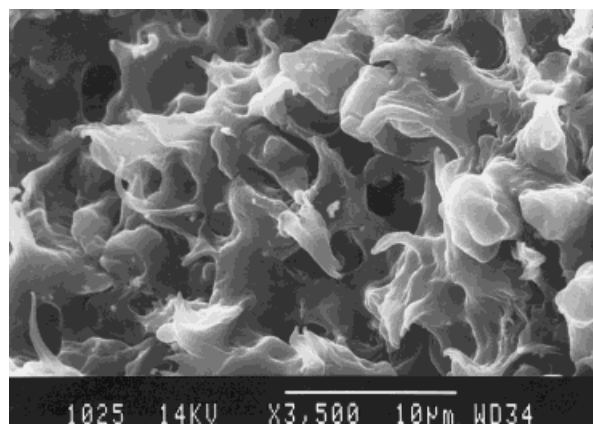


**Figure 20** SEM photomicrograph of isotactic polypropylene.

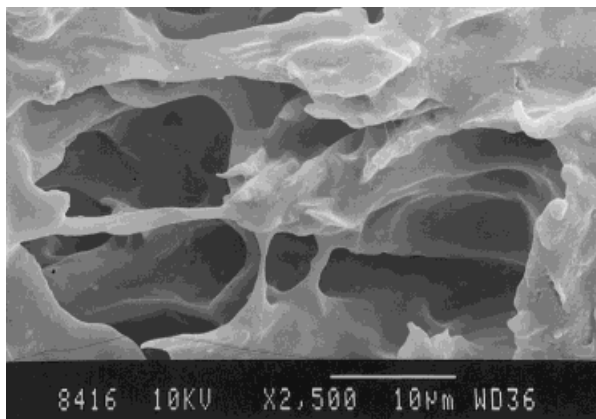


**Figure 21** SEM photomicrograph of etched sample of unvulcanized PP/EPDM Blend (10 wt % EPDM rubber content).

tracted by cyclohexane are shown in Figures 21–24, respectively. The black spaces visible in these micrographs represent EPDM droplets that have been dissolved out on etching with cyclohexane. This is due to the higher melt viscosity and lower content of EPDM compared with PP in the blend. These micrographs show irregular shapes of the inclusions (EPDM domains). The domains are quite small in the case of samples (about 2  $\mu\text{m}$  to 2.5  $\mu\text{m}$ ) with the lowest content (i.e., 10 wt % and 20 wt %). Occurrence of larger domains (about 2.5  $\mu\text{m}$  or more, lengthwise) is apparent at EPDM content above 20 wt %. The bigger particle size of the rubber phase with an increase in EPDM content is attributed to reagglomeration or coalescence of the dispersed rubber particles. The occur-



**Figure 22** SEM photomicrograph of etched sample of unvulcanized PP/EPDM Blend (20 wt % EPDM rubber content).

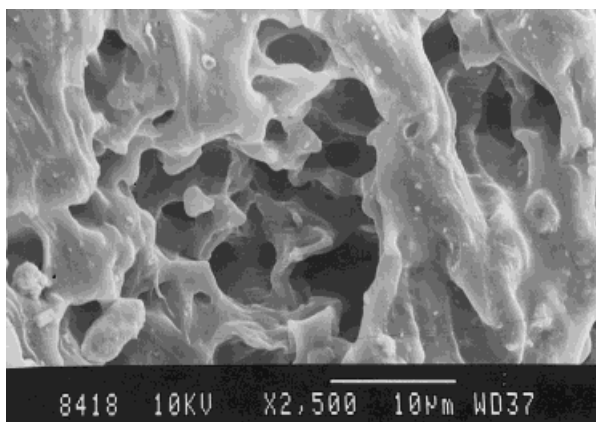


**Figure 23** SEM photomicrograph of etched sample of unvulcanized PP/EPDM Blend (30 wt % EPDM rubber content).

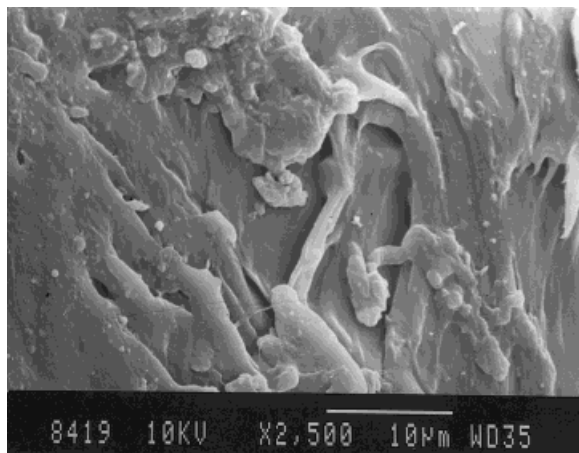
rence of the coalescence at higher concentrations of one of the components has been reported by the many authors.<sup>32–35</sup>

There is a considerable distribution of droplet size and shape in the studied range of blend composition. The droplets are spherical and smallest at low EPDM content (i.e., 10 wt %) and somewhat nonspherical at higher EPDM content ranging from 20–40 wt % EPDM content where some smaller droplet retaining their shape and size can also coexist.

The spherical shape of dispersed phase at lower EPDM content is quite consistent with the findings of theoretical analysis of tensile properties where yield stress data was found to be closer to the two-thirds power law that is applicable for spherical inclusions. It is believed by various au-



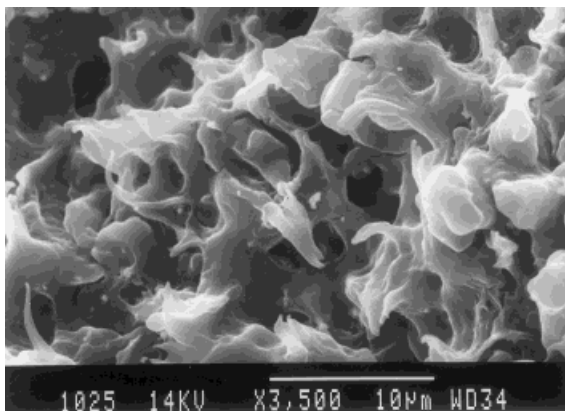
**Figure 24** SEM photomicrograph of etched sample of unvulcanized PP/EPDM blend (40 wt % EPDM rubber content).



**Figure 25** SEM photomicrograph of etched sample of vulcanized PP/EPDM blend (10 wt % EPDM rubber content).

thors<sup>36,37</sup> that the greater the size of inclusions, the greater the stress concentration, and that the stress concentration is lower for the case of rounded or spherical inclusions than the inclusions with sharp corners or irregular shapes. The increase in stress concentration at higher EPDM loading is in total agreement with increase in size and nonspherical shape of the rubber domains in that region in unvulcanized blends. In blends with 40 wt % of EPDM, large and elongated droplets are observed, apparently formed by coalescence of several small droplets. On careful examination of the micrograph, the voids also seem to be continuous. The phase morphology change can be inferred from stress-strain curves also. From the disappearance of necking and sharp reduction in tensile strength for this blend it is concluded that EPDM and PP are forming continuous phases. Thus, a change from dispersed phase to co-continuous phase morphology is observed in unvulcanized blends range of 30–40 wt % EPDM rubber content. The continuous thermoplastic phase retains its thermoplastic fabricability whereas dispersive elastomeric phase imparts high elastomeric nature in blends. Similar behavior at 40 wt % EPDM content during tensile testing where flattened yield stress vs. yield strain curve without necking is observed.

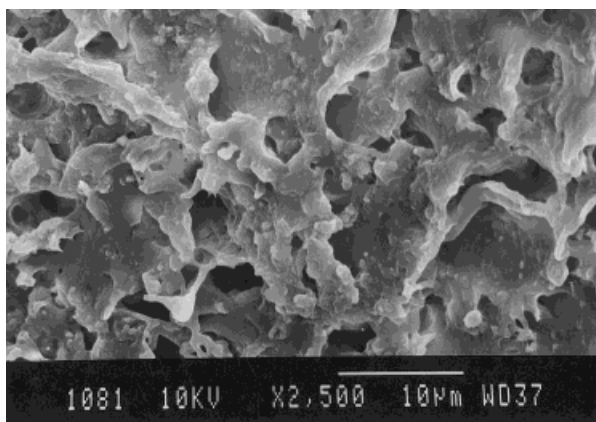
The SEM photomicrographs of vulcanized blends (Figs. 25–28) do not depict the voids due to EPDM clearly because no extraction of the rubber phase was possible due to the gelled nature. This is true except in blend compositions having lower EPDM content, where the gel content is low and



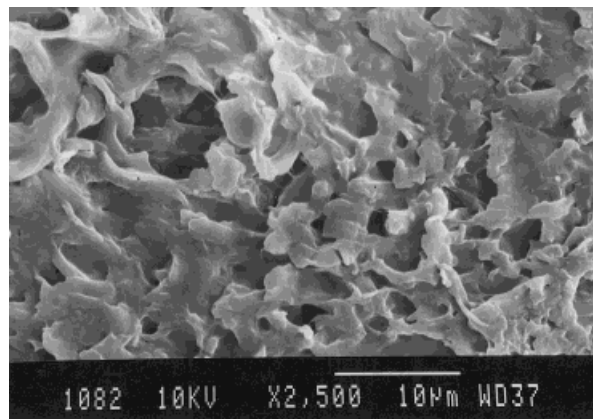
**Figure 26** SEM photomicrograph of etched sample of vulcanized PP/EPDM blend (20 wt % EPDM rubber content).

the system is not fully cross-linked. At lower rubber content the percent of curing agent is low and there is possibility of some swelling. If the rubber phase and the hard phase materials each were to swell to the same extent in a rubber-plastic composition and if there were no voids formed during swelling, then the volume swelling of the hypothetical composition would be the average of the volume swelling of the plastic and rubber phases, weighted by their initial volume fraction. However, if the two different materials swell to different extents, and if there is adhesion there between, constrained swelling must result, at least with most morphological phase relationships.

During mixing and dynamic vulcanization, rubber droplets are likely drawn into threads, which are broken into very small droplets, stabi-



**Figure 27** SEM photomicrograph of etched sample of vulcanized PP/EPDM blend (30 wt % EPDM rubber content).



**Figure 28** SEM photomicrograph of etched sample of vulcanized PP/EPDM blend (40 wt % EPDM rubber content).

lized by cross-linking against reagglomerations. The thermoplasticity of the dynamic vulcanizates is in itself an indication of the continuity of the thermoplastic (PP) phase and discontinuity of the thermoset (EPDM rubber) phase.

On increasing rubber content from 20 to 40 wt % in the blend, the EPDM particles appeared to cover the continuous PP matrix. The covered particles suggest that a graft copolymer of PP/EPDM may produce on the interface during the cross-linking and strengthen the interfacial adhesion. If these copolymers are formed they can act as an emulsifier at the interface and reduce the interfacial tension and improve the interfacial adhesion. As pointed out by Illing,<sup>33</sup> a graft copolymer stays preferentially on the surfaces of dispersed domains acting as an interfacial agent. The presence of an interfacial agent would require less energy for breaking large dispersed particles during melt blending and thus make it possible for domains to adhere the continuous phase.

The absence of void after solvent etching, higher gel content value with increasing EPDM content in vulcanized blends indicates that the cross-link reaction of the rubber particles proceeds predominantly and production of graft copolymer may proceed as a side reaction. This leads to a conclusion that the structure of most of the graft copolymer is not PP-(noncross-linked EPDM) type but PP-(cross-linked EPDM) type.

When the degree of cross-linking of the EPDM phase increases sufficiently, the relatively immobilized rubber particles break up to lower sizes under the prevalent shear level and become dis-



persed in continuous PP phase. Thus, the degree of vulcanization attained, the PP/EPDM blend ratio selected, and the shear level applied in the dynamic process together will ultimately decide size and shape of broken dispersed EPDM particles, their state of dispersion or distribution in continuous polypropylene matrix, and hence the overall morphology.

## CONCLUSION

The morphology and mechanical properties of blends from PP and EPDM have been studied with special reference to the effects of blend ratio and degree of cross-linking. The morphology of the blends indicates a two-phase structure in which the rubber phase is dispersed as domains in the continuous PP matrix at lower proportion of EPDM, and size of domains increases with increase in rubber content. A change in morphology from dispersed phase to co-continuous phase takes place in composition range of 30–40 wt % in unvulcanized blends and in composition range of 20–30 wt % in vulcanized blends, which is reflected in variation in stress-strain behaviors. The high interfacial activity of vulcanized blends reduces the dispersed phase size and provides more uniform particle size distribution. However, dynamic vulcanization markedly improved the plastic deformation and tensile properties.

The mechanical properties of the blends are strongly influenced by the blend ratio. The Young's modulus and tensile stresses of the blends were decreased with increase in EPDM content. Various models have been used to fit the experimental mechanical results. As regards the first power and two-thirds power laws, the yield stress of the blend shows first power law type behavior at lower EPDM contents and two-thirds power law type behavior at higher EPDM content. The one-parameter incorporation of stress concentration effect in these power laws did not describe satisfactorily the behavior of this blend, over the entire study, with a single value of the parameter. However, the porosity model with one stress concentration parameter was found adequate to describe the behavior of the blend over the whole range. In other models, two-parameter expressions were expected to be more appropriate. Further, stress concentration effect is less and interfa-

cial addition is more in vulcanized blends than in the unvulcanized blends.

The authors gratefully acknowledge Dr. D. A. Dabholkar, Director, Shriram Institute for Industrial Research, Delhi for his support, encouragement, and for all help during experimental work.

## REFERENCES

1. Dao, K. C. *Polymer* 1984, 25, 1527.
2. Kresge, E. N.; Lohse, D. J.; Datta, S. *Makromol Chem, Macromol Symp* 1992, 53, 173.
3. Krulis, Z.; Fortelny, I.; Kovar, J. *Collect Czech Chem Commun* 1993, 58, 2642.
4. Inoue, T. *J Appl Polym Sci* 1994, 54, 723.
5. Kresge, E. N. *Rubber Chem Technol* 1991, 64, 469.
6. Abdou-Sabet, S.; Patel, R. P. *Rubber Chem Technol* 1991, 64, 769.
7. Danesi, S.; Porter, R. J. *Polymer* 1978, 19, 448.
8. White, J. L. *Polym Eng Sci* 1973, 13, 46.
9. Lattimer, R. P.; Kinsey, R. A.; Layer, R. W.; Rhee, C. K. *Rubber Chem Technol* 1989, 62, 107.
10. Hultsch, K. *J Prakt Chem* 1941, 158, 275.
11. Hultsch, K. *Chemie der Phenolharze*, Springer Verlag, Berlin, 1950.
12. Cunneen, J. I.; Farmer, E. H.; Koch, H. P. *J Chem Soc* 1943, 472.
13. Schwarz, A. G.; Kamenskii, B. Z. *Kautsch, Resina* 1963, 22, 8.
14. Fitch, A. *Interaction of Alkylphenol—Formaldehyde Condensates with Trialkylethylenes*; Ph.D Thesis, London, 1978.
15. Ginsburg, L. B.; Scherschnew, W. A.; Dogadkin, B. A. *Ber Akad, Wiss UdSSR* 1973, 152, 335.
16. vander Meer, S. *Rev Gener, Caoutchue* 1943, 20, 230.
17. vander Meer, S. *Rev Trav Chim, Pays Bas* 1944, 63, 157.
18. Giller, A. *Kautsch Gummi* 1961, 14, WT 201.
19. Giller, A. *Kautsch Gummi* 1964, 17, 3.
20. Giller, A. *Kautsch Gummi* 1965, 18, 1304.
21. Popsisl, J. *Polym Adv Techno* 1992, 3, 443.
22. George, S.; Joseph, R.; Thomas, S. *Polymer* 1995, 36, 4405.
23. Coran, A. Y.; Patel, R.; Willams, D. *Gummi Fasern, Kunstst* 1998, 39, 658.
24. Coran, A. Y.; Patel, R.; Willams, D. *Rubber Chem and Technol* 1985, 58, 1014.
25. Elliot, D. J. In *Thermoplastic Elastomers from Rubber Plastic Blends*; De, S. K.; Bhowmick, A. K.; Eds.; Ellis Harwood: New York, 1990; chap. 4.
26. Coran, A. Y.; Patel, R. *Rubber Chem Technol* 1980, 53, 141.
27. Kunori, T.; Geil, P. H. *J Macromol Sci Phys* 1980, B (18), 93.

28. Piggott, M. R.; Leidner, J. *J Appl Polym Sci* 1974, 18, 1619.
29. Neilsen, L. E. *J Appl Polym Sci* 1966, 10, 97.
30. Gupta, A. K.; Purwar, S. N. *J Appl Polym Sci* 1984, 29, 3513.
31. Nicolais, L.; Narkis, M. *Polym Eng Sci* 1971, 11, 194.
32. Piggott, M. R.; Leidner, J. *J Appl Polym Sci* 1974, 18, 1619.
33. Martuscelli, E.; Riva, F.; Sellitti, C.; Silvestre, C. *Polymer* 1985, 26, 270.
34. Thomas, S.; Gupta, B. R.; De, S. K. *J Vinyl Technol* 1987, 9(2).
35. Walczak, Z. K. *J Appl Polym Sci* 1973, 17, 169.
36. Heiken, D.; Barentsen, W. *Polymer* 1977, 69, 18.
37. Sabu, S.; Broutman, L. J. *Polym Engg Sci* 1972, 12, 91.
38. Illing, G. In *Polymer Blends, Processing, Morphology and Properties*; Martuscelli, E.; Palumbo, R.; Kryszewski, M. Eds.; Plenum: New York, 1980; P. 167.