Effect of Dynamic Crosslinking on Impact Strength and Other Mechanical Properties of Polypropylene/Ethylene-Propylene-Diene Rubber Blends

A. K. JAIN,[1] A. K. NAGPAL,[2] R. SINGHAL,[2] NEERAJ K. GUPTA[1]

[1] Department of Material Science, Shriram Institute for Industrial Research, 19 University Road, Delhi 110 007, India

[2] Department of Plastic Technology, Harcourt Butter Technological Institute, Kanpur 208 002, India

ABSTRACT: The deformation and fracture behavior of several dynamic vulcanizate blends of isotactic polypropylene with ethylene-propylene-diene rubber (EPDM) was examined and compared with those of uncrosslinked blends of PP/EPDM. These blends were prepared by melt mixing in an internal mixer at 190°C in a composition range of 10−40 wt % EPDM rubber. The variation in yield stress, the strength of fibrils of the craze, and the number density of the EPDM rubber domains (morphology fixation) that are dominant factors for enhancing interfacial adhesion and toughness in dynamic vulcanizate blends were evaluated. The ductility and toughness of these materials were explained in light of the composition between crack formation and the degree of plastic deformation through crazing and shear yielding. The physicomechanical properties including the hardness, yield stress, Young's modulus, percentage elongation, impact strength, flexural strength, and flexural modulus of dynamic vulcanized blends were found to be consistent and displayed higher values compared with uncrosslinked blends. The nucleation effect of the crosslinked particles and the decrease of crystallinity of the EPDM rubber were also considered to contribute to the improvement in the impact strength. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2089−2103, 2000

Key words: polypropylene; ethylene-propylene-diene rubber; polymer blend; impact strength; dynamic mechanical properties; fracture mechanics

INTRODUCTION

The commercial importance of toughened polymer blends has rapidly increased in recent years. Impact strength or toughness is a complex mechanical property of a material that reflects the absorption of impact energy during different processes preceding fracture of the specimen. Viscoelastic deformation, yielding, voiding, crazing, and finally formation and propagation of true cracks leads to fracture. As is well known, the toughness of most thermoplastics can be considerably enhanced by the incorporation of a dispersed rubbery phase. The toughening mechanisms involved are influenced by the properties of the matrix material and by the morphology of the blend.[1] Thus, the dominant energy absorbing process is different in different blends. Figure 1 shows schematic diagrams of some toughening mechanisms.

Toughening is typically explained by invoking the two major deformation mechanisms of crazing and shear yielding,[2] but cavitation and deformation also play an important role.
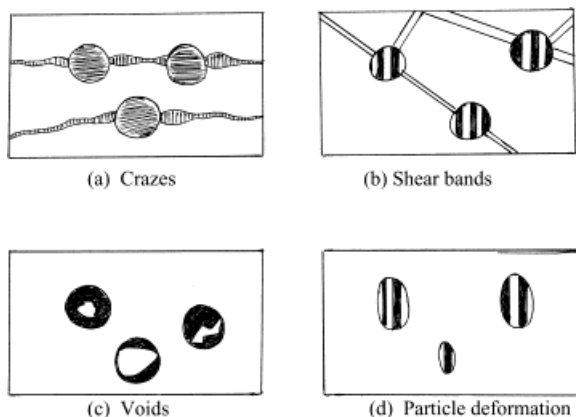
Figure 1 A schematic of four toughening mechanisms.

Polypropylene (PP) is characterized by poor low temperature impact behavior because of its relatively high glass-transition temperature (T_g). The incorporation of elastomer particles offers a classical solution of these problems. Although there were many intensive studies to explain the toughening effect of the dispersed phase, the subject still has many controversial points.[3] Numerous studies were carried out to investigate the toughening of PP by the effects of dispersed phase properties or structures, such as the rubber concentration, particle size, shape and spatial packing of the rubber particles, and the degree of functionalization. However, few studies were concerned with the crosslinking of the rubber particles. Bucknall[1] states that crosslinking of the rubber particle is desirable because the rubber phase is subjected to very large tensile strains during impact, giving a crazelike structure. Dao[4] found that a highly crosslinked ethylene-propylene-diene terpolymer (EPDM) rubber was slightly more effective than uncrosslinked EPDM. A moderate degree of crosslinking allows the rubber to reach high strains by fibrillation and at the same time renders mechanical strength to the fibrils.

It is also well known that the brittle–tough transition depends on particle size. Wu[5] stated that a sharp brittle–tough transition occurred at a critical rubber particle size. Because of the fixed morphologies of dynamic vulcanized blends, they have improved property profiles. In order to optimize conditions, it would appear to be an attractive technique to change finely and uniformly dispersed particles of EPDM in the PP matrix (which can be obtained by a common melt blending process, when higher molecular weight PP and

EPDM are blended) to crosslinked EPDM particles. This could be accomplished by certain crosslinking systems under melt blending conditions, the so-called dynamic crosslinking.[6] Dynamic vulcanization is a melt mixing technique wherein the rubber component is crosslinked with a *in situ* process. The resulting blend has small, uniform, and finely distributed crosslinked rubber particle matrices.

The purpose of this article was to more precisely investigate the effects of the crosslinking of EPDM rubber particles in the PP matrix on the impact energy absorption behavior. The basic mechanical properties and phase morphology investigation of fracture surfaces by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) analysis, and dynamic mechanical analysis (DMA) were conducted.

EXPERIMENTAL

Materials

The polymers used in this study are listed in Table I. The isotactic PP (i-PP) and the EPDM with ethylidene 2-norbonene (ENB) as a termonomer were all commercially available grades. The polymers were vulcanized with RESOLE type dimethylol phenolic resin. The stannous chloride used as an accelerator was obtained from BDH Limited (India).

Methods

Blend Formulations

The unvulcanized EPDM rubber blends of 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 was approximately 185 g/batch. The vulcanized blends were prepared under identical conditions. At the onstart of the fifth minute of the 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 the EP(D)M rubber component was monitored online until 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 a heavy-duty grinder

Table I   Materials and Characteristics

Material	Properties	Source
Isotactic polypropylene	MFI = 10 g/10 min Specific gravity = 0.9 g/mL M_w = 530,000 M_n = 106,000 Degree of crystallinity = 41.63%	Grade Koylene M0030 (Indian Petrochemical Corporation Ltd., India)
Ethylene-propylene-diene rubber	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/mL	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)

The degree of crystallinity of the virgin polypropylene was calculated by differential scanning calorimetry.

and 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_{100}, $PP_{90}EL_{10}$, $PP_{80}EL_{20}$, $PP_{70}EL_{30}$, and $PP_{60}EL_{40}$ and vulcanized blends were designated as $PP_{90}EB_{10}$, $PP_{80}EB_{20}$, $PP_{70}EB_{30}$, and $PP_{60}EB_{40}$; the subscripts indicate the amount of PP and EPDM, respectively, in the blend.

Gel Content

The gel contents of the vulcanized blends were determined by extraction of 0.3 g of powdered sample through a 120-mesh stainless steel pouch in boiling cyclohexane in accordance with ASTM D-2765.

Mechanical Properties

Fine notched Izod impact strength was measured according to ASTM D-256 using a Ceast impact tester (model RESIL 25). Measurements were done at room temperature (RT, 27 ± 2°C). The tensile properties were determined on an Instron tester with a computerized data acquisition system at a crosshead speed of 5 mm/min. Specimens for tensile testing were prepared at room temperature (27 ± 2°C) according to the ASTM D-638 type IV method. The flexural strength and modulus at 5% strain were analyzed at a 16 mm/min crosshead speed and a span length of 50.8 mm according to ASTM D-790. The melt flow rate

(MFR) was measured at 230°C under a load of 2.16 kg according to ASTM D-1238.

DMA Testing

The viscoelastic properties were studied using a DuPont model 983 dynamic mechanical analyzer. Rectangular 50 × 10 × 3 mm samples were cut from the compression-molded sheets and subjected to a fixed frequency of 1 Hz over a temperature range of −130 to +140°C at a ramp of 5°C/min.

SEM

The morphologies of the samples were studied by preferential etching of the EPDM phase in cyclohexane. Prior to etching, the samples were cryogenically fractured. The dried samples were sputter coated with gold and the photographs were taken on a Jeol (model JSM-840) SE microscope.

RESULTS AND DISCUSSIONS

Toughness: Impact Strength and Its Mechanisms

The effects of the rubber crosslinking on the basic mechanical properties are summarized in Table II.

Figure 2 shows the Izod impact strength of PP blended with EPDM following selective crosslinking in comparison with that of the PP blend before crosslinking. Before crosslinking (unvulcanized system) the impact strength increases gradually

Table II   Effects of Crosslinking of EPDM Particles on Mechanical and Crystallization Properties of PP/EPDM Blends

Sample Code	MFR (g/10 min)	Gel Content (%)	Hardness Shore D	Mechanical Properties				Impact Strength (Type A)		
				Tensile Stress at Yield (MPa)	Ultimate Elongation (%)	Flexural Stress at Yield (MPa)	Flexural Modulus (MPa)	Notched Izod (J/m)	Crystal. Temp. (°C)	Degree of Crystal. (%)
PP_{100}	10	—	88	33.25	46	44.46	1383	25	117.01	41.63
$PP_{90}EL_{10}$	9.1	—	82	23.50	52	36.51	1127	39	118.80	36.09
$PP_{80}EL_{20}$	8.3	—	80	20.45	66	29.51	973	57	118.90	31.36
$PP_{70}EL_{30}$	4.6	—	73	16.20	122	21.5	585	113	120.17	27.86
$PP_{60}EL_{40}$	4.2	—	70	13.00	285	17.7	547	190	119.78	23.97
$PP_{90}EB_{10}$	7.5	7.4	84	24.65	56	37.1	1179	58	116.68	37.47
$PP_{80}EB_{20}$	4.5	15.6	80	20.75	76	31.1	1013	86	115.16	34.39
$PP_{70}EB_{30}$	1.8	24.9	76	17.80	140	23.4	738	935	115.79	32.44
$PP_{60}EB_{40}$	0.3	34.8	71	13.94	350	18.8	560	1150 (PB)	116.99	23.43

PB, partial break.

from 25 to 190 J/m as the EPDM rubber content increases from 0 to 40 wt % in the blend. After crosslinking (vulcanized system) a quite sharp rise in the impact strength values from 25 to 86

Figure 2 The variation of the notched Izod impact strength with the blend composition for polypropylene/ethylene-propylene-diene rubber blends.

J/m in the region of 0–20 wt % EPDM rubber content in the blend is observed. A dramatically rise in impact strength is achieved from 86 to 1150 J/m (partial break) in the region of 20–40 wt % rubber content in the blend.

The increase in impact strength as the EPDM content increases from 0 to 40 wt % in both blend systems is attributed to the fact that rubber domains act as stress concentation sites for dissipation of shock or impact energies by controlling and promoting matrix deformation. The addition of rubber leads to relaxation of the stress concentration due to release of constraints of strain by Poisson's contraction between voids at the EPDM domains–polyolefin interfaces. As a result, nucleation of catastrophic cracks at the sites of crazes or matrix deformation is suppressed and toughness is improved.

The results showed that the EPDM rubber content required to improve the impact strength of the PP blend before crosslinking is above 30 wt %. On the other hand, in the blend of PP after crosslinking the impact strength is improved by an increase of 20 wt %. This suggests that the stand impact strength (IIS) of PP/EPDM blends or the impact energy absorption behavior of these change dramatically when the content of the EPDM reaches a certain critical value. This point is called "a transition point" (TP) for impact energy absorption behavior.

The i-PP homopolymer is taken as the reference material in order to evaluate the impact performance of the blend. At 27°C PP is a ductile
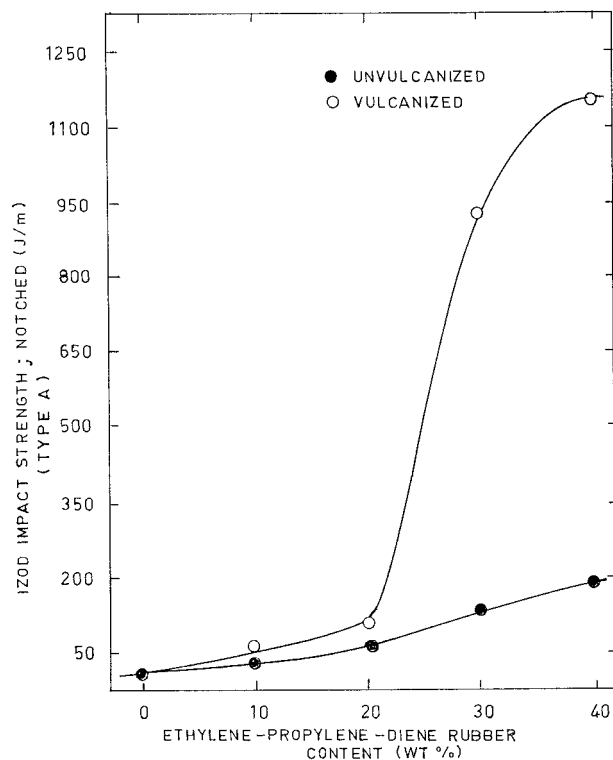
polymeric material, being above its T_g, and shear yielding is the primary mode of energy absorption under deformation.

The low impact values for the control unvulcanized blend are attributed to the fact that the rubber droplets formed during blend preparation coalesce during static melt cooling, giving rise to irregularly sized rubber domains that are larger than the critical size desired for impact toughening. This size enlargement and shape irregularity also reduces the number density of stress concentration sites and the interfacial adhesion. At higher rubber content (40 wt %) the impact strength also slightly increases. This is because of the poor interface between the EPDM rubber and PP matrix debonds during the deformation before the interaction is attained; not only is the stress relieved, reducing the possibility of the interaction, but also voids or flaws are produced. This poor interfacial adhesion may be because of the big EPDM domain size in the continuous PP matrix.

In the vulcanized blends the rubber particles are crosslinked and their size is greatly reduced because of a shear induced size reduction during vulcanizate preparation. The crosslinked structure of these discrete particles greatly inhibits the probability of rubber cohesion during cooling, so the number density of rubber at constant volume fraction domains are manyfold with good interfacial adhesion promoted by physical interlocking during meltdown (i.e., enhanced molecular entanglements in and around the crosslinked structures). At RT these blends are above the glass-transition temperatures of either components; therefore, as soon as the stress around the crosslinked rubber particles overcomes the yield stress of the matrix, the shear yielding mechanism of fracture becomes predominant over crazing and enhanced toughness is achieved. This is also evident from the stress whitening effects observed in the corresponding fractured surfaces.

In order to promote shear yielding in the PP matrix, it is important that the stress concentration fields developed from the EPDM particles interact effectively with each other in the PP matrix. If the interface between the particle and the matrix debonds during the deformation before the interaction is attained, not only is the stress relieved, reducing the possibility of the interaction, but also voids or flaws are produced. On the other hand, if sufficient interaction is attained, a kind of continuous stress concentration zone is realized in the matrix and the blend. This allows shear yielding to occur easily and, as the result, the energy absorption in the blends increases dramatically.

The MFR is an inverse function of viscosity and can be used to qualitatively assess the interaction between the phases. Because the viscosity of EPDM is much higher than that of the matrix (elastomer MFR could not be measured under standard conditions) and PP and EPDM are not miscible in the melt, the blend melt could be treated as a suspension of solid particles in a fluid. Table II shows the decrease of MFR with the increase of elastomer concentration. The differences in the MFR among PP/EPDM samples reflect differences in compositions, the molecular weight of the compositions, and the morphology (particle shape and size). Generally, a decrease in the MFR can be approximated with a linear function in the concentration range used in this work. At a 30 wt % concentration in the unvulcanized blend, the MFR fell to approximately one-half of the original value. This rise in the melt viscosity is in turn reflected in reduced values of melt flow indices: 9.1–4.2 g/10 min for unvulcanized blends and 7.5–0.3 g/10 min for vulcanized blends as the EPDM content increases from 10 to 40 wt %, respectively, in the blend. On increasing the rubber content, the number density of dispersed rubber particle sizes increases considerably while a small increase in the average diameter is also observed. The bigger particle size of the rubber phase with the increase of EPDM content is attributed to reagglomeration or coalescence of dispersed particles. These big size domains might be because of greater obstruction of the flow, which might account for the observed high melt viscosity in the blends with higher EPDM content. The same is also evidenced from our findings of gel contents of the systems. The gel content of various vulcanized blends are compiled in Table II.

Morphology Fixation

Figure 3(a–d) shows the micrographs of samples of unvulcanized blends etched with cyclohexane. These micrographs show the irregular shapes of the inclusions (EPDM domains). The domains are quite small in the samples (about 2–2.5 μm) with the lowest EPDM content (i.e., 10–20 wt %). The occurrence of larger domains (about 2.5 μm or more lengthwise) is apparent at EPDM contents above 20 wt %. The fracture surface observations after crosslinking by SEM [Figure 4(a–d)] reveals that the EPDM particles appear to be covered
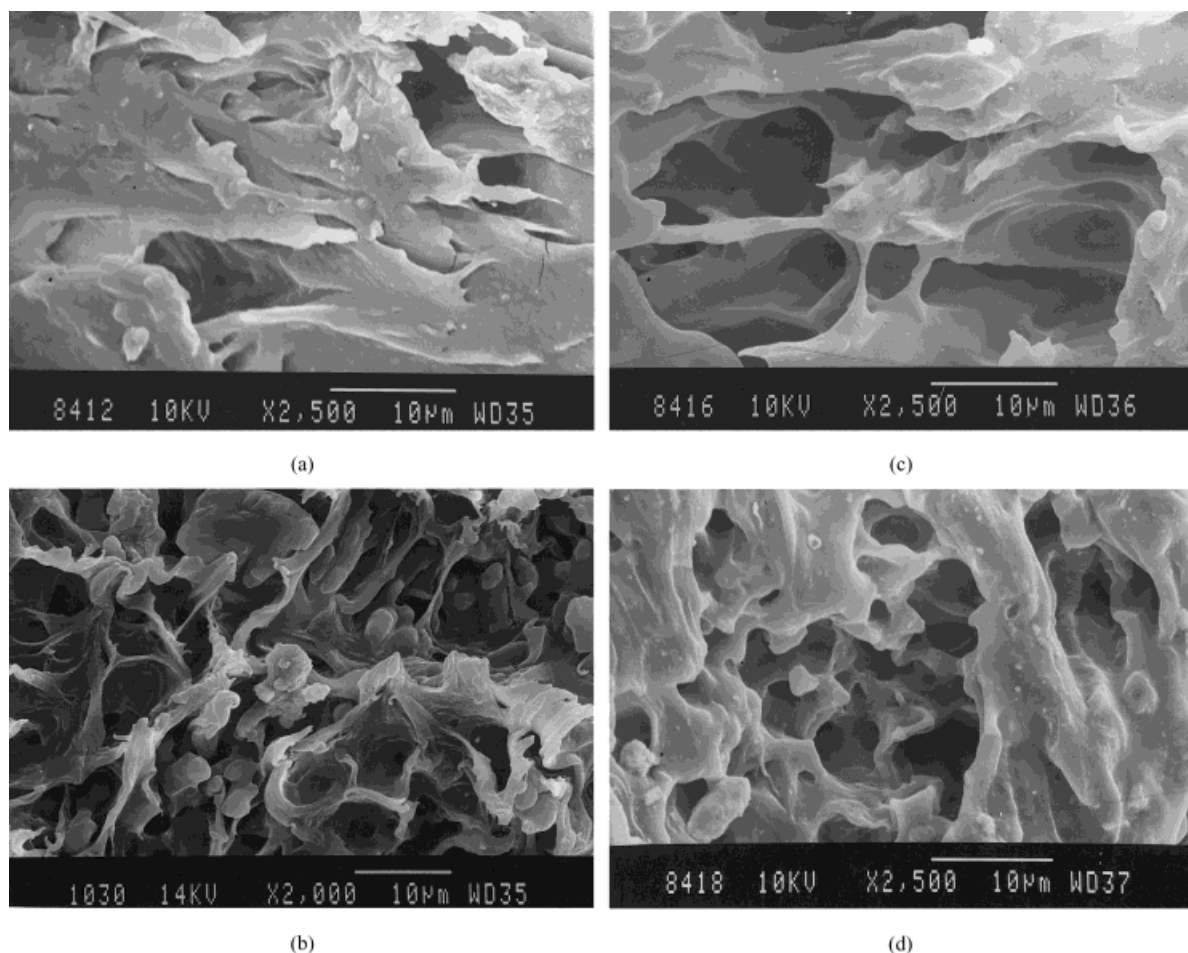
Figure 3 Scanning electron micrographs of the cryogenically fractured unvulcanized polypropylene/ethylene-propylene-diene rubber blend with rubber loadings of (a) 10, (b) 20, (c) 30, and (d) 40 wt %.

with the PP. The covered particles suggest that PP/EPDM graft copolymers are produced on the interface and 3-dimensional (3-D) network structure during the crosslinking and strengthen the interfacial adhesion. Because the graft copolymer produced under the crosslinking of the EPDM particles increases the interfacial adhesion, the result indicates that the transition occurs when relatively small concentrations of the graft copolymer are produced. In other words, the critical interfacial adhesion, which is strong enough to increase the possibilty of the interaction of stress concentration zones facilitating the shear yielding of the PP matrix, can be attained by relatively small amounts of the graft copolymer and they are produced by the early stages of the crosslinking reaction. It is also indicated that when the interaction or the overlapping is attained by a certain point in the increase of the interfacial

adhesion, a further increase cannot improve the impact strength. However, another possible interpretation is that the further improvement in impact strength cannot be obtained because all of surfaces of the elastomer particles are covered. The interfacial adhesion is indicated as one of the most important factors affecting the impact strength of this blends.

The impact strength of PP increases on the addition of 10 wt % EPDM because of the presence of rubber droplets of desirable size ($\sim$ 0.5 μm). In the region of 10–30 wt % rubber concentration, there is a gradual increase in the average size and number density of rubber domains, which seems consistent with the gradual increase in impact strength in this region. The change in morphology from the dispersed phase to the co-continuous phase in the composition range of 30–40 wt % rubber content, which imparts a high
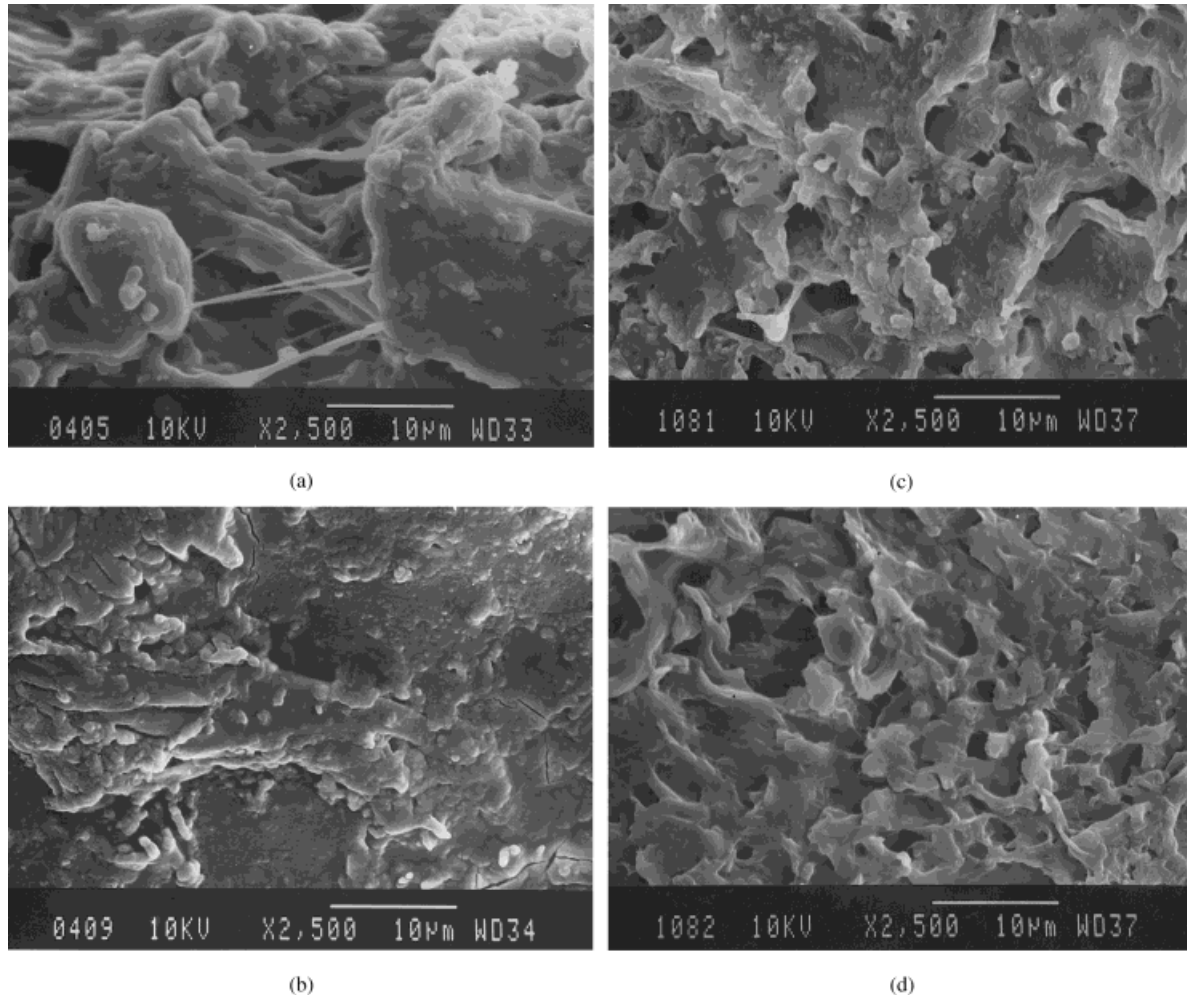
Figure 4 Scanning electron micrographs of the cryogenically fractured vulcanized polypropylene/ethylene-propylene-diene rubber blend with rubber loadings of (a) 10, (b) 20, (c) 30, and (d) 40 wt %.

elastomeric nature to the blend, is responsible for the increase in impact strength in the unvulcanized system in that region.

The disappearance of the yield peak and remarkably high impact strength of the vulcanized blend at 30 wt % EPDM suggests a continuous elastomeric phase at that composition and a change in morphology from a dispersed to a cocontinuous phase in the composition region of 20–30 wt % EPDM rubber content. The covalent crosslinks in vulcanized blends, although providing a distinct and stable structure to EPDM particles, might become labile through heat activation or during a thermoplastic processing step and can undergo exchanges at higher concentration, resulting in coalescence and a continuous rubber phase. There is a significant interaction

between the thermoplastic matrix and the rubber particles themselves. This aggregate of interactions or synergistic interactions results in surprisingly improved properties, and a drastic increase in the impact strength is observed in the region of 20–30 wt % EPDM rubber content in the blend.

Tensile Strength at Yield, Ultimate Elongation, and Strength of Craze

The results of tensile strength at yield (YTS) and ultimate elongation (UEL) of various blend compositions are given in Table II. It can seen that the yield stress (which is resistant to plastic deformation) and strength of the fibril (which constitutes the craze) are characteristic values for
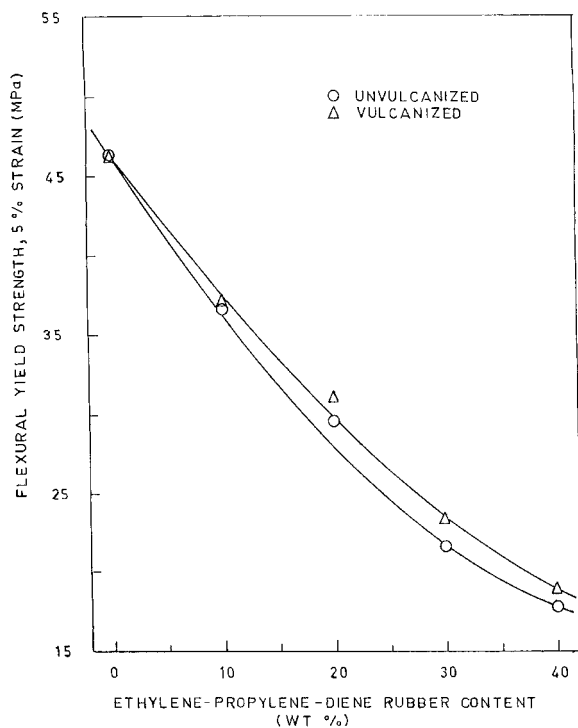
Figure 5 The variation of the flexural yield strength with the blend composition for polypropylene/ethylene-propylene-diene rubber blends.

Figure 6 The variation of the flexural modulus with the blend composition for polypropylene/ethylene-propylene-diene rubber blends.

brittle fracture of a ductile polymer. In either case, the characteristic value decreases with increasing content of modifier. The strength of the craze increases because the interfacial adhesion between the EPDM particles and the PP matrix is increased by the graft copolymer and/or the strength of the EPDM particles is improved after the crosslink reaction. On the other hand, the yield stress decreases because it seems that the crystal growth is suppressed. The YTS decreases but the UEL markedly increases with the addition of EPDM rubber in the PP matrix. The area under the stress–strain curve increases after the reaction, demonstrating that energy absorbed by the specimen before fracture also increases.

PP shows a well-defined yield peak, breaks in a brittle manner, and finally fails by a necking type of rupture. In all the modified samples studied, extensive stress whitening is observed before the general yield point and this whitening phenomenon continues to intensify in the unnecked zone. In the cross section of tensile specimens of PP/ crosslinked EPDM blends, neck formation is facilitated over a wider region as the deformation increases. This change is due to increases of the interfacial adhesion and interaction between the
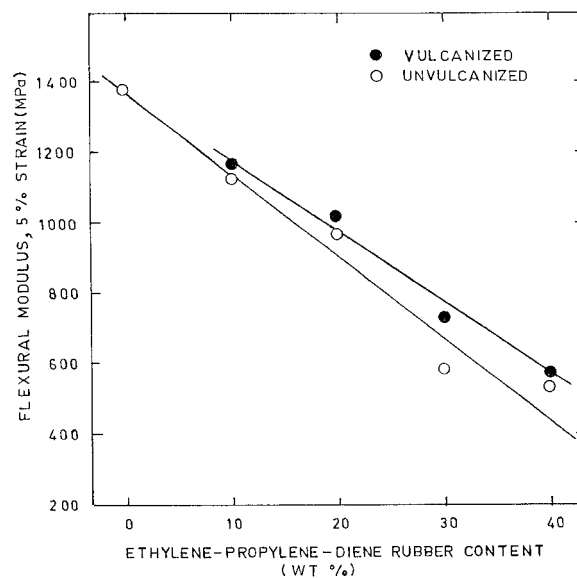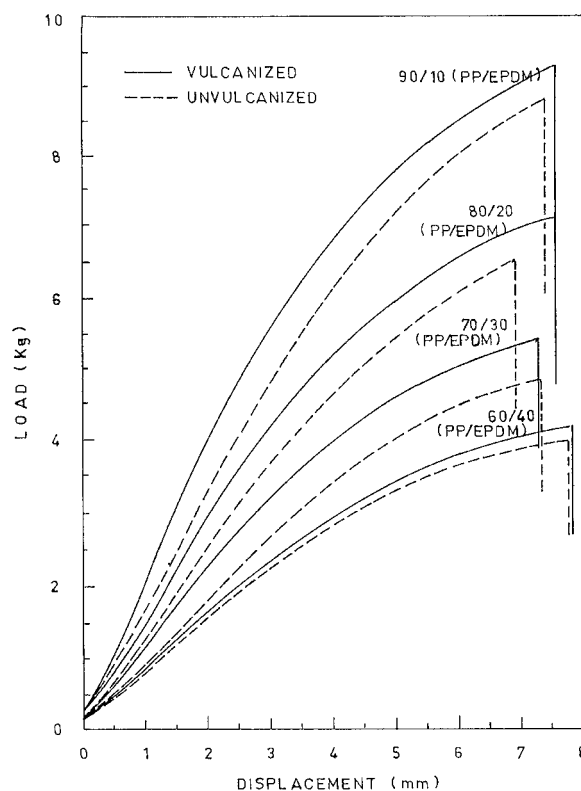

Figure 7 The variation of load–displacement curves for polypropylene/ethylene-propylene-diene rubber blends.
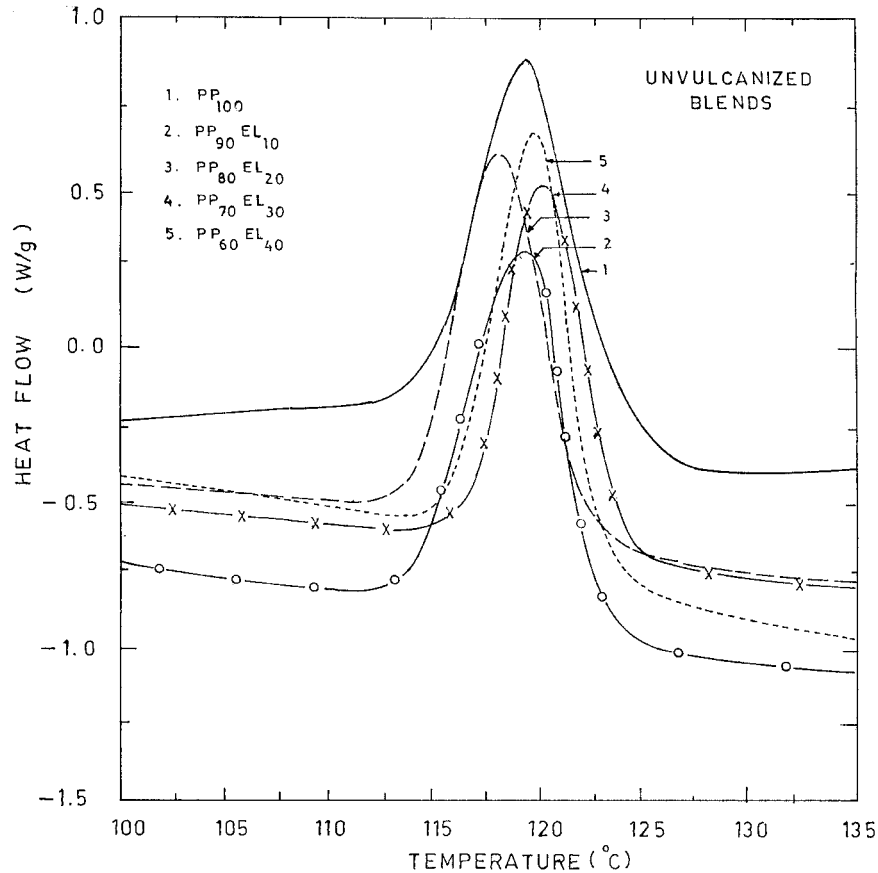
Figure 8 The variation of the various crystallization parameters with the blend composition for unvulcanized polypropylene/ethylene-propylene-diene rubber blends.

stress concentration zones in the PP matrix, both of which are caused by a 3-D network structure and maybe formation of the graft copolymer similar to the case of impact strength improvement. Therefore, vulcanized blends have higher values because an increase of the interfacial adhesion suppresses production of voids or flaws in the PP matrix, which might grow into cracks, and shear yielding can be promoted by the interaction between the stress concentration zone. Following the onset of yielding, the increased interfacial adhesion enables the deformation to occur easily in the cross section and facilitates shear yielding.

However, vulcanized blends have comparatively higher elongation at break because the craze fibrils are stabilized by molecular entanglements and can sustain high stresses for long periods. In unvulcanized systems the molecular entanglement is unable to prevent rapid flow and fracture in response to applied stress.

Flexural Modulus and Crystallization Temperature

The flexural strength and flexural modulus results are depicted in Table II and variations with rubber content are compiled in Figures 5 and 6. Flexural strength and flexural modulus show a negative deviation from the additivity. The negative deviation is generally seen in immiscible blends of polyolefins[7] and is mainly caused by poor interfacial adhesion. The decrease in flexural yield strength with increasing EPDM rubber content in the blends indicates a reduction in the rigidity and an increase in the elastomeric nature of the blend. An elastomeric nature improves the bending properties of the systems.

As the concentration of the soft rubbery component EPDM rubber increases in the blend, the hardness of the material decreases (see Table II for the results of shore D hardness) and the flexural strength and flexural modulus decrease. The observed behavior can be analyzed as a combined effect of both components of the blend.
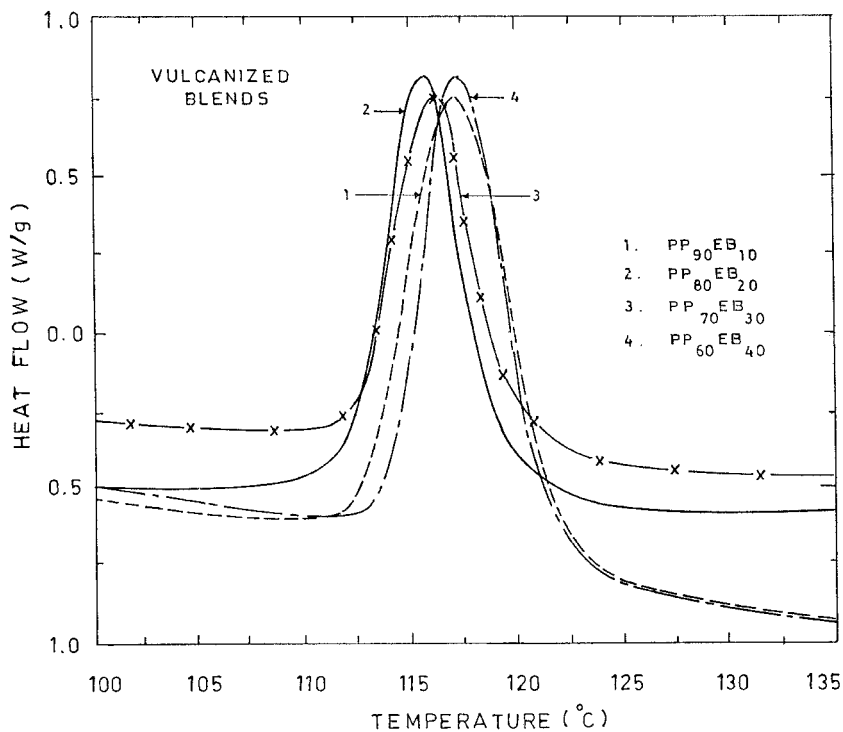
Figure 9 The variation of the various crystallization parameters with the blend composition for vulcanized polypropylene/ethylene-propylene-diene rubber blends.

The vulcanized blends having higher flexural strength and flexural modulus than the corresponding unvulcanized blends is also well docu-
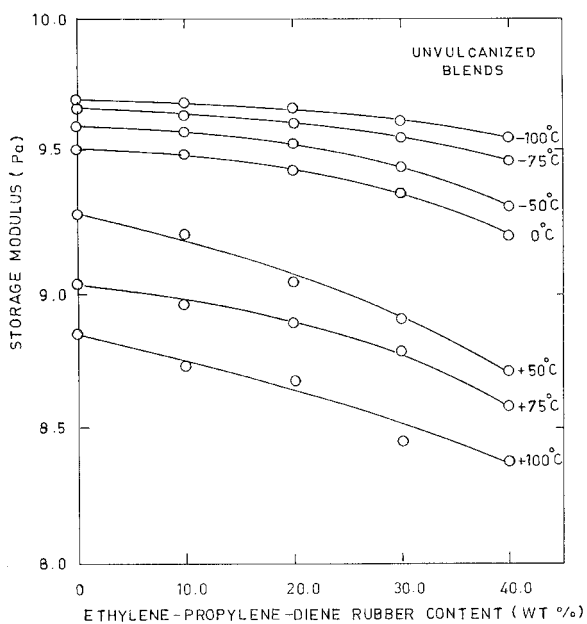

Figure 10 The variation of the storage modulus (E') with temperature for unvulcanized polypropylene/ethylene-propylene-diene rubber blends.
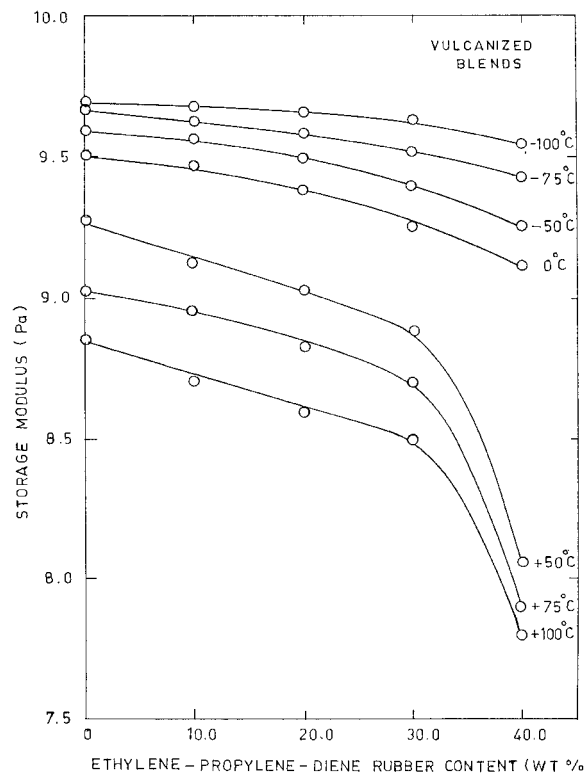

Figure 11 The variation of storage modulus (E') with temperature for vulcanized polypropylene/ethylene-propylene-diene rubber blends.

mented and is an effect of the crosslinking that forms a network structure. This crosslinking effect strengthening the interfacial adhesion would be accompanied by an increase in the flexural strength and flexural modulus in vulcanized blends.

The bending moment (load)–displacement curves of unvulcanized and vulcanized blends are presented in Figure 7. They show that the mode of fracture of the PP blend is brittle with a slight addition of modifier. The mode of deformation changes from brittle fracture to ductile deformation, showing general yielding when the addition of modifier is over a critical content. For the blend of PP before crosslinking, as much as 30–40 wt % modifier is required for the mode of deformation to change to ductile deformation; for the blend of PP after crosslinking, its content is about 20–30 wt %. The modifier content required to change the mode of deformation from brittle fracture to ductile deformation depends on the bending. The brittle to ductile transition takes place with a slight addition of modifier at low bending. The addition for the brittle to ductile transition increases with increasing bending.

The higher load required to propagate a crack in vulcanized blends indicates stronger adhesion between PP and EPDM rubber. This may be due to the dimethylol phenolic resin being interface compatible, and crosslinking the EPDM rubber particles at the same size results in a tough stabilized PP/EPDM matrix.

The crystallization temperature was determined by DSC analysis to determine the nucleation. Equal weight samples (8–9 mg) of the blends were analyzed under a cooling rate of 5°C/min from 230 to 27°C (RT). The variation in the crystallization temperature of the blends is shown in Figures 8 and 9, and the results are depicted in Table II.

The nucleation ability of the crosslinked EPDM rubber particles is believed to not only compensate for the expected decrease but to also overcome it, resulting in an increase in the flexural
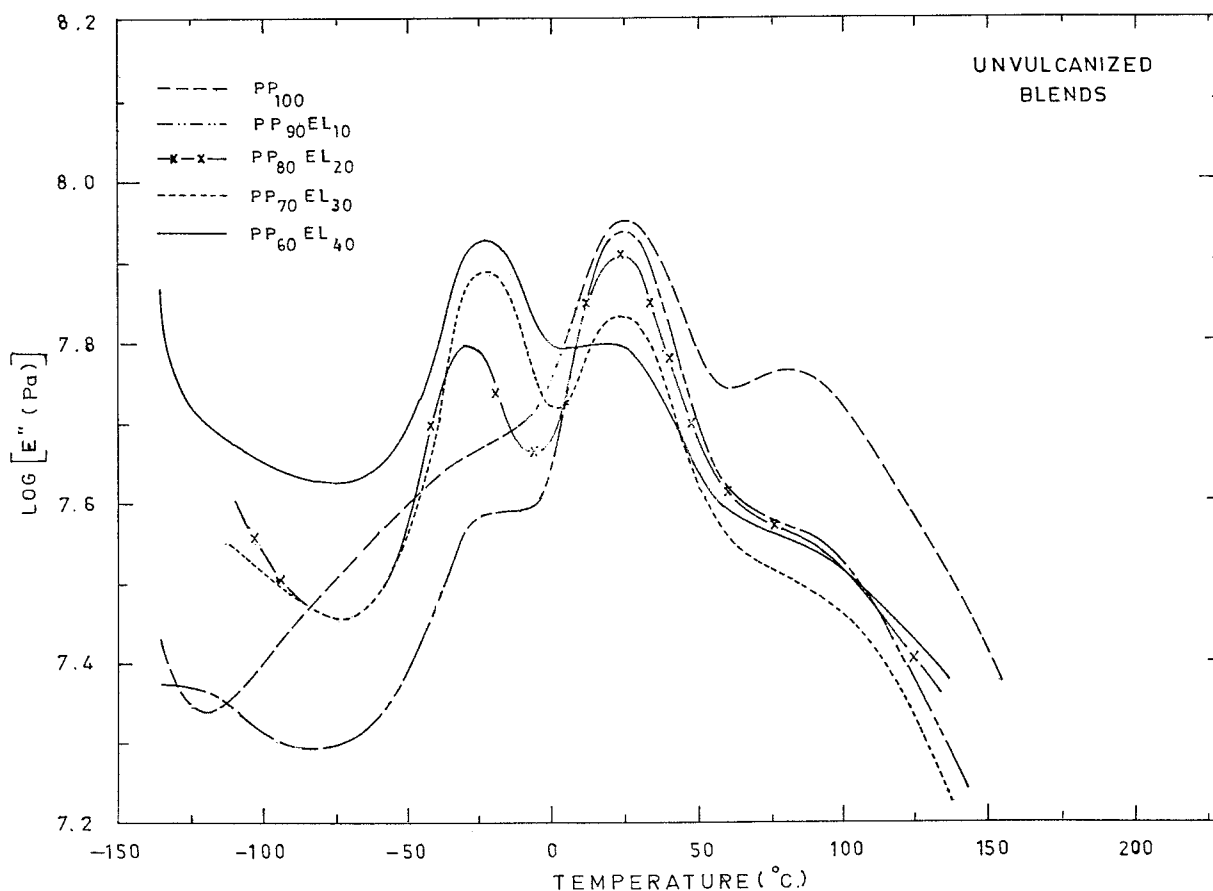

Figure 12   The variation of the loss modulus (E'') with temperature for unvulcanized polypropylene/ethylene-propylene-diene rubber blends.
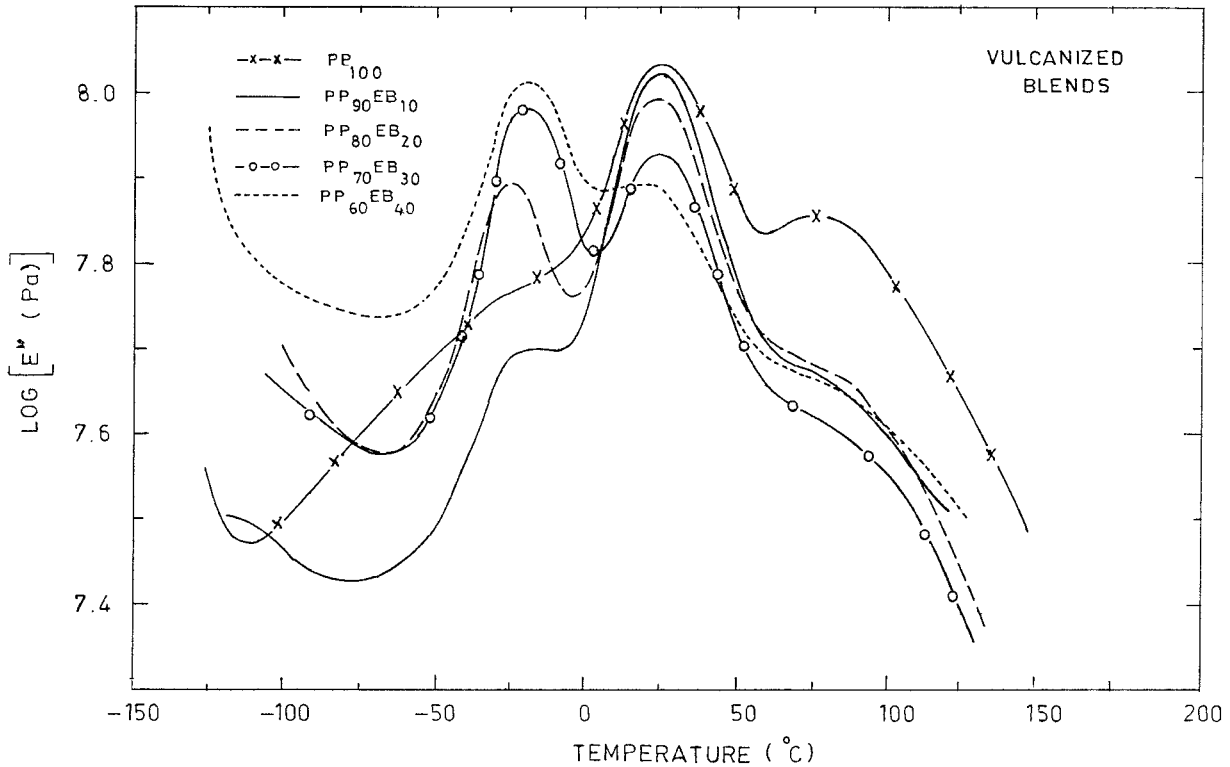
Figure 13 The variation of the loss modulus (E'') with temperature for vulcanized polypropylene/ethylene-propylene-diene rubber blends.

strength and flexural modulus in vulcanized blends. The nucleation effect probably changes the size of the spherulites, the crystalline form, and impact properties of the PP matrix, as reported in the literature.[8] The impact strength improvement obtained in the samples indicates that the effect of nucleation on the impact strength is smaller compared with that of the interfacial adhesion, considering that most nucleating agents decrease the impact when they increase the crystallization temperature; it is interesting that the produced crosslinked particles increased both of them at the same time.

DMA

The effect of blend composition and crosslinking on the dynamic mechanical properties was investigated in the -130 to $+140°C$ temperature range. The investigation indicated that PP/EPDM blends are incompatible, as shown by the presence of two relaxation peaks corresponding to the T_g's of PP and EPDM. For each blend the peak at the lower temperature is the glass-transition temperature of the elastomeric phase whereas the peak at the higher temperature is that of PP.

Interaction between the rubber and matrix can provide a shift and broadening of this peak. The broadening of the T_g peak of PP is quantified by introducing the ratio between the peak width and height (W/H). However, some compatibility is achieved as a result of dynamic crosslinking that is evident from the peak broadening. As the concentration of rubber increases, the storage modulus of the system decreases (Figs. 10, 11) while the loss modulus (Figs. 12, 13) and tan δ increase (Figs. 14, 15). The decrease in the storage modulus with increasing EPDM is sharp in the composition ranges of $30-40$ wt % in the unvulcanized blends and $20-30$ wt % in vulcanized blends, which suggests a change in morphology at these composition ranges that is also indicated by the SEM studies. The temperature where tan δ rapidly increases (E' rapidly decreases) shifted upward after the crosslinking. This indicates that the EPDM is crosslinked and the interaction between the EPDM and the PP has increased. Byrne and Hourston[9,10] investigated the dynamic mechanical behavior of EPDM and reported that the $\tan_{max}$ is increased by crosslinking, which is ascribed to the decrease of the degree of crystal-
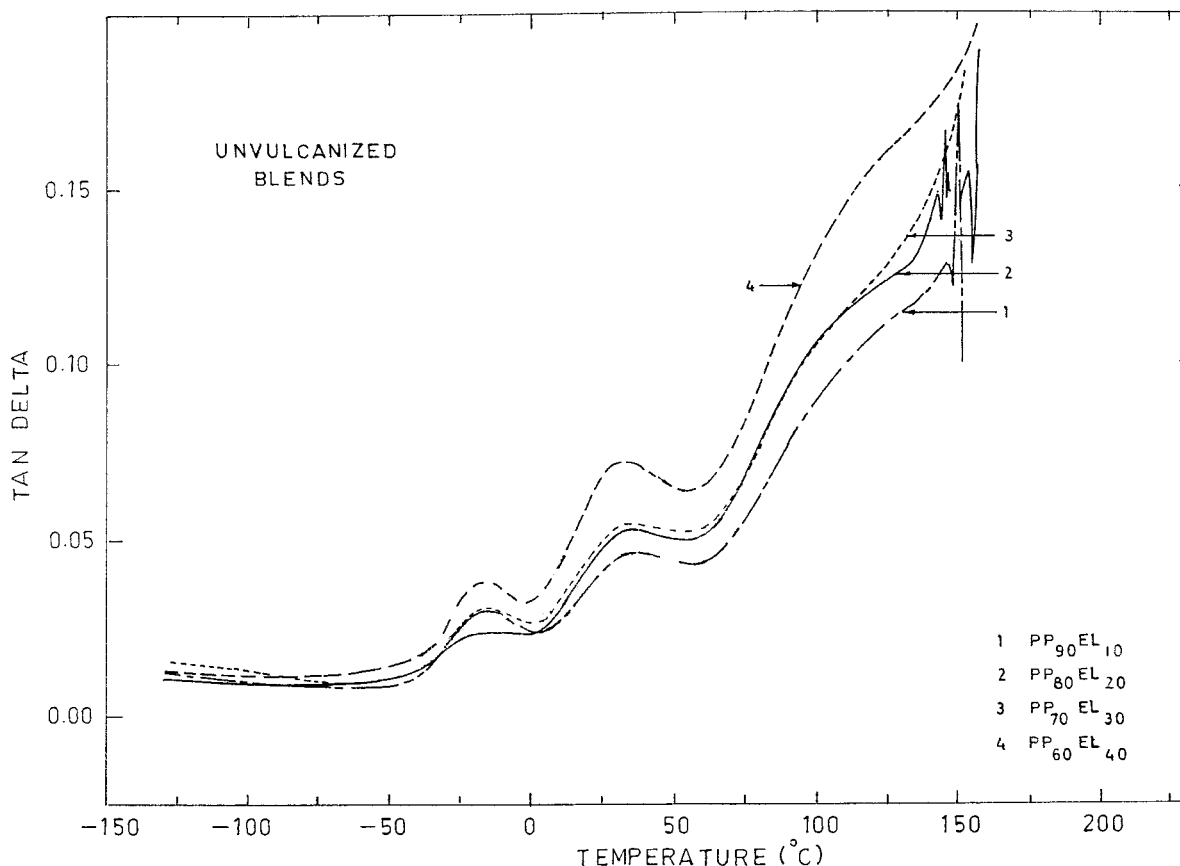
Figure 14 The variation of the tan δ with temperature for unvulcanized polypropylene/ethylene-propylene-diene rubber blends.

linity from 41.63 to 23.73 as the EPDM content increases from 0 to 40 wt % in the blend. The same phenomenon was observed by Coran and Patel.[11] It is also believed to crosslink the EPDM particles selectively because the addition reaction of the phenolic resin occurs only at unsaturated bonds in the EPDM. The results indicate that the interaction between the PP and the EPDM are strengthened by the crosslinking reaction because graft copolymer may be formed at the interface. The formation of graft copolymer was not confirmed; the tentative explanation given in the study must be verified with further experiments.

Reportedly, any molecular process that promotes distribution and dissipation of energy would enhance the impact resistance of polymers. Because viscoelastic relaxation of polymers is an important molecular mechanism of energy dissipation, it contributes to the impact resistance of polymers, although shear yielding and crazing are the main mechanisms of toughening. Correlation of impact and dynamic mechanical proper-

ties in terms of the tan δ peak values of the rubber component in the PP blend has been done. Because viscoelastic relaxation of the loss peaks of both PP and EPDM rubber occur at a temperature below the impact test temperature, it is more appropriate to include the tan δ peak values of the matrix (i.e., PP) also. The variation of the impact strength as a function of the total loss tangent peak values due to PP and EPDM rubber of the blends is shown in Figure 16. The curves show a nonlinear shape and features similar to those of curves depicting the variation of the impact strength with the blend ratio. The increase of the impact strength with the total loss tangent peak values indicates the role of the viscoelastic energy dissipation mechanism in the impact enhancement of these blends. The slope of these curves increases with an increasing EPDM rubber fraction with a rapid increase in the region of 30–40 and 20–30 wt % in unvulcanized and dynamically vulcanized blend systems, respectively. This behavior indicates viscoelastic energy dissipation
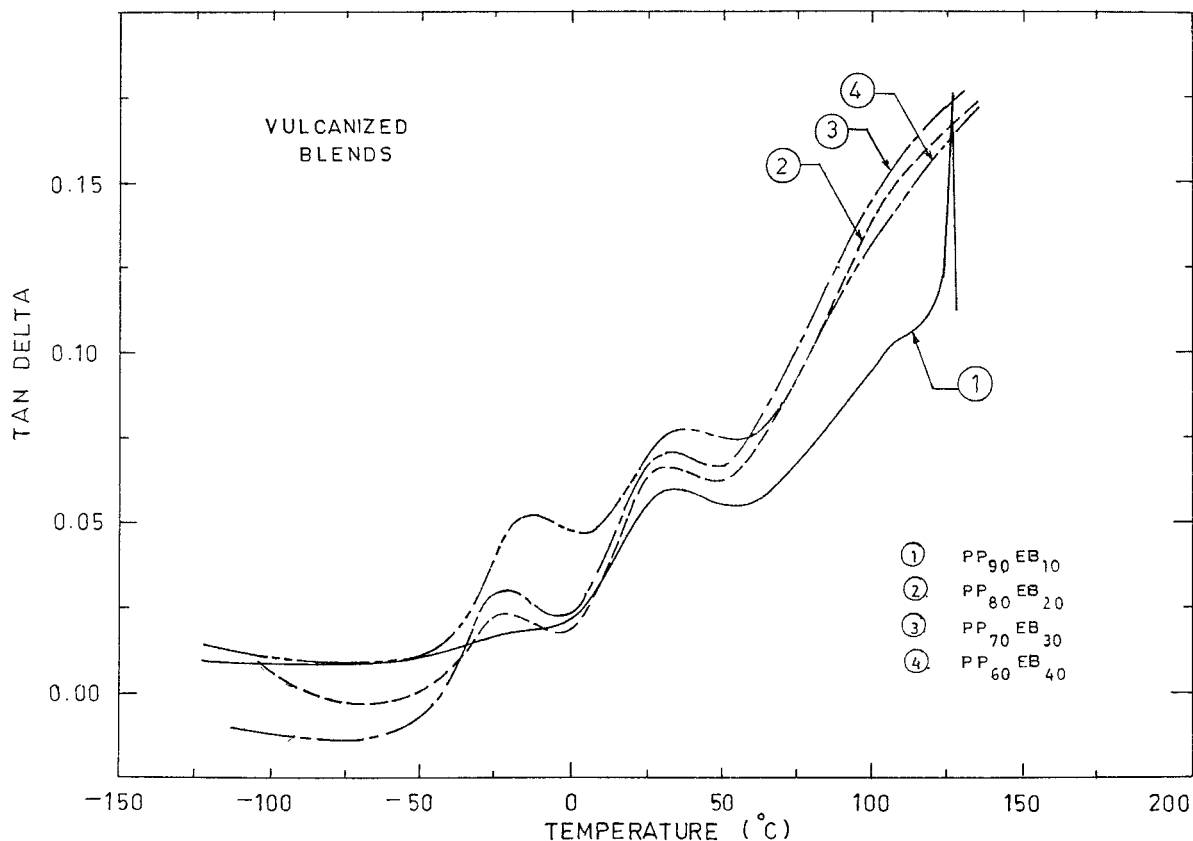
Figure 15 The variation of the tan δ with temperature for vulcanized polypropylene/ethylene-propylene-diene rubber blends.

crystallization behavior of the PP blends. PP shows a prominent crystallization exotherm in all the blend samples, as well as in unblended PP (Figs. 8, 9). The addition of EPDM rubber to PP leads to a decrease in the crystallization of the PP matrix and hence improves the energy dissipation by the matrix itself. This behavior indicates that viscoelastic energy dissipation is not the only mechanism responsible for the impact strength enhancement: other mechanisms like shear yielding and crazing are also operative.

CONCLUSION

1. PP is ductile above its T_g; the impact strength increases dramatically when the EPDM weight percentage reaches a critical value. The crosslinking of the EPDM and the increased interfacial adhesion reduce this critical value.
2. The high interfacial activity of crosslinked blends reduces the dispersed phase size
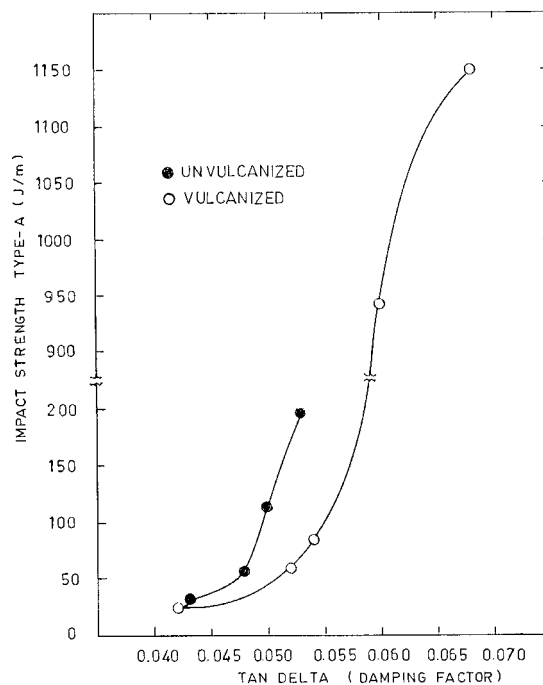

Figure 16 The correlation of the impact strength with the loss tangent peak value (tan δ) in polypropylene/ethylene-propylene-diene rubber blends.

and provides a more uniform particle size distribution.

3. A small amount of PP/EPDM graft copolymer is produced by the coupling of radicals, causing a slight reduction in the size of the EPDM particles. Production of graft copolymer is not investigated in this research and other studies are needed.

4. The crosslinking of the EPDM particles stabilizes the morphology of the blends. From the tensile strength impact strength and morphology data it is clear that the properties of the vulcanized blends are substantially improved by crosslinking with dimethylol phenolic resin.

5. The increased interfacial adhesion permits the interaction of the stress concentration zone developed from the elastomer particles under deformation and promotes shear yielding in the PP matrix.

6. The crosslinked EPDM particles act as nucleating agents and can lead to a decrease in the dimension of the PP spherulites.

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