RESEARCH ARTICLE

Investigation on the improvement of physico-mechnical, viscoelastic and morphological properties of isotactic polypropylene (iPP)/ethylene-propylene diene rubber (EPDM)/ nitrile rubber (NBR) elastomeric blends

Krishna Dutt Chauhan · Rakesh Kumar Soni · Harjeet Singh

Abstract An attempt has been made to study the mechanical, viscoelastic and morphological behavior of various dynamically cross-linked blends of isotactic polypropylene (iPP) with ethylene-propylene diene rubber (EPDM) and nitrile rubber (NBR) were examined and compared with these of uncross-linked blends of iPP/EPDM/NBR. These blends were prepared by melt blending in an internal mixer at 190 °C in the composition range of 10–40 wt. % EPDM/NBR elastomeric content. The variation in the strength of fibrils of the craze, yield stress and the number density of the EPDM/NBR elastomeric domains (morphology) which are important factors for enhancing the interfacial adhesion and toughness in dynamically cross-linked blends were determined. The toughness and ductility of these blends were discussed with main emphasis on the composition between crack formation and the degree of plastic deformation through crazing and shear yielding. The physico-mechanical properties such as hardness, impact strength, flexural strength and flexural modulus of dynamically cross-linked blends were found to be consistent and displayed enhanced mechanical properties values as compared with uncross-linked blends. The decreases in crystallinity and nucleation effect in cross-linked blends of iPP/EPDM/NBR were considered to contribute in the improvement in the impact strength behavior of the blends prepared.

Keywords Isotactic polypropylene (iPP) · Ethylene propylene-diene rubber (EPDM) · Nitrile rubber (NBR) · Polymer blend · Impact strength · Physico-mechanical properties · Fracture mechanics · Crystallinity · Nucleation

K. D. Chauhan (✉) · R. K. Soni · H. Singh
Department of Chemistry, Ch .Charan Singh University, Meerut, UP, India 200005
e-mail: kkdchauhan@gmail.com

Introduction

The commercial importance of the thermoplastic vulcanized (TPV'S) especially toughened polypropylene has rapidly increased in recent years. Toughness or impact strength is a complex mechanical property of a material which indicates the absorption of impact energy during different processes before final fracture of the test specimen. Viscoelastic deformation, voiding, yielding, crazing, deformation and propagation of true cracks finally lead to fracture.

As it is well known that the toughness of most thermoplastics can be considerably improved by the incorporation of a dispersed elastomeric phase. The toughening mechanisms involved are governed by the properties of the matrix material and by the morphology of the blend [1]. Hence, the dominant energy absorbing properties are different in different blends. Toughening can be explained by involving two major deformation mechanisms of shear yielding and crazing [2], but deformation and cavitations also plays an important role in polymeric blends. Polypropylene (PP) is characterized by poor low temperature impact behavior due to its relatively high glass-transition temperature (T_g). This can be overcome by the incorporation of elastomer particles. There are many intensive studies to explain the toughening effect of dispersed phase but the subject has still many controversies [3].

Number of studies was conducted in order to investigate the toughening of PP by the effects of dispersed phase properties viz., concentration of elastomer, particle size, shape, tightness in packing of the elastomeric particles and degree of functionalization. Bucknall [1] states that cross-linking of the elastomer particles is desirable because the elastomeric phase is subjected to very large tensile strains during impact thus giving it a craze like structure. Dao [4] found that a highly cross-linked EPDM elastomer was slightly more effective as compared to that of uncross-linked EPDM. A moderate degree of cross-linking allows the elastomer 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 elastomer particle size. Due to the enhanced morphologies of dynamically cross-linked blends, they possess improved property profiles. Dynamic cross-linking is an attractive technique to disperse finely and uniformly elastomer phase of EPDM in the PP matrix. This could be obtained by utilizing common melt blending process, but the process is limited to a lower molecular weight (MW). When higher molecular weight (PP) and EPDM are blended utilizing insitu cross-linking in the presence of cross-linking agents, the process so-called is termed as dynamic vulcanization [6]. The resulting blend possesses a small, uniform and finely distributed cross-linked elastomer particle matrices dispersed in thermoplastic phase.

However, elastomeric blends of iPP with various elastomers such as EPDM, NBR, Butyl rubber, natural-rubber etc., are reported but little work has been done to prepare ter blends without making much compromise in properties. Hence, in this study isotactic polypropylene (iPP) is blended with a unique elastomeric system of EPDM/NBR. The blends exhibited good physico-mechanical properties in terms of toughness or impact strength property. Hence, a unique melt blending system was developed with the incorporation of Dicumyl peroxide (DCP) which besides being a cross-linker also acts as a flow promoter during the blend formation. The principle of

dynamic vulcanization has gained interest in reactive processing of polymer blends. Thermoplastic blends with large polarity differences can be made by reactive compatibilisation of the two phases by the incorporation of block co-polymers [7].

Many other areas of development on TPV'S mainly focus on the improvement of the curing systems of the TPV'S [8]. Various cross-linking systems based on peroxides, sulfur are widely used to make TPV'S based on PP/ EPDM. The advantages of the cross-linking agents in the preparation of thermoplastic blends are listed in reference [9]. The effect of sulphur as a cross-linker on the physico-mechanical properties of PP/EPDM (TPV) is given in reference [10]. As far as superior physico- mechanical properties are concerned the blends of PP/EPDM [11] are widely used in automotive industry.

Recent development for EPDM based thermoplastics vulcanizates with emphasis on general purpose TPV, based on resole- cross-linked PP/ EPDM/oil blends are listed in reference [12].

The morphology and melt rheology of immiscible polymer blends filled with silica nano particles are described in reference [13]. Rheology and phase structure of PP/EPDM/SiO$_2$ ternary composites are well described by Hong Yang et al. [14]. The effect of dynamic cross-linking on mixing torque behavior and tensile yield behavior of isotactic polypropylene (iPP)/ ethylene- propylene diene rubber (EPDM)/nitrile rubber (NBR) elastomeric blends is well described by Rakesh Kumar Soni et al. [15].

The objective of this paper is to investigate more precisely the effects of the cross-linking of EPDM/NBR elastomeric particles on the iPP matrix and to study its impact absorption behavior. The basic mechanical properties and phase morphology investigation of fractured surface by scanning electron microscopy (SEM), modulated differential scanning calorimetry (MDSC) analysis and dynamic mechanical analysis (DMA) were conducted.

Experimental

Materials

The polymers used in this study are listed in (Table 1). The isotactic polypropylene (iPP), EPDM with ethylidene 2-norbonene (ENB) and nitrile rubber (NBR) were all commercially available grades. The polymers were cross-linked with resole type dimethylol phenolic resin.

Methods

Blend formulation

The uncross-linked iPP/EPDM/NBR blends of 10, 20, 30, and 40 wt. % EPDM/NBR elastomer content were prepared by melt blending at 190 °C for 10 min. at 80 rpm in the internal mixer of a torque rheometer (Haake Rhecord RC-90). The sample size in the mixing chamber was approximately 190 gm/ batch. The crosslinked blends were prepared under identical conditions. At the on start of the fifth minute of the

Table 1 Shows materials and its characteristics

Material	Properties	Source
Isotactic polypropylene (iPP)	MFI=11.0 g/10 min, Specific Gravity=0.91 g/cc, M_n=1,06,250, M_w=5,30,170, Degree of Crystallanity*=41.65%	Grade REPOL H 110 MA (Reliance Industries Ltd., India)
Ethylene-propylene-diene rubber (EPDM)	E/P weight ratio=68/32, ENB=4.5 wt %, Mooney Viscosity, ML1+4 (125 °C)=50 min, & 65 max, Specific gravity=0.86 g/cc	Grade Herlene-512 Herdillia Unimer Ltd., Mumbai, India
Nitrile Rubber(NBR)	Bound (ACN),%=33, Ash,%=0.3, Volatiles,%=0.4, Specific gravity=0.98, Mooney Viscosity, ML1+4 (100 °C)=(45–55)	Grade Chemigum-N685 Elio Kem Industries Ltd., Ankeleshwar, Gujrat, India
Dimethylol phenolic resin (Resole type)	Pale yellow lumps, Methylol content=8–13 %, Softening range=80–100 °C, Specific gravity=1.02–1.06	Hylax HR-6415 Bakelite Hylam Ltd., India

• Degree of crystallinity of the virgin iPP was calculated by differential Scanning Calorimetry (DSC) method

blending cycle, Dimethylol phenol resin (cross-linking agent), 10 wt. % based on EPDM/NBR elastomer and stannous chloride (accelerator), 2 wt. % based on EPDM/NBR elastomer was introduced into the blend. Subsequently after seventh minute N-Phenyl-2-naphthyl amine (antidegrant), 1 wt. %, [Zinc Stearate, (1 wt. %) / Tris nonyl phenyl phosphite (0.5 wt %) (Thermal stabilizers)] and Di cumyl peroxide (flow promoter/cross-linker) (0.2 wt. %) were introduced into the blend system and the cross-linking of EPDM/NBR elastomer component was monitored online until torque stabilization was achieved. The in situ elastomer cross-linking process took 10 min. The resultant blends were then discharged from the internal mixer in the form of lumps. The cooled lumps were then shredded in a heavy duty grinder 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. Formulations of blends (wt. % wise) are depicted in (Table 2).

The uncross-linked blends were designated as **iPP_{100}, $iPP_{90}EUC_{10}$, $iPP_{80}EUC_{20}$, $iPP_{70}EUC_{30}$** and **$iPP_{60}EUC_{40}$** and cross-linked blends were designated as **$iPP_{90}EC_{10}$, $iPP_{80}EC_{20}$, $iPP_{70}EC_{30}$** and **$iPP_{60}EC_{40}$,** the subscripts indicates the amount of iPP and EPDM/NBR respectively in the blends.

Characterization

Mechanical properties

Izod impact strength; notched The impact strength Type-A was measured according to ASTM D-256 on notched izod specimen of 63.5×12.7×3.0 mm

Table 2 Shows Formulations of blends (Weight percentage (%) wise)

S.No.	Sample Notation	Isotactic poly-propylene (iPP)	Ethylene-Polypropylene diene Rubber (EPDM)	Nitrile Rubber (NBR)	Zinc stearate**	TNPP**	N-phenyl 2-naphthyl amine	Dimethylol Phenolic Resin[a]	Dicumyl peroxide (DCP)	Stannous Chloride[a]
A	Uncrosslinked Control Blends									
	iPP_{90} EUC_{10}	90	7.5	2.5	1.0	0.5	1.0	–	–	–
	iPP_{80} EUC_{20}	80	15.0	5.0	1.0	0.5	1.0	–	–	–
	iPP_{70} EUC_{30}	70	22.5	7.5	1.0	0.5	1.0	–	–	–
	iPP_{60} EUC_{40}	60	30.0	10.0	1.0	0.5	1.0	–	–	–
B	Crosslinked Blends									
	iPP_{90} EC_{10}	90	7.5	2.5	1.0	0.5	1.0	–	–	–
	iPP_{80} EC_{20}	80	15.0	5.0	1.0	0.5	1.0	10.0	0.2	2.0
	iPP_{70} EC_{30}	70	22.5	7.5	1.0	0.5	1.0	10.0	0.2	2.0
	iPP_{60} EC_{40}	60	30.0	10.0	1.0	0.5	1.0	10.0	0.2	2.0

[a] Weight % based on EPDM/NBR elastomer

** Weight % based on isotactic polypropylene

dimensions with 2 mm deep triangular notches of 45 °C using CEAST impact tester, model RESIL 25 at 27±1°C.

Flexural properties The flexural properties including flexural modulus and flexural stress were determined in accordance with ASTM D-790 with an Instron Universal Tester (Model-4302). The samples were cut from compression molded sheets, having a dimension of 80 mm×25 mm×3 mm and conditioned at RT 27±1°C and 50% RH.

Hardness The hardness Shore-D of each blend composition was obtained in accordance with ASTMD-2240 using a shore hardness durometer (Shore-D).

Total insoluble content (gel content)

The gel content (insoluble fraction) is the main criteria to determine the (%) cross-linking in accordance to ASTM D-2765, wherein about 0.3 gm ground was extracted through a 120-mesh stainless steel pouch measuring approximately 80 by 40 mm in boiled cyclo hexane for 24 h.

Modulated differential scanning calorimetry (MDSC)

Modulated Differential Scanning Calorimetry (MDSC) measurements were undertaken on a TA analysis system Model-2910.

Dynamic mechanical analysis (DMA)

The viscoelastic properties were studied using a Du Pont model -938 dynamic mechanical analyzer (DMA). 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 uniform rate of heating of 5 °C/min.

Morphological observations

The prepared 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 discussions

Toughness; impact strength and its mechanisms

The effects of the EPDM/NBR elastomeric cross-linking on the basic mechanical properties are given in (Table 3). (Figure 1) depicts the Izod impact strength of iPP blended with EPDM/NBR elastomer particles following selective cross-linking as compared with that of the iPP blends before cross-linking. Before cross-linking (unvulcanized system) the impact strength increases gradually from 24 to 179 J/m as

Table 3 Shows different mechanical properties, crystallinity peak temperature and Degree of crystallinity

S.N	Sample code	MFR (g/min)	Mechanical properties				Crystallization peak temperature	Degree to crystallanity%
			Hardness shore	Flexural of stress at yield MPδ	Flexural modulus MPδ	Notched impact strength (type A) J/m		
1	iPP$_{100}$	11	89	46.85	1385	24	117.03	41.65
2	iPP$_{100}$ EUC$_{10}$	9.2	84	38.56	1189	37	118.82	36.60
3	iPP$_{100}$ EUC$_{20}$	8.1	82	31.12	1026	54	118.91	31.38
4	iPP$_{100}$ EUC$_{30}$	4.3	75	22.68	617	106	120.19	27.84
5	iPP$_{100}$ EUC$_{40}$	4.0	72	18.67	577	179	119.77	23.99
6	iPP$_{100}$ EUC$_{10}$	7.2	86	39.19	1244	55	116.67	37.49
7	iPP$_{100}$ EUC$_{20}$	4.1	82	32.81	1069	81	115.15	34.37
8	iPP$_{100}$ EUC$_{30}$	1.7	78	24.69	778	879	115.80	32.42
9	iPP$_{100}$ EUC$_{40}$	0.4	73	19.89	591	1081[a]PB	116.98	23.75

[a] *PB* PARTIAL BREAK

the EPDM/NBR elastomer content increases from 0 to 40 wt. % in the blend. After cross-linking (vulcanized system) a quite sharp increase in the impact strength values took place from 24 to 81 J/m in the region of 0–20 wt. % EPDM/NBR elastomer content in the blend was observed. A dramatically rise in impact strength is achieved from 81 to 1081 J/m (Partial break) in the region of 20–40 wt. % of elastomer content in the blend.
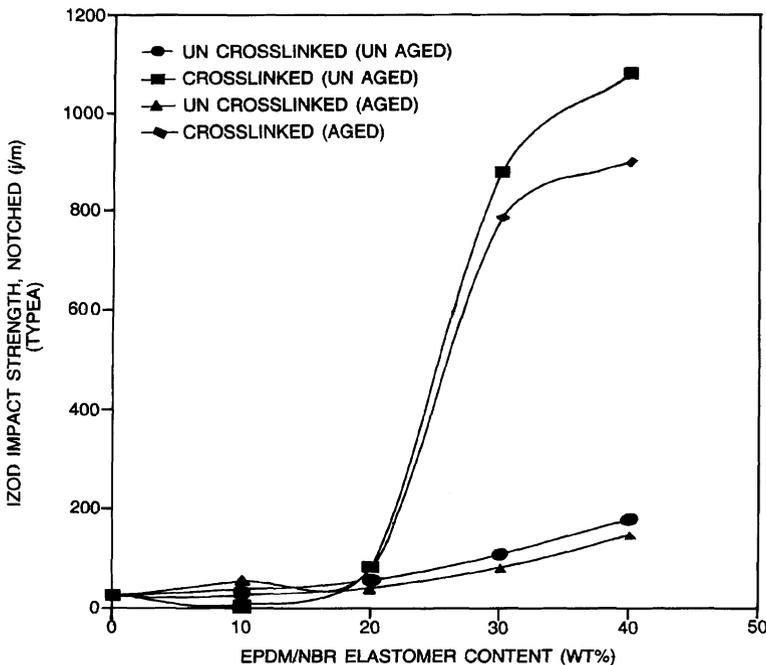
Fig. 1 Variation of izod impact strength notched (Type A) with blend composition for iPP/EPDM/NBR elastomer blends

The increase in impact strength as the EPDM/NBR content increases from 0 to 40 wt .% in both the blend systems is due to the fact that elastomer domains act as stress concentration sites for dissipation of shock or impact energies there by reducing the tendency of matrix deformation. The addition of elastomer leads to relaxation of the stress concentration due to release of constants of strain by Poisson's contraction between voids at the EPDM/NBR domains/ poly olefin 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/NBR elastomer content required to improve the impact strength of the iPP blend before cross-linking is over 30 wt .%. However, in the blends of iPP after cross-linking the impact strength is improved by an increase of 20 wt. %. This behavior suggests that the impact strength of iPP/EPDM/NBR blends or the impact energy absorption behavior of these blends change dramatically when the EPDM/NBR content reaches a certain critical value. This point is known as "Transition point" (TP) for impact energy absorption behavior.

The iPP homopolymers is taken as the reference material in order to evaluate the impact performance of the blend. At 30 °C iPP is a ductile polymeric material, being above its T_g, and shear yielding is the prime mode of energy absorption under deformation.

The low impact values for the control uncross-linked blends are attributed to the fact that the elastomeric droplets formed during blend preparation coalesce during static melt cooling, giving rise in irregular sized elastomer domains that are larger than the critical size desired for impact toughening. The size enlargement and shape irregularity also reduces the number density of stress concentration sites and then interfacial adhesion. At higher elastomer content (40 wt. %) the impact strength slightly increases. This is due to the poor interface between the EPDM/NBR elastomer and iPP matrix debonds during the deformation before the interaction is attained resulting in the stress reduction there by reducing the possibility of the interaction, but flaws or voids are also produced. This poor interfacial adhesion may be because of the big EPDM/NBR domain size in the continuous iPP matrix.

In the cross-linked blends the elastomer particles are cross-linked and their size is greatly reduced due to shear induced size reduction during blend preparation. This cross-linked structure inhibits the probability of elastomer cohesion during cooling, so the number density of elastomer at constant volume fraction domains are many fold with good interfacial adhesion promoted by physical interlocking during melt down viz., molecular entanglements in and around the cross-linked structure. At room temperature these blends are above the glass transition temperatures of either component. Hence, as soon as the stress around the cross-linked elastomer particles overcomes the yield stress of the matrix, the shear yielding mechanism of fracture becomes prevalent over crazing and improved toughness is achieved. This is also evident from the stress whitening effects observed in the resulting fractured surfaces.

In order to promote shear yielding in the iPP matrix, it is important that the stress concentration fields developed from the EPDM/NBR elastomer particles interact effectively with each other in the iPP matrix. If the interface between the particle and the matrix debonds during the deformation before interaction is attained, the stress is relieved but also reduces the possibility of interaction with a drawback that voids/

flaws are produced. On the other hand, if interaction is sufficient a continuous stress concentration zone is realized in the matrix and the blend. This allows shear yielding to occur easily resulting in increased energy absorption dramatically.

The melt flow rate (MFR) is an inverse function of viscosity and can be used to qualitatively assess the interaction between the phases. As the viscosity of EPDM/NBR is much higher than that of the matrix and iPP and EPDM/NBR are not miscible in the melt, the blend melt may be treated as a suspension of solid particles in a fluid. (Table 3) shows the decrease of MFR with an increase in elastomer concentration. The differences in the MFR among iPP/EPDM/NBR blends reflect differences in compositions, the molecular weight of the composi- tions, and the morphology (Particle size and shape). At a 30 wt. % concentration in the uncross-linked blend, the MFR fell to approximately one- half of the original value. The rise in the melt viscosity is reflected in reduced values of melt flow indices from 9.2 to 4.0 g/10 min for cross-linked blends and 7.2–0.4 g/10 min for cross-linked blends as the EPDM/NBR content increases from 10 to 40 wt. % respectively in the blend. On increasing the elastomer content, the number density of dispersed elastomer particle sizes increases considerably while a small increase in the average diameter is also observed. It is due to the reagglomeration or coalescence of dispersed particles. The big size domains may be due to greater obstruction in the flow, which account for the observed higher melt viscosity in the blends with higher EPDM/NBR content. The same is evidenced from our findings of gel content of the systems. The gel content of various cross-linked blends is shown in (Table 3).

Gel content

From (Fig. 2), it was observed that gel content increases linearly as the concentration of EPDM/NBR elastomer content or cross-linked density increases from 0 to 40 wt. %. During dynamic cross-linking process, phenolic modified– polypropylene Ph-(iPP) reacts with EPDM and nitrile rubber to yield a cross-linked product as shown in (Fig. 3). HYLAX HR-6415 (Dimethylol Phenolic resin) used is a thermal reactive modified phenolic resin based on alkyl phenol. It has two independent O-hydroxy methyl groups. The first step is dehydration in the presence of Lewis acid ($SnCl_2$), induced by heat to produce Quinone methide. Isotactic polypropylene (iPP) then reacts with Quinone methide to give phenolic modified iPP. This is then added to EPDM (via 1, 4 cyclo- addition) and nitrile rubber to give a cross-linked product with a Chroman structure and also graft copolymer formed between iPP and EPDM/NBR due to emulsifying action (Products I & II). These two products in the presence of Dicumyl peroxide (DCP) forms a complex cross-linked dispersed phase of cross-linked EPDM/NBR elastomers in a continuous phase of isotactic polypropylene (iPP). DCP also acts as flow regulator by maintaining proper consistency in the blend formation.

Lattimer et al. [16] gives a good survey of results of studies for the resole curing of elastomer. The product structures of resole cured elastomers as suggested by Cunneen et al. [17], Hultzsch [18, 19], Schwarz and Kamenskii [20] are therefore confirmed. However, other structures have been proposed in combinations with quite a variety of resole curing mechanism (Table 4) [21–27].
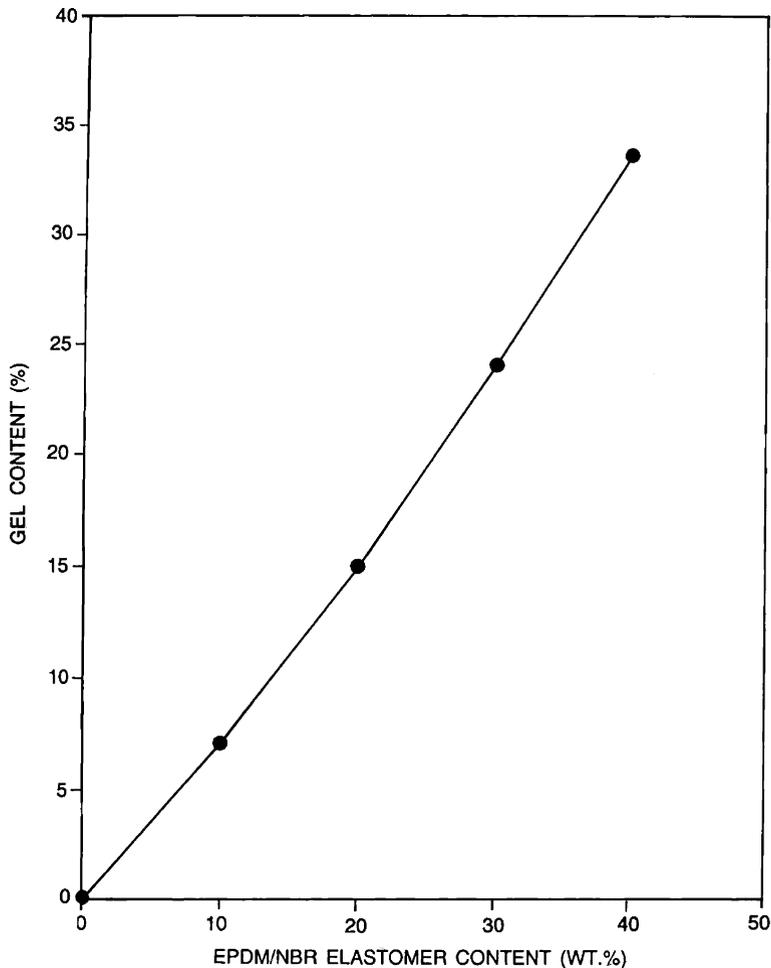
Fig. 2 Variation of Gel content with blend composition of cross-linked iPP/EPDM/NBR elastomer blends

Flexural modulus and crystallization temperature

The flexural strength and flexural modulus results are shown in (Table 3) and its variations with elastomer content are shown in (Figs. 4 and 5). Flexural strength and modulus shows a negative deviation from the additivity line. This deviation is generally seen in immiscible blends of poly olefins [28] and is generally caused by poor interfacial adhesion. The decrease in flexural yield strength with increasing EPDM/NBR elastomer content in the blends indicates a reduction in the rigidity and an increase in the elastomeric nature of the blend. Elastomeric nature improves the bending properties of the systems.

    As the concentration of the elastomeric component EPDM/NBR increases in the blends, the hardness (Shore- D) of the material decreases, refer (Fig. 6) and the flexural strength and flexural modulus decrease as shown in (Figs. 4 and 5). This behavior can be analyzed as a combined effect of both components of the blend. The cross-linked blends showed higher flexural strength and flexural modulus than the
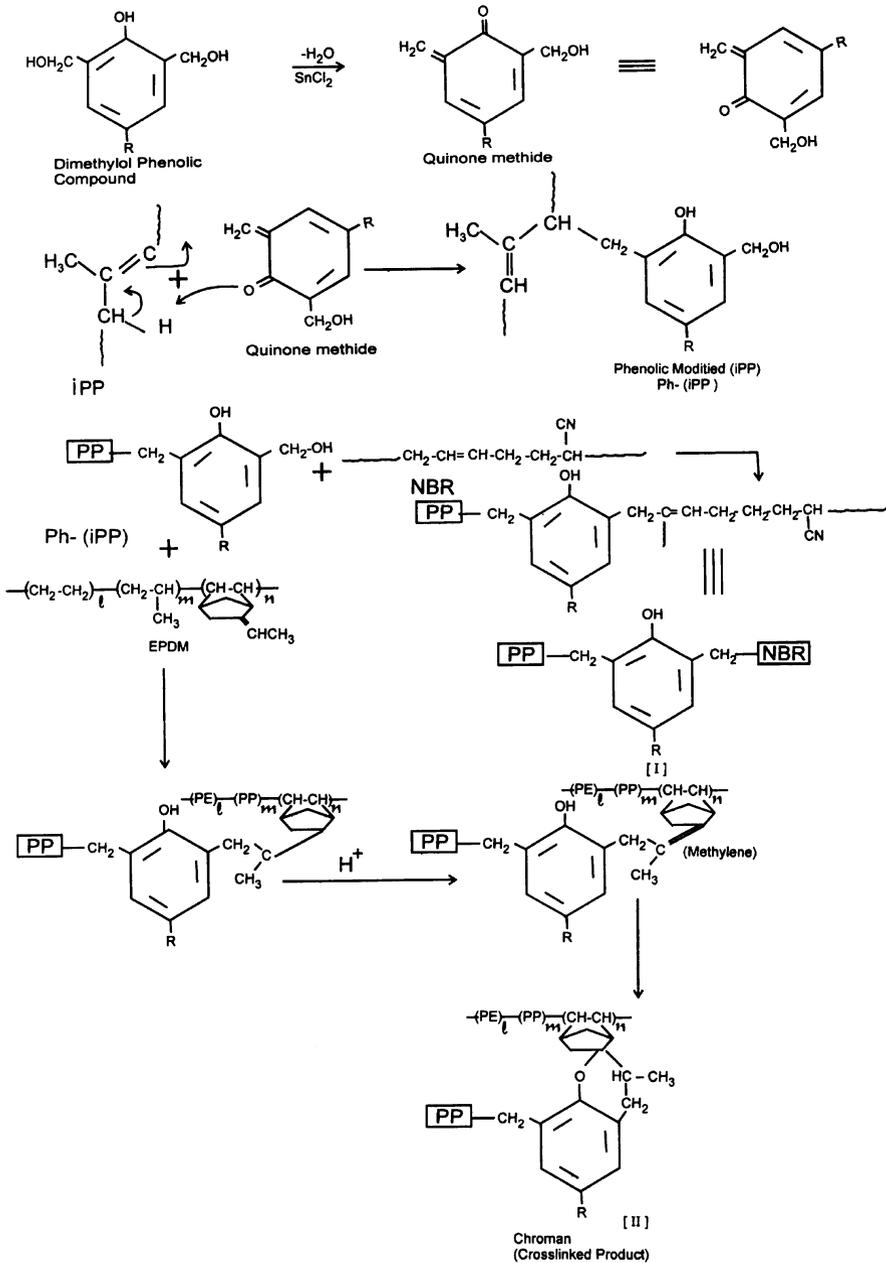
(I) + (II) $\xrightarrow{\text{DCP}}$ **Complex dispersed phase of phenolic modified (iPP) with EPDM and NBR in a continuous matrix of isotactic polypropylene (iPP).**

Fig. 3 Proposed schematic representation of the dimethylol phenolic modification of iPP resulting in the formation of iPP/EPDM/NBR Elastomer blends

Table 4 Shows Mechanism and reaction products of the phenolic resin cross-linking of elastomer

Intermediate	Reaction Product	
	Chroman	Chroman/Methylene methylene
Benzyl Cation	–	Giller [21–23]
Methylene Quinone	Fitch [24]	Ginsburg et al. [25], Vander Meer [26, 27]
	Lattimer et al. [16]	
	Cunneen [17]	
	Sahwarz [20]	
	Hultzsch [18, 19]	

corresponding uncross-linked blends which is well documented and is due to the effect of the cross-linking which forms a three – dimensional network structure. This cross-linking effect strengthens the interfacial adhesion which results in an increase in the flexural strength and flexural modulus in cross-linked blends. The blending
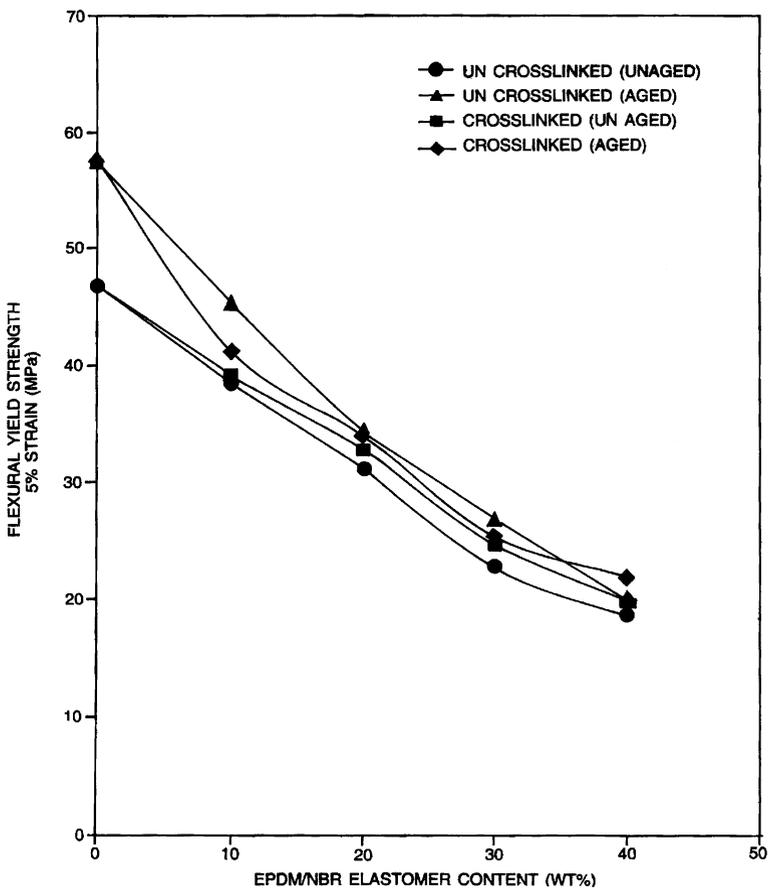
Fig. 4 Variation of flexural yield strength with blend composition for iPP/EPDM/NBR elastomer blends

Fig. 5 Variation of flexural modulus with blend composition for PP/EPDM/NBR elastomer blends
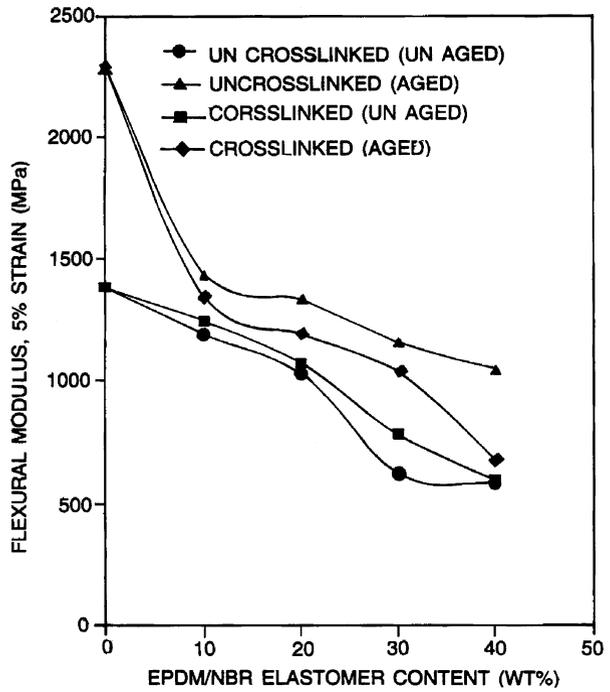
Fig. 6 Variation of hardness shore (D) with blend composition for iPP/EPDM/NBR elastomer blends
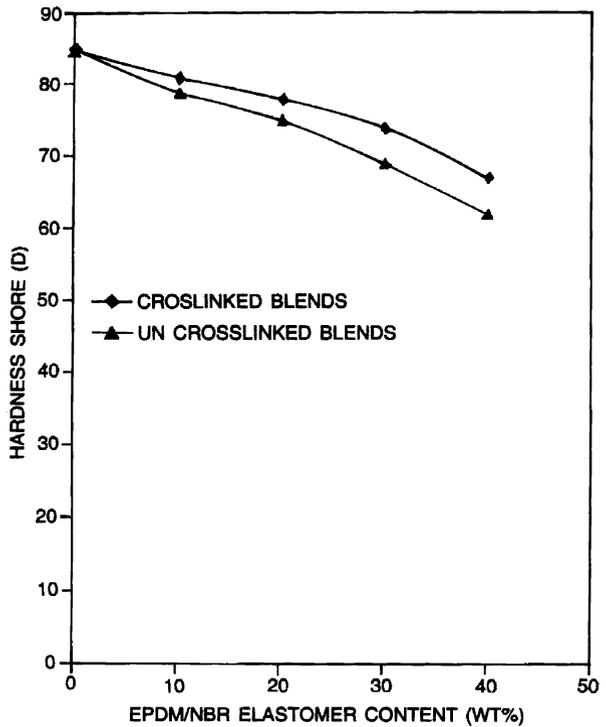
moment viz, load- displacement curves of uncross-linked and cross-linked blends are presented in (Figs. 7 and 8). They showed that the mode of fracture of iPP blend is brittle with a slight addition of elastomer. The mode of deformation changes from brittle fracture to ductile deformation showing general yielding when the addition of elastomer is over a critical content. In iPP blends before cross-linking about 30–40 wt. % elastomer is required for the mode of deformation to change to ductile deformation but for the blend of iPP after cross-linking its content is about 20–30 wt. % elastomer content.

The brittle to ductile transition takes place with a slight addition of elastomer at low bending. The addition for the brittle to ductile transition increases with increasing bending. The higher load required to propagate a crack in cross-linked blends indicates a stronger adhesion between iPP and EPDM/NBR elastomer. This is due to resole resin being interface compatible and cross-linking the EPDM/NBR elastomer particles at the same size resulting in a tough stabilized iPP/EPDM/NBR matrix.

The crystallization temperature was determined by MDSC analyses to determine the nucleation. Weighed samples (8–10 mg) of the blends were analyzed under a cooling rate of 5 °C / min from 230 °C to 27 °C (RT).The variation in the crystallization temperature of the blends is shown in (Figs. 9 and 10) and the results
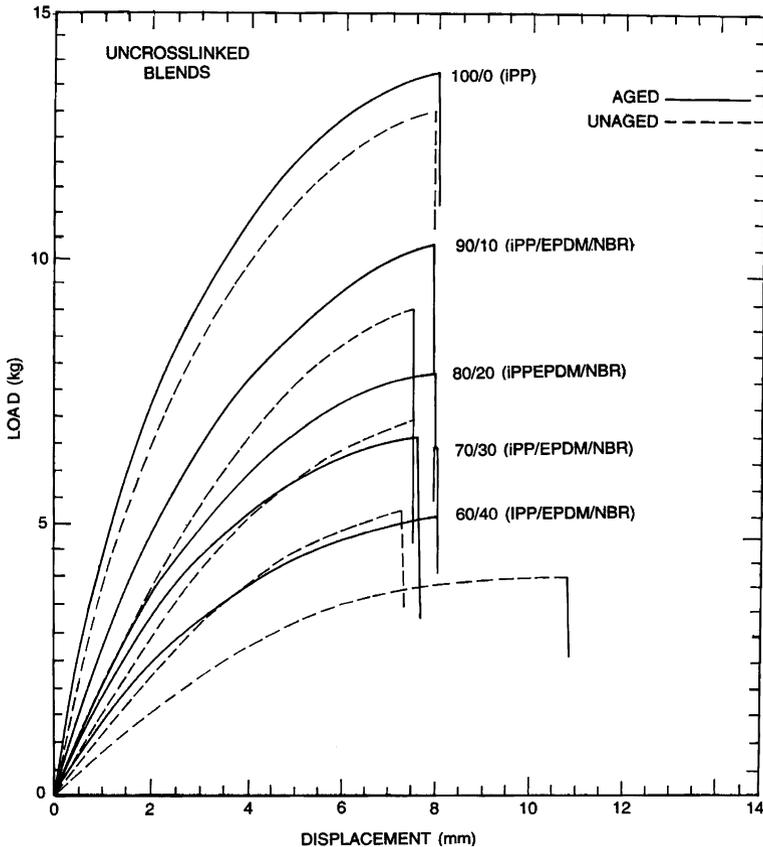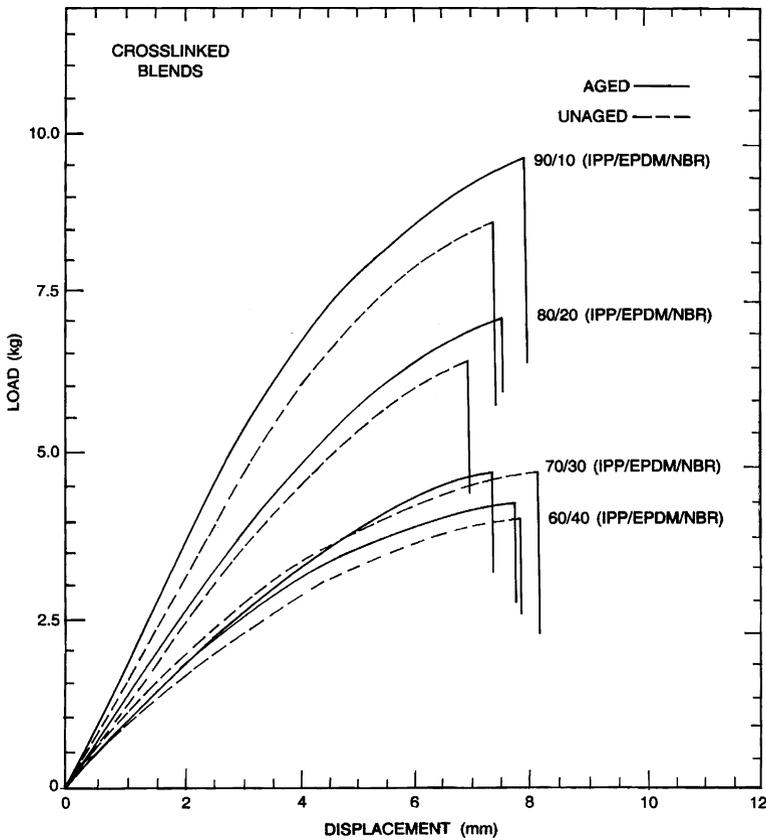

Fig. 7 Variation of load-displacement curves of uncross-linked iPP/EPDM/NBR elastomer blends

Fig. 8 Variation of load-displacement curves of cross-linked iPP/EPDM/NBR elastomer blends

are shown in (Table 3). The nucleation ability of the cross-linked EPDM/NBR elastomer particles is believed to not only compensate for the expected decrease but to also over come it, resulting in an increase in the flexural strength and flexural modulus in cross-linked blends.

The nucleation effect changes the size of the spherulites to the crystalline form there by resulting in overall improvement in impact properties of the iPP matrix as reported in the literature [29]. The impact strength improvement of the blends indicates that the effect of nucleation on impact strength is smaller as compared to that of interfacial adhesion. This shows that most nucleating agents decrease the impact when they increase the crystallization temperature. It is observed that produced cross-linked elastomer particles increase both of them at the same time.

Dynamic mechanical analysis (DMA)

The effect of blend compositions and its cross-linking on the dynamic mechanical properties (DMP) was investigated in the region −130 to 140 °C temperature range. The results showed that the blends of iPP/EPDM/NBR are incompatible as is evident by the presence of two relaxation peaks corresponding to the Tg's of iPP and EPDM/NBR
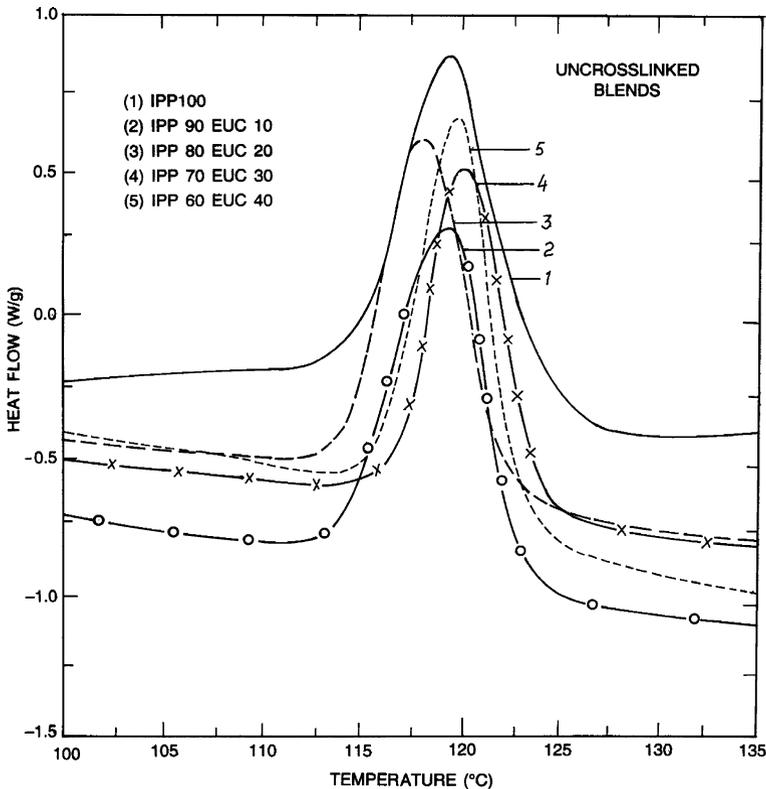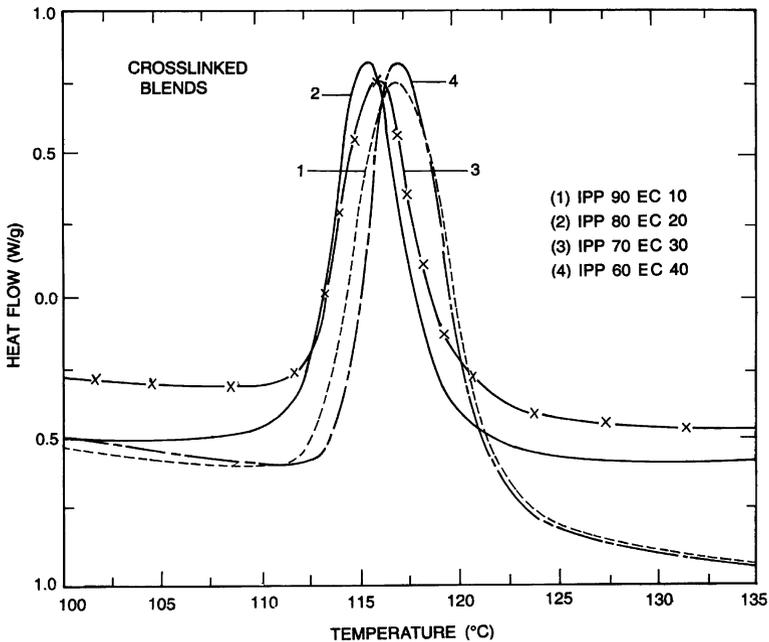
Fig. 9 MDSC Exotherm representing crystallization behaviour of iPP in uncross-linked iPP/EPDM/NBR elastomer blends

(elastomeric phase). For each blend the peak at the lower temperature is the Tg of the elastomeric phase, where as the peak at the higher temperature is that of iPP.

An interaction between the elastomer and matrix results in a shift and broadening of this peak. The broadening of the Tg peak of iPP is quantified by introducing the ratio between the peak width and height (W/H). But, same compatibility is observed as a result of dynamic cross-linking that is evident from the peak broadening. As the loading of elastomer increases, the storage modulus of the system decreases (Figs. 11 and 12) while the loss modulus (Figs. 13 and 14) and tan (δ) increase (Figs. 15 and 16). The decreasing trend in the storage modulus with increasing EPDM/NBR content is sharp in the composition range of 30–40 wt. % in the uncross-linked blends and 20–30 wt. % in cross-linked blends, which results in a change in morphology at these composition ranges (also confirmed by the SEM studies).

The temperature where tan δ rapidly increases, (E') rapidly decreases and is shifted upward after cross-liking. This shows that EPDM/NBR is cross-linked and the interaction between the EPDM/NBR and the iPP has increased. Hourston and Byrne [30, 31] investigated that the dynamic mechanical behavior of EPDM and reported that the tan δ_{max} is increased by cross-linking which is shown with the decrease of the degree of crystallinity from 41.65 to 23.75 as the loading of EPDM/NBR content increases from 0 to 40 wt. % in the blend. This was also observed by Coran and Patel [32]. It may also be possible that the addition reaction of the resole type phenolic resin

Fig. 10 MDSC Exotherm representing crystallization behaviour of iPP in cross-linked iPP/EPDM/NBR elastomer blends

cross-linked the EPDM/NBR particles at the unsaturated bands in the EPDM and NBR. The result also indicates that the interaction between the iPP and the EPDM/NBR are strengthened by the cross-linking reaction due to formation of graft copolymer at the interface (further investigation is sought).

Reportedly, any molecular process which promotes distribution and dissipation of energy would enhance the impact resistance of polymer. As viscoelastic relaxation of polymer is a very important molecular mechanism of energy dissipation and it contribute to the impact resistance of polymers although shear yielding and crazing are the main mechanism of toughening. An attempt has been made to correlate the impact and dynamic mechanical properties in terms of the tan δ peak values of the elastomer component in the iPP blend.

As viscoelastic relaxation of the loss peaks of both iPP and elastomeric phase occurs at a temperature below the impact test temperature, it is more relevant to include the tan δ peak values of the matrix (i.e., iPP). The variation of the impact strength as the function of the total loss tangent peak values due to iPP and EPDM/NBR elastomer of the blends is depicted in (Fig. 17). The curves exhibit a nonlinear shape and are similar to those of curves showing the variation of impact strength with blend ratio. The increase of the impact strength with the total loss tangent peak values indicates the role of viscoelastic energy dissipation mechanism in the impact improvement of these blends.

The slope of these curves increase with an increasing EPDM/NBR elastomer content with a rapid increase in the region of 30–40 and 20–30 wt. % in an uncross-linked and dynamically cross-linked blend systems.

This indicates the viscoelastic energy dissipation and crystallization behavior of the iPP/ EPDM/NBR elastomeric blends. iPP exhibits a prominent crystallization exotherm in
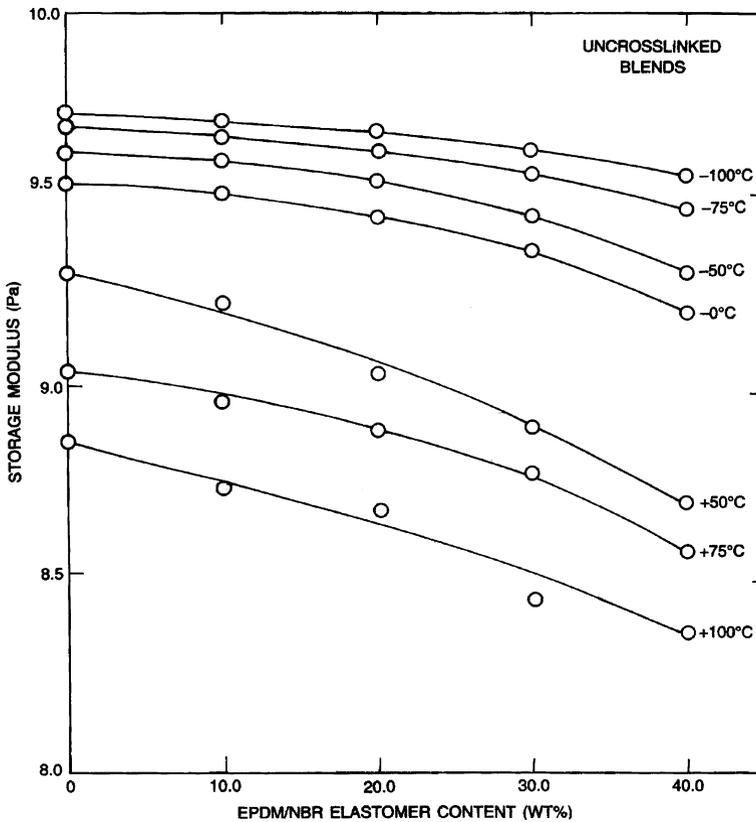
Fig. 11 Variation of storage modulus (E') with temperature of uncross-linked iPP/EPDM/NBR elastomer blends

all the blends composition, as well as in unblended iPP (Figs. 9 and 10).With the addition of EPDM/NBR elastomer in iPP a decrease in crystallization of the iPP matrix was observed which exhibits an improved energy dissipation by the iPP (matrix) itself. This study indicates that viscoelastic energy dissipation is not the only mechanism responsible for the impact strength enhancement but other mechanism such as crazing and shear yielding are also operative for enhancing the impact strength of the blends.

Morphology fixation

The micrographs of samples of uncross-linked blends etched with the cyclohexane at elastomer loading (20–40) wt. % is depicted in (Figs. 18, 19 and 20). They depict the irregular shapes with the inclusions of EPDM/NBR domains. The domains are quite small in the blends (about 2–2.7 μm) in the low elastomer loadings of 10–20 wt. %. The occurrence of larger domains (about 2.7 μm or more length wise) is apparent at EPDM/NBR contents above 20 wt. %.

   The fracture surface observation after cross-linking by SEM (Figs. 21, 22 and 23) reveals that the EPDM/NBR particles appear to be covered with the iPP. These covered particles suggest that iPP/ EPDM/NBR graft copolymers are produced on the interface and three dimensional network structures is formed during the cross-
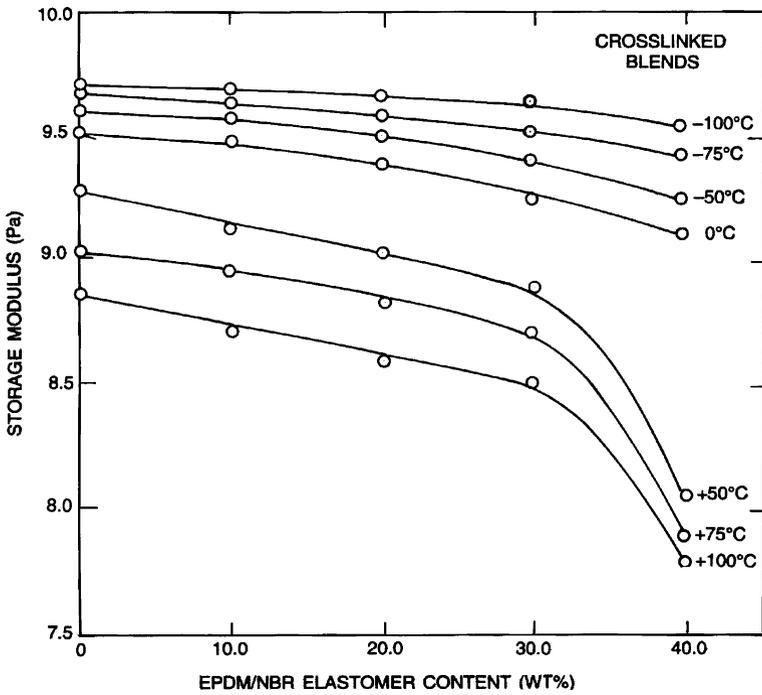
Fig. 12 Variation of storage modulus (E') with temperature of cross-linked iPP/EPDM/NBR elastomer blends

linking and strengthen the interfacial adhesion. As the graft copolymer produced under the cross-linking of the EPDM/NBR domains increases the interfacial adhesion, the result indicates that the transition occurs when relatively small amount of the graft copolymer is produced.
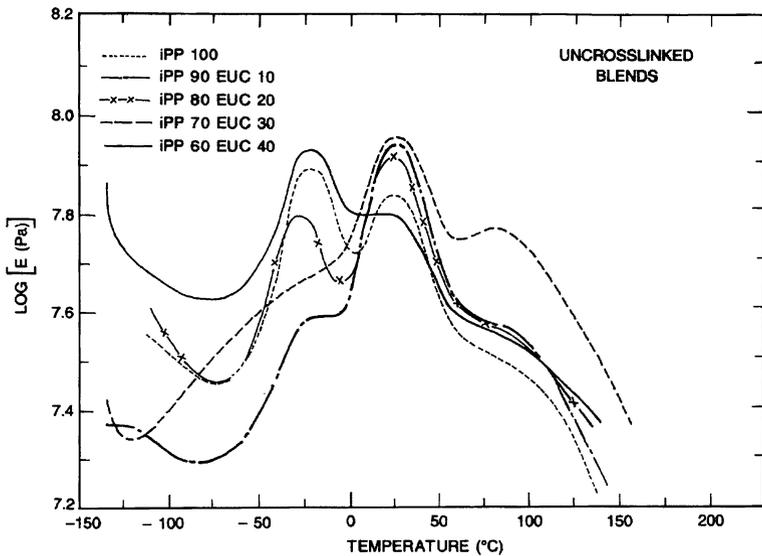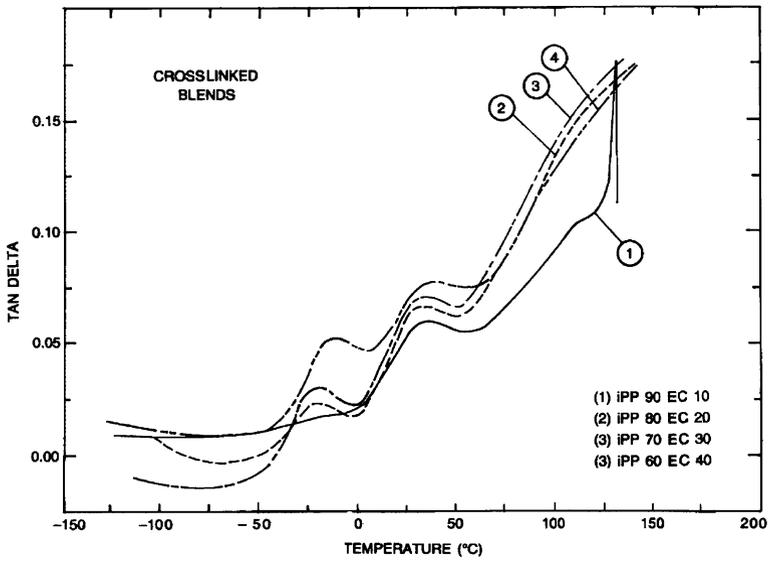

Fig. 13 Variation of loss modulus (E") with temperature of uncross-linked iPP/EPDM/NBR elastomer blends

Fig. 14 Variation of loss modulus (E") with temperature of cross-linked iPP/EPDM/NBR elastomer blends

In other words, we can say that the critical interfacial adhesion, which is strong enough to increase the possibility of the interaction of stress concentration zone which facilitates the shear yielding of the iPP matrix, can be achieved with relatively small amount of the graft copolymer and they are produced at early stages of the cross-linking reaction . When the interaction or the overlapping is achieved by a certain point with further increase in interfacial adhesion the impact strength can not be improved further. Another possible interpretation is that further improvement in impact strength is not possible because all the surfaces of the elastomer particles are covered .This interfacial adhesion is indicated as one of the most important factor which affects the impact

Fig. 15 Variation of loss tangent (tan δ) with temperature of uncross-linked iPP/EPDM/NBR elastomer blends

Fig. 16 Variation of loss tangent (tan δ) with temperature of cross-linked iPP/EPDM/NBR elastomer blends

Fig. 17 Variation of impact strength of cross-linked and uncross-linked blend
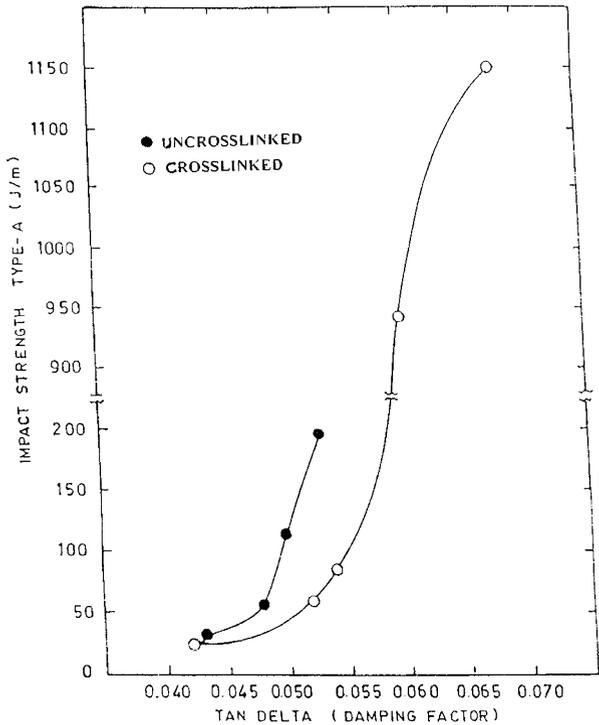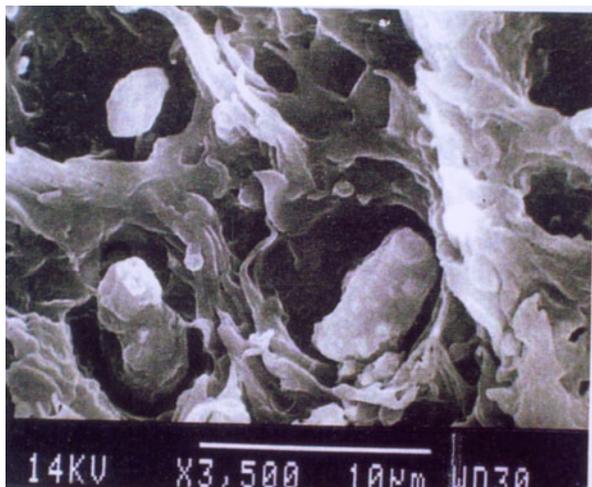
Fig. 18 Scanning Electron Micrograph (SEM) of cryogenically fractured etched with cyclohexane of uncrossed-linked iPP/EPDM/NBR elastomer blend at 20% elastomer loading
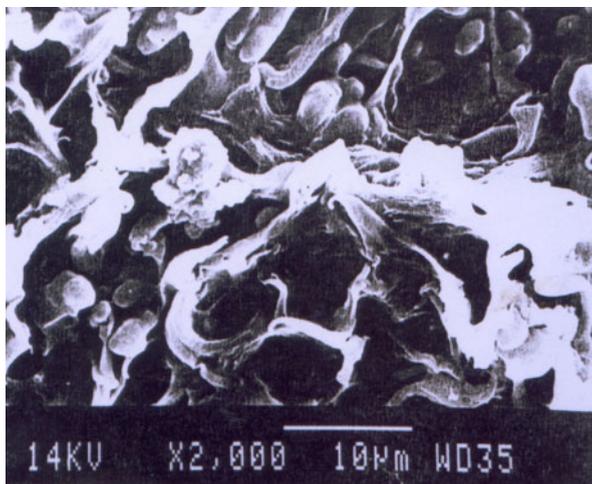

strength of these blends. The impact strength of iPP increases on the addition of 10 wt. % EPDM/NBR due to the presence of elastomeric droplets of desirable size (approx. 0.6 μm). In the region of 10–30 wt. % elastomer content, there is a gradual increase in the average size and number density of elastomer domains which is 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.% elastomer content, imparts a high elastomeric nature to the blend which is responsible for the increase in impact strength in the uncrossed -linked system in that region.

The disappearance of the yield peak and remarkably high impact strength of the cross-linked blend at 30 wt. % EPDM/NBR suggest a continuous elastomeric phase at that composition and a change in morphology from a dispersed to a co-continuous phase in the composition range of 20–30 wt. % EPDM/NBR elastomer content .The covalent cross-links in cross-linked blends provides a distinct and stable structure of EPDM/NBR

Fig. 19 Scanning Electron Micrograph (SEM) of cryogenically fractured etched with cyclohexane of uncrossed-linked iPP/EPDM/NBR elastomer blend at 30% elastomer loading

Fig. 20 Scanning Electron Micrograph (SEM) of cryogenically fractured etched with cyclohexane of uncrossed-linked iPP/EPDM/NBR elastomer blend at 40 wt % elastomer loading
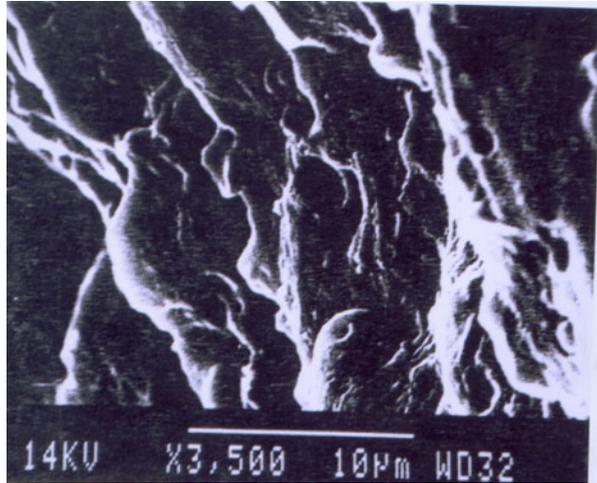

elastomer particles which might become labile through heat activation or during thermo plastic processing step at higher concentration, resulting in coalescence and a continuous elastomer phase. There is a prevalent interaction between the thermoplastic matrix and the elastomer particles themselves.

These interactions results in synergistically improved properties with a drastic increase in the impact strength values in the region of 20–30 wt.% EPDM/NBR elastomer content in the prepared polyolefin elastomeric blends.

Conclusions

1. Isotactic poly propylene (iPP) is ductile above its glass transition temperature (Tg) and its impact strength increases drastically when the EPDM/NBR wt. %

Fig. 21 Scanning Electron Micrograph (SEM) of cryogenically fractured etched with cyclohexane of crossed-linked iPP/EPDM/NBR elastomer blend at 20 wt % elastomer loading
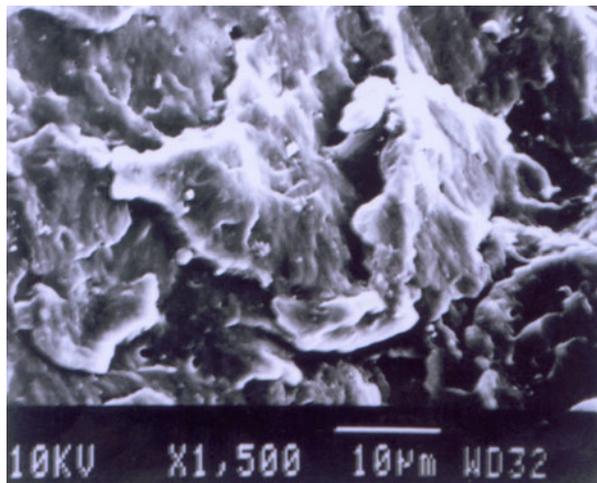
Fig. 22 Scanning Electron Micrograph (SEM) of cryogenically fractured etched with cyclohexane of crossed-linked iPP/EPDM/NBR elastomer blend at 30 wt % elastomer loading
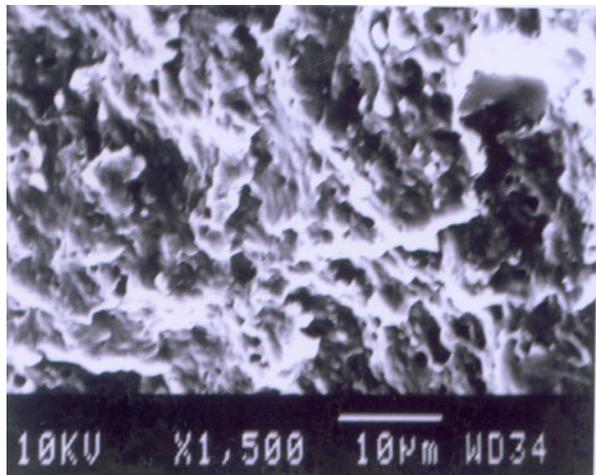

reaches a critical value. The cross-linking of the EPDM/NBR increases the interfacial adhesion to a greater extent resulting in the formation of strong covalent bond between the dispersed and co-continuous phase of the blend.

2. The high interfacial adhesion of the cross-linked blend reduces the dispersed phase size and provides a more uniform distribution of particle size.

3. The cross-linking of the EPDM/NBR elastomer particles stabilizes the morphology of the blends. From the result of the tensile strength, impact strength and morphology data it is clear that the properties of the cross-linked blend are improved substantially by cross-linking with a unique cross-linked system well described in the study.

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

5. The cross-linked EPDM/NBR particles act as nucleating agent which leads to the decrease in the dimension of the iPP Spherulites.

Fig. 23 Scanning Electron Micrograph (SEM) of cryogenically fractured etched with cyclohexane of crossed-linked iPP/EPDM/NBR elastomer blend at 40 wt % elastomer loading
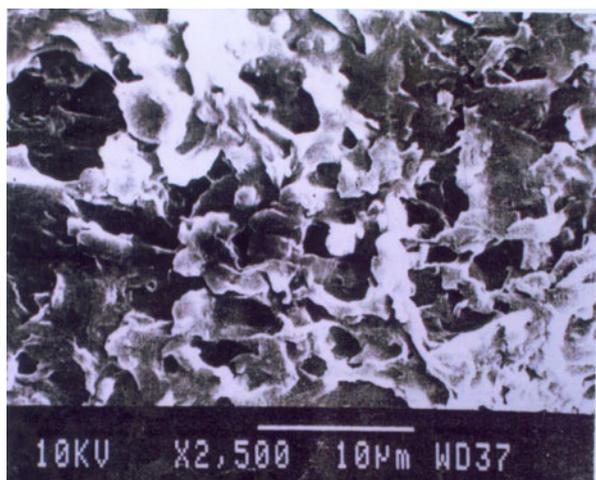
References

1. Bucknall CB (1977) Toughened plastics. Applied Science. London
2. Hourstan DJ, Lane S, Zhang HX (1991) Polymer 32:2215
3. Fukui T, Kikuchi Y, Inouse T (1991) Polym Eng Sci 31:1029
4. Dao KC (1982) J Appl Polym Sci 27:4799
5. Wu S (1982) Polymer 26:1855
6. Coran AY, Patel R (1980) Rubber Chem Technol 53:141
7. Joseph S, Ommen Z, Thomas S (2002) Mat Lett 53:1268
8. Naskar K (2004) Ph D Thesis, Twente University, Enschede
9. Van DM (2002) Kautsch Gummi Kunstst 55:150
10. John B, Varughese KT, Ommen Z, Postschke P, Thomas S (2003) J Appl Polym Sci 87:2083
11. Mousa A, Al-Balque (2005) J Polym Mater 54:619–631
12. Van DM (2006) Macro molecular Symposia 233:11–16, Eng
13. Elias L, Fenouillot F, Majeste JC, Cassagnau PH (2007) Polmer 48:6029–6040
14. Hong Y, Sun T, Wang S, Qin Z, Qiang F, Xia D, Charles C (2008) Eur Polym J 44:113–123
15. Soni RK, Singh H, Dutt K, Arora P (2010) J Polym Res 17:411
16. Lattimer RP, Kinsey RA, Layer RW, Rhee CK (1989) Rubber Chem Technol 62:107
17. Cunnen JI, Farmer EH, Koch HP (1943) J Chem Soc 7:472
18. Hultzsch K (1950) Chemieder Phenolharze. Springer Verlag, Berlin
19. Hultzsch KJ (1941) Prakt Chem 158:275
20. Schwarz AG, Kamenskii BZ (1963) Kautsch Resina 22:8
21. Giller A (1964) Kautsch Gummi 17:3
22. Giller A (1965) Kautsch Gummi 18:1304
23. Giller A (1961) Kautsch Gummi 14:WT201
24. Fitch A (1978) Interaction of alkyl phenol- formaldehyde condensates with trialkyl ethylenes. Ph.D. Thesis, London
25. Ginsburg LB, Scherschnew WA, Dogadkin BA (1973) Ber Akad Wiss U SSR 152:335
26. Vander MS (1943) Rev Gever Caoutchue 20:230
27. Vander MS (1944) Rev Trav Chim 63:157
28. Kim KH, Cho WJ, Ha CS (1996) J Appl Polym Sci 59:407
29. Han CD, Jang HH (1987) J Appl Polym Sci 33:122
30. Byrne LF, Hourston DJ (1979) J Appl Polym Sci 23:1607
31. Byrne LF, Hourston DJ (1979) J Appl Polym Sci 23:2899
32. Coran AY, Patel R (1980) Rubber Chem Technol 53191