

Dynamically Vulcanized Blends of Polypropylene and Ethylene-Octene Copolymer: Comparison of Different Peroxides on Mechanical, Thermal, and Morphological Characteristics

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ABSTRACT: Thermoplastic vulcanizates (TPVs) are prepared by the dynamic vulcanization process, where crosslinking of an elastomer takes place during its melt mixing with a thermoplastic polymer under high shear. TPVs based on polypropylene (PP) with different grades of ethylene-octene copolymers (EOC) were prepared with a coagent assisted peroxide crosslinking system. The effect of dynamic vulcanization and influence of various types and concentrations of peroxide were mainly studied on the basis of the mechanical, thermal, and morphological characteristics. Three structurally different peroxides, namely dicumyl peroxide (DCP), *tert*-butyl cumyl peroxide (TBCP), and di-*tert*-butyl peroxy isopropyl benzene (DTBPIB) were investigated. The mechanical properties of the TPVs are primarily determined by the extent of crosslinking in the EOC and the degree of degradation in the

PP phase. Among all peroxides used DCP gives best overall properties with low-molecular-weight EOC, whereas TBCP shows best property level with high-molecular-weight EOC-based TPVs. These can be explained on the basis of the molecular characteristics of EOC and the nature of the peroxide used. Differential scanning calorimetry (DSC) and morphological analysis reveal that PP and EOC are a thermodynamically immiscible system. The melting endotherm was studied to determine the influence of various peroxides on crystallinity of the PP phase. Tensile fracture patterns were also analyzed to study the failure mechanism of the samples. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1836–1852, 2009

Key words: dynamic vulcanization; polypropylene; ethylene-octene copolymer; peroxide

INTRODUCTION

Thermoplastic vulcanizates (TPVs) are prepared by the dynamic vulcanization process, where crosslinking of an elastomer takes place during its melt mixing with a thermoplastic polymer under high shear. The resulting morphology consists of micron-sized finely dispersed crosslinked rubbery particles in a continuous thermoplastic matrix of which the rheological behavior can be compared with that of highly filled elastomers.^{1,2} TPVs were first introduced by Gessler and Haslett³ and earlier work of Fisher⁴ in PP/EPDM TPVs with peroxide as crosslinking agent resulted in the commercialization of “Uniroyal TPR” thermoplastic rubber in 1972. Greater industrial attention was generated only after extensive study of TPVs based on various blend components by Coran and Patel in 1980s.^{5,6} A recent survey indicates that the global annual growth rate of TPE based on TPVs

is about 15%. Now TPVs are widely used in automobiles, wires/cables, biomedical, soft-touch applications, etc. In principle, a large number of rubber-thermoplastic TPVs are possible and this number is increasing day by day with the introduction of new polymers. But technologically useful blends can only be obtained by the close match of surface energies of the blend components.⁷ Besides these blend components, the crosslinking agent also plays an important role in determining the selection of a process, performance and properties of the system. Generally, if the elastomer particles are small enough and fully crosslinked, significant improvement in the properties such as reduced permanent set, improved elastic recovery, improved mechanical properties, improved high temperature utility, resistance to attack by fluids, stability of phase morphology and better thermoplastic processability can be obtained.⁸

TPVs based on polypropylene (PP) and ethylene propylene diene terpolymer (EPDM) were extensively studied, and to a lesser extent those based on butyl rubber-PP, natural rubber-PP, and nitrile rubber-PP. Very recently, Naskar⁹ reviewed extensively the thermoplastic elastomers based on PP-EPDM

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blends by dynamic vulcanization. Impact modification of PP using ethylene- α olefins in the place of traditional EPDM has attracted much attention.^{10–12} Walton¹³ and Williams and Miller¹⁴ reported that these ethylene-octene copolymers (EOCs) are compatible with most olefinic materials and offer excellent impact modification in semicrystalline materials. There have been increasing applications of EOC in the automotive field and also as impact modifiers. Nevertheless, TPVs based on EOC or plastomer and PP are not well explored. Msakni et al.¹⁵ studied the crosslinking process of EOC by DCP under static and dynamic condition and reported that dynamically vulcanized samples developed hyperbranched structure, which is reprocessable, meaning that the final microstructure is totally different from that obtained from static vulcanization. Lai et al.¹⁶ studied the fracture mechanism of a PP-metallocene based EOC thermoplastic vulcanizate by peroxide crosslinking. Li et al.¹⁷ investigated the effects of reactive blending of PP and EOC using organic peroxide as initiator. Naskar and Noordermeer^{18,19} reported the influence of different types of peroxides including multifunctional ones in conventional PP/EPDM TPVs. When a peroxide is added to PP-EOC blends, two major competing reactions can take place: crosslinking in the EOC phase and degradation of the PP phase by β -chain scission. Johnston²⁰ successfully used a Monte Carlo simulation to model the effects of DCP on the EOC and concluded that chain scission/crosslinking ratio is 0.24. This indicates that crosslinking in the EOC is dominant one and that the chain scission can be neglected for these copolymers. However, chain scission reactions can be partially overcome by using a suitable coagent.²¹ Coagent-assisted peroxide systems can diminish PP degradation and enhance crosslink density in EOC. The effect of a peroxide on a particular polymer blend depends on the nature and type of the polymers, nature, and concentration of the peroxide and reactivity of other components in the composition. The rate of crosslinking of a peroxide depends on the decomposition temperature and the rate of formation of free radicals; these two parameters are related by a term called “half-life time” of the peroxide ($t_{1/2}$) at a particular temperature. This is defined as the time required to reduce the original peroxide content by 50% at a given temperature.^{21,22} The morphology evolution of TPVs is governed by several parameters, including blend composition, viscosity ratio, shear force, and interfacial interaction between the two phases.^{1,2,8,9} Initially, with the addition of curative, viscosity ratio plays a major role in the morphology evolution (less viscous phase encapsulate the more viscous phase). With further increase in curative dosage, degree of crosslinking increases in the dispersed phase, although there is an abrupt

increase in viscosity ratio resulting decrease in particle size. It is expected that applied shear fields overrides the viscosity ratio factor. It is further clarified as, with enough crosslinking in the rubber part cause an immobilisation of the particles and therefore breakdown to smaller particles under the applied shear field. Because curing occurs under shearing, it is of significant interest to understand the influence of structural parameter of the blend components (molecular weight) on the size and degree of crosslinked rubber particle network formation.

The main objective of the present work is to study the effect of different types of peroxides with varying concentrations at a fixed blend ratio of PP and EOC. The study was also broadened to understand the influence of molecular characteristics (particularly molecular mass) on the crystallizing tendency of PP, on the morphological evolution of the blend components and on the property enhancement of the samples prepared by dynamic vulcanization process. Two types of EOCs having the same octene content and molecular mass distribution but differing in their molecular masses were taken. This investigation reports the mechanical and thermal properties of these peroxide cured TPVs based on PP and EOC, which could be a potential alternative to the conventional PP-EPDM TPVs.

EXPERIMENTAL

Materials

Isotactic PP and two different types of EOC were used as blend components. Metallocene catalyzed EOC (Exact[®] grades) were used in this study. The octene content of these Exact copolymers was determined from ¹H-NMR measurement. The material characteristics of PP and EOCs are given in Table I.

Three different types of peroxides were used as crosslinking agents, obtained from Akzo-Nobel Polymer Chemical Company, The Netherlands. Their commercial name, chemical name, structure, and molecular characteristics are given in Table II. Triallyl cyanurate (TAC) (SR 507A; specific gravity, 1.12 g/cm³ at 23°C) was used as coagent, obtained from Sartomer Company (Exton, PA).

Preparation of TPVs

PP-EOC TPVs were prepared by melt mixing of PP with EOC in a Haake Rheomix 600s with a mixing chamber of 85 cm³ at a temperature of 180°C. Batch sizes were about 60 g. Total mixing time for each batch was 14 min. At first, PP was allowed to soften

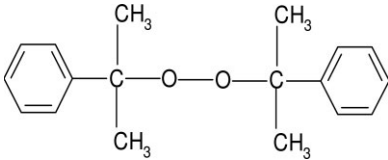
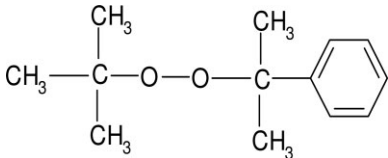
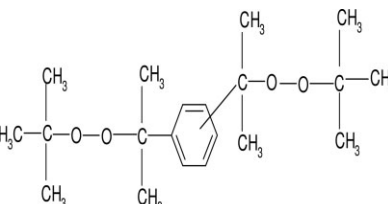
TABLE I
Characteristics of Polymers

Polymer used	Polypropylene (PP)	Exact [®] (EH)	Exact [®] (EL)
Source	Indian Petrochemicals, India	Exxon Mobil Chemical Company (USA)	Exxon Mobil Chemical Company (USA)
Grade	Koylene ADL (AS030N)	5061	5371
Octene content (mol %)	–	~ 13%	~ 13%
Melt flow rate (MFR)	3.0 at 230°C/2.16 kg (g/10 min)	0.5 at 190°C/2.16 kg (1.0 g/10 min)	5.0 at 190°C/2.16 kg (1.0 g/10 min)
Density (g/cm ³) at 23°C	0.905	0.868	0.870
Mooney viscosity ML(1+4) at 125°C	–	31	9.5

for 3 min and then EOC was added to the chamber and melt mixing was done for 5 min. Dynamic vulcanization was carried out by adding coagent-assisted peroxide for 2 min and then mixing was continued for another 4 min to complete the vulcanization. The compositions of PP/EOC TPVs used for this study are shown in Table III. TPVs prepared by different peroxides are designated as D for DCP, T for TBCP, and DT for di-*tert*-butyl peroxy isopropyl benzene (DTBPIB). The first number corresponds to the concentration of peroxide and EH corresponds to the high-molecular-weight copolymer (lower MFR) and EL corresponds to the low-molecular-weight copolymer (higher MFR) used for the prepa-

ration of the TPVs. For example, D5EL corresponds to the composition of 5 milliequivalents (meq) DCP in the low-molecular-weight EOC. The different peroxides differ in their molecular weight and also have different relative functionalities, so 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 at hot condition and sheeted out on a two roll mill at 25°C in a single pass. Sheets were then cut and pressed in a compression molding machine (Moore Press, Birmingham, United Kingdom) at 190°C for 4 min at 5-MPa pressure. Aluminum foils were placed between the

TABLE II
Chemical Structures and Characteristics of Various Peroxides

Commercial name	Chemical name	Structure	Crosslinking temperature ^a [°C]	Temperature at which $t_{1/2} = 0.1$ h [°C]
Perkadox-BC-40B PB (40%)	Dicumyl peroxide (DCP)		170	162
Trigonox-T-50D-PD (50%)	<i>Tert</i> -butyl cumyl peroxide (TBCP)		175	169
Perkadox-14-40B-PD (40%)	Di-(2- <i>tert</i> -butyl peroxy isopropyl) benzene (DTBPIB)		175	169

^a Temperature at which 90% of the total possible crosslinks are formed within 10–15 min.

TABLE III
TPV Compositions in Phr With Varying Peroxide Concentration

Compound name	PP-EH	D0.5EH	D1EH	D3EH	D5EH	D7EH	T0.5EH	T1EH	T3EH	T5EH	T7EH	DT0.5EH	DT1EH	DT3EH	DT5EH	DT7EH
EH ^a	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
PP	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
DCP	-	0.12 (0.5) ^b	0.675 (1)	2.027 (3)	3.378 (5)	4.729 (7)	-	-	-	-	-	-	-	-	-	-
TBCP	-	-	-	-	-	-	0.21 (0.5)	0.42 (1)	1.26 (3)	2.1 (5)	2.94 (7)	-	-	-	-	-
DTBPIB	-	-	-	-	-	-	-	-	-	-	-	0.21 (0.5)	0.425 (1)	1.27 (3)	2.125 (5)	2.975 (7)
TAC	-	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

^a Similar compositions for the EL grade were prepared and were designated as EL.

^b Values in the parenthesis correspond to the concentration of corresponding peroxide expressed in milliequivalents.

mold plates. The molded sheets were then cooled down to room temperature under the same pressure.

Testing procedures

Mechanical testing

The dumb-bell 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. Tensile strength was measured according to ASTM D418-98A using a universal testing machine Hounsfield H10KS (United Kingdom) at a constant cross head speed of 500 mm/min. Tear strength was determined according to ASTM D-624-81 test method using the unnicked 90° angle test piece. Cross-head 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 the ASTM D412-98 method. To study the effect of ageing 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 ageing were then determined as per ASTM standard. Three specimens were performed for each composition.

Cure characteristics

Cure characteristics of the compounds were determined with a Rubber Process Analyzer RPA2000 (Alpha Technologies, Akron, OH). The compound consisted of only EOC without any PP along with the different peroxides taken for the study. Concentrations of curatives selected were 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.

Crosslink density

Equilibrium solvent swelling measurements were carried out on the PP/EOC TPVs to determine the crosslink density of the EOC in presence of PP. The crosslink density was calculated using modified Flory-Rehner equation²³ as shown below [eq. (1)]. In case of TPVs, crosslinked EOC is embedded in the relatively less swellable matrix like PP. Crosslinked EOC swells against the compressive force exerted by the PP matrix. From the degree of swelling, the overall crosslink density was calculated relative to the (EOC + PP) phases and expressed as ($\nu + PP$). 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 48 h to achieve equilibrium swelling condition. Initial weight, swollen weight, and

deswollen or dried weight were measured and substituted in the following equation.

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

where v = number of moles of effectively elastic chains per unit volume of EOC [mol/mL] (crosslink density), $(v + PP)$ = crosslink density of EOC phase in the presence of PP (overall crosslink density), V_s = molar volume of cyclohexane [cm³/mol], χ = polymer swelling agent interaction parameter, which in this case is 0.306²⁴ and V_r = volume fraction of EOC 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 EOC after swelling.

Differential scanning calorimetry

DSC measurements were carried out in a TA Instrument (New Castle, DE) (Model DSC Q100 V 8.1) to study the melting behavior. The samples of about 6 mg sealed in aluminum pans were heated from -80 to 200°C at a scanning rate of 10°C/min under nitrogen atmosphere. The degree of crystallinity of PP was determined from the heating curve by using the following relation.

$$X = \frac{\Delta H_f}{\Delta H_{C100\%} \times W_i} \times 100 \quad (3)$$

where X = Percentage of crystallinity (%).

ΔH_f = Apparent enthalpy of crystallinity of PP (J/g).

$\Delta H_{C100\%}$ = Extrapolated value of the enthalpy of crystallization of a 100% crystalline sample, for PP the value is 209 (J/g).^{2,10,12}

W_i = Weight fraction of PP in the blend.

Morphology

Morphology studies were carried out using a scanning electron microscope (SEM) (JEOL JSM 5800, Japan). Molded samples of PP/EOC TPVs were cryofractured in liquid nitrogen to avoid any possibility of phase deformation during the fracture process. In the case of uncrosslinked blends, the EOC phase was preferentially extracted by treating with hot xylene at 50°C for 15 min, whereas in dynamically vulcanized blends 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 solvents present. Treated surfaces were then sputtered with gold before examination. Tensile fracture surface of

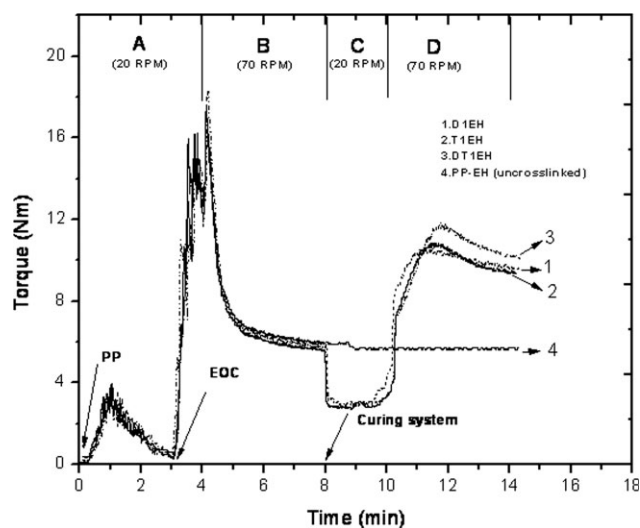


Figure 1 Mixing torque as a function of time for PP/EH TPVs dynamically cured by different peroxides at a concentration of 1 meq.

uncrosslinked and dynamically crosslinked blends were also examined by SEM to understand the failure mechanism.

RESULTS AND DISCUSSION

Mechanical properties

The effects of dynamic vulcanization of the PP/EOC blends by different peroxides were measured by torque - time values, under the same mixing conditions, as obtained from the Haake rheomix (Fig. 1). In the Figure 1, four distinct mixing intervals can be clearly observed with varying rotor speed. Stage A corresponds to the melting of PP at 20 RPM followed by melt blending of PP and EOC at 70 RPM (Stage B). The sudden drop at 8 min is attributed to the addition of curing agent (coagent + peroxide) with lowering the rotor speed to 20 RPM. In all the batches, dynamic vulcanization time was maintained to 4 min at 70 RPM. When a crosslinking agent is added after melt blending of PP and EOC (ensured by the appearance of constant torque values), dynamically vulcanized blends show a substantial increase in the torque values due to the crosslinking in the EOC phase (Stage D). Initially, after the addition of crosslinking agent, vulcanization takes place in the EOC phase and results in an increase in torque, thereby exerting greater resistance to rotation. With continued mixing, the torque values tend to decrease; that can be explained by breakdown of crosslinked rubber particles²⁵ along with an influence of peroxide on the PP phase. Generally, the effect of peroxide on the polymer depends on the nature of the polymer, type and concentration of peroxide and the reactivity of other components. When the peroxide is added to the PP-EOC blends,

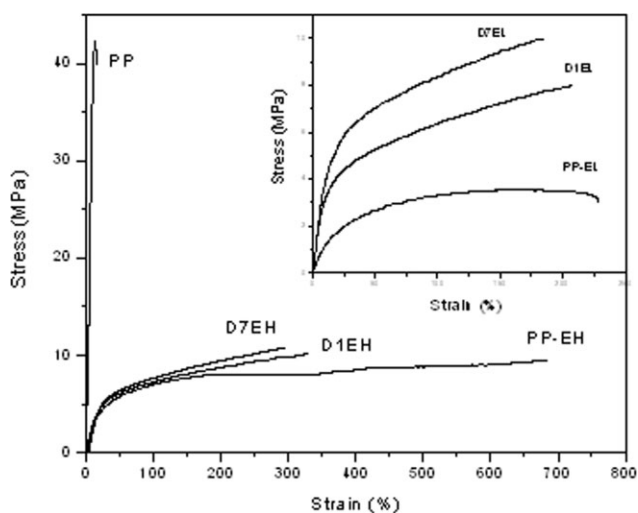


Figure 2 Tensile stress-strain curves of uncrosslinked and dynamically vulcanized PP/EOC blends (main graph) and PP/EH TPVs (inset graph) PP/EL TPVs.

mainly two competing reactions take place, crosslinking in the EOC as well as degradation of the PP via β -chain scission.

The mechanical properties of PP/EOC TPVs by TAC assisted peroxide are the results of extent of crosslinking in the EOC elastomer phase and the degree of PP degradation. The stress-strain curves of pure PP, PP/EOC uncrosslinked, and dynamically crosslinked blends with 1 and 7 meq concentration of DCP are shown in Figure 2. Main graph corresponds to PP-EH TPVs and inset graph for PP-EL TPVs. By dynamic vulcanization and with an increase in the concentration of the vulcanizing agent, the tensile strength and modulus at 100% elongation increase because of crosslinking in the

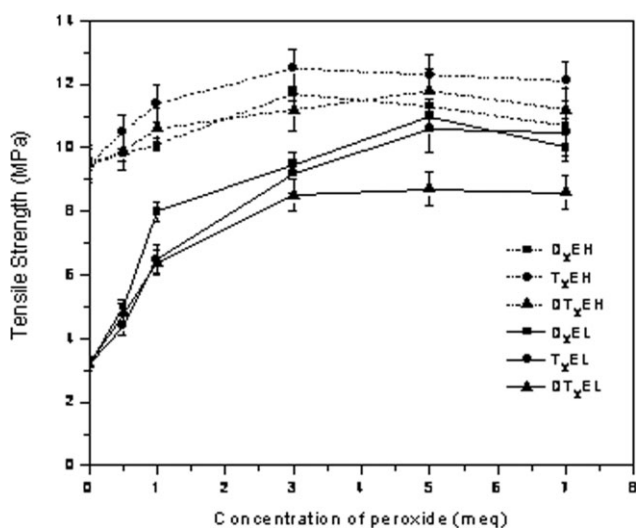


Figure 3 Tensile strength as a function of concentration of different peroxides for both the series of TPVs.

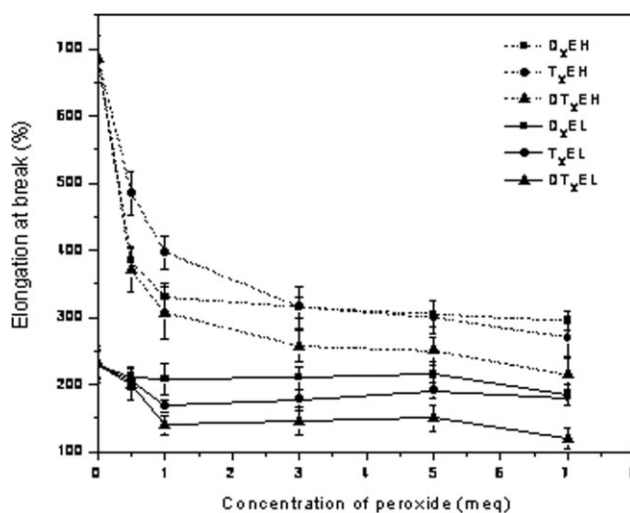


Figure 4 Elongation at break as a function of concentration of different peroxides for both the series of TPVs.

EOC phase, which helps in dissipation of the large amount of energy. Various types of peroxides have dissimilar crosslinking efficiencies and undergo different decomposition patterns under a given condition. Figures 3–7 show the tensile strength (stress at break), elongation at break, modulus at 100% elongation, tear strength and tension set values, respectively, as a function of concentration of the various peroxides. The trend appeared to be different for various peroxides and also changed with the type of EOC used. Increase in tensile strength, modulus and decrease in tension set (increase in elastic recovery property) corresponds to the crosslinking of the EOC phase in the blends.

In case of PP/EH TPVs, in most cases it is observed that tensile strength and modulus values

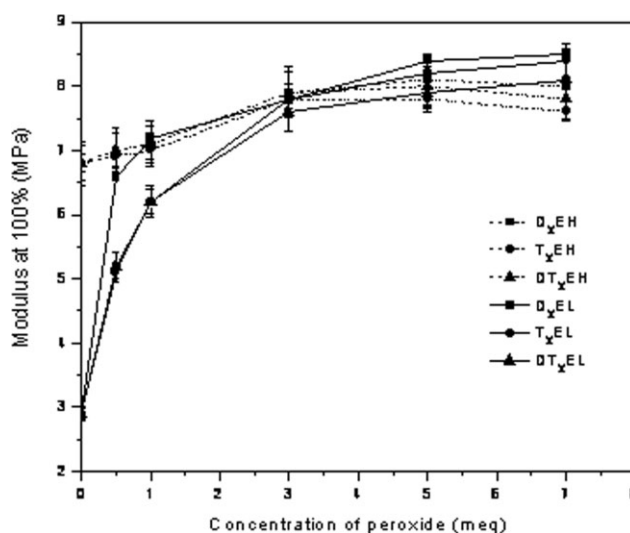


Figure 5 Hundred percent modulus as a function of concentration of different peroxides for both the series of TPVs.

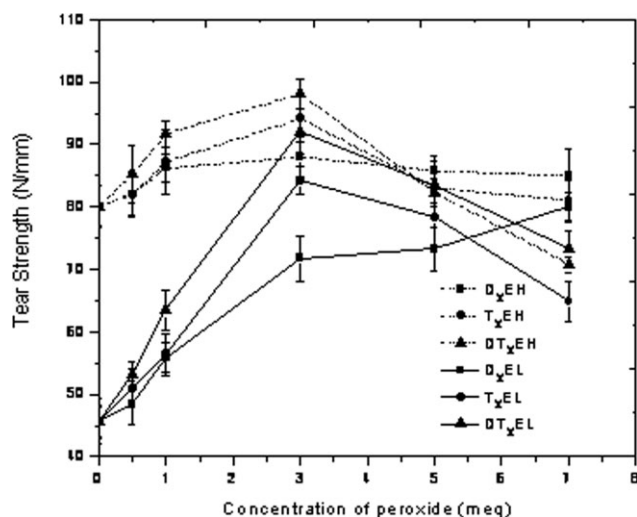


Figure 6 Tear strength as a function of concentration of different peroxides for both the series of TPVs.

initially increase reach a maximum followed by marginal decrease and elongation at break shows continuous decrease with increasing concentration of peroxide. Increasing trend in tensile strength and modulus corresponds to the crosslinking taking place in the EOC phase whereas the decreasing trend at higher concentration may be attributed to the degradation of the PP phase.^{18,19} It seems that two opposite behaviors are in competition to determine the final physical properties. Among the three different peroxides taken for investigation, TBCP shows the highest tensile strength followed by DCP and DTBPIB. The influence of different peroxides on the 100% modulus value is not well discriminated (only a marginal change in the values); still DCP and DTBPIB show higher modulus values than TBCP. Elongation at break value shows a continuous decrease and TBCP shows the maximum value as the function of concentration of different peroxides. In general, the most effective peroxides can produce primary free radicals, which are very reactive to abstract hydrogen atoms from the polymer chain, to form the corresponding macroradicals. The relative reactivity or stability of the free radicals generated is again related to the hydrogen bond dissociation energy of the parent compound. From the values of bond dissociation energy, it has been demonstrated²² that radicals such as phenyl, methyl, *tert*-butoxy, and alkoxy are highly reactive and are good hydrogen abstractors. On the other hand, radicals such as ethyl, isopropyl, and *tert*-butyl are lower in energy and are poor hydrogen abstractors. It is evident from the relative amounts of decomposition products of the different peroxides in pentadecane,¹⁸ TBCP produces less reactive primary radicals as

compared with DCP and DTBPIB, which is reflected in the modulus values of the TPVs.

On the other hand, in the PP/EL TPVs, the trends of physical properties seem to be different when compared with PP/EH TPVs. From the Figure 3 it is clear that, different peroxides exhibit varied response with increasing peroxide concentration, DCP initially increases and then decreases, TBCP keeps on increasing and DTBPIB reaches a plateau. The trend seems to be interesting for elongation at break (Fig. 4), for DCP and DTBPIB cured TPVs, it initially decreases and then shows a marginal increasing trend with increasing concentration and falls down at higher concentration (7 meq), whereas for TBCP it initially decreases and keeps on increasing within the given concentration limits. The modulus values continuously increase and this rise becomes marginal at higher concentrations. In a nutshell, DCP shows the highest tensile strength, elongation at break and modulus followed by DTBPIB and TBCP. The effect of curatives on the physical properties is more pronounced in the PP/EL grades, which can be explained by the nature of molecular characteristics of the polymer. In general, mechanical properties increase as the molecular weight of a polymer rises. However, above some limiting molecular weight the mechanical properties are usually unaffected. EL by its nature, is a low molecular weight compound (high MFR) that combines together to form a higher molecular weight compound during vulcanization. So, with the addition of curatives the latter shows a significant improvement in physical properties. But, when the final values of physical properties, i.e., tensile strength, elongation at break and modulus are compared, PP/EH TPVs shows still better properties, possibly because of its

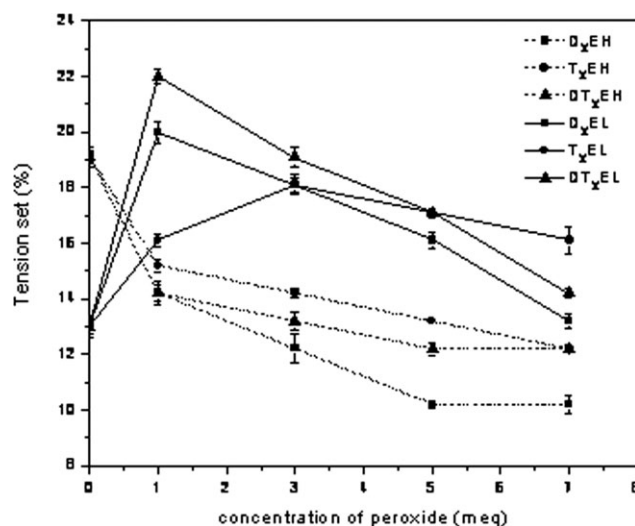


Figure 7 Tension set as a function of concentration of different peroxides for the both the series of TPVs.

inherent high molecular weight: Figures 3–5. An optimum level of curative is required to get the best overall physical properties, because beyond that point deterioration takes place due to saturation of the EOC macromolecules for crosslinking and a degradation effect of the peroxide on the PP phase. Still PP/EL requires a higher curative dosage than PP/EH to achieve a similar degree of crosslinking. It is to be noted that the PP/EH TPVs show a marginal decrease in modulus values at high concentration of peroxide which may be attributed to the degradation in the PP phase, whereas the PP/EL TPVs still show a marginal improvement.

Figure 6 shows the tear strength as a function of concentration of different types of peroxides. From the graph, it is observed that PP/EL shows a drastic increase in tear strength and PP/EH shows only a marginal rise in tear strength. In both series, the tear strength reach a maximum at a concentration of 3–5 meq of peroxide, and DTBPIB shows the highest value in both EH and EL. Interestingly, DCP cured TPVs show continuous increase in tear values with increase in concentration of peroxide. Generally, when tensile stress is applied to a rubber – plastic blend, tearing occurs at the interface between the rubber particle and plastic phase. Comparing the unvulcanized and dynamically vulcanized blends, the latter experiences higher hindrance in the crack propagation path because of micron size crosslinked rubber particles uniformly dispersed in the continuous thermoplastic matrix. These deviates the crack propagation path in an irregular manner and some kind of extension by rubbery particles also increases the tear strength values. A speculative model illustrating the tearing behaviour of the uncrosslinked and dynamically crosslinked HDPE/NBR blends is shown by Thomas et al.²⁶ When the coagent-assisted peroxide curative is added to the PP/EOC blends under dynamic condition, some *in situ* grafting of PP with EOC occurs at the interface.^{27,28} The latter acts as a compatibilizer and improves the interface interaction of the crosslinked rubber particles and the matrix part as reflected in the tear strength values. The decrease in tear strength values at higher concentration of peroxide can be explained by the inextensibility of highly crosslinked rubbery particles during tearing. From the above test results, DTBPIB show best compatibilising effect for both systems.

Tension set (elastic recovery after removal of an applied tensile strain) of the TPVs was modeled by Kikuchi et al.²⁹ by the outcome of two-dimensional (2D) finite element modeling (FEM). According to them, 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 fractions around the rubber particles are pulled back during the removal of applied strain by the improved elastic nature of crosslinked EOC domains.⁹ Tension set values as function of concentration of different peroxides is shown in Figure 7. With increasing concentration of curatives there is a continuous decrease in tension set values, which indicates better elastic recovery. In both series, DCP shows the lowest tension set values followed by TBCP and DTBPIB. Interestingly, the unvulcanized PP/EL blend shows a lower set value than the dynamically vulcanized blends. In the unvulcanized blend, the EOC forms a continuous phase and PP acts as dispersed phase according to the composition. Thereby, the elastic recovery property is mainly determined by the EOC phase, whereas after dynamic vulcanization phase inversion occurs, resulting in crosslinked EOC as the dispersed phase and PP as the matrix. It is reported that EOC exhibits better elastic characteristics than PP homopolymer.¹⁰ By a further increase of the degree of vulcanization in EOC by raising the curative level the elastic recovery property of all TPVs improves. This may be due to the formation of a highly cross-linked network in the EOC phase.

Heat aging

From a practical point of view, it is important to study the effect of heat aging on the physical properties. An aging study was carried out for all the TPVs prepared with the different peroxides and various EOC grades. Generally, peroxide crosslinked polymers show good retention of mechanical properties after aging due to the formation of the thermally stable C—C bonds. Table IV indicates the variation in tensile strength, elongation at break and 100% modulus value of the uncrosslinked and dynamically crosslinked blends of both the grades of EOCs. Both PP/EL and PP/EH unvulcanized blends show increase in tensile strength and modulus values with decrease in elongation at break. It is expected that during the aging process the rubber network stabilizes, which results in overall change in physical properties. Among the peroxide used, DTBPIB-based TPVs show the best retention of properties followed by DCP and TBCP. Since DTBPIB is a highly efficient and low reactive peroxide, the amount of peroxide used is not fully used during dynamic vulcanization. In particular, DT7EL shows increases in tensile, elongation and modulus values after aging. It is believed that an unreacted residual amount of peroxide still present may cause predominant crosslinking. In other words, the crosslinking reaction overrides chain scission during aging at high concentration of DTBPIB.

TABLE IV
Percentage Change in Physical Properties of TPVs After Aging for the PP/EH and PP/EL Series

Compound name	Tensile strength [MPa]		Elongation at break [%]		Modulus at 100% [MPa]	
	EH	EL	EH	EL	EH	EL
PP + EOC	23.2	50.0	-9.8	-23.5	1.5	65.5
D1	-13.3	-1.2	-15.8	-21.8	2.8	18.6
D3	-10.2	-5.3	-12.7	-2.4	1.3	1.3
D5	-2.7	-11.7	-5.3	-9.8	3.7	1.2
D7	-9.7	-4.0	1.6	-5.4	2.4	2.4
T1	-12.3	29.3	-20.6	33.3	4.3	25.8
T3	12.8	1.1	6.0	-10.1	7.6	3.9
T5	0.8	-1.9	-6.0	-3.0	3.9	1.2
T7	-7.4	-6.7	-17.0	-17.2	6.6	1.2
DT1	2.8	12.5	-7.2	-12.9	7.0	16.1
DT3	-4.5	0.0	-16.3	-1.4	7.6	3.9
DT5	1.7	2.3	-7.2	-1.3	7.5	2.5
DT7	-2.7	7.5	-2.0	8.3	7.7	1.2

D, dicumyl peroxide (DCP); T, *tert*-butylcumyl peroxide (TBCP); DT, di(*tert*-butylperoxyisopropyl)benzene (DTBPIB); EH, high-molecular-weight ethylene-octene copolymer; EL, low-molecular weight ethylene-octene copolymer.

Cure characteristics and crosslink density

To understand the effect of the different peroxides on the PP/EOC TPVs prepared, it is necessary to understand the curing characteristics of EOC part alone, with increasing concentration of different peroxides. Therefore, cure tests were carried out using a

torsional dynamic rheometer RPA 2000 from Alpha Technologies. The recipes taken for the cure study correspond to the recipes of the TPVs prepared, with PP omitted. Table V shows the RPA 2000 rheo-data for the corresponding compositions. The parameters used to characterize the peroxide efficiency and effectiveness are cure rate index and delta torque (ΔS). Cure rate index can be calculated from $t_{c90} - t_{10}$ and ΔS is measured from maximum torque minus minimum torque. In a very fast crosslinking system, t_{10} can be taken for the calculation for cure rate index, and it is generally defined as the time of 10% completion of vulcanization and t_{c90} corresponds to the time required for 90% completion of vulcanization at a given condition. Irrespective of the nature of peroxides used, increase in peroxide concentration causes increase in ΔS and rate of cure. The more peroxide is added, the more radicals are formed and thus the higher the cure rate and ΔS . Among the three peroxides under investigation, DCP gives the highest cure rate indices followed by DTBPIB and TBCP for both the EOC grades (Table V). ΔS values can be correlated with the degree of crosslinking for the different peroxides. TBCP shows the lowest degree of crosslinking, while DCP and DTBPIB exhibit similar crosslinking efficiencies and show higher values for both the EOC grades used in the study. Decomposition efficiencies and the relative amounts of reactive products are in line with the ΔS values. In brief, the peroxides taken for the investigation can be described as follows. DCP has a

TABLE V
RPA 2000 Rheometer Data for Pure EOC Vulcanizates

Compound name	Minimum S [dNm]	Maximum S [dNm]	ΔS [dNm]	t_{10} [m : s]	t_{c90} [m : s] ^a	Cure rate [%]	Crosslink density(v) $\times 10^{-4}$ [mol/mL]
RD1EH	0.24	2.988	2.748	0.50	4.02	28.40	1.61
RD3EH	0.644	4.027	3.383	0.32	25.4	45.04	2.33
RD5EH	0.747	5.118	4.371	0.33	2.22	52.91	3.05
RD1EL	0.042	1.264	1.222	0.57	5.59	19.92	0.41
RD3EL	0.180	3.364	3.184	0.39	3.47	32.46	1.55
RD5EL	0.392	4.049	3.657	0.34	3.14	35.71	2.18
RT1EH	0.170	1.501	1.331	1.08	7.48	15.62	0.85
RT3EH	0.259	3.786	3.527	0.49	4.20	26.95	1.51
RT5EH	0.403	4.292	3.889	0.39	3.47	32.46	1.76
RT1EL	0.025	0.342	0.317	1.16	8.44	13.73	0.13
RT3EL	0.039	3.042	3.003	0.49	6.01	18.11	1.36
RT5EL	0.093	4.142	4.049	1.01	6.17	19.37	1.42
RDT1EH	0.238	2.617	2.379	0.51	5.25	21.09	1.30
RDT3EH	0.359	4.385	4.026	0.41	4.23	26.17	2.31
RDT5EH	0.535	4.677	4.142	0.35	3.54	31.34	2.96
RDT1EL	0.025	1.433	1.408	1.17	8.01	14.61	0.43
RDT3EL	0.070	3.470	3.40	0.52	6.26	17.42	1.67
RDT5EL	0.135	4.104	3.969	0.43	5.42	20.04	2.24

R denotes the compound composition in the Table III without PP.

^a m : s, minutes : seconds.

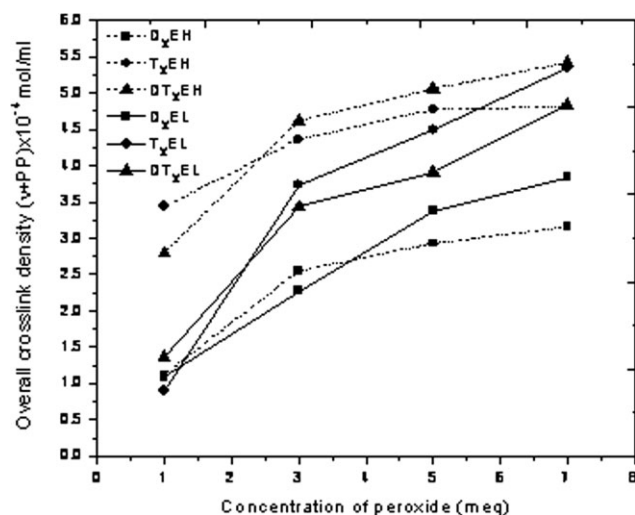


Figure 8 Overall crosslink density of TPVs prepared as a function of concentration of different peroxides for both the series of TPVs.

high reactivity and high efficiency, TBCP has a low reactivity and low efficiency and DTBPIB has a low reactivity and high efficiency.

The crosslink densities (ν) of the cured EOC vulcanizates with same amounts of curatives as that of PP/EOC TPVs were measured: Table V. DCP and DTBPIB show higher crosslinking densities as compared with TBCP. This correlates well with the ΔS and amount of reactive products by decomposition at a particular temperature. The overall crosslink density ($\nu + \text{PP}$) of the TPVs as a function of concentration of different peroxides is shown in Figure 8. With increasing concentration of peroxide, the value of overall crosslink density

increases. DCP is found to give relatively lower overall crosslink density values compared to TBCP and DTBPIB. DCP apparently has a more pronounced effect on the PP phase to reduce the molecular weight through β -chain scission. Because, PP forms the matrix phase, a significant contribution to the overall crosslink density value is also governed by the PP molecular characteristics.

There is a clear trend of increase in modulus of the TPVs with increase in overall crosslink density. A similar correlation also exists between ΔS values obtained from RPA rheograph for the vulcanized compounds and the overall crosslink densities of the corresponding TPVs. An attempt was made to correlate the change in tensile strength and elongation at break of the TPVs with the crosslink density at various concentrations of different peroxides, but a poor correlation was found, which may be due to the different extent of degradation in the PP-phase for different peroxides.

Differential scanning calorimetry

The influences of the various peroxides on the thermal properties of PP/EOC TPVs were quantified by DSC. DSC melting characteristics of virgin PP, PP/EOC simple blends, and PP/EOC TPVs with varying concentrations of different peroxides are given in Table VI. Generally, in the simple blends and in the TPVs four transitions are observed, glass to rubber transition (T_g) of EOC at -45 to -55°C and glass to rubber transition for PP at 0 – 10°C due to the movement of chains in the amorphous portion, the melting peak of EOC at 45 – 55°C and melting peak of PP at 160 – 170°C . Typical DSC thermograms of the PP,

TABLE VI
DSC Data of PP/EH and PP/EL TPVs With Different Peroxides and Concentrations

Compound name	EOC				PP			
	T_g [$^\circ\text{C}$]	T_m [$^\circ\text{C}$]	ΔH_f [J/g]	CRY [%]	T_g [$^\circ\text{C}$]	T_m [$^\circ\text{C}$]	ΔH_f [J/g]	CRY [%]
PP	–	–	–	–	9	165	98.88	47.76
EH	–54	49	17.24	5.94	–	–	–	–
PP-EH	–50	53	12.88	6.73	4	165	29.57	43.29
D1EH	–51	48	13.82	7.22	4	165	30.45	44.58
D5EH	–48	48	13.05	6.82	9	163	28.37	41.53
T1EH	–50	56	13.53	7.07	3	164	28.25	41.36
T5EH	–46	49	11.02	5.76	8	162	26.54	38.85
DT1EH	–53	50	13.23	6.91	5	164	29.23	42.79
DT5EH	–49	49	10.88	5.68	7	162	25.60	37.48
EL	–54	49	23.16	7.98	–	–	–	–
PP-EL	–49	55	17.05	8.91	4	165	29.03	42.49
D1EL	–47	52	17.58	9.18	5	165	29.47	43.14
D5EL	–47	55	15.78	8.24	9	164	25.36	37.12
T1EL	–50	49	15.00	7.84	5	165	29.61	43.35
T5EL	–47	57	13.43	7.02	6	163	26.08	38.18
DT1EL	–48	54	17.23	9.00	4	165	28.86	42.25
DT5EL	–46	53	14.66	7.66	7	163	26.73	39.13

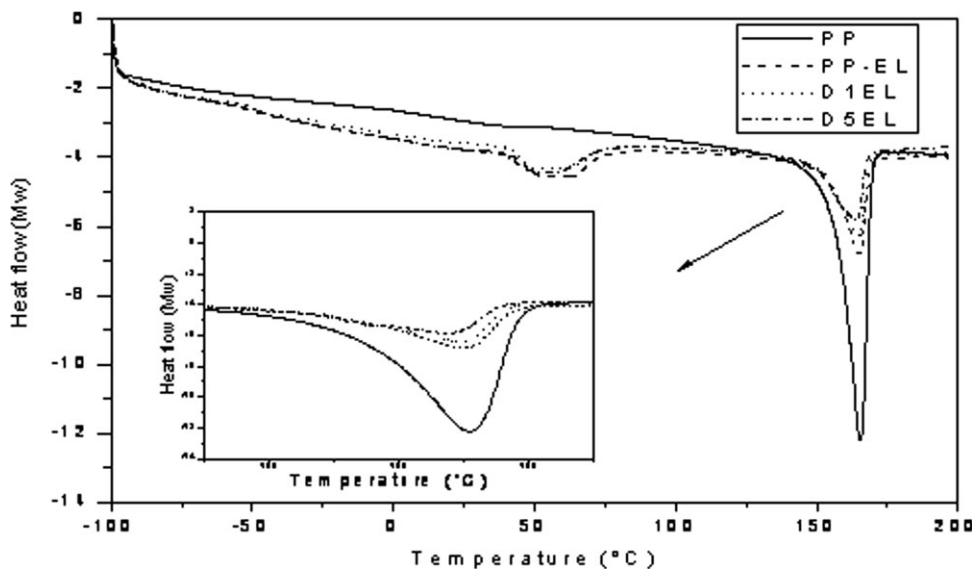


Figure 9 DSC thermograms of virgin PP, PP-EL simple blends, D1EL, and D5EL (inset) Enlarged view of crystalline melting endotherm of PP phase.

PP-EL simple, and PP-EL TPVs are shown in Figure 9 (enlarged view of crystalline melting endotherm of PP phase is shown as inset in Fig. 9). The melting endotherm of the samples shows two distinct T_g -relaxations and T_m 's, indicating heterogeneity of the blend components. It is expected that during melt blending, there occurs an inter-diffusion and molecular level of mixing to some extent between the non-crystalline portion of PP and the amorphous portion of EOC. This is reflected in a move of the T_g values of EOC and PP from their parent position, together with a decrease of heat of fusion. Bielinski et al.³⁰ also reported similar observations on PP/EPDM blends. The heat of fusion value corresponds to the degree of crystallinity of the material. Generally, with the addition of rubbery material to the semi-crystalline thermoplastic, the rubber particles will pass through and be present in the inter- and intra-spherulitic region of the crystalline component of the thermoplastic phase.³¹ Low-molecular-weight EOC in PP/EL blend can easily be trapped inside the spherulites of PP to lower percent crystallinity value of PP than PP/EL simple blend.

It can be observed that, irrespective of the nature of the peroxide used, with increase in concentration of peroxide two major events take place. First the T_g values increase for both EOC and PP components, which is mainly due to restricted chain mobility by crosslinking. Second, the melting endotherm gets diffused for both EOC and PP, which in turn decreases the melting point and lowers the onset of melting. This may be due to the limited extent of crosslinking in PP phase^{32,33} and grafting of EOC on PP^{27,28} (and/or curing of PP and EOC) inhibit the crystallization process of the PP. The marginal

decrease in melting peak of the PP with the peroxide addition indicates a small influence on lamellar thickness. With increasing concentration of peroxide, the percentage crystallinity of PP decreases also for the same reason. DCP and DTBPIB provide typically high crosslinking efficiency and highly reactive radicals for grafting^{27,28,34,35} and may cause some extent of crosslinking in the PP phase as well.^{32,33,36}

Morphology

The mechanical and rheological properties of the blends depend not only on the blend compositions but also on their morphology. In general, the major factors affecting blend morphology are blending ratio, viscosity ratio, and interfacial tension.³⁷ PP and EOC have a very good affinity, which leads to low-interfacial tension.^{38,39} In general, continuity of a phase is favored by a higher volume fraction and low viscosity relative to that of other component.

A qualitative equation has been proposed to predict the point of dual phase continuity based on the blend composition and torque ratio.^{37,40,41}

$$\frac{\phi_1}{\phi_2} \sim \frac{T_1}{T_2} \quad (4)$$

Where ϕ_1 , ϕ_2 are volume fractions and T_1 , T_2 are torque values of phase 1 and phase 2, respectively. Torque values are measured in Haake Rheomix for each polymer at 180°C with a rotor speed of 70 RPM. The use of torque values is a better reflection of the mixing condition since it includes all the viscous and elastic deformations under shear and extension. Despite limitations, eq. (4) can be

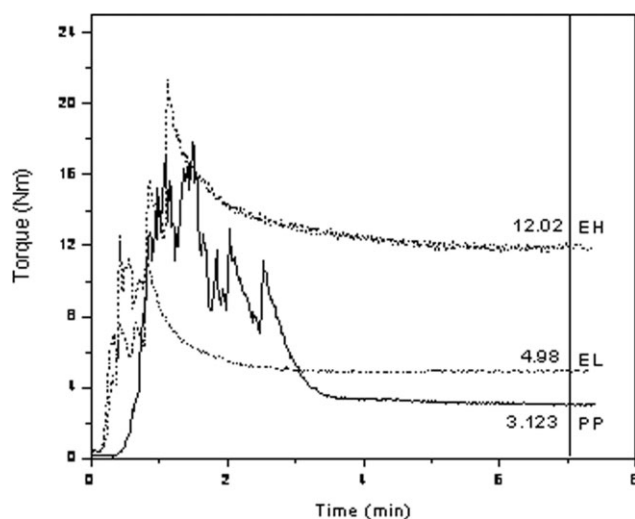


Figure 10 Mixing torque as a function of time for PP, EH, and EL polymers at 180°C under the constant rotor speed of 70 RPM.

modified accordingly for a two phase blend system to qualitatively analyze the morphology evolution.^{40,41}

$$\frac{\phi_1}{\phi_2} \cdot \frac{T_2}{T_1} = X \quad (5)$$

which results in the following morphology variants⁴¹:

$X > 1$: Phase 1 is continuous or matrix and phase 2 is dispersed.

$X < 1$: Phase 2 is continuous or matrix and phase 1 is dispersed.

$X = 1$: dual phase continuity or phase inversion region.

Figure 10 shows the mixing torque-time values for pure polymers, torque values are stabilized at around seventh minute and the corresponding values are taken for calculation. The calculated X values for both 50/100 PP/EH and PP/EL uncrosslinked blends are 1.92 and 0.798, respectively. Hence the deviation of the values from the unity shows that PP forms the continuous phase in PP/EH whereas EOC constitutes the continuous phase in the PP/EL uncrosslinked blends. However dynamic vulcanization leads to drastic change in morphology as a result of crosslinking in the rubbery phase. An ideal thermoplastic vulcanizate is characterized by major crosslinked rubber domains dispersed in a minor continuous thermoplastic matrix although the rubber content is higher than the thermoplastic component to maintain the thermoplasticity of blends.

To get a good insight into the morphology, for the uncrosslinked blends the EOC phase was preferentially extracted and for the dynamically crosslinked

blends the PP phase was preferentially extracted before the SEM observations. The phase morphologies of uncrosslinked and dynamically crosslinked PP/EH blends with varying peroxide type and concentration are illustrated in Figures 11(a–e). In the PP/EH, uncrosslinked blends [Fig. 11(a) with EOC etched], a high degree of cocontinuity is observed, i.e., both components form an interpenetrating network-like phase morphology. According to the theoretical prediction, PP forms the matrix phase in PP/EH uncrosslinked blend, but SEM analysis shows cocontinuous phase morphology. Because EH is a high-molecular-weight copolymer that exhibits higher viscosity, and the composition is also double that of PP composition. Therefore, EH exhibits higher tendency toward coalescence and shows sign of cocontinuous phase morphology. This may be held responsible for the higher elongation at break value during tensile testing. In fact, at various compositions above the threshold, various levels of continuity exist. It is expected that percentage continuity of PP is more than that of EOC in 50/100 PP/EH blend ratio. This leads to the inference that the coalescence of the uncured rubber droplets played an important role in controlling the morphology of the uncured blend samples. Further with the addition of curatives under dynamic conditions, EOC gets crosslinked and PP undergoes degradation. This leads to an increase in viscosity ratio, which plays an important role in driving the morphology from cocontinuity to dispersed phase morphology. The less viscous PP encapsulates the most viscous crosslinked EOC phase to minimize mixing energy.^{25,41,42} Larger crosslinked domains is observed at lower concentration of peroxide (1 meq DCP) [Fig. 11(b)], further with increase in the concentration of peroxide (5 meq DCP) effective particle break down predominates to form smaller crosslinked domains dispersed uniformly in the matrix [Fig. 11(c)]. A speculative model of morphology development in the dynamically vulcanized samples with special reference to the extent of curing is depicted by Thomas et al.²⁶ Among the three different peroxides, the efficiency and reactivity of these peroxides have an important effect on the morphology formation of the TPVs. DCP and DTBPIB produce highly reactive radical and their amount is also high enough to give a higher degree of vulcanization than TBPCP. It is clear from Figures 11(c–e) that the DCP and DTBPIB cured TPVs show very small crosslinked rubber domains dispersed throughout the PP matrix in the form of aggregates and/or agglomerates.²⁵ The aggregates and/or agglomerates are embedded in the PP macromolecules via a joint shell mechanism and/or segmental interdiffusion mechanism.⁴² The TBPCP-cured TPV shows relatively large and nonuniform crosslinked rubber domains.

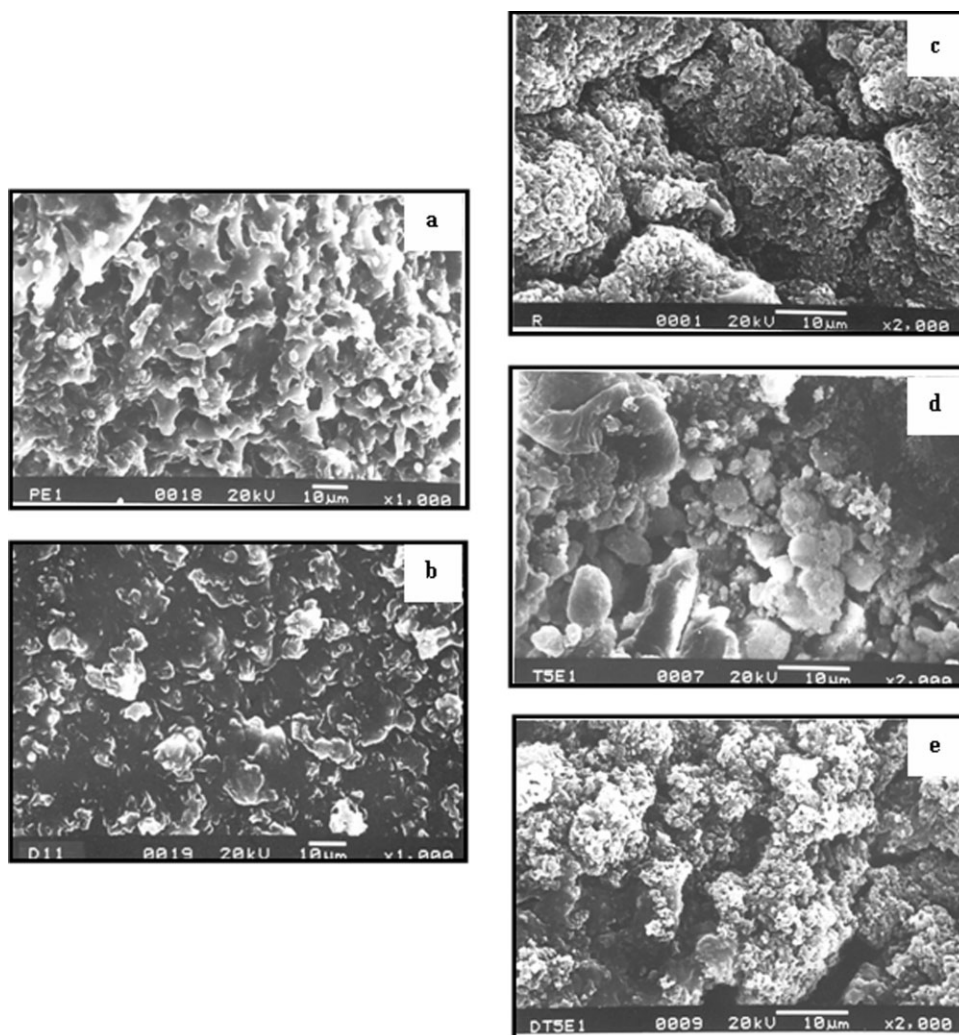


Figure 11 SEM photomicrographs of 50/100 PP/EH TPVs without and with various peroxides: (a) uncrosslinked, (b) DCP (1 meq), (c) DCP (5 meq), (d) TBCP (5 meq), and (e) DTBPIB (5 meq).

Although the DCP- and DTBPIB-cured TPVs show small crosslinked rubber domains, the mechanical properties are not good, which may be due to severe degradation of the PP matrix phase.

Figures 12(a–e) show the PP/EL-based uncrosslinked and dynamically crosslinked blends. Because EL is a low-molecular-weight polymer and is also present in greater proportion than PP, it tends to form the matrix phase and PP as dispersed phase. In the uncrosslinked blend [Fig. 12(a) with EOC etched], elongated and spherical particles of PP are seen, as dispersed in the EOC matrix. During dynamic vulcanization a complete phase inversion occurs, to form crosslinked EOC dispersed in the PP matrix. It is to be noted that in PP/EH the dynamic crosslinking progresses to form a dispersed phase morphology from a dual cocontinuous morphology, whereas in PP/EL a complete phase inversion occurs. This is reflected in the tension set measurements (Fig. 7) and elongation at break values

(Fig. 4). In PP/EH, there exists a gradual decrease in set values with increasing peroxide concentrations, but in case of PP/EL the uncrosslinked blend shows the lowest set value, whereas the dynamically crosslinked ones show higher set values. In PP/EL, there exists a minimal effect of peroxide on the elongation at break, EL is a low-molecular-weight copolymer, which forms the matrix phase in uncrosslinked blends, thereby shows lower elongation at break. After dynamic vulcanization, PP forms the matrix phase which limits the extensibility of TPVs and the dispersion of crosslinked EL domains is more pronounced in reinforcement effect which is reflected in the improvement in 100% modulus values. It is clear from the Figures 12(b,e), coarse distribution pattern of crosslinked EOC domains are narrow down as the concentration of peroxide (DTBPIB) is increased. When comparing the phase morphology of the three different peroxides [Fig. 12(c–e)], DCP shows small crosslinked rubber domains, uniformly dispersed in

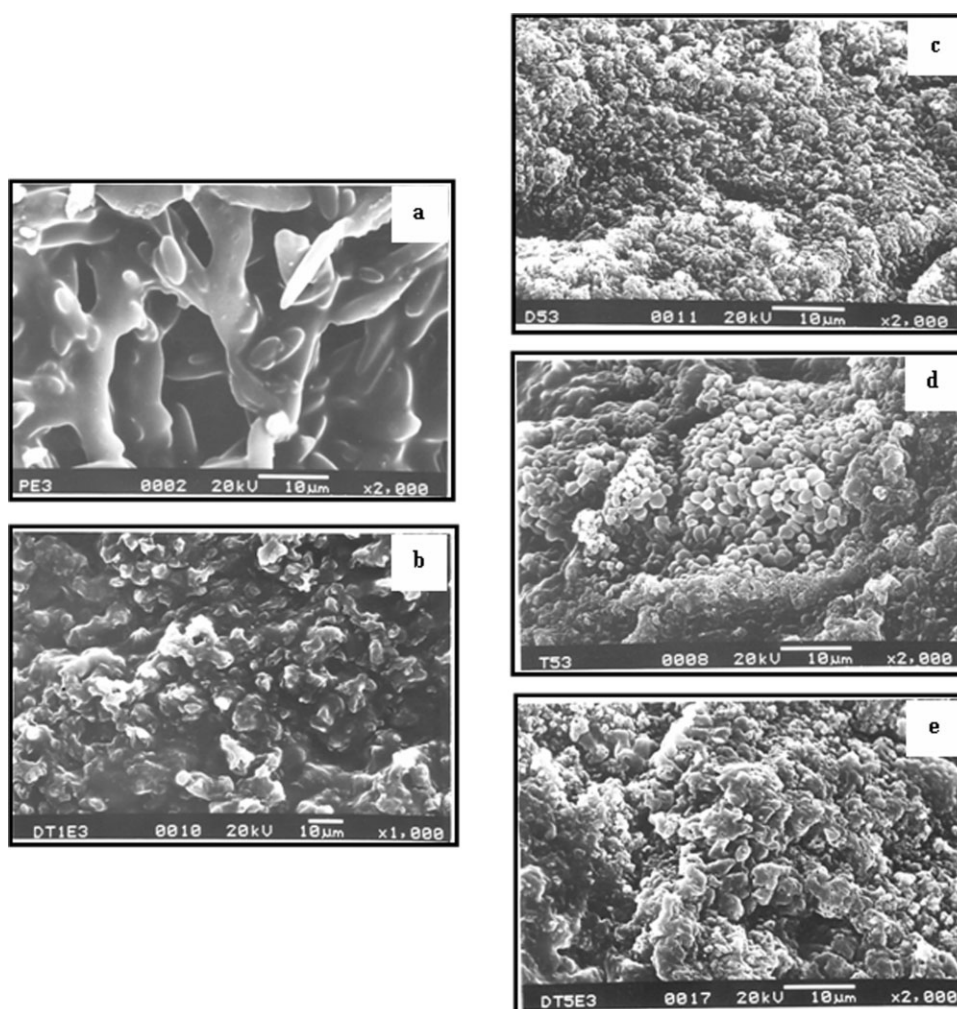


Figure 12 SEM photomicrographs of 50/100 PP/EL TPVs without and with various peroxides: (a) uncrosslinked, (b) DTBPIB (1 meq), (c) DCP (5 meq), (d) TBCP (5 meq), and (e) DTBPIB (5 meq).

the PP matrix, whereas TBCP and DTBPIB show relatively large crosslinked rubber domains. The above-mentioned morphological evaluations are in good agreement with the theoretical prediction and in line with the effectiveness of corresponding peroxides. The above morphological evaluation is reflected in the mechanical properties of the corresponding PP/EOC TPVs.

The SEM investigation shows that irrespective of different peroxide used, finer dispersion of crosslinked domains are developed in the TPVs containing low-molecular-weight EOC, i.e., in PP/EL TPVs. This can be explained by the decrease in the viscosity difference between the two phases. In other words, phase viscosity ratio of dispersed and matrix phase is responsible for the determination of domain size i.e., size of the crosslinked domains decrease as the viscosity ratio is lowered. Similar conclusions were reached by Goharpey et al.⁴² on studying PP/EPDM TPVs.

In brief, with the addition of a coagent-assisted peroxide cure system in the PP/EOC blends, two major competing reactions take place simultaneously: (i) EOC crosslinking and (ii) PP degradation along with two minor reactions (i) *in situ* grafting of PP with the EOC and (ii) a limited extent of crosslinking in the PP phase. The selection of the best peroxide for a particular blend system depends primarily on the extent of all the four reactions, and it is necessary to understand the intricate behavior of the different peroxides as to their performance characteristics.

Tensile fractography

Tensile fracture surfaces of the uncrosslinked and dynamically crosslinked PP/EOC blends of both series are shown in Figures 13(a–g), which were examined to study the deformation characteristics and mode of failure under applied tensile load. Low

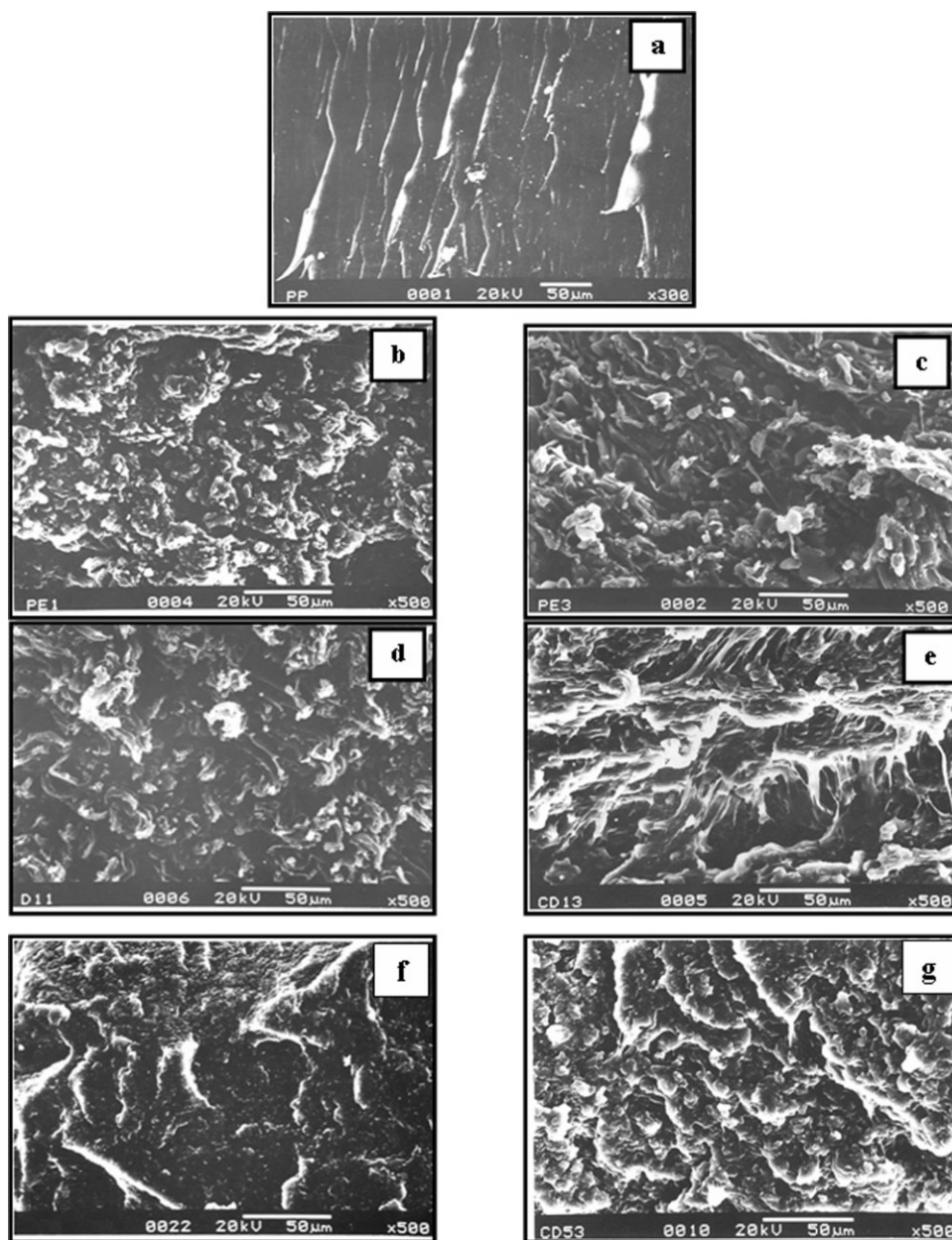


Figure 13 SEM photomicrographs of tensile fracture surface (a) neat PP, (b) PP-EH, (c) PP-EL, (d) PP-EH with 1 meq of DCP (D1EH), (e) PP-EL with 1 meq of DCP (D1EL), (f) PP-EH with 5 meq of DCP (D5EH), (g) PP-EL with 5 meq of DCP (D5EL).

magnification SEM micrograph of neat PP [Fig. 13(a)] shows that fracture occurs through the formation of planes of cracks parallel to each other, such observation agree with the brittle mechanism of fracture.⁴³ Binary blends of PP-EH [Fig. 13(b)] shows rough surface with rounded dimples due to existence of highly interpenetrating network structure (sea sponge structure)⁴⁴. When the test specimen undergoes failure high molecular weight EOC species recoil in to spherical lumps due to their inherent elasticity. The high elongation at break is due to higher content of high molecular weight EOC phase

with PP phase. In case of PP-EL, PP particles adhere strongly to the low-molecular-weight EOC matrix resulting to exhibit numerous thin ligaments connected to PP particles to the deformed matrix [Fig. 13(c)]. This indicates that PP and EL adhesion is good enough to prevent de-bonding during tensile test. The above behavior of the blends is guided by the morphology of the two phase system. The nature of the stress-strain curves also supports these micrographs.

Addition of 1 meq concentration of peroxide in PP-EH blend [Fig. 13(d)] results to show clear coarse

fibrous surface with highly stretched regions. It is expected that limited extent of degradation of PP phase may cause to produce plastic deformation, and thus ductile fracture mechanism is active. In case of PP-EL [Fig. 13(e)], ductile type of failure with the formation of thin ligaments or microfibrils of matrix phase is observed. Addition of 5 meq concentration of peroxide in both PP-EH and PP-EL blends drastically modifies the fracture mechanism from ductile to brittle [Fig. 13(f,g)]. High degree of crosslinking in EOC coupled with the severe degradation of PP phase results to exhibit brittle type of failure, with the formation of smooth surface with discontinuous fracture path in different planes.⁴³ Similar observation is observed in the tensile failure of styrene butadiene styrene block copolymer.⁴⁵

CONCLUSIONS

TPVs based on PP and EOC were prepared using coagent-assisted peroxide crosslinking systems. The effects of various types and concentrations of the peroxides on the two series of PP/EH and PP/EL vulcanizates were investigated. The choice of the best peroxide to fulfill specific requirements should not be made entirely on the basis of the peroxide efficiency and reactivity at a particular temperature. The above study clearly illustrates the complexity associated with the peroxide activity for a given polymer system.

From the cure characteristics and relative decomposition products the peroxides under investigation can be depicted as follows: DCP has a high reactivity and high efficiency; TBCP has a low reactivity and low efficiency; and DTBPIB has a low reactivity and high efficiency. The physical properties of the TPVs of both series depend not only on the extent of crosslinking in the EOC phase, but also on the extent of degradation of the PP phase, as evidenced in the crosslink density values and mechanical properties. The modulus of the TPVs shows a good correlation with the ΔS values of corresponding equivalent crosslinked EOC compounds without PP. DSC and phase morphology studies clearly indicate the heterogeneity of the blends. In PP/EH, dynamic crosslinking progresses to form a dispersed phase morphology from a dual cocontinuous morphology, whereas in PP/EL complete phase inversion occurs to form crosslinked rubber dispersed as domains in a continuous PP matrix. A good correlation is observed between the phase morphology and mechanical properties for both the series of TPVs. The tensile fracture surface of PP/EOC TPVs showed that failure mechanism changes from ductile to brittle with increase in concentration of peroxide. Degradation in PP is more prominent than crosslinking effect in EOC phase to exhibit brittle failure.

In general, *tert*-butyl cumyl peroxide (TBCP) gives the best overall balance of properties for the PP/EH system, whereas DCP shows the best for the PP/EL system. The PP/EL blend system requires a relatively higher concentration of curatives as compared with the PP/EH system, to achieve an optimum level of physical properties.

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