# Effect Of Dynamic Cross-Linking On Melt Rheological Properties Of Polypropylene/Ethylene-Propylene-Diene Rubber Blends

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**ABSTRACT:** Study of melts rheological properties of unvulcanized and dynamically vulcanized polypropylene (PP)/ethylene-propylene-diene rubber (EPDM) blends, at blending ratios 10–40 wt %, EPDM, are reported. Blends were prepared by melt mixing in an internal mixer at 190°C and rheological parameters have been evaluated at 220°C by single screw capillary rheometer. Vulcanization was performed with dimethylol phenolic resin. The effects of (i) blend composition; (ii) shear rate or shear stress on melt viscosity; (iii) shear sensitivity and flow characteristics at processing shear; (iv) melt elasticity of the extrudate; and (v) dynamic cross-linking effect on the processing characteristics of the blends were studied. The melt viscosity increases with increasing EPDM concentration and decreased with increasing intensity of the shear mixing for all compositions. In comparison to the unvulcanized blends, dynamically vulcanized blends display highly pseudoplastic behavior provides unique processing characteristics that enable to perform well in both injection molding and extusion. The high viscosity at low shear rate provides the integrity of the extrudate during extrusion, and the low viscosity at high shear rate enables low injection pressure and less injection time. The low die-swell characteristics of vulcanizate blends also give high precision for dimensional control during extrusion. The property differences for vulcanizate blends have also been explained in the light of differences in the morphology developed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1488–1505, 2000

**Key words:** cross-linking level; polypropylene/rubber blends; rheological properties; curing agent

## INTRODUCTION

Dynamic cross-linking of ethylene-propylene-diene rubber (EPDM) during its melt mixing with polypropylene (PP) can improve some properties of high-impact PP.[1–4] But little attention has been focused so far on the study of the rheological properties of dynamically cross-linked PP/EPDM blends. Ha et al.[5] studied the viscosity of the PP/EPDM blends dynamically cured by dicumyl peroxide. They found that dynamically cross-linked blends with higher content of EPDM exhibit a high viscosity in the range of low shear rates. Their viscosity steeply decreases with increasing shear rate. A similar dependence of viscosity versus shear rate was also found for other blends containing cross-linked rubber inclusions[6–8] and for filled systems with higher contents of mineral filler.[9–10]

**Table I   Materials and Characteristics**

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

[a] Degree of crystallinity of the virgin PP was calculated by Modulated differential scanning calorimetry (MDSC) method.

The organic peroxide/coagent cross-link system, which is the most commonly used one, degrades the PP matrix and changes its mechanical and rheological properties because highly active radicals produced from the organic peroxide abstract hydrogen radicals not only from the allylic carbons of EPDM but also from the tertiary carbon of PP.

The cross-link reactions effected by sulfur/accelerator or sulfur donor/accelerator systems also cross-link the EPDM with no problem of degradation. However, the produced polysulfide cross-link, i.e., (Sn : n = 2–6)-type linkage, is unstable at the required temperature for the melt-blending process and the molding process of PP/EPDM blends. Thus, this system is not suitable to material of commercial use.

Dynamic vulcanized blends are judicial control of morphologies accomplished by choice of mixing methods, mixing conditions, rheological properties of blend components, control of surface energy, and chemical reaction during formulative mixing have resulted in production of high-quality materials to meet a great variety of end-use applications. In blends where the rubber phase is cross-linked during the mixing process, the cross-linked phase must be discontinuous. The break up mechanism(s) that control particle size in dynamically vulcanized systems has not been extensively investigated. However, shear stress in intensive mixing produces particles by fracture of the cross-linked rubber phase. A high concentration of the dispersed rubber phase is required to achieve excellent elastomeric recovery, however such a high concentration generally produces high viscosity material similar to a highly filled polymer. However, dynamically cured blends also have important technical advantages in processing also because the blends can be fabricated by such methods as extrusion and molding, though they possess a cross-linked elastomer as one component.

The purpose of the research described here is to develop cross-linking systems that are able to cross-link unsaturated rubber particles in a polyolefin matrix selectively, especially EPDM particles in a PP matrix, without causing the chain scission, degradation, and agglomeration problems described above. A further aim of this paper is the better understanding of the rheological properties of the blends with dynamically cross-linked rubber phase and study of the relation between the shape of the dependence of rheological properties on the blend composition and change of the type of the blend phase structure.

## EXPERIMENTAL

### Materials

The polymers used in this study are listed in Table I. The isotactic polypropylene (iPP) and the

EPDM with ethylidene 2-norbonene (ENB) as a termonomer were all commercially available grades. The polymers were vulcanized with RE-SOLE-type dimethylol phenolic resin. Stannous Chloride used as accelerator was obtained from BDH (India) Limited.

## Blend Formulations

The unvulcanized PP/EPDM rubber 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. This continued for 6 min, when torque stabilization was obtained. The resultant blends were discharged in the forms 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 sheet were cut into desired sample sizes for detailed characterizations. The unvulcanized blends were designated as $PP_{100}$ ($PP_{90}EL_{10}$, $PP_{80}EL_{20}$, $PP_{70}EL_{30}$, $PP_{60}EL_{40}$), and vulcanized blends were designated as $PP_{90}EB_{10}$, $PP_{80}EB_{20}$, $PP_{70}EB_{30}$, $PP_{60}EB_{40}$, where the subscripts indicate the amount of PP and EPDM, respectively, in the blend.

## Polymer Characterization

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 h.

The rheological properties were measured with a Capillary Rheometer using a Haake Rheocord RC-90 equipped with a single screw extruder type Rheomex 252 in several shear rates at 220°C. Dried chips of PP and blend samples were extruding using a barrel ¾ inch (19.05 mm); a screw of L : D ratio 25 : 1; and the dimension of a rod capillary of 2.0 cm length and 0.2 cm diameter, compression ratio 3 : 1 and the pressure sensor of 300 bar. The temperature profile 190°C (first zone); 200°C (second zone); 210°C (third zone);

and 220°C (die zone) was maintained during the study of rheological properties. Fit (corrected) values of the experimental rheological data were calculated by instrument software program based on the method of Bagley's correction.

Melt flow indices of the samples were determined at 230°C and 2.16 kg load using ASTM D-1238 specification.

Melt elasticity such as die-swell ratio, first normal stress differences, recoverable shear strain, and the shear modulus are evaluated. Die-swell ratio and percentage extrudate swell were determined according to ASTM D-3835. The die-swell ratio is Di/D and percentage extrudate swell is Di-D/D × 100, where Di and D are the diameters of the extrudate and the die respectively. The first normal stress differences ($\tau_{11}-\tau_{22}$) is calculated according to the Tanner's eq. (1):

$$(\tau_{11} - \tau_{22}) = 2(\tau_w)_{\text{fit}}[2(Di/D]^6 - 2]^{1/2} \qquad (1)$$

Recoverable shear strain ($\gamma_R$) and fit shear modulus (G) are calculated from the following equations:

$$(\gamma_R) = (\tau_{11} - \tau_{22})/2(\tau_w)_{\text{fit}} \qquad (2)$$

$$G = (\tau_w)_{\text{fit}}/(\gamma_R) \qquad (3)$$

The thermal analysis was performed under nitrogen, with a heating rate of 5°C /min using modulated differential scanning calorimetry (MDSC) of TA analysis system model 2910. The samples were then cooled to the room temperature at constant cooling rate of 5°C/min., at identical settings of the instrument for all the samples. The samples were again heated as accordance to ASTM D-3417 & 3418 to measure the wt % crystallinity. The wt % crystallinity of PP in the blend was evaluated from the second melt by comparing the enthalpy change of the samples to that of fully crystalline sample. (Δ Hpp = 209 J/g was used for calculation.)

The blend morphology was studied by using a scanning electron microscope (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 DISCUSSIONS

### Gel Content

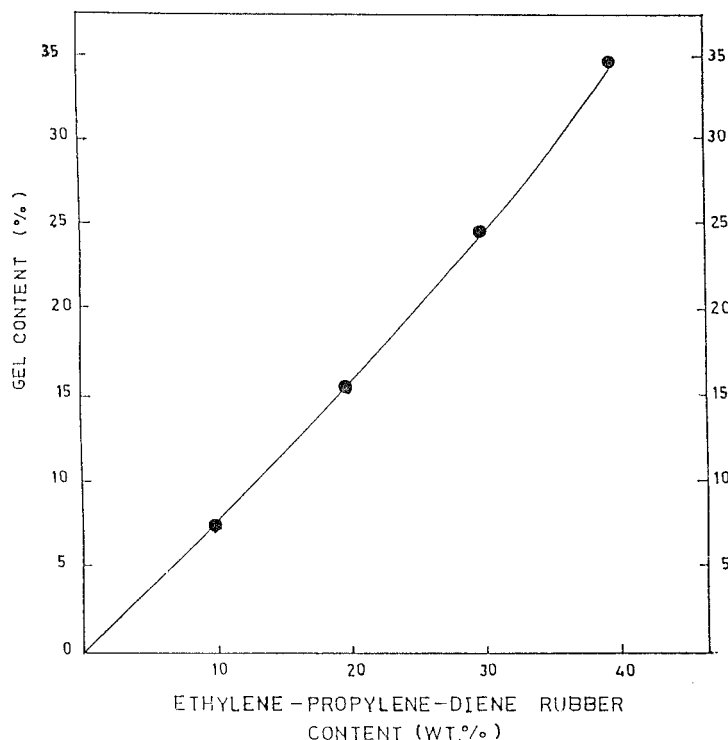From Figure 1, it is observed that gel content increases linearly as the concentration of EPDM

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

rubber content, i.e., cross-link density, increases from 0 to 40 wt %. Dynamic vulcanization process causes cross-linking of norborene (diene part) of the EPDM rubber 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 ($SnCl_2$), induced by heat to produce an o-methylene quinone intermediate. This than add to unsaturated rubber (or any alkene) via, 1, 4 cycloaddition to give a product cross-link with a chroman structure. At the same time polypropylene may react with second o-hydroxyl methyl group to enhance the functionality of polypropylene to produce modified phenolic polypropylene structure (not confirmed in this study). Continuation of this process via addition of a second molecule or rubber (or alkene) to give a cross-link with a bischroman structure.

Lattimer et al.[11] gives a good survey of results of studies for the resole curing of rubber. They conclude 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 Hultzsch,[12,13] Cunneen et al.,[14] and Schwarz and Kamenskii[15] 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 the PP is charged into the mixer, there is sharp increases in torque a maxima of 109.3 Nm. This sudden rise in torque is due to cold polymer charging 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 semi-equilibrium state for the remaining mixing period. A slight gradual decrease in torque is detected though not very significant. This slight decrease is due to reduction in melt viscosity because torque is an indirect indication of viscosity. This viscosity reduction due to thermo-oxidative degradation of polypropylene. Thermo-oxidative degradation occurs due to the formation of labile

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

| Intermediate | Chroman | Reaction Product | |
|---|---|---|---|
| | | Chroman/Methylene | Methylene |
| Methylene Quinone | Hultzsch[12,13] Cunneen[14] Schwarz[15] Fitch[16] Lattimer et al.[11] | Ginsburg et al.[17] | Vander Meer[18,19] |
| Benzyl Cation | | | Giller[20–22] |

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 versus 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-loading 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 rubber are cold. Whereas rubber undergoes shear thinning, PP has to undergo softening before fusion and finally melting. The rubber also acts as a plasticater for the rigid matrix of polypropylene. 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
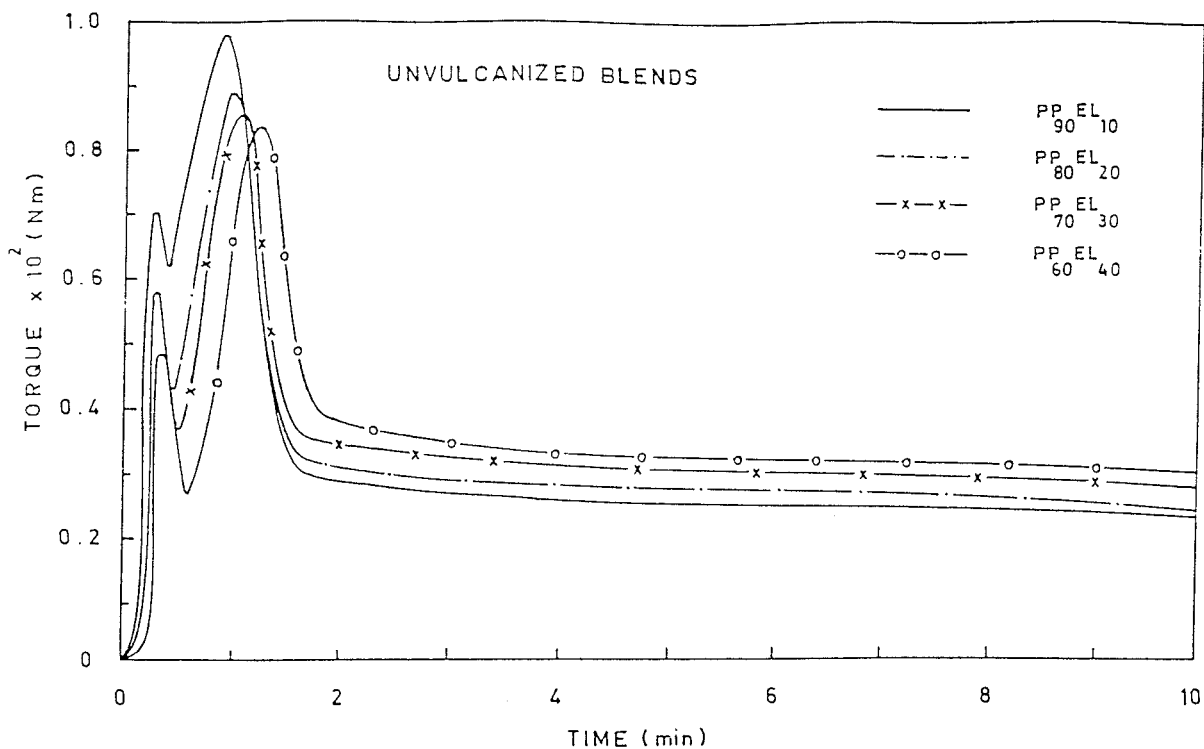


**Figure 2**   Comparison plots of torque development during blend formation of unvulcanized PP/EPDM blends at 190°C and at 80-rpm rotor speed.
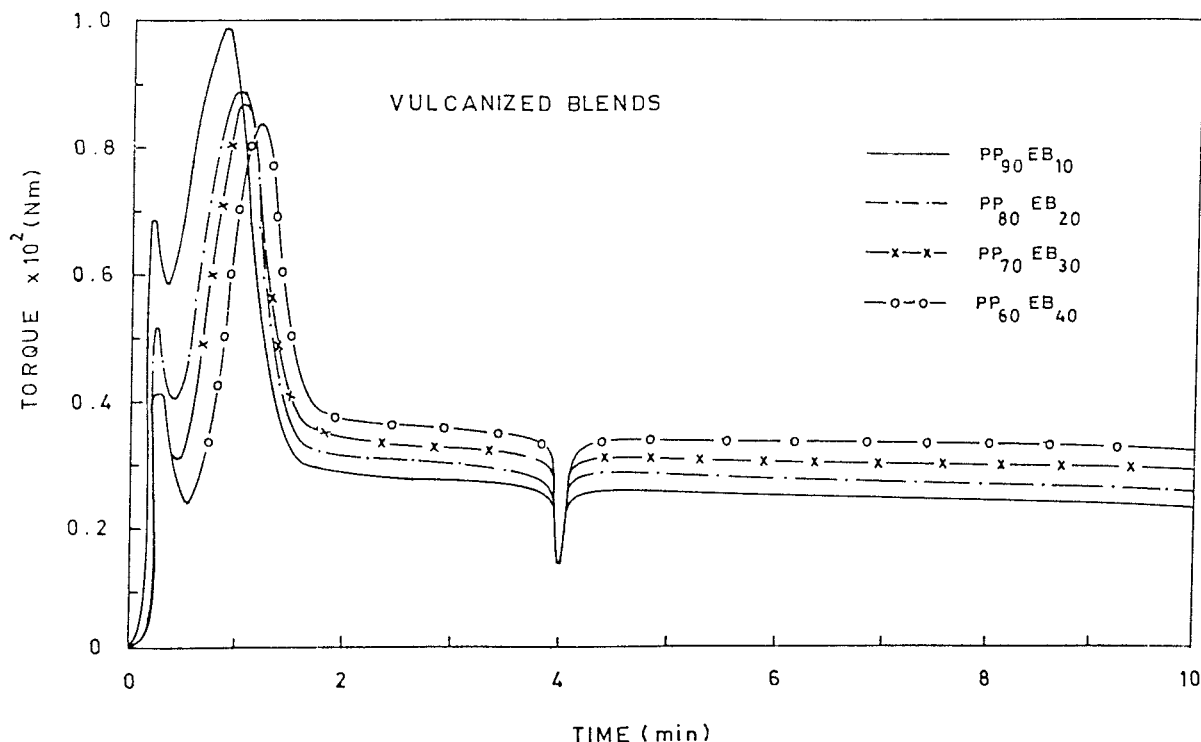
**Figure 3**  Comparison plots of torque development during blend formation of dynamically vulcanized PP/EPDM blends at 190°C and at 80-rpm rotor speed.

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 same as that of unvulcanized blends as all the conditions of mixing are the same (Fig. 3). At the onstart of the fifth minute 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 rubber loading, because more phenolic curative is re-

quired. Once all the curative melts and the dilation effect reach maxima, cross-linking of EPDM rubber is effected immediately. The final torque develop 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 untill 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. 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 this increase is more conspicuous in vulcanized blends. This rise in melt viscosity in turn is reflected in increasing
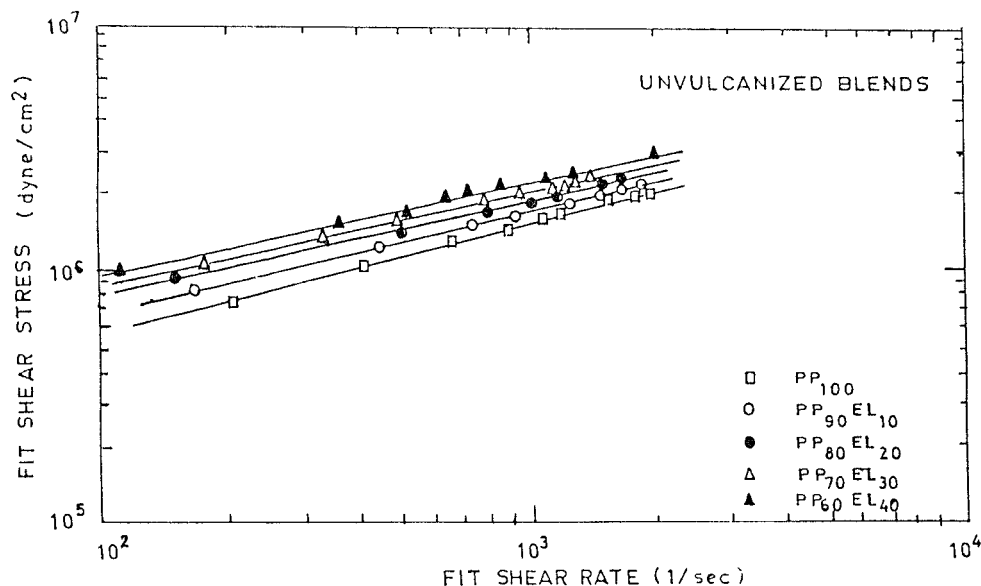
**Figure 4**  Fit shear stress–fit shear rate plots showing the effect of rubber content in PP/EPDM blends at 220°C.

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

### Capillary Rheometry Studies

#### *Effect of Blend Ratio and Dynamic Cross-Linking on Shear Stress–Shear Rate Curves*

The apparent wall shear stress and apparent wall shear rate can be calculated using Poiseuille law from knowledge of barrel diameter, screw speed, length, and diameter of the capillary according the following expression:

$$\text{Wall Shear Stress, } (\tau_w)_{\text{app}} = \Delta PR/2L \quad (4)$$

$$\text{Wall Shear Rate, } \gamma = 4\,Q/\pi R^3 \quad (5)$$

where $\Delta P$, the pressure drop over the capillary length, is measured as a pressure entrance and exit difference of between the capillary, L is the

capillary length, Q is the volumetric flow rate, and R is the radius of the capillary. Interpretation of capillary rheometry data using the Poiseuille equation yields an apparent rather than a true (fit) measure of viscosity at the operating temperature. A series of corrections are appropriate to derive the fit viscosity but of these only one, the ends (or Bagley) correction, is recommended. Using Bagley correction the following rheological parameters can be recalculated by computer software using the following equations:

$$\text{Fit shear rate} = 4Q/\pi R^3 \quad (6)$$

$$\text{Fit shear stress} = \frac{(P_L - P_O)R}{2L} \quad (7)$$

$$\text{Fit viscosity}, \eta_{\text{fit)}} = \tau_{\text{fit}}/\gamma_{\text{fit}} \quad (8)$$

where $P_L$ is the pressure drop through a long die and $P_0$ is the pressure drop through an orifice die of the same diameter at the same flow rate.

The variations of shear stress $(\tau)_{\text{fit}}$ versus shear rate $(\gamma)_{\text{fit}}$ in log-log scale are quite linear over the entire study, confirming the validity of the power-law relationship. The logarithmic plots of shear stress-shear rate in Figures 4 and 5 illustrating the effects of blend ratio and cross-linking effect on PP/EPDM Blends at 220°C. The shear stress is
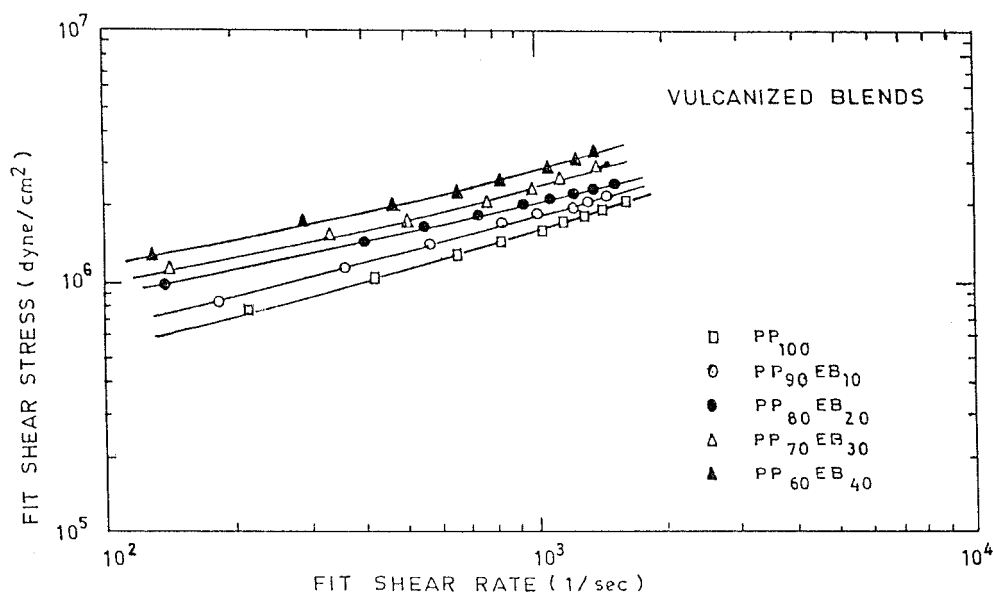
**Figure 5** Fit shear stress–fit shear rate plots showing the effect of blend ratio and dynamic crosslinkings effects on PP/EPDM blends at 220°C.

increased as EPDM content increase at the same shear rate for both blend systems. The increase in shear stress should be expected as the result of the rubbery nature of EPDM rubber. The dynamically vulcanized blends exhibited higher shear stress than the unvulcanized blends over the overall composition ranges was observed.

Values of the exponent n or the flow behavior index of the power law eq. (9) were calculated from the slope of shear stress and the shear rate.

$$(\tau_w)_{\text{fit}} = k(\gamma_{\text{fit}})^n \qquad (9)$$

It was observed that n values are less than unity also supports the pseudoplastic nature of the melts. Large variation in n values with blend composition in unvulcanized blend indicates that there is an inhomogeneity mixing in between the matrix. These observations reveal the inhomogeneity appreciable the dispersion of larger and irregular shape of rubber domains in the continuous polypropylene matrix. In cross-linked blends, n values did not change significantly with blend composition and this may be due to the effect of rubber on dispersion having a high cross-link density results in uniform and fine dispersion matrix. This fine dispersion apparently results from the effective role of cross-linking in restricting particle reagglomeration.

### Effect of Blend Ratio, Dynamic Cross-Linking, and Shear Stress on Melt Viscosity

The effect of blend ratio and dynamic cross-linking effect on melt viscosity- shear stress plots at 220°C are shown in Figures 6 and 7 for these samples. At lower shear stresses, the viscosity of the blend increases with increase of EPDM rubber content in the blend. The viscosity decreases with increase in shear stress, and at high shear stresses the difference between the viscosity of the blends containing various proportions of PP and EPDM rubber is reduced. As the mixer rotation became faster, the melt viscosity of the blends decreased overall in the compositions examined. The rubber droplets are large in size with increases the EPDM content in uncross-linked samples, as is evidenced in SEM studies, and at low shear stress coalescing of rubber droplets is predominant. As the shear stress increases smearing of rubber droplets takes place faster than their ability to associate, causing a decrease in melt viscosity. The rate decrease in melt viscosity with increase in shear stress is because of there is a simultaneous occurrence of shear induced break-up. However, the system deviates somewhat from non-Newtonian behavior.

The dynamically vulcanized blends exhibited higher viscosity than the unvulcanized blend over the overall composition range. It should be noted, however, that the dynamically vulcanized blends
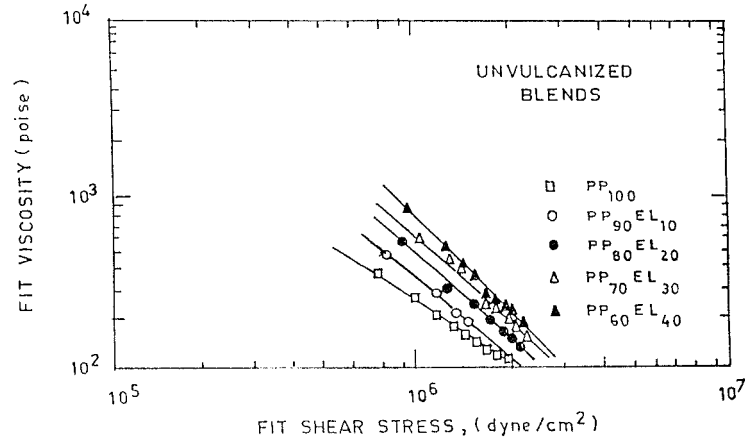
**Figure 6** Fit melt viscosity–fit shear stress plots showing the effect of rubber content in PP/EPDM blends at 220°C.

showed the thermoplastic nature, although they contain cross-linked EPDM as one component. It has been reported that the formation of the continuous three-dimensional network was constrained effectively, even at low shear intensity.

As free volume is less and intermolecular slippage is restricted in a cross-linked structure, the vulcanized blend showed higher melt viscosity, which is more conspicuous at higher rubber loading having a higher degree of cross-linking. It has been reported that the degree of cross-linking increasing the number density of small rubber particles in continuous PP matrix, resulting in drastic improvement in viscosity. At equal formulation volume fractions, smaller particles will impart greater viscosities because of greater surface area. Cross-linking of EPDM rubber phase

increases its viscosity and decreases the deformation of dispersed particles as indicated by the increase in melt-mixing torque values.[23] The uncross-linked rubber particles in the blend are elongated at the entrance of the capillary and are broken down into smaller particles where the cross-linked particles, which are less deformable, retain the morphology of the blend even at high shear stresses. Thus, differences in viscosities in both blend systems is due to changes of phase morphology.

### Flow Behavior

#### Effect of Blend Ratio, Screw Speed, and Dynamic Cross-Linking on Flow Behavior Index

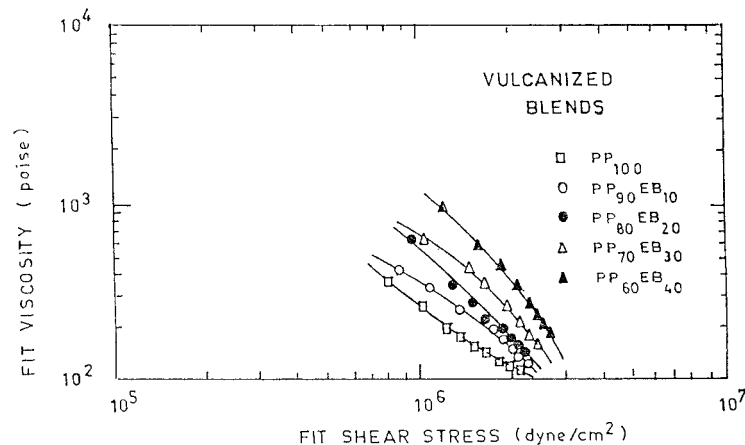Figure 8 shows the flow behavior index of the blends at 220°C. The drop of the melt flow index



**Figure 7** Fit melt viscosity–fit shear stress plots showing the effect of blend ratio and dynamic cross-linking effect on PP/EPDM blends at 220°C.
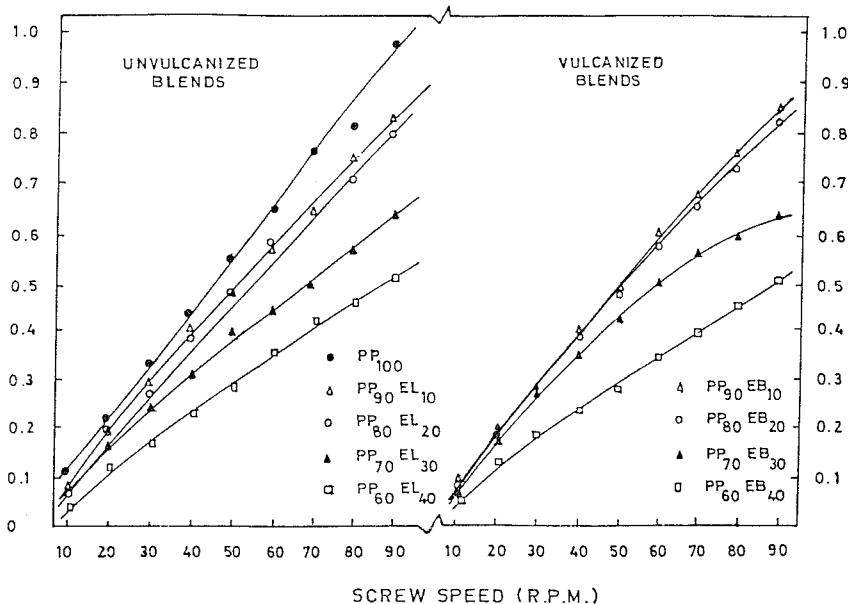
**Figure 8**   Comparison plots of melt flow indices versus screw speed showing the effect of blend ratio and dynamic cross-linking on PP/EPDM blends at 220°C.

with increasing EPDM content implies higher pseudoplasticity for PP/EPDM blends. The dynamically vulcanized blends have lower flow indices because mobility of the polymer chain from the higher molecular weight EPDM microgel increased due to the chemical cross-link of EPDM rubber. The increase trend of melt viscosity with rubber content and comparative higher melt viscosity values of vulcanized blends is well determined and fully established in the previous studies by the capillary rheometry technique and also is indicated in steady-state torque values in melt mixing studies. There is also evidence that may be seen in melt flow index results at 230°C and load of 2.16 kg determined by Plastometer capillary rheometer. These observations reveal that dynamically vulcanized blends are more thermally stable (low melt flow index even at high temperature) and more shear sensitive.

### Melt Elasticity

#### *Effect of Blend Ratio and Dynamic Cross-Linking on Melt Elasticity*

Various parameters characterizing melt elasticity, namely, die swell ratio (Di/D), the first normal stress difference ($\tau_{11} - \tau_{22}$), recoverable shear strain ($\gamma_R$), and fit shear modulus (G) at several shear stresses are evaluated and results are presented in Figures 9–12, respectively.

At any given shear rate, $\gamma_R$ decrease and G increases with increasing EPDM content of the blend, and the sigmoidal shapes of these variation with the aforesaid characteristics were observed.

During the flow of a viscoelastic fluid through a capillary, the pressure is highest at the entrance and decays along the length of the capillary depending on the properties of the material and finally reaches its lowest value at the exist called exit pressure ($P_{exit}$). The decay of the pressure amplitude may be treated analogous to the damping characteristics of a viscoelastic material for its dependence on time and elasticity of the material. The decay of pressure amplitude in an element of the fluid flowing from one end of the capillary would thus be greater if its residence time is longer. Hence exit pressure would be inversely proportional to melt viscosity.

The effect of elasticity on the damping characteristics implies that greater the elasticity the lower the damping. Hence an increase in melt elasticity should account for an increase in exit pressure. Higher values of first normal stress, recoverable shears strain, or Di/D and lower values of G for unvulacnized blends imply greater elastic recoverability, hereafter referred to as the higher melt elasticity. Unvulcanized blends show lower melt elasticity than PP. This suggests a significant role of the EPDM rubber in the reduction of melt elasticity.
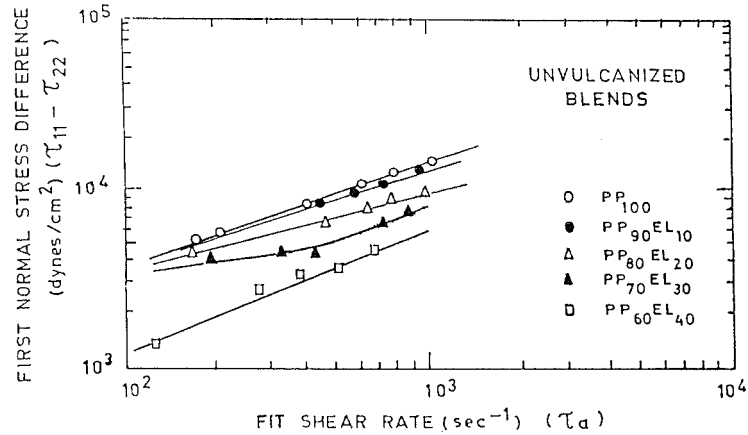
**Figure 9** First normal stress difference–fit shear rate plots showing the effect of rubber content in PP/EPDM blends at 220°C.

Vulcanized blends have lower melt elasticity than PP and unvulcanized blends. This mean that vulcanized blends is more elastic as the cross-linking increases. Blends with lower $(\tau_{11}-\tau_{22})$ have higher $\eta_{fit}$ indicate a decrease in melt elasticity accompanied by an increase in melt viscosity. The results of both $\eta$ and $\tau_{11}-\tau_{22}$ for both vulcanized blends also attributed here have prompted us to suggest that they might have formed three-dimensional network as well as flexible, long-chain branching. When modification yields gel particles (cross-linking occurs), discrete particles may be formed and dispersed in the matrix, as postulated by Narkis and Miltz.[24] In such an instance, the increase in normal stresses observed here is not expected. This is because the normal stresses of two-phase polymeric system containing either rigid particles or barely deformable rubber particles, when plotted against shear stress, are expected to decrease as the amount of the discrete phase is increased.

## Material Processing Characteristics

The polymer materials show lot to lot variances in processing and in product quality. The variance occurs are difficult to detect in the production line because they are dealt with in mass. A single-screw extruder in conjunction with the Rheocord are used for characterized the processing of materials by measuring the total torque development, residence time, shear rate, and specific output. This information provides uniformity of solid conveying, melting, and pumping mechanisms of the screw is being used.
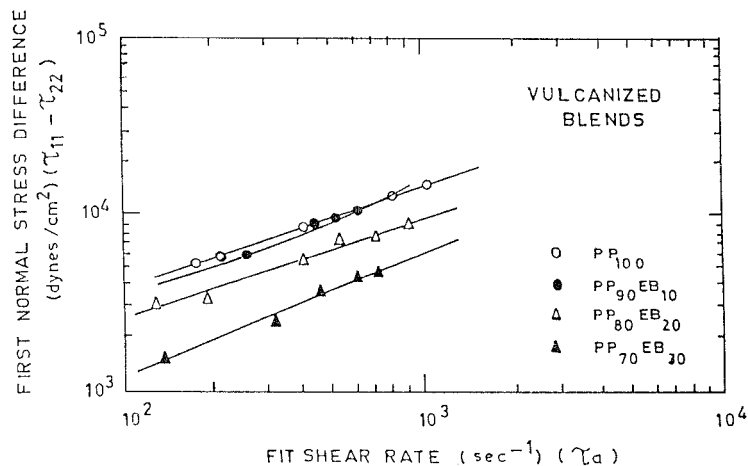


**Figure 10** First normal stress difference–fit shear rate plots showing the effect of blend ratio and dynamic cross-linking effect on PP/EPDM blends at 220°C.
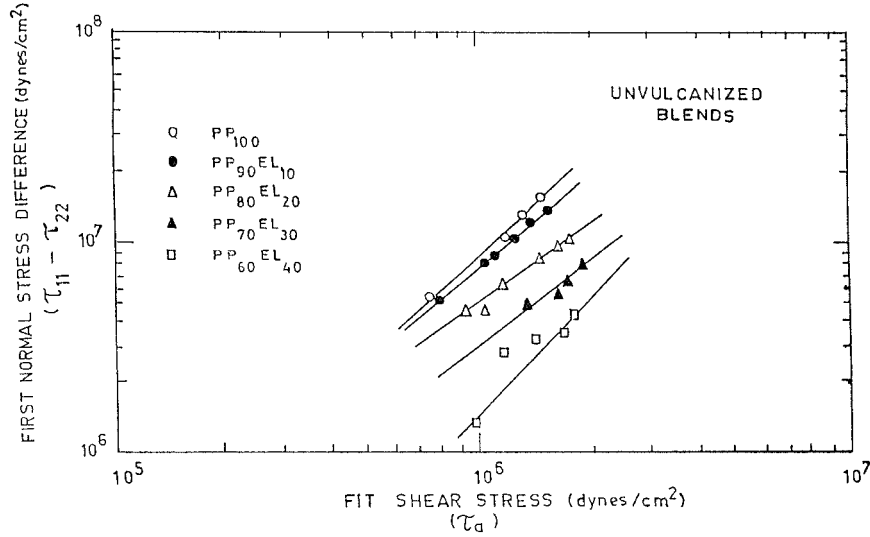
**Figure 11**   First normal stress difference–fit shear stress plots showing the effect of rubber content in PP/EPDM blends at 220°C.

## Total Torque Development

The total torque in extruder barrel during the processing of PP/EPDM rubber blends is presented in Table III; it increases with screw speed increase, even though overall output increases as screw speed increases because of melt limitations of the material in the system. The torque values of unvulcanized blend systems decreases with increasing wt % of EPDM rubber content in the blend. However, the soft EPDM rubber increases the flexibility of the material in barrel during the melt processing of the material. There is a nonlinear torque values variations in unvulcanized

blends also evidence the inhomogeneity mixing of the materials. The dynamically vulcanized blends also follows the same trends but has higher values as compared to unvulcanized blend. This is because of three-dimensional network structure of vulcanized blends having higher melt viscosity.

## Total Shear Energy

The effect of blend ratio and dynamic cross-linking on shear energy is shown in Figure 13 for these samples. Total shear energy (TE) is the energy introduced to the polymer materials by the motor
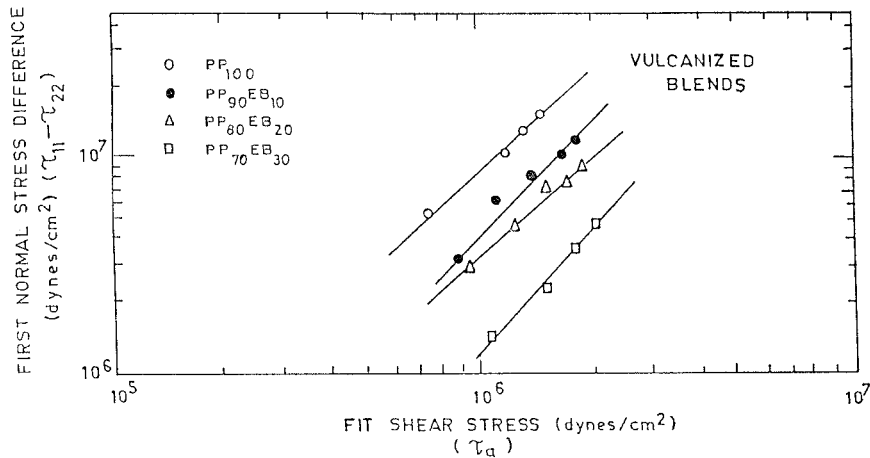


**Figure 12**   First normal stress difference–fit shear stress plots showing the effect of blend ratio and dynamic cross-linking effect on PP/EPDM blends at 220°C.

**Table III   Effect on Torque Developed in Barrel of Single Screw During Processing of PP/EPDM Blends**

| Blend Notation | Sample Notation | TORQUE (Nm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Screw Speed (rpm) | | | | | | | | |
| | | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
| Unvulcanized control blends | $PP_{100}$ | 5.9 | 8.2 | 10.5 | 12.2 | 13.8 | 15.1 | 18.1 | 18.3 | 20.2 |
| | $PP_{90}EL_{10}$ | 4.8 | 7.0 | 8.6 | 10.2 | 11.2 | 12.3 | 13.2 | 14.2 | 15.0 |
| | $PP_{80}EL_{20}$ | 5.0 | 7.6 | 9.3 | 10.8 | 11.8 | 12.8 | 12.9 | 13.0 | 13.1 |
| | $PP_{70}EL_{30}$ | 5.6 | 8.1 | 8.6 | 8.7 | 9.0 | 9.4 | 10.0 | 10.2 | 10.3 |
| | $PP_{60}EL_{40}$ | 4.6 | 6.2 | 6.9 | 7.2 | 8.1 | 9.2 | 10.7 | 10.5 | 11.0 |
| Vulcanized blends | $PP_{90}EB_{10}$ | 5.2 | 8.2 | 9.3 | 10.5 | 11.9 | 13.1 | 13.9 | 14.9 | 15.7 |
| | $PP_{80}EB_{20}$ | 5.4 | 8.2 | 9.7 | 11.0 | 11.1 | 11.7 | 12.6 | 12.7 | 13.6 |
| | $PP_{70}EB_{30}$ | 5.4 | 7.9 | 9.0 | 10.0 | 10.3 | 11.0 | 11.5 | 11.6 | 12.0 |
| | $PP_{60}EB_{40}$ | 6.5 | 8.5 | 8.8 | 9.3 | 10.3 | 11.1 | 11.0 | 11.1 | 11.7 |

drive during processing. This is calculated from the measured torque multiplied by screw speed (N).

$$TE = Torque \times N \times 9.807 \times 10^{-3} \quad (10)$$

This data gives information about total mechanical energy that is required for material processing. The vulcanized blends have higher specific energy compared with that of unvulcanized blends; this indicates that higher viscosity materials require more shear energy because vulcanized blends have higher torque values.

**Specific Energy**

The effect of blend ratio and dynamic cross-linking on specific energy is shown in Figure 14 for
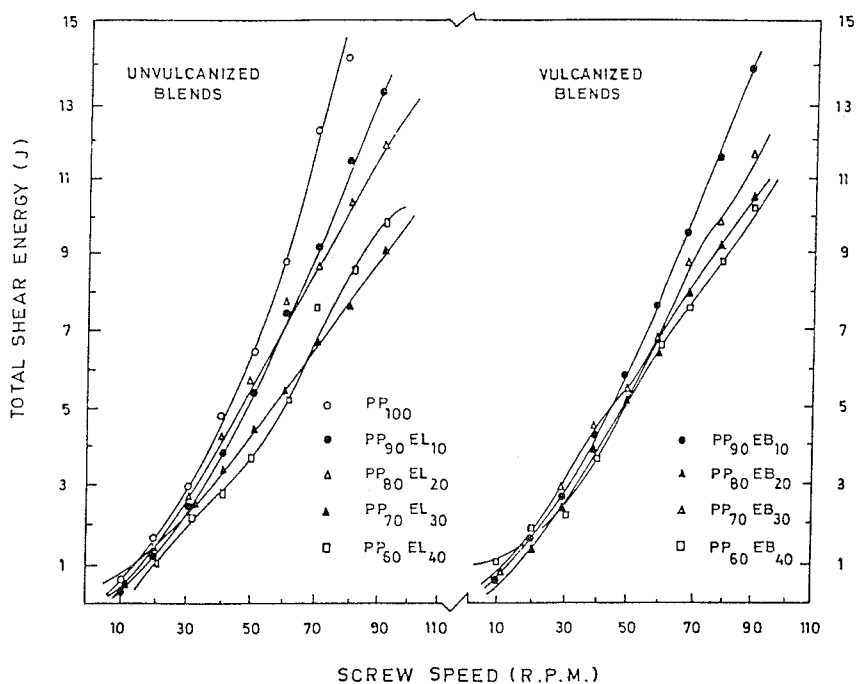


**Figure 13**   Comparison of total shear energy versus screw speed showing the effect of blend ratio and dynamic cross-linking effect on PP/EPDM blends at 220°C.
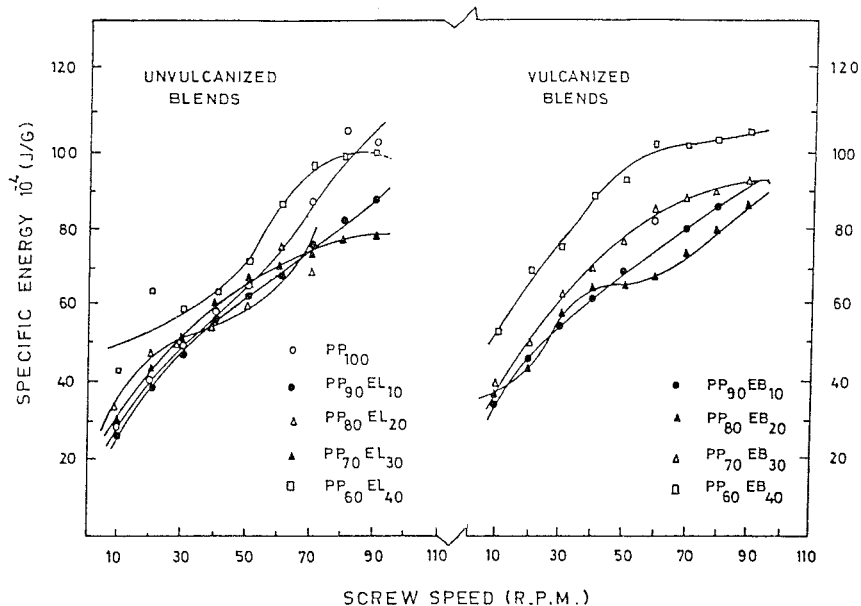
**Figure 14**   Comparison of total shear energy specific versus screw speed showing the effect of blend ratio and dynamic cross-linking effect on PP/EPDM blends at 220°C.

these samples. Specific energy (SE) is defined as energy required to process a unit mass of material. This is calculated from total shear energy divided by the total mass flow rate, as shown in eq. (11):

$$SE = \frac{0.0167 \, TE}{m} \qquad (11)$$

where TE is the total shear energy and m is the total mass flow rate. These data give information about viscous dissipation heat build-up in the system based on screw speeds.

The specific energy of PP/EPDM rubber blend increases steadily as screw speed increases because the overall viscosity of the material in the system increases and residence time (RT) decreases with increases screw speed. The vulcanized blends having slightly higher specific energy compared with that of unvulcanized blends, indicating that the more viscous (higher viscosity) materials require more energy for processing.

**Specific Output**

The effect of blend ratio and dynamic cross-linking in overall output is shown in Figure 15. Specific output (SO) is defined as mass flow rate per unit rpm of screw and is calculated from total

mass (m) divided by RPM (N) used, as shown in the following equation:

$$SO = m/N \qquad (12)$$

Insignificant variation of specific output in both blend systems at different screw rotation speed is attributed to the fact that both systems have uniformity of solid conveying, melting, and pumping mechanism during processing, even though overall output increases with increasing screw speed.

However, a total simulation of the behavior of polymer blends in different zones in a single screw extruder is necessary for detailed production of immiscible PP/EPDM blend. The lesson to be learned from this study is how can one material be vulcanized and yet be processed as a thermoplastics. All these tests gives a microscopic viewpoint of the polymer blends processing characteristics, showing differences that normally would not be seen individually in the overall macroscopic view seen in the production line. The processing of a blend is determined primarily by the properties of its thermoplastic phase, yet the properties of the same blends are determined primarily by the nature of the cross-linked rubber phase. Thus, an PP/EPDM blend has essentially the same melting point as rigid PP and is processed in much the same manner as PP. The
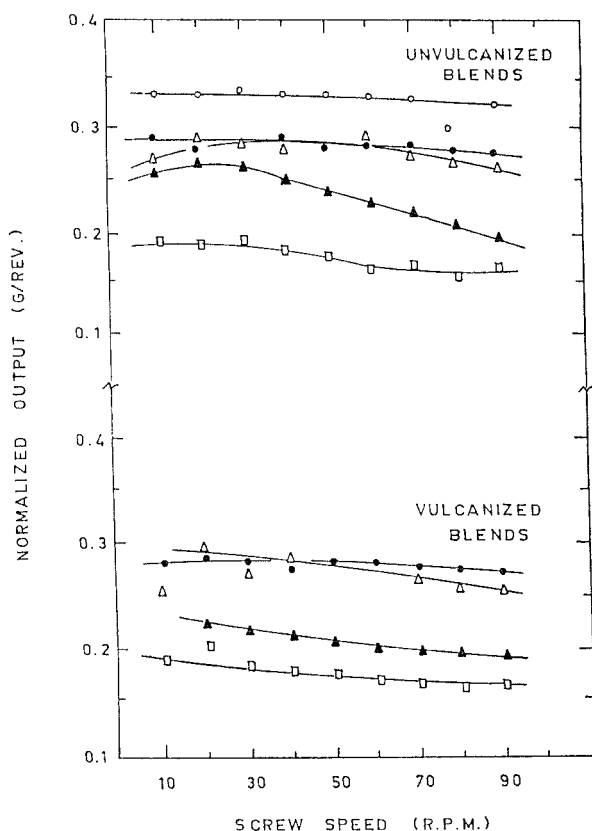
**Figure 15** Normalized output and screw speed plots showing the effect of blend ratio and dynamic cross-linking effect on PP/EPDM blends at 220°C.

rheology of the vulcanized blends is extremely non-Newtonian. Thus the viscosity of these materials is highly sensitive to the applied shear rate. Thus vulcanized blends have in practice been found to flow well at high shear rates and to flow poorly at low shear rate. This knowledge has been used extensively in the fabrication of vulcanized blend articles by injection molding, a method normally using high shear rates.

## Thermal Properties

The effect of EPDM on the thermal properties of PP was determined from MDSC. Results are presented in Table IV. Melting point of blends decreased with increasing EPDM contents for both unvulcanized and dynamically vulcanized blends. The inclusion of EPDM caused a PP smaller crystalline domain size for those blends. For the dynamically vulcanized blends, however, the vulcanization of EPDM had a more synergic effect on the decrease of the melt temperature by restricting the mobility of the polymer chain. As EPDM content increase, relative percent crystallinity decreases. Comparing unvulcanized blends with dynamically vulcanized blends, we find cross-linked blend systems having higher percent degree of crystallinity. The effect of dynamic vulcanization on the wt % crystallinity seems marginal, even though the EPDM chemically cross-linked by dimethylol phenolic resin restricts the crystallization of PP.

## Scanning Electron Microscopy

SEM of fracture surfaces of samples and etched in cyclohexane to dissolve out the EPDM component, are shown in Figures 16a–d for unvulcanized and Figure 17a–d for dynamically vulcanized systems of various blend compositions. Owing to the irregular shapes and varying sizes of

**Table IV  Effect on Melting and Degree of Crystallinity of PP/EPDM Blends**

| Blend Systems | Sample Notation | Heat of Fusion $(\Delta H)$, J/g | Melting Temperature $(Tm)$, °C | Crystallization Peak Temperature $(Tp)$, °C | Degree of Crystallinity, (%) |
|---|---|---|---|---|---|
| Unvulcanized control blends | $PP_{100}$ | 87.02 | 167.81 | 117.01 | 41.63 |
| | $PP_{90}EL_{10}$ | 76.66 | 164.90 | 118.80 | 36.59 |
| | $PP_{80}EL_{20}$ | 65.71 | 164.92 | 118.90 | 31.36 |
| | $PP_{70}EL_{30}$ | 58.38 | 165.35 | 120.17 | 27.86 |
| | $PP_{60}EL_{40}$ | 50.22 | 164.89 | 119.78 | 23.97 |
| Vulcanized blends | $PP_{90}EB_{10}$ | 78.51 | 165.87 | 116.68 | 37.47 |
| | $PP_{80}EB_{20}$ | 72.06 | 164.80 | 115.16 | 34.39 |
| | $PP_{70}EB_{30}$ | 67.98 | 164.90 | 115.79 | 32.44 |
| | $PP_{60}EB_{40}$ | 49.72 | 166.03 | 116.99 | 23.73 |
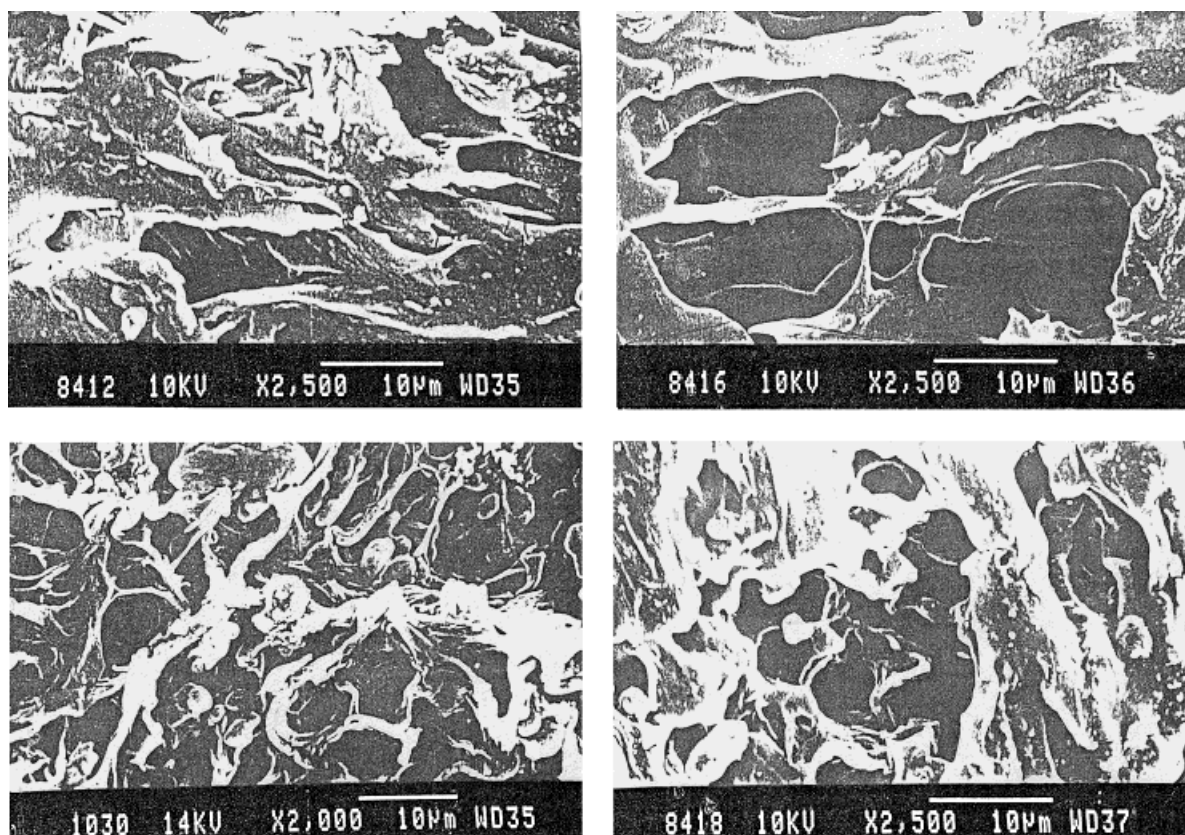
**Figure 16** SEM micrographs of the unvulcanized PP/EPDM blends: (a) 90/10; (b) 80/20; (c) 70/30; (d) 60/40.

state of dispersion (or average domain size) for these samples could not be possible from these SEM studies. However, information based on shapes, number density, and sizes of the EPDM domains at various blend compositions described below, supports some of the finding stated in a previous section.

On increasing the rubber content from 0 to 40 wt % in the blend, the number density of the dispersed rubber particles size increases considerably, whereas a small increase in average diameter is also observed. The bigger particle size of the rubber phase with increase in EPDM rubber content is attributed to reagglomeration or coalescence of the dispersed rubber particles. Many authors[25–27] have reported the occurrence of the coalescence at higher concentration of one of the component. These big size domains might be the because of greater obstruction to flow, which might account for the observed high melt viscosity in the cases of blends with higher rubber content. At lower EPDM content, the decrease of melt viscosity seems to effect plasticization pro-

duced by smaller size domains, which are apparently elongated and aligned along the flow line and thereby ease the flow.

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 rubber content and somewhat nonspherical at higher rubber content, where some smaller droplet retaining their shape and size can also coexist.

Deformability of viscoelastic domains is related to the capacity of storing recoverable elastic energy. Elasticity of melt, the recoverable shear strain ($\gamma_R$) is lower for the blends with high-EPDM rubber content, which is consistent with the lower deformability of the large EPDM rubber domains in the blends revealed by SEM micrographs.

The two-phase morphology is clearly visible at all the composition conforming the immiscibility of PP and EPDM blend systems.

The micrographs of vulcanized blends in Figure 17a,b have 10–20 wt % EPDM rubber con-
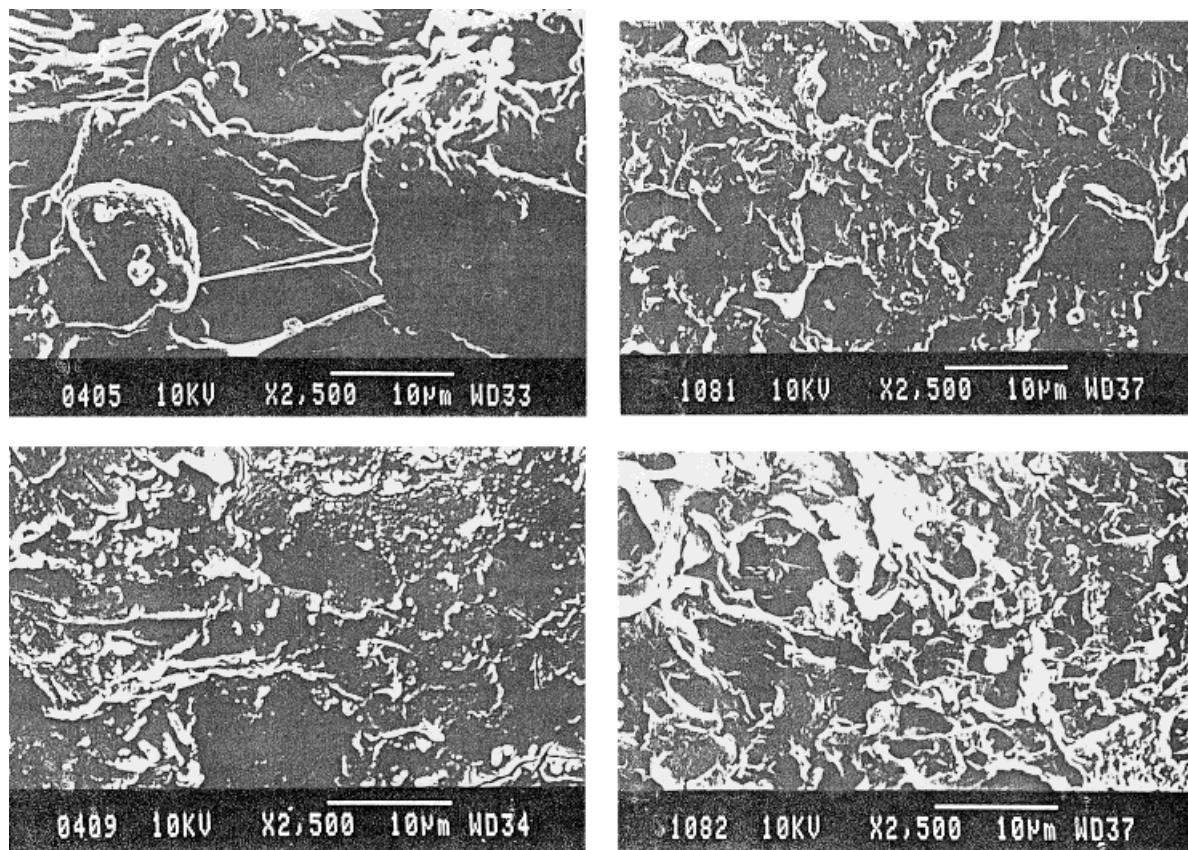
**Figure 17** SEM micrographs of the dynamically vulcanized PP/EPDM blends: (a) 90/10; (b) 80/20; (c) 70/30; (d) 60/40.

tent, and they show spherical rubber domains finely dispersed in continuous polypropylene matrix. The number density of the rubber domains in vulcanized blends is more whereas the average sized is less because of its higher mixing torque than the corresponding unvulcanized blends. The number density of rubber domains provides larger number of potential craze initiation sites and is responsible for higher impact strength in vulcanized blends. The tenacity of the cross-linked rubbers prevents the particles from continually shearing apart or reagglomerating, thus establishing an equilibrium and standard size range.

On increasing the rubber content from 20 to 40 wt % in the blend (see Fig. 17c,d), rubber particles appeared to be covering the continuous polypropylene matrix. The covered particles suggest that a graft copolymer of PP/EPDM rubber blend may produce on the interface during the cross-linking and strengthen the interfacial adhesion. These copolymers between phenolic-PP and EPDM rubber can act as emulsifier at the interface, result-

ing in reduction of the interfacial tension and leading too small and uniform distribution of the EPDM rubber phase. As pointed out by Illing,[28] a graft copolymer stays preferentially on the surfaces of dispersed domains acting as an interfacial agent. The presence of such an interfacial agent would require less energy for breaking large dispersed particles during melt blending and thus make it possible for domains to adhere to the continuous phase.

The absence of void after solvent etching and higher gel content values with increasing EPDM rubber content in vulcanized blends indicates that the cross-link reaction of the rubber particles proceeds predominantly and the production of the 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-(non-crosslinked EPDM rubber) type but PP-(cross-linked EPDM rubber) type.

As the EPDM rubber phase is cross-linked under high shear, the viscosity of the rubber phase initially increases markedly, resulting in an effect

that starts playing a role in disturbing the continuity of the phases. When the degree of cross-linking of the rubber phase increases sufficiently, the relatively immobilized rubber particles break up to lower sizes under the prevalent shear level and become dispersed in the continuous PP phase. Thus, the degree of vulcanization attained, the PP/EPDM rubber blend ratio selected, and the shear level applied in the dynamic process together will ultimately decide the size and shape of the dispersed rubber particles, their state of dispersion or distribution in the continuous PP matrix, and hence the overall morphology.

## CONCLUSION

The cross-link system used in this study exhibits unique selectively in PP/EPDM blends. It is considered to be a useful technique to produce polyolefin/cross-linked rubber blends when it is needed to retain the rheological properties of the polyolefin in the resulting blends.

Under intensive mixing of the dynamic cross-linking procedure free radicals are produced on carbon at the allylic position in unsaturated EPDM particle in saturated PP matrix. Coupling of radicals causing slight reduction in the size of EPDM particles may produce a small amount of PP/EPDM graft copolymer. Production of graft copolymer was not investigated in this research and needs further investigation. However, dimethylol phenolic resin/stannous chloride is a cross-link system which also facilitates the better compatibility for a mixture of PP and EPDM rubber.

Rheology and polymer processing are very closely related. A proper rheological characterization is necessary.

The morphological analysis showed that the dynamically vulcanized blends exhibited enhanced property profiles because interfacial adhesion is better because of compatibility between the two immiscible phases.

## 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.; Fortenlny, I.; Kovar, J. Collect Czech Chem Commun 1993, 58, 2642.
4. Inouse, T. J Appl Polym Sci 1994, 54, 723.
5. Ha, Ch. S.; Ihm, D. J.; Kim, S. Ch. J Appl Polym Sci 1986, 32, 6281.
6. Munstedt, H; Polym Eng Sci 1981, 21, 259.
7. Castellani, L.; Lomellini, P. Plast Rubber Compos Process Appl 1991, 16, 25.
8. Castellani, L.; Lomellini, P. Rheol Acta 1994, 33, 446.
9. Malkin, A.Y. Adv Polym Sci 1990, 96, 69.
10. Husband, D. M.; Aksel, N.; Gleissle, W. J Rheol 1993, 37, 215.
11. Lattimer, R. P.; Kinsey, R. A.; Layer, R. W.; Rhee, C. K. Rubber Chem Technol 1989, 62, 107.
12. Hultzsch, K. J Prakt Chem 1941, 158, 275.
13. Hultzsch, K.; Chemie der Phenolharze; Springer Verlag: Berlin, 1950.
14. Cunneen, J. I.; Farmer, E. H.; Koch, H. P. J Chem Soc 1943, 472.
15. Schwarz, A. G.; Kamenskii, B. Z. Kautsch, Resina 1963, 22, 8.
16. Fitch, A. Interaction of Alkylphenol – Formaldehyde Condensates with Trialkylethylenes. PhD. Thesis, London, 1978.
17. Ginsburg, L. B.; Scherschnew, W. A.; Dogadkin, B. A. Ber Akad, Wiss UdSSR 1973, 152, 335.
18. van der Meer, S. Rev Gener, Caoutchue 1943, 20, 230.
19. van der Meer, S. Rev Trav Chim, Pays Bas 1944, 63, 157.
20. Giller, A. Kautsch Gummi 1961, 14, WT 201.
21. Giller, A. Kautsch Gummi Kunstst 1964, 17, 3.
22. Giller, A. Gummi Asbest Kunstst 1965, 18, 1304.
23. Kuriakose, B.; De, S. K. Polym Engg Sci 1985, 25, 630.
24. Narkis, M.; Milz, J. Polym Engg Sci 1970, 9, 153.
25. Martuscelli, E.; Liva, F.; Sellitti, C.; Silverstre, C. Polymer 1985, 26, 217.
26. Thomas, S.; Gupta, B. R.; De, S. K. J Vinyl Technol 1987, 9(2).
27. Walezak, Z. K. J Appl Polym Sci 1973, 17, 169.
28. Illing, G. in Polymer Blends, Processing, Morphology and Properties; Martuscelli, E.; Palumbo, R.; Kryszewski, M., Eds.; Plenum: New York, 1980, p. 167.