

# Dynamically Vulcanized Blends of Polypropylene and Ethylene Octene Copolymer: Influence of Various Coagents on Mechanical and Morphological Characteristics

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**ABSTRACT:** Dynamically cured blends of polypropylene (PP) and ethylene octene copolymer (EOC) with coagent-assisted peroxide curative system were prepared by melt-mixing method. It was well established that PP exhibits  $\beta$ -chain scission in the presence of peroxide. Principally, incorporation of a coagent increases the crosslinking efficiency in the EOC phase and decreases the extent of degradation in the PP phase. The present study mainly focused on the influence of three structurally different coagents, namely, triallyl cyanurate (TAC), trimethylol propane triacrylate (TMPTA), and *N,N'*-*m*-phenylene dimaleimide (MPDM), on the mechanical properties of the PP/EOC thermoplastic vulcanizates (TPVs). The reactivity and efficiency of different coagents were characterized by cure study on EOC gum vulcanizate. TAC showed the highest torque values followed by MPDM

and TMPTA. Significant improvements in the physical properties of the TPVs were inferred with the addition of coagents. Among the three coagents used, MPDM showed the best balance of mechanical properties in these TPVs. The results indicated that torque values obtained during mixing and the final mechanical properties can be correlated. Different aspects were explained for the selection of a coagent that forms a product with desired properties. The phase morphologies of the TPVs prepared were studied by scanning electron microscopy. Tensile fracture patterns were also analyzed to study the failure mechanism of the samples. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3207–3221, 2009

**Key words:** dynamic vulcanization; polypropylene; ethylene–octene copolymer; coagent; peroxide

## INTRODUCTION

Thermoplastic elastomers (TPEs) have the potential to exhibit performance properties like conventional vulcanized rubbers, yet can be processed at elevated temperatures like thermoplastic materials.<sup>1,2</sup> In general, TPEs can be broadly grouped into two different classes: block copolymers and rubber-thermoplastic blends. Melt mixing of rubber with thermoplastic gained much importance because of their easy method of preparation and tailored properties. Many combinations of rubber–plastic blends were possible, in which the selection of polymers is mostly based on semicrystalline thermoplastic and amorphous rubbery material.<sup>3</sup> The process of dynamic vulcanization is the route to produce thermoplastic vulcanizate (TPVs), in which melt mixing of rubber and thermoplastic proceeds at high temperature and the former is vulcanized under dynamic conditions. Unlike static vulcanization, dynamic vulcanization is performed at a high shear

rate, which leads to formation of dispersed phase morphology of the blend components.<sup>4,5</sup> Dynamically vulcanized blends show significant improvement in mechanical properties, reduced permanent set, higher oil and heat resistance, and improved high-temperature utilization over the unvulcanized blends.<sup>6</sup> TPVs have proven themselves to perform in a wide range of demanding engineering requirements mainly in automobile sectors. These materials were continuously replacing the vulcanized thermoset rubbers because of their reprocessability and process flexibility (i.e., can be extruded, injection molded, thermoformed, and blow molded, etc.).<sup>7</sup>

The selection of polymers plays a major role in determining the end use applications and final properties. Ethylene octene copolymers (EOC) are metallocene-based polymers with unique molecular characteristics and the physical properties span the range between plastic and elastomer. These ethylene copolymers have narrow molecular weight distribution and controlled comonomer distributions and exhibit good combination of high tensile strength with rubbery properties.<sup>8,9</sup> These dual characteristics and compatibility with most olefinic polymers lead to use in the area of polypropylene (PP) impact modification, replacing conventional ethylene propylene rubber or ethylene propylene diene rubber (EPDM) to produce thermoplastic polyolefin.

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Laughner et al.<sup>10</sup> reported that the amorphous version of these ethylene- $\alpha$ -olefin polymers exhibit better ambient and low temperature properties to PP. New thermoplastic vulcanizates based on these ethylene octene copolymers were studied and such PP/EOC TPVs would be a potential alternative to the conventional PP/EPDM TPVs.<sup>8</sup>

Several crosslinking agents are used in the preparation of TPVs, such as phenolic resin, peroxide, and a silane crosslinking system. Phenolic resin gained considerable commercial importance but still the formation of black specks motivates the development of other potential crosslinking systems.<sup>7</sup> In this particular PP/EOC blend system, phenolic resin is ineffective, because the latter needs the presence of a double bond to form a crosslinked network structure. Peroxides can crosslink both saturated and unsaturated polymers without any reversion characteristics. The formation of strong C—C bonds provides substantial heat resistance and good compression set property without any discoloration. However, the activity of peroxide depends on the type of polymer and presence of other ingredients in the system.<sup>6,11</sup> It has been well established that PP exhibits  $\beta$ -chain scission reaction (degradation) with the addition of peroxide. Hence, the use of peroxide only is limited to the preparation of PP-based TPVs. An alternative approach to overcome the abovementioned drawback could be the introduction of a compound that not only improves the efficiency of peroxide during crosslinking but also decreases the extent of degradation. Generally, coagents are multifunctional vinyl monomers that are highly reactive toward free radicals either by addition reaction and/or by hydrogen abstraction. Some of the benefits that coagents afford are improved heat aging, high tensile and tear strength, high modulus and hardness, increased abrasion resistance, better hot tear properties, improved dynamic properties, and excellent adhesion characteristics. Chain scission also could be retarded by stabilizing the PP macroradicals by the addition reaction across the double bond in the vinyl monomer (coagent).<sup>12</sup> Hence, addition of coagent in the PP/EOC blend increases the crosslinking efficiency in the EOC phase and decreases the degradation in the PP phase. It not only improves the end use properties but also decreases the peroxide concentration and aids in flow characteristics during processing. The coagents are broadly classified into two different types: Type I coagents increase both rate and state of cure. Acrylate, methacrylate, bismaleimide, etc. belong to this type. They mainly undergo addition reaction rather than hydrogen abstraction. Type II coagents increase only state of cure, which includes polybutadiene, triallylcyanurate, triallylisocyanurate, etc. They have both readily accessible vinyl unsaturation and abundant number

of easily abstractable allylic hydrogen atoms. However, it has been reported previously that these multifunctional monomers during vulcanization undergo intramolecular cyclization or homopolymerization to give coagent bridges.<sup>13,14</sup> Influences of the different methacrylates coagents on the mechanical and rheologic properties of the peroxide-cured PP/EPDM TPVs were reported by De Risi and Noordermeer.<sup>15</sup> Among the coagents taken, trimethylol propane trimethacrylate shows the best overall balance of properties. The authors interpreted the results in terms of solubility parameter and cure kinetics. The effects of coagent on both processing and properties of the compound depend on the nature of polymer, type of peroxide, and other compounding ingredients. Naskar and Noordermeer reported the influence of multifunctional peroxides 1-(2-*tert*-butylperoxyisopropyl)-3-isopropenyl benzene and 2,4-diallyloxy-6-*tert*-butylperoxy-1,3,5-triazine (DTBT), consisting of peroxide and coagent functionality in a single molecule, in PP/EPDM TPVs.<sup>16</sup> Generally, decomposition of peroxides produces smelly byproducts and blooming effects and these multifunctional peroxides avoid the same. The solubility parameter, kinetic aspects, and decomposition products of these multifunctional peroxides are highlighted with respect to the avoidance of smelly byproducts. DTBT performs the better of the two and is a potential alternative for the conventional dicumyl peroxide/triallyl cyanurate combination.

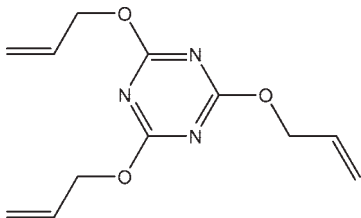
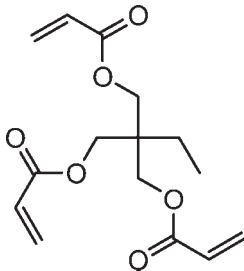
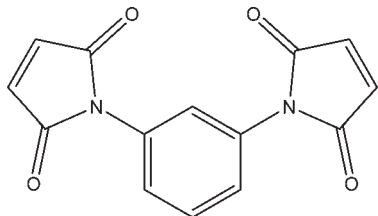
The authors previously reported the influence of three different peroxides at a fixed blend ratio of PP/EOC TPVs by using triallyl cyanurate (TAC) as a coagent. Dicumyl peroxide was found to give the best overall performance in PP/EOC TPVs.<sup>17</sup> However, different coagents have different reactivity and efficiency in terms of increasing the degree of crosslinking and decreasing the extent of degradation. The main objective of the present investigation was to study the influence of three structurally different coagents as a function of concentration on the dicumyl peroxide cured PP/EOC TPVs. In brief, the experimental variables include type and concentration of different coagents.

## MATERIALS AND METHODS

### Materials

The general purpose polyolefin elastomer Exact<sup>®</sup> 5371 [specific gravity, 0.870 g/cm<sup>3</sup> at 23°C; co-monomer (octene) content, 13 (mol %); melt flow index (MFI), 5.0 g/10 min at 190°C/2.16 kg] was procured from Exxon Mobil Chemical (USA). The octene content of these Exact<sup>®</sup> copolymers was determined from <sup>1</sup>H-NMR experiment. PP (specific gravity, 0.9 g/cm<sup>3</sup> at 23°C; MFI, 3.0 g/10 min at 230°C/2.16 kg)

TABLE I  
Chemical Names and Structures of Coagents Employed

Chemical name	Structure	Designation
Triallyl cyanurate (TAC) (Type-II coagent)		C
Trimethylol propane triacrylate (TMPTA) (Type I coagent)		A
<i>N,N'</i> - <i>m</i> -Phenylene dimaleimide (MPDM) (Type I coagent)		M

was obtained from IPCL (India). Dicumyl peroxide (DCP; Perkadox-BC-40B-PD), having active peroxide content of 40%; temperature at which half-life time ( $t_{1/2}$ ) is 1 h at 138°C; specific gravity 1.53 g/cm<sup>3</sup> at 23°C, was used as the crosslinking agent obtained from Akzo Nobel Chemical. (The Netherlands). Three different types of coagents, used as boosters for DCP-cured TPVs, were obtained from Sartomer Company (USA). Their chemical names and corresponding structures are given in Table I.

### Preparation of TPVs

PP/EOC TPVs were prepared by melt mixing of PP with EOC in a Haake Rheomix 600s with a mixing

chamber volume of 85 cc at a temperature of 180°C with a rotor speed of 70 rpm. Total mixing time for each batch was around 14 min. First, PP was allowed to soften and then EOC was added; melt mixing was continued until reaching a constant torque value. Dynamic vulcanization was carried out by adding coagent-assisted peroxide curative system and vulcanization time (4 min) was maintained constant for all the compositions. The compositions of PP/EOC TPVs employed for this study are shown in Table II. TPVs prepared by different coagents were designated as C for TAC, A for trimethylolpropane triacrylate (TMPTA), and M for *N,N'*-*m*-phenylene dimaleimide (MPDM). Dicumyl peroxide was used as curing agent in all compositions and

TABLE II  
TPV Compositions in phr with Varying Types and Concentrations of Coagents

Compound Name	DC0	DC10	DC20	DC30	DA10	DA20	DA30	DM10	DM20	DM30
EOC	100	100	100	100	100	100	100	100	100	100
PP	50	50	50	50	50	50	50	50	50	50
DCP	3.38 <sup>a</sup>	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38
TAC	–	0.83(10) <sup>b</sup>	1.66(20)	2.49(30)	–	–	–	–	–	–
TMPTA	–	–	–	–	0.98(10)	1.97(20)	2.96(30)	–	–	–
MPDM	–	–	–	–	–	–	–	1.39(10)	2.79(20)	4.18(30)

<sup>a</sup> Concentration of DCP was optimized at 3.38 phr which corresponds to 5 mequiv concentration.<sup>17</sup>

<sup>b</sup> Values in parentheses correspond to the milliequivalent concentration of the corresponding coagent.

designated as D (first letter in all composition). The second letter in the designation represents the type of coagent and the number followed corresponds to the concentration of coagent. For example, DC20 corresponds to the composition containing 20 mequiv triallyl cyanurate. The different coagents have different molecular weights and also have different relative functionalities; therefore, their concentrations were expressed in terms of milliequivalents per 100 g of pure EOC instead of parts per 100 g of pure EOC (phr). After mixing, the blends were removed from the chamber hot and sheeted out in a two-roll mill at room temperature in a single pass. Sheets were then cut and pressed in a compression-molding machine (Moore Press, Birmingham, UK) at 190°C for 4 min at 5 MPa pressure. Aluminum foil was placed between the mold plates. The molded sheets were then cooled down to room temperature under the same pressure.

### Testing procedures

#### Cure characteristics

Cure characteristics of the compounds were determined with a rubber process analyzer RPA2000 (Alpha Technologies). The compound consists of only EOC without any PP along with the different coagents taken for the investigation. Concentrations of curatives were selected similar to those used to produce the TPVs. Testing conditions were maintained at 180°C for 30 min at 2.79% strain and a frequency of 1 Hz.

#### Mechanical testing

The dumbbell-shaped specimens of the TPV used for testing were die-cut from the compression-molded sheet and the testing was done after 24 h of maturation at room temperature. Samples were punched out along the mill grain direction from the molded sheet. Tensile strength was measured according to ASTM D 418-98A by using a universal testing machine (Hounsfield H10KS, UK) at a constant crosshead speed of 500 mm/min. Tear strength was determined according to ASTM D 624-81 test method by using an unnicked 90° angle test piece. Crosshead speed was maintained the same as that of the tensile test. Tension set was performed at room temperature with a stretching condition for 10 min at 100% elongation according to ASTM D 412-98 method. To study the effect of aging on the mechanical properties of the TPVs, the representative samples of the blends were aged in a hot-air aging oven at 70°C for 72 h. Tensile strength, elongation at break, and modulus after aging were then determined as per ASTM standard. A minimum of three samples was tested for each composition.

#### Crosslink density

Equilibrium solvent swelling measurements were carried out on the PP/EOC TPVs to determine the crosslink density of the EOC in the presence of PP. The crosslink density was calculated by using the modified Flory–Rehner equation<sup>11,15,18</sup> as shown in eq. (1). From the degree of swelling, the overall crosslink density was calculated relative to the (EOC + PP) phases and was expressed as  $(v + PP)$ . The latter was done to avoid the need to correct for a part of the PP, being extracted as amorphous PP. A circular piece of 2-mm thickness was made to swell in cyclohexane for about 48 h to achieve an equilibrium swelling condition. Initial weight, swollen weight, and de-swollen or dried weight were measured and substituted as

$$(v + PP) = -\frac{1}{V_s} \times \frac{\ln(1 - V_r) + V_r + \chi(V_r)^2}{(V_r)^{1/3} - 0.5V_r} \quad (1)$$

where  $V_s$  is the molar volume of cyclohexane ( $\text{cm}^3/\text{mol}$ ),  $\chi$  is the polymer swelling agent interaction parameter, which in this case is 0.306,<sup>19</sup> and  $V_r$  is the volume fraction of ethylene–octene copolymer in the swollen network, which can be expressed by

$$V_r = \frac{1}{A_r + 1} \quad (2)$$

where  $A_r$  is the ratio of the volume of absorbed cyclohexane to that of ethylene–octene copolymer after swelling.

#### Morphology

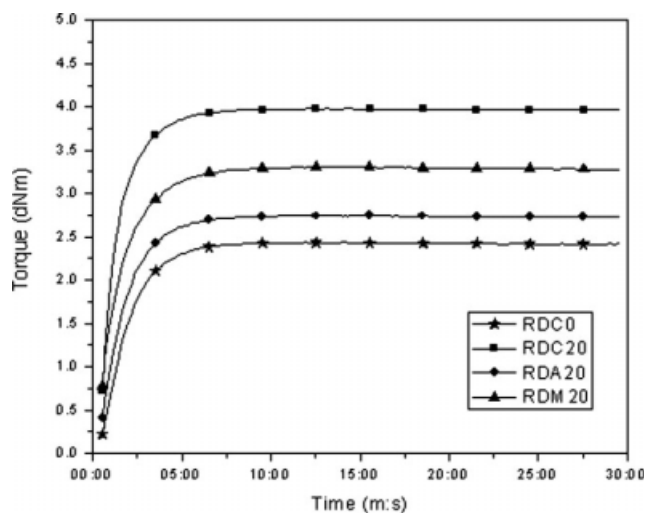
Morphology studies were carried out by using a field emission scanning electron microscope (FESEM; Supra 40; Carl Zeiss SMT, Germany). Molded samples of PP/EOC TPVs were cryofractured in liquid nitrogen to avoid any possibility of phase deformation during the fracture process. The PP phase was preferentially extracted by etching with hot xylene at 100°C for 45 min. The samples were then dried in a vacuum oven at 70°C for 5 h to remove the traces of solvent present. Treated surfaces were then sputter-coated with gold before examination. Tensile fracture surface of PP/EOC TPVs were also examined by a scanning electron microscope (SEM; JEOL JSM 5800, Japan) to understand the failure mechanism.

## RESULTS AND DISCUSSION

### Cure characteristics: Coagent effectiveness in EOC gum vulcanizates

To understand the effectiveness of various coagents in the PP/EOC TPVs, it is necessary to understand the performance of different coagents only in the

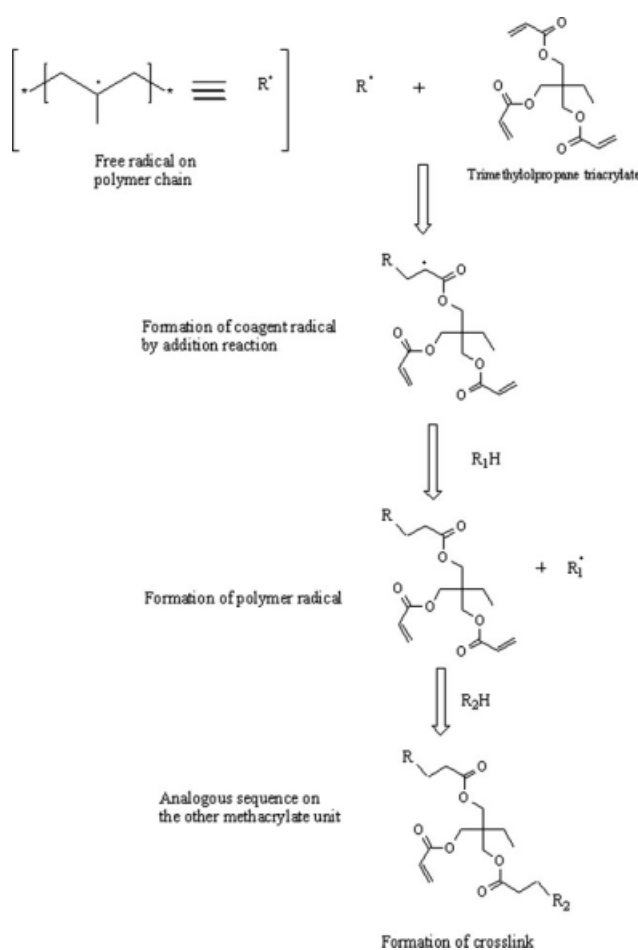




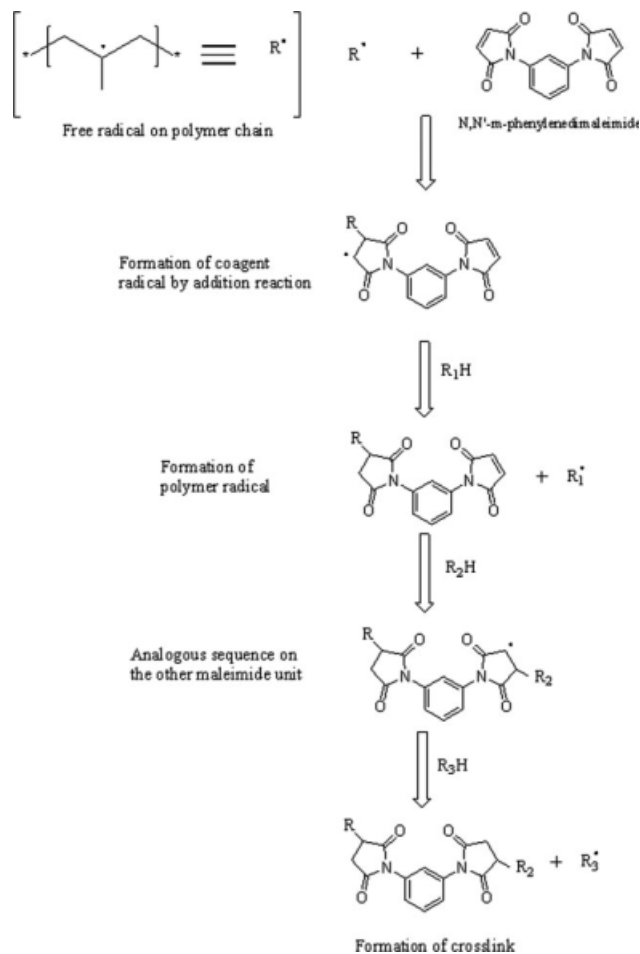
**Figure 1** Rheograms for equivalent thermoset EOC compound with 20 mequiv concentration of various coagents at 180°C.

EOC compound (without PP). The reactivity and efficiency of different coagents were characterized by cure study on gum EOC vulcanizates. Figure 1

shows the rheographs of peroxide-cured EOC vulcanizates containing various coagents at 20 mequiv concentration and compares them with the control sample (without addition of any coagent). Irrespective of different coagents taken for the investigation, a considerable improvement in the maximum torque (Max S) and delta torque (Max S – Min S) values were inferred upon addition of coagent. This is mainly due to the improved crosslinking efficiency of DCP in the presence of coagent. It is clear from Figure 1 that TAC shows the higher torque values followed by MPDM and TMPTA. As mentioned before, Type I and Type II coagents differ in their reactivity during vulcanization; accordingly, their reaction mechanism differs. Figures 2 and 3 show the plausible reaction mechanism of TMPTA and MPDM coagents (Type I coagent) in which, once a macroradical is formed, it adds to the coagent to produce an active radical on the coagent molecule. Subsequently, chain transfer reaction takes place, which leads to the formation of new polymeric radical. The same sequence takes place on the other coagent molecules and results in the formation of a

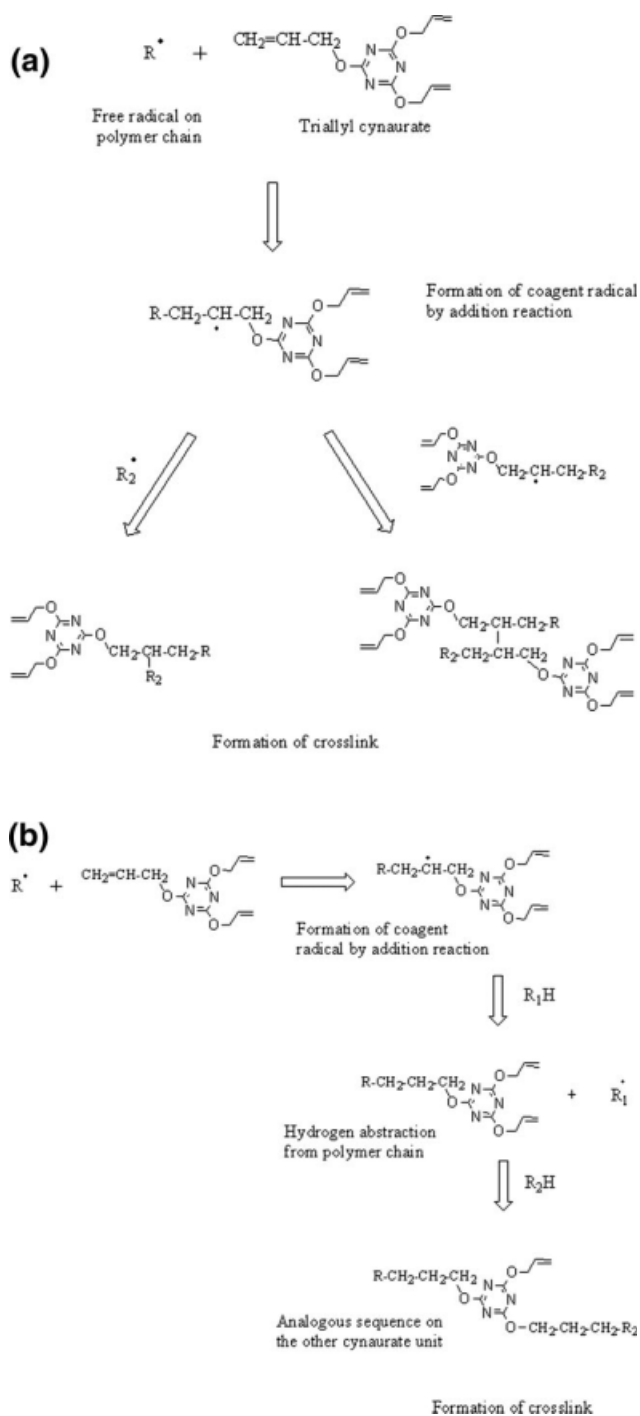


**Figure 2** Plausible reaction mechanism of TMPTA coagent (Type I coagent).<sup>20</sup>



**Figure 3** Plausible reaction scheme of MPDM coagent (Type I coagent).<sup>21</sup>

crosslinked structure.<sup>20–22</sup> Unlike the coagents of first type (Type I), most of the coagents of the second type (Type II) contain both readily accessible vinyl unsaturation (sites for radical addition) and an ample amount of easily abstractable allylic hydrogen atoms. Figure 4(a,b) shows the plausible reaction scheme of TAC (Type II coagent) and explains how an allylic hydrogen-containing coagent incorporates



**Figure 4** Plausible reaction mechanism of TAC coagent (Type II coagent) (a) suggested by Endstra<sup>23</sup> (b) according to Simunkova et al.<sup>24</sup>

in the polymer network formation.<sup>23,24</sup> To obtain a better understanding of crosslinking behavior (reactivity) of different coagents, cure rate index values were calculated. Table III shows the rheodata and corresponding cure rate index and crosslink density value of EOC vulcanizate. Scorch time  $t_{s2}$  ( $t_{10}$  for very fast curing system) generally defines the time of onset of vulcanization and  $t_{c90}$  corresponds to the time required for 90% completion of vulcanization at a given condition. The value of  $100/(t_{c90} - t_{10})$  can be taken as an indication of rate of cure or cure rate index. The decrease in the scorch time ( $t_{10}$ ) and optimum cure time ( $t_{c90}$ ) were observed in the compounds with the addition of coagents. It is noticeable that there is little difference in the scorch time values between different coagents. Therefore the  $t_{c90}$  value mainly decides the cure rate of the respective compound. TAC is found to exhibit the fastest rate of cure followed by TMPTA and MPDM. Interestingly, MPDM shows the same rate of cure as that of control compound, but with a considerable improvement in the maximum torque value. Because MPDM and TMPTA belong to Type I coagents, which are expected to increase the rate and state of cure, in this particular case, there is no significant influence in the rate of cure. The concentration of peroxide is rather high (5 mequiv–3.38 phr), which may obscure the performance of coagents in terms of rate. Also, Type I coagents are more prone to secondary reaction (i.e., homopolymerization of coagent compound, which is an ineffective utilization of coagent compound).<sup>13</sup> Therefore, it is expected that homopolymerization of MPDM compound could reduce the cure rate values. Generally, in a coagent-assisted peroxide cure system, it is well established that along with the favorable reaction (i.e., crosslink via coagent molecule), several competing reactions, like the formation of coagent bridges or domains (homopolymerized coagent compound), may also occur between two effective crosslink points and pendent coagent bridge grafted on the polymer chains. When a coagent domain is grafted to the polymer chain, the effect can be similar to the addition of reinforcing filler with high modulus.<sup>13,14</sup> A conceptual model of crosslink formation and coagent bridge formation of the coagent-assisted peroxide system is shown in Figure 5. It is generally believed that Type I coagents (like TMPTA and MPDM) undergo homopolymerization more readily than Type II coagents (like TAC), but the results described by Dikland suggest that homopolymerization is also a prevailing mechanism for Type I coagents.<sup>24</sup>

### Mixing torque

The mixing characteristics of the blends were studied in the Haake Rheomix during the preparation of

TABLE III  
RPA 2000 Rheometer Data for Pure EOC Gum Vulcanizate

Compound name	Min. $S$ (dNm)	Max. $S$ (dNm)	$\Delta S$ (Max $S$ - Min $S$ ) (dNm)	$T_{10}$ (m:s)	$t_{c90}$ (m:s)	Cure rate index (%)	Crosslink density (v) $\times 10^{-4}$ (mol/ml)
RDC0 <sup>a</sup>	0.142	2.435	2.293	0.43	4.07	27.47	1.01
RDC20	0.431	3.979	3.548	0.33	3.18	35.08	1.93
RDA20	0.278	2.747	2.469	0.37	3.58	31.15	1.14
RDM20	0.546	3.308	2.762	0.33	3.96	27.54	1.52

<sup>a</sup> R denotes the cure study of EOC gum vulcanizate.

TPVs. The peak torque values of PP/EOC TPVs prepared by three different coagents are shown in Table IV. Before addition of the curative package, formation of homogeneous blend of PP and EOC was ensured; this can be inferred from the constant torque values during mixing. With the addition of curative, torque values first reach a maximum and then gradually decrease. Dynamic vulcanization is evident from the increase in the torque values, although a decreasing trend after reaching maximum may be due to the combined effect of disintegration of dispersed domain and the degradation in the PP phase. A similar trend has been reported by Varghese et al.<sup>25</sup> It has been well established that the addition of even a small amount of peroxide can cause a considerable degradation in the PP through  $\beta$ -chain scission. Generally, peak torque values obtained after the addition of curative is related to the amount of crosslink formed. Irrespective of the nature of different coagents, the blends with coagent give a stronger crosslinking effect than the blends without coagent. However, different coagents show different behavior with respect to increase in concen-

tration. It is interesting to note that with an increase in the concentration of TAC (Table IV), there is a gradual decrease in the maximum torque values. When TMPTA is used as a coagent, marginal improvement in the torque value is inferred only at the higher concentration (30 mequiv). Unlike TAC and TMPTA, the MPDM-containing system shows a more consistent trend for which the improvement is more linear as the concentration increases up to the study limit of 30 mequiv (Table IV). It has been previously reported that MPDM can act as a reactive compatibilizer in the NR-PP blend system.<sup>1,25</sup> It generates a low degree of crosslinking in the NR phase and forms a block or graft copolymer in the NR-PP interface. Many other polymer systems have been studied by using MPDM such as in PP/EPDM, PP/PE/EPDM PP/styrene-isoprene-styrene, and PP/styrene-butadiene-styrene, etc.<sup>26-28</sup>

Generally, a block or graft copolymer reduces the interfacial tension and improves adhesion between immiscible polymer systems, thus increasing the extent of compatibilization of immiscible polymer blend constituents. Similar behavior is expected in the PP/EOC blends as well. Figure 6 shows the comparative mixing torque values of three different coagents with 20 mequiv concentration. It is clearly seen that MPDM shows the higher peak torque values followed by TMPTA and TAC.

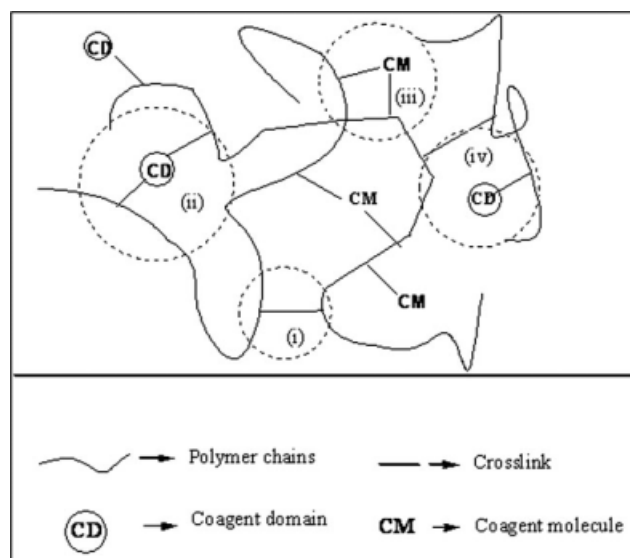
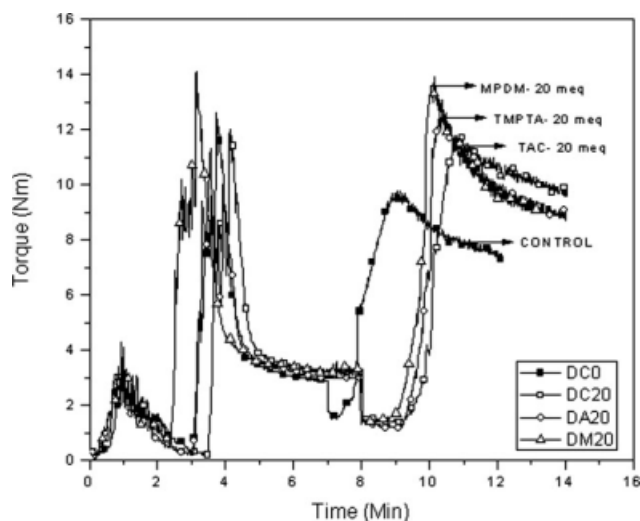


Figure 5 A conceptual model of coagent-assisted peroxide-cured polymer network.

TABLE IV  
Peak Mixing Torque Values Obtained from Haake Rheomix During the Preparation of PP/EOC TPVs

Compound name	Peak mixing torque values (Nm)
DC0 <sup>a</sup>	9.34
DC10	11.90
DC20	11.40
DC30	10.54
DA10	12.30
DA20	12.40
DA30	12.80
DM10	12.20
DM20	13.60
DM30	13.90

<sup>a</sup> DC0 compound does not contain any coagent.

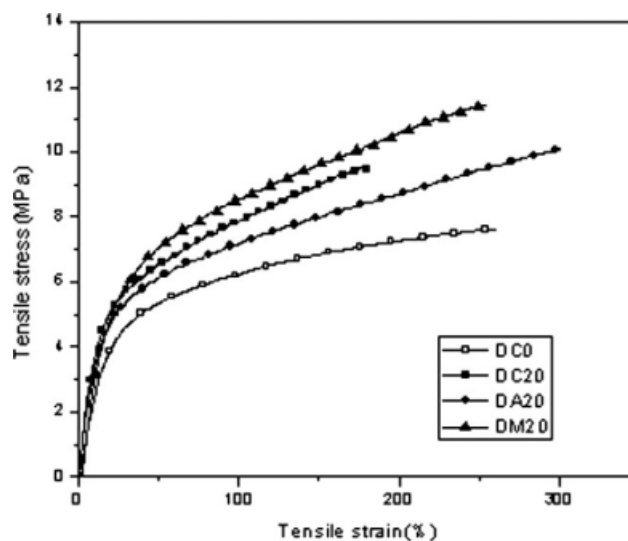


**Figure 6** Comparative mixing torque vs. time for PP/EOC TPVs using various coagents of equal concentration (20 mequiv).

A clear divergence is inferred when comparing the performance of different coagents on the delta torque values obtained from the cure study in the EOC vulcanizate (without PP) and the mixing torque of the PP/EOC TPVs. In the cure study mentioned before, TAC shows the higher rate and state of cure on pure EOC vulcanizate. However, when examining the mixing torque vs. time of PP/EOC TPVs by using different coagents, MPDM shows higher peak torque values, which may be due to its compatibilizing efficiency of immiscible polymers.

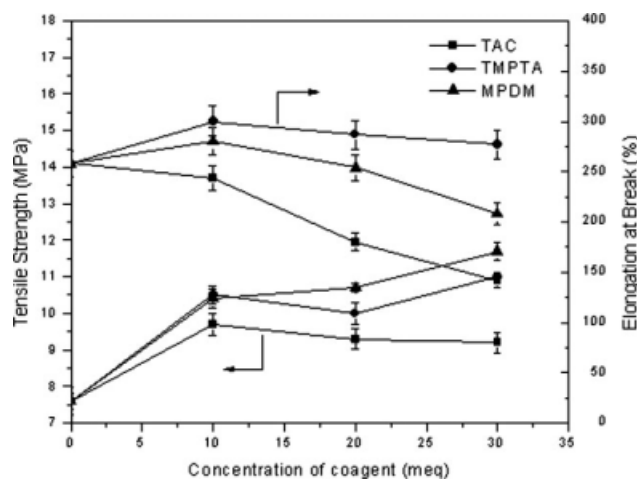
### Mechanical properties

The stress-strain plots of PP/EOC TPVs without and with coagents of three different types at 20 mequiv concentration are given in Figure 7. The mechanical properties of PP/EOC TPVs with varying types and concentrations of different coagents are shown in Figures 8–11. Tensile strength as a function of concentration of different coagent is shown in Figure 8. TPVs prepared by using MPDM as coagent exhibit gradual increase and provide superior tensile strength relative to the other coagents used. TAC shows an initial increase and then gradual decrease and finally exhibits lowest tensile strength values. TAC is an aromatic and trifunctional coagent, allowing the clustering and homopolymerization of the coagent compound to form hard domains, which provide the compound a hardening effect.<sup>29,30</sup> It has been reported that coagents that produce hard domains exhibit poor elongation and tensile strength than softer domains.<sup>13</sup> In an extensive study by Dikland et al.,<sup>30</sup> it was reported that the coagent TAC of Type II can form coagent domains during vulcanization. The effect on mechanical properties of these



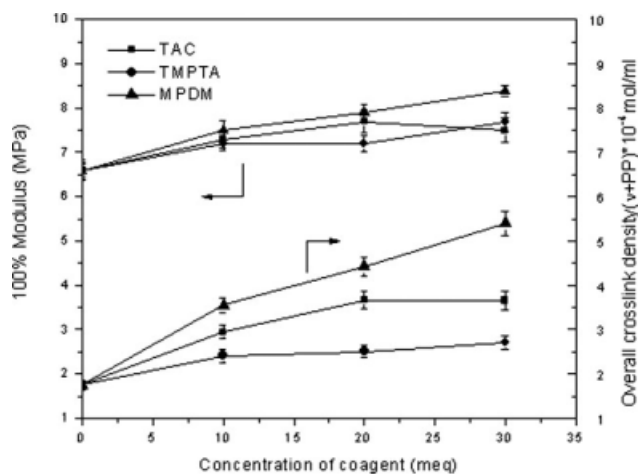
**Figure 7** Tensile stress-strain curves of PP/EOC TPVs.

coagent domains depends on the rigidity of the coagent molecules. These rigid domains can act as stress concentration points during extension and eventually cavitation may take place followed by tearing. On the other hand, coagent molecules with difunctional and aliphatic structure (like TMPTA and MPDM) tend to form softer domains, which may have a reinforcing effect and may therefore improve mechanical properties. The ratio of homopolymerization over polymer grafting presumably depends on coagent concentration, polarity differences between coagent and polymer, and adequacy of mixing.<sup>30</sup> It is expected that due to the formation of hard domains at high (30 mequiv) concentration of TAC, a premature failure with inferior tensile strength is favored. The above observations are in line with the mixing torque value obtained from Haake Rheomix (Table IV). Figure 8 shows the performance of different coagents on elongation at



**Figure 8** Tensile strength and elongation at break as a function of concentration of different coagents.





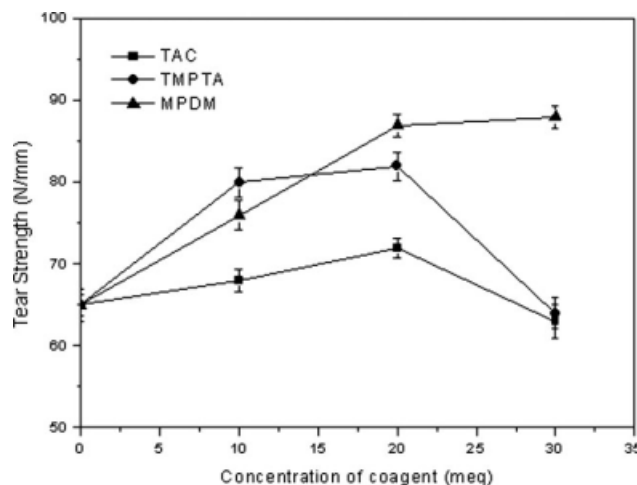
**Figure 9** 100% Modulus and overall crosslink density ( $v + PP$ ) as a function of concentration of different coagents.

break value of the TPVs. The values are continuously decreasing in the case of TAC, whereas MPDM and TMPTA show an initial increase and then gradual decrease. Decreasing trend may be due to the stiffening of the material. It was generally accepted that a low crosslink density compound is indeed accompanied with the higher elongation at break. It is clearly seen that TMPTA shows lower delta torque value and thereby exhibits higher elongation at break. TAC shows the lowest value and MPDM shows the intermediate value of elongation in TPVs. It can be argued as compatibilized blends would show somewhat higher elongation at break than the uncompatibilized blends.<sup>31</sup> Because MPDM can act as a crosslinking agent as well as a compatibilizing agent, where crosslinking decreases, the elongation and compatibilization increases. In this case, both the effects are very sensitive in determining the final elongation at break.

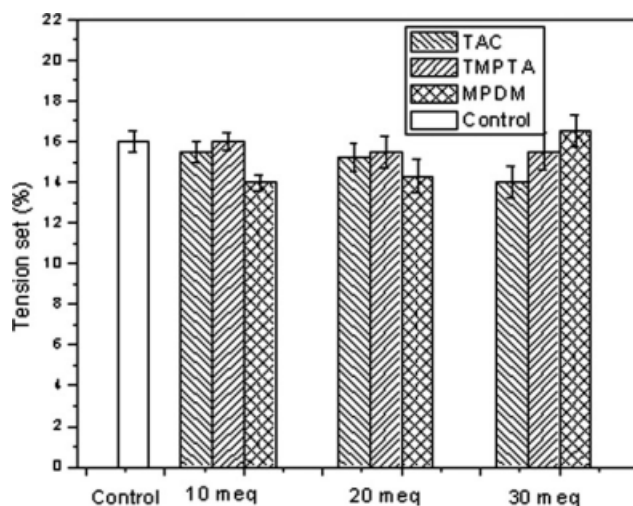
Modulus at 100% and overall crosslink density were found to increase continuously with the increasing concentration coagent; corresponding plots are shown in Figure 9. Performance of different coagents on the 100% modulus is in agreement with the overall crosslink density values ( $v + PP$ ) calculated. An attempt was made to interpret the results of the modulus value of TPV with the delta torque values obtained from the cure study of pure EOC vulcanizate. Interestingly, the trends of different coagent efficiency on the modulus values of TPVs are not in agreement with the torque values obtained from the cure study on the pure EOC vulcanizate. It has been previously reported that modulus of TPVs were mostly governed by the extent of crosslinking in the rubbery phase and also by the molecular integrity of matrix phase.<sup>11,17</sup> However, in this particular system, apart from the abovementioned presumptions, compatibility of the blend

system also plays an important role in the determination of modulus values. The above observation can be intercepted in a sense that MPDM not only crosslinks the rubbery phase, it also performs as a compatibilizer to promote the interaction of dissimilar polymers. It is important to note that, at high concentration of TAC (30 mequiv), 100% modulus decreases marginally. As previously mentioned, TAC is a trifunctional and aromatic-based coagent that shows higher tendency to form hard homopolymerized coagent domains, which in turn acts as stress concentration points to exhibit poor physical properties.<sup>13,23,30</sup> Influence of the different coagents on the tear strength is shown in Figure 10. As previously mentioned, addition of coagent not only aids in the crosslinking process but also improves in formation of grafting of either polymer through the coagent bridges; the latter improves the interfacial adhesion. MPDM shows a continuous increase in tear strength, whereas TMPTA and TAC initially increase and then decrease at higher concentrations of coagent. Because MPDM acts also as a compatibilizer, it decreases the interfacial tension and also decreases the dispersed particle size. Smaller and more uniformly distributed particles are more effective in deviating in the propagation of crack and thereby limiting the catastrophic failure. A speculative model of the tearing behavior of dynamically vulcanized blend is suggested by Thomas et al.<sup>31</sup>

Kikuchi et al.<sup>32</sup> studied the deformation behavior and elastic recovery property (tension set) of the PP/EPDM TPVs by using two-dimensional Finite Elemental Analysis. It was found that during stretching PP phase around the crosslinked rubber particles acts as glue and yielding of PP occurs in the equatorial region (perpendicular to the loading direction) of the crosslinked particle. The nonyielded PP



**Figure 10** Tear strength as a function of concentration of different coagents.



**Figure 11** Tension set as a function of concentration of different coagents.

fractions around the rubber particles are pulled back during the removal of applied strain by the improved elastic nature of crosslinked EOC domains. Even at highly deformed states at which almost the whole matrix has been yielded, the ligaments matrix between the rubber inclusions is locally preserved within the elastic limit and helps in the recovery. Tension set values as a function of concentration of different coagents are shown in Figure 11. The trend seems to be varying nonlinearly and in fact there is no particular trend in the values observed. Within the experimental limit of the concentration of different coagents, the variation of the set values is not more than 2% as compared to the control sample. The correlation fails with the trend of overall crosslink density values observed. Because different factors determine the set values, such as type and concentration of coagent, coagent functionality, homopolymerization tendency, relaxing tend-

ency of homopolymerized coagent domains, polarity difference between matrix and coagent, adhesion between crosslinked particles and matrix ligaments, particle size of the dispersed domains, the difference in the crosslink structure type and mechanism involved for various coagents might result in different relaxation characteristics.

Table V shows the percentage change in physical properties of TPVs prepared by three different coagents after aging in a hot-air oven at 70°C for 72 h. MPDM-based TPVs show the best retention of physical properties followed by TAC and TMPTA. Formation of peroxide/coagent complex C—C bonding has high dissociation energies and provides vulcanizates with better strength and heat-aging resistance. From the literature, it has been already mentioned that the maleimide curing system is less susceptible to oxygen attack.<sup>1,27</sup>

Different factors can account for the explanation of the abovementioned various experimental results. However, MPDM shows the best overall balance of properties (optimized performance of vulcanizates) and TAC shows the worst overall balance of properties in PP/EOC TPVs. This clearly reveals that only by improving the extent of crosslinking in the rubbery phase does the final mechanical properties of TPVs improve. Coran and coworkers<sup>2,4</sup> pointed out the parameters that affect the properties of the TPVs; particularly, surface tension of the blend components plays a crucial role in determining the final mechanical properties. A poor interaction is usually accompanied by a sudden failure as a result of a crack-opening mechanism. Also, vulcanizate with hard domains (coagent domains) reduces the mechanical properties, probably due to the induction of the cavitation process on vulcanizate deformation.

Table VI shows the evaluation of overall performance of various coagents, which gives an impression

**TABLE V**  
Percentage Change in Physical Properties of TPVs Prepared by Three Different Coagents on Aging at 70°C for 72 h

Compound name	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% (MPa)
DC0 <sup>a</sup> (Control)	-16.6	-25.6	1.1
DC10	-10.3	-16.3	1.5
DC20	-8.9	-14.8	1.8
DC30	-9.6	-15.9	2.6
DA10	-12.6	-18.3	2.1
DA20	-11.3	-20.5	1.5
DA30	-14.2	-16.6	2.2
DM10	-8.9	-10.3	2.2
DM20	-5.3	-12.6	4.5
DM30	-6.2	-11.4	4.8

<sup>a</sup> DC0 compound does not contain any coagent.

**TABLE VI**  
Overall Performance of Different Coagents in PP/EOC TPVs

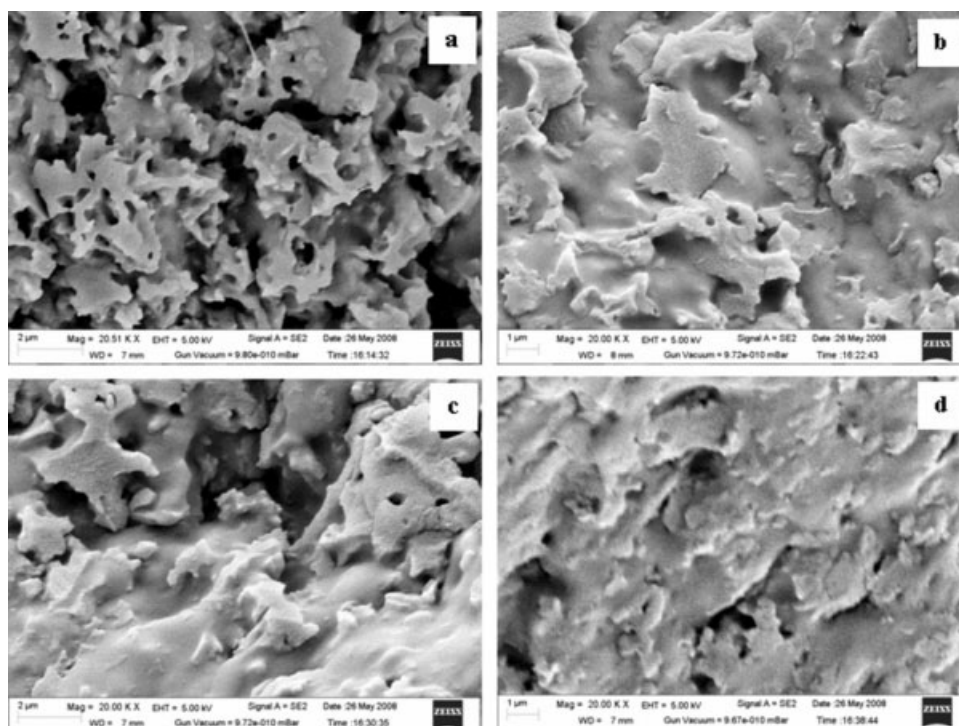
Property	TAC	TMPTA	MPDM
Processing and handling	Moderate	Moderate	Good
100% modulus	Poor	Moderate	Good
Tensile strength	Poor	Moderate	Good
Elongation at break	Poor	Good	Moderate
Tension set	Good	Moderate	Moderate
Tear strength	Poor	Good	Good
Aging at 70°C for 72 h	Moderate	Poor	Good

of the selection of a particular coagent depending on the final property requirements.

### Morphology

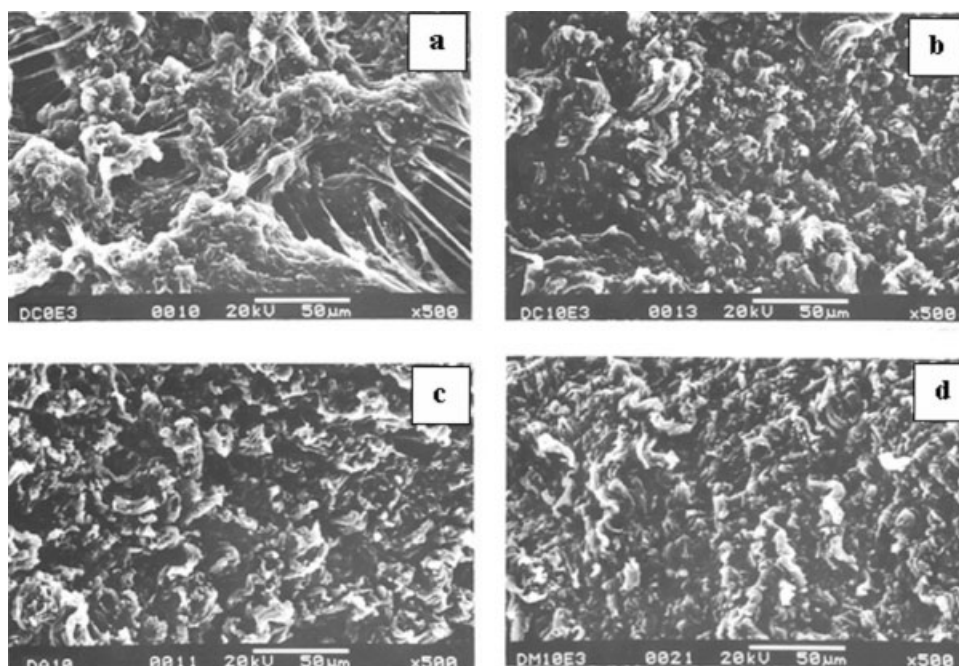
The mechanical and rheologic properties of the blends depend not only on the type of polymer used but also on the morphology finally formed. Morphology of the immiscible polymer blends are generally determined by the blend composition, viscosity ratio, and processing conditions.<sup>33</sup> Principally, dynamically vulcanized blends show droplet and matrix morphology. As the rubber phase is cross-linked under high shear rate, viscosity of rubbery phase increases, which drives the low viscosity (uncrosslinked plastic phase) to form a matrix phase (i.e., less viscous material encapsulates the more viscous phase to minimize the mixing energy). From the photomicrograph of PP/EOC TPV without

coagent, the Control [Fig. 12(a)] shows that cross-linked rubber particles are dispersed throughout the PP matrix. For high rubber composition, the particle–particle association is strong enough to form aggregates and these aggregates can agglomerate with further increase in concentration. The cross-linked rubber aggregates are embedded in the PP macromolecules via joint shell mechanism and/or segmental interdiffusion mechanism.<sup>34</sup> As hot xylene could extract out the PP, absorbed on the surface of crosslinked rubber particles, these constitute to form a network of crosslinked structures. Figure 12(b–d) shows the effect of TAC, TMPTA, and MPDM, respectively, as coagent with 20 mequiv concentration on the phase morphology of blend components. From the photomicrographs of the coagent incorporated TPVs, interfacial boundaries were obscured or blurred. Similar observations were reported in the case of PP/EPR/PE and PP/epoxidized natural



**Figure 12** FESEM photomicrographs of dynamically vulcanized PP/EOC TPVs without and with 20 mequiv concentration of various coagents: (a) Control; (b) TAC; (c) TMPTA; (d) MPDM.





**Figure 13** SEM photomicrographs of tensile fracture surface: (a) DC0, (b) DC10, (c) DA10, (d) DM10.

rubber (ENR) blend systems.<sup>35,36</sup> It has been previously mentioned that coagent incorporation might increase the interaction between the two phases and decrease the extent of degradation in the PP phase. As the extent of compatibilization increases, adhesion between the blend components increase; hence, more molecular interlocking at the interface resists the effect of xylene on PP and is absorbed in the interface. High molecular weight PP species also experience greater resistance toward solvent extraction. Among the three different coagents used, MPDM exhibits less phase heterogeneity and lower particle size. This again confirms that MPDM not only acts as the crosslinking agent but also as a compatibilizer, which thereby decreases the interfacial tension and retards the feasibility of dynamic coalescence of dispersed domains.<sup>37</sup> These results are in agreement with the mechanical properties of TPVs prepared by the different coagents.

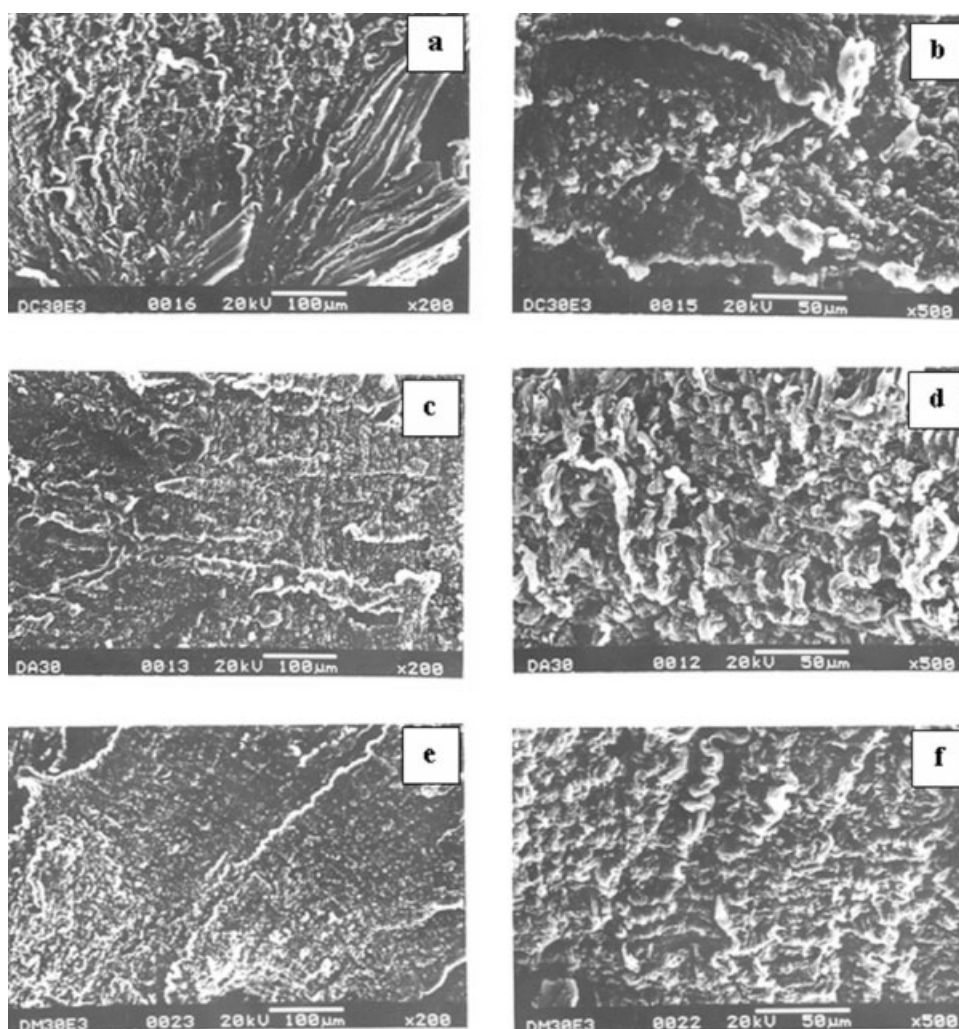
### Tensile fractography

Tensile fracture surface of the coagent-assisted peroxide PP/EOC TPVs was observed by SEM and their micrographs are shown in Figures 13 and 14. Fractography gives information about the deformation characteristics and mode of failure of the blends. Tensile fracture surface of DC0 (without coagent or control) [Fig. 13(a)] shows the ductile type of failure: formation of long thin fibrils and peaks of rubber mass normal to the direction of applied strain. Fibril formation is a characteristic feature of ductile failure with high plastic deforma-

tion.<sup>38</sup> Addition of only peroxide causes crosslinking in the EOC phase and chain scission in the PP phase. The net result of the two effects may cause restricted flow of matrix. Evidence of some type of adhesion between dispersed particles (crosslinked EOC) and matrix (PP) is provided where long fibrils connecting dispersed domains and matrix can be seen. Coagent-assisted peroxide systems can diminish PP degradation and enhance crosslink density in EOC. Despite the difference in the type of coagent, fracture surface topography of DC10, DA10, and DM10 [Fig. 13(b–d)] is more or less similar. In general, it can be observed that the elastic nature of the samples is found to increase as the crosslinking level in the EOC phase is increased. The absence of long fibrils and matrix flow indicates the deformation of elastic type.<sup>39</sup>

SEM micrographs of tensile fracture surface of TPVs with 30 mequiv concentration of different coagents were shown in Figure 14(a–f). Irrespective of different coagents, the fractography of higher magnification clearly shows the formation of pulled up wavy crest or sinusoidal folding. The presence of such wavy crest suggests the occurrence of a tearing process during tensile testing. The macromolecular chains undergo a high degree of orientation and are elongated before rupture, thereby causing the dissipation of a large amount of energy. These patterns are generally observed in the tear fractography of plasticized polyvinyl chloride (PVC), PVC-ENR blend, 1,2-polybutadiene, and some TPES.<sup>40,41</sup> Akhtar et al.<sup>42</sup> reported a similar type of tensile fracture surface for pure semicrystalline low-density





**Figure 14** SEM photomicrographs of tensile fracture surface: (a) DC30 (low magnification,  $\times 200$ ); (b) DC30 (higher magnification,  $\times 500$ ); (c) DA30 (low magnification,  $\times 200$ ); (d) DA30 (higher magnification,  $\times 500$ ); (e) DM30 (low magnification,  $\times 200$ ); (f) DM30 (higher magnification,  $\times 500$ ).

polyethylene. In general, the folding on the fracture surface is intense and prominent for strong material.<sup>43</sup> The fracture surface of DM30 [Fig. 13(f)] shows the closely packed wavy crest better than DA30 [Fig. 14(b)] and DC30 [Fig. 14(d)]. The tensile properties of DM30 are also relatively high, supporting the development of sinusoidal folding. The low magnification of fracture surface of TPVs [Fig. 14(a,c,e)] shows the formation of the stress concentration point or the induction point for the failure. On the fracture surface of DC30, it is possible to see the stress concentration point followed by tearing. The fracture surface of DA30 [Fig. 14(c)] and DM30 [Fig. 14(f)] shows that there is no fracture induction region and the fracture occurs through shearing action. Such observations are in agreement with the elastic mechanism of fracture.

To sum up, when using only peroxide in PP/EOC-based TPVs, final morphology and mechanical

properties are controlled by the following different factors:

1. Increase in viscosity ratio (two competing reactions: crosslinking in EOC phase and chain scission in PP phase) favors the formation of dispersed phase morphology in which PP forms matrix with crosslinked EOC as dispersed. However, degradation in the PP phase is undesirable, which has a negative influence on the mechanical properties and dispersion characteristics.
2. Limited extent of interfacial tension is also favored by co-curing characteristics of peroxide, which has a positive effect on mechanical properties of TPVs.

The use of coagent in the peroxide cure system has enlarged the range of application by limiting the

PP degradation to a minimum and maximizing the degree of crosslinking in EOC phase in the fixed blend ratio of PP/EOC blend. In addition, there is a possibility of improving the interfacial interaction by forming the *in situ* graft-like structure between two phases during dynamic vulcanization. The improvement in the interfacial adhesion is supported by the mechanical, micromorphology, and macromorphology (tensile fractography) of the PP/EOC TPVs. Comparing well-known coagents such as TAC, TMPTA, and MPDM in PP/EOC TPVs, the latter provides improved mechanical properties and less phase heterogeneity. Therefore, MPDM has the potential to be used as an effective coagent for the preparation of peroxide-cured PP/EOC TPVs.

### CONCLUSIONS

The present study demonstrated the influences of three structurally different coagents on the mechanical and morphological properties of PP/EOC TPVs. Significant improvement in the mechanical properties were inferred with the addition of coagents. Different coagents show different behavior in the physical properties due to the variation in the rate and crosslinking mechanism. This in turn depends on the number of functionalities present and is also governed by the structural member bridging the functional components. In the case of TAC and TMPTA, low concentration is sufficient to exhibit optimum mechanical properties, whereas for MPDM, a more consistent trend is noticed even at higher concentration.

Among the various coagents taken for the investigation, the most interesting properties were observed for MPDM containing TPVs. A clear divergence is inferred when comparing the performance of different coagents on the delta torque values obtained from the cure study in EOC gum vulcanizate and the final mechanical properties of PP/EOC TPVs. In the cure study, TAC shows the higher state of cure on pure EOC vulcanizate but, when examining the properties of PP/EOC TPVs, MPDM shows the best balance of mechanical properties. MPDM is shown to effectively behave as a compatibilizer for the PP/EOC blend system and thereby improvement is significant. Tension set values initially decrease and then increase with increasing concentration of coagents, which may be due to the relaxing tendency of the coagent domains in the system. MPDM shows a slightly poorer set of properties than TAC and TMPTA. Different aspects can account for the explanation of different mechanical behaviors. Two-phase morphology is observed for all the blend components. A better dispersion and lowering of the particle size of the crosslinked EOC phase dispersed in the PP matrix is promoted by the addition of

coagent. The phase boundaries are obscured when coagents are added. These may be attributed to the strengthening of interfacial adhesion between blend components. MPDM-containing samples exhibit less phase heterogeneity and lower particle size than other coagents used. The mechanical properties are found to be in agreement with the morphological evaluation. Tensile fracture surface showed a failure mechanism, changing from ductile to elastic type with the addition of 10 mequiv concentration of coagent (irrespective of different types). Fracture surface of TAC-based TPVs at 30 mequiv concentration clearly showed the stress concentration point expected to be initiated by the presence of hard coagent domains. The above observation supports the stress-strain characteristics of the corresponding TPVs prepared.

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