

Dynamically Vulcanized Blends of Polypropylene and Ethylene Octene Copolymer: Influence of Various Coagents on Thermal and Rheological Characteristics

R. Rajesh Babu, Nikhil K. Singha, Kinsuk Naskar

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

Received 22 September 2009; accepted 27 December 2009

DOI 10.1002/app.32023

Published online 29 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The present study focuses on the influence of the three structurally different coagents, namely triallyl cyanurate (TAC), trimethylol propane triacrylate (TMPTA) and *N,N'*-*m*-phenylene dimaleimide (MPDM) on the thermal and rheological properties of thermoplastic vulcanizates (TPVs) based on the polypropylene (PP) and ethylene octene copolymer (EOC). Depending on the structure and reactivity, different coagents show different behaviors. All the TPV compositions were made by melt mixing method in a Haake Rheomix at 180°C. Rheological properties have also been evaluated at the same temperature. Viscoelastic properties of the TPVs were analyzed by a dynamic oscillatory rheometer in the melt state in a Rubber Process Analyzer (RPA 2000). Morphologically, TPVs consist of dense cross-linked rubber domains dispersed in a continuous thermo-

plastic matrix. The crosslinked rubber particles have a tendency to form agglomerates and build local clusters which undergo disintegration by shearing. A variety of rheological characteristics such as Payne effect, shear rate sensitivity, modulus recovery and dynamics of relaxation were studied by performing strain sweep, frequency sweep and stress relaxation tests. Among the various coagents taken for investigation, MPDM-based TPVs show improved dynamic functions (complex modulus and complex viscosity) and lower rate of stress relaxation over TAC, TMPTA and the control sample without any coagent. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1578–1590, 2010

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

INTRODUCTION

Thermoplastic vulcanizates (TPVs) are a very special type of thermoplastic elastomers (TPEs) prepared by melt blending technique and comprise of the fastest growing in the family of TPEs.^{1,2} They are prepared by reactive blending of rubber and thermoplastic, in which the rubber phase is crosslinked under dynamic condition using a suitable crosslinking agent. TPVs based on polypropylene (PP) and ethylene propylene diene rubber (EPDM) using activated phenolic resins were widely studied because of their commercial importance.^{1–3} Naskar et al.^{3,4} extensively studied the structure–property relationship of various peroxides cured PP/EPDM TPVs. Ethylene octene copolymer provides better toughening characteristics to PP. Lai et al.⁵ studied the fracture mechanism of a PP-metalocene-based EOC thermoplastic vulcanizate by peroxide crosslinking. Effect of differ-

ent peroxides on the PP/EOC TPVs was recently investigated by the authors.⁶

To extend the scope of investigation, influence of different coagents at fixed concentration of peroxide on the mechanical and morphological characteristics of PP/EOC TPVs were studied and reported.⁷ Among the various coagents taken, *N,N'*-*m*-phenylene dimaleimide (MPDM) showed the best overall balance of mechanical properties. Morphology analyzes support the same with the formation of the smallest particle size. MPDM is shown to effectively behave as a booster as well as a reactive compatibilizer to enhance the formation of *in situ* copolymer at the interface in presence of peroxide in PP/EOC TPVs. To further support the compatibilizing efficiency of MPDM, melt rheological characterization is carried out to get valuable information about the interfacial adhesion in the melt state. Knowledge of rheological properties can provide better understanding about the compatibility of the blend in the melt state together with melt processing characteristics.^{8,9}

Rheological behavior of the blends mainly depends on the type of morphology formed as well as interfacial interaction. In the solid state, the properties of the TPVs are determined primarily by the matrix molecular weight (which has a direct consequence on the percent crystallinity and entanglement density), extent of crosslinking, degree of dispersion, size and

Correspondence to: K. Naskar (knaskar@rtc.iitkgp.ernet.in).

Contract grant sponsor: Council for Scientific and Industrial Research, CSIR, New Delhi, India.

deformability of dispersed phase as well as morphology produced. In the melt state, changes in the morphology originating from matrix molecular weight can be excluded and the influence of other factors can be of more importance. Numerous studies related to the rheological properties of dynamically vulcanized blends have been reported.^{10–13} They demonstrated that the TPV has a yield stress and that increases with increasing loading of rubber and show more shear thinning characteristics than that of neat PP or its uncrosslinked blends. Morphologically, TPVs consist of dense crosslinked rubber domains dispersed in the thermoplastic phase and their rheological behavior can be compared to that of highly filled polymers. The crosslinked particles tend to agglomerate and build local cluster which tends to disintegrate by shearing. Information obtained from rheological studies such as strain sweep and frequency sweep of TPVs can be used to understand the mechanism of reinforcement and shear rate sensitivity. Coran and Patel¹⁴ studied the reactive compatibilization and dynamic vulcanization on the PP/nitrile rubber (NBR) blends using phenolic resin as a curative. The added phenolic resin acts as crosslinking agent for NBR and also as a compatibilizer to intensify the phase interaction. Corley and Radusch¹⁵ studied the physically compatibilized dynamic vulcanization using maleic anhydride grafted PP and an amine terminated NBR for compatibilization in PP/NBR blends. Both *in situ* and premade block and graft copolymers were successfully used to intensify the interfacial interactions of PP and NBR to gain a thermoplastic vulcanizates with both improved mechanical and oil resistance properties. It is expected that coagents can be effectively used as a reactive compatibilizer for peroxide cured PP/EOC TPVs.

The present article deals with a comprehensive insight into the thermal and rheological behavior of PP/EOC TPVs with special reference to the addition of different coagents.

EXPERIMENTAL

Materials

The general purpose polyolefin elastomer Exact[®] 5371 (specific gravity of 0.870 g/cm³ at 23°C; comonomer (octene) content of 13 (mol %); melt flow index (MFI) of 5.0 g/10 min at 190°C/2.16 kg), was procured from Exxon Mobil Chemical Company. The octene content of these Exact copolymers was determined from ¹H-NMR experiment. Polypropylene (PP; specific gravity of 0.9 g/cm³ at 23°C; MFI of 3.0 g/10 min at 230°C/2.16 Kg) 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 of 1.53

g/cm³ at 23°C) was used as the crosslinking agent obtained from Akzo Nobel Chemical Company, The Netherlands. Three structurally different coagents namely, triallyl cyanurate (TAC), trimethylol propane triacrylate (TMPTA) and *N,N'*-*m*-phenylene dimaleimide (MPDM) were obtained from Sartomer Company. Their chemical names and corresponding structures were given in elsewhere.⁷

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 constant torque value was reached. Dynamic vulcanization was carried out by adding coagent assisted peroxide curative system and time of vulcanization (4 min) was kept constant for all the compositions. The compositions of PP/EOC TPVs employed and the corresponding designation is shown in Table I. The different coagents have different molecular weight 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 at hot condition 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 foils were placed between the mold plates. The molded sheets were then cooled down to room temperature under the same pressure.

Testing procedures

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements (around 6 mg of sample weight) were carried out in a TA instrument, (Model DSC Q100 V 8.1) in the temperature range of –100°C to 200°C at a heating (scanning) rate of 10°C/min under nitrogen atmosphere. The sample underwent a series of scans: (a) first heating followed by (b) cooling, and (c) second heating at the same rate of 10°C/min. The degree of crystallinity of PP was determined from the heating curve by using the following relation:

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

where X = Percentage of crystallinity (%)

TABLE I
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 ^a	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38
TAC	–	0.83 (10) ^b	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)

^a Concentration of DCP was optimized as 3.38 phr⁶ which corresponds to 5 milliequivalent concentration.

^b Values in the parentheses correspond to the milliequivalent concentration of respective coagent.

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

$\Delta H_{C100\%}$ = Extrapolated value of the melting enthalpy of crystallization of

100% crystalline sample, for PP the value is 209 (J/g)^{6,7}

W_i = Weight fraction of PP in the blend

Morphology

Phase morphology of the cryofractured samples of various blends was investigated by a JEOL JSM 5800 digital scanning electron microscope (SEM). All the blends were cryofractured in liquid nitrogen to avoid any possibility of phase deformation during cracking 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.

Rheological characterizations

Melt rheological behaviors of the TPVs were analyzed in a Rubber Process Analyser (RPA 2000, Alpha Technologies) equipped with conical test fixtures. All the specimens were directly loaded between the dies maintained at 180°C and the tests were carried out in both frequency and strain sweep modes.

Frequency sweep

The frequency was logarithmically increased from 0.33 to 33 Hz at constant strain amplitude of 5%. A strain of 5% was selected to ensure that the rheological behavior was located in the linear viscoelastic region.

Strain sweep

The strain amplitude sweep was performed from 1–1200% at a constant frequency of 0.5 Hz. The duration of each step strain is around 24 sec.

Modulus recovery

To determine the recovery kinetics, each sample underwent the following test sequences: (a) frequency sweep, (b) strain sweep (c) relaxation time of 2 min, (d) frequency sweep, (e) strain sweep, (f) relaxation time of 2 min, (g) frequency sweep, and (h) strain sweep. All the tests were carried at a temperature of 180°C. Average of three measurements was reported for each sample.

Stress relaxation

Stress relaxation experiments were also carried out in RPA 2000 with the step strain of 70% (5° arc) at 100°C. In general, for rubbery materials like TPEs and TPVs, the applied or step strain might be far above the linear viscoelastic limit.¹⁶ A preheating time of 60 sec is given to all the samples prior to the application of step strain. Stress relaxation decay time was selected up to 100 sec.

Capillary rheometer

Flow properties were determined using a capillary rheometer (Smart Rheo, Ceast, Italy). The flow curves and melt fracture behavior were measured at different temperatures by using 40 : 1 *L* : *D* ratio capillary die.

RESULTS AND DISCUSSION

Reaction mechanism

The reaction mechanism of peroxide vulcanization of saturated polymer is well known. Generally in peroxide vulcanization, along with desirable reactions (which lead to effective crosslink formation) several competing reactions (rearrangement, transfer, scission, etc.) also occur simultaneously. The balance between the productive and competitive reactions depends on type of polymer and other additives (fatty acids, oils, antioxidants, etc.) present in the system.¹⁷ Addition of coagent suppresses the competing reactions and also imparts additional

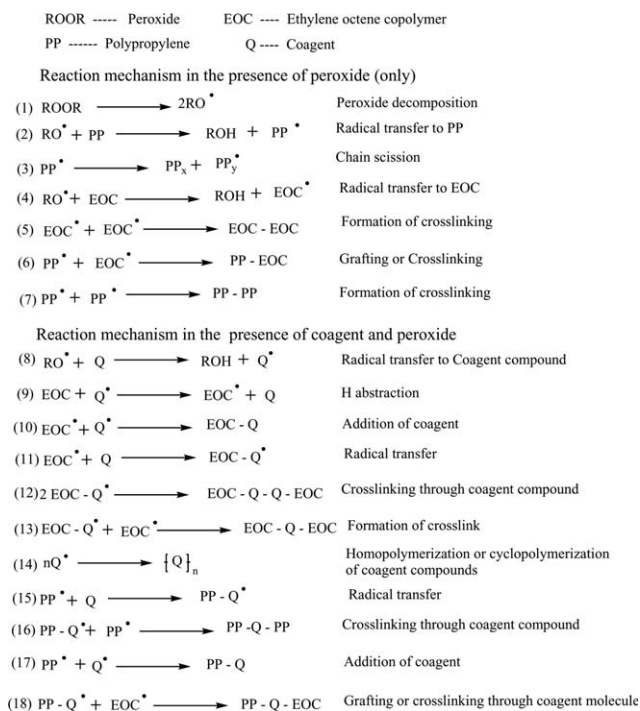


Figure 1 Simplified reaction scheme of coagent assisted peroxide cured PP/EOC blend.

crosslinks. The mechanism of coagent assisted peroxide system has been a topic of debate for many years.^{17,18} The major component in this blend system is EOC (50/100 PP/EOC), generation of free radicals and subsequent crosslink formation in EOC are the major reactions. However, chain scission of PP by peroxide also occur simultaneously (more pronounced at higher concentration of peroxide). Figure 1 shows the simplified reaction of coagent assisted peroxide crosslinking in PP/EOC TPVs.

The reactivity and efficiency of a coagent depend mainly on the chemical structure of the coagent and the type of polymer used.¹⁸ It is very clear from Figure 1 that the reactions occur in more complex way and the final properties are basically the interplay of aforementioned reactions. Different coagents have different dimensions to the aforementioned reactions. Equations (1)–(7) show the plausible reactions in absence of coagent and eqs. (8)–(18) represent the reaction in presence of coagent in peroxide cured PP/EOC TPVs. Although cross-curing at the interface [eq. (6)] and PP crosslinking [particular at higher concentration of peroxide; eq. (7)] were possible in the absence of coagent, but crosslinking in EOC [eqs. (4) and (5)] and degradation in PP [eqs. (2) and (3)] overrides the former. It is expected that, coagent molecules stabilize the reactive radicals and aid in formation of additional crosslinks. As all the coagents contain terminal unsaturation, addition reaction and hydrogen abstraction are the principle mechanism by which coagents react with the poly-

mer. Coagent molecules generate additional crosslinks in the EOC via eqs. (8)–(13). Furthermore, PP fragmentation is not completely eliminated by the use of coagent, but can be limited to greater extent. Coagent molecules react directly to the PP radicals before deleterious chain scission [eqs. (15)–(17)] and form a more stable polymer radical. This intermediate shows a favorable tendency towards crosslinking or grafting to another polymer radical [eq. (18)]. Coagent molecules can also homopolymerize and/or cyclopolymerize due to the presence of vinyl unsaturation sites [eq. (14)]. Thereby in the final network, polymer chains may be connected with the coagent molecules ranging from one to several between the crosslinks.¹⁹

Thermal properties

DSC thermograms were investigated to study the crystallization and melting behavior of the samples. DSC provides information about the microstructural changes that take place in both the phases with the addition of coagent assisted peroxide crosslinking system. The effect of addition of coagent on the thermal properties such as glass transition temperature (T_g), melting temperature (T_m), heat of fusion (ΔH_f) and % crystallinity (X_c) of PP/EOC TPVs were listed in Table II. Melting endotherm and crystallization exotherm at 20 mequiv concentration of different coagents are shown in Figure 2. Irrespective of nature of different coagents used, T_g increases marginally, T_m decreases, and X_c decreases gradually for both EOC and PP components as a function of coagent concentration. These results clearly emphasizes the addition of coagent affects the microstructural arrangements of polymer chains in both the phases (EOC and PP). In general, addition of coagent increases the crosslink density in EOC phase and decreases the degradation in the PP phase. The changes in the EOC phase are mainly attributed due to the increase in crosslink density in the EOC phase. With increasing crosslink density, the freedom of movement of polymer chains decreases and thereby limits the crystallizing tendency (decrease of perfectness of crystals). In PP matrix, the melting characteristics were determined by various factors and discussed in our previous paper.⁶ It is a matter of fact, lowering of molecular weight by chain scission reaction favors to increase the % crystallinity. Decrease in chain length have higher tendency to orient in the crystallization process without any restrictions imposed by entanglements.²⁰ Interestingly, X_c of PP decreases continuously with addition of concentration. Coagent sufficiently absorbs the free radicals in the PP chains before β -chain scission and thereby limits the degradation effect. Apart from that, addition of coagent aid in enhancing the

TABLE II
DSC Data of Dynamically Vulcanized Blends with Varying Coagent Concentrations

Compound name	EOC				PP			
	T_g (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%)
DC0	-47	59	16.06	8.39	6	166	28.84	42.21
DC10	-46	58	13.74	7.17	5	166	28.17	41.23
DC20	-46	56	13.26	6.92	5	165	27.65	40.47
DC30	-46	53	12.17	6.35	6	165	26.23	38.39
DA10	-45	54	14.52	7.58	5	165	28.59	41.82
DA20	-46	50	14.21	7.41	6	163	27.76	40.63
DA30	-46	50	14.14	7.38	6	163	26.38	38.61
DM10	-47	54	15.13	7.90	7	163	27.89	40.82
DM20	-46	53	14.96	7.81	6	162	27.31	39.97
DM30	-42	53	11.71	6.11	6	162	25.79	37.75

cross curing tendency [grafting of either components; eq. (18)], and grafting or addition of only coagent molecules in the PP chains [eqs. (10) and (17)] and limited extent of crosslinking in the PP macromolecules [eqs. (15) and (16)]. The combined effects of aforementioned reactions result to restrict the spherulithes growth of PP and correspondingly decrease the crystallinity. Among the coagents taken, MPDM-based TPVs show most favorable thermal properties of reduced % crystallinity. At 30 mequiv concentration of MPDM, T_m of PP decreased from 165°C to 161°C and X_c of PP decreased to about 5% than control (TPV without any coagent) sample. MPDM is expected to be acting as both crosslinking agent and compatibilizer (in terms of increasing interfacial reaction by *in situ* graft copolymer formation or cross curing) and correspondingly affect the melting characteristics of both PP and EOC.

Morphology

The morphological features as obtained from the field emission scanning electron microscopy (FESEM) for PP/EOC TPVs without and with three different types of coagents at equal concentration were discussed in our previous article.⁷ However, in order to visualize the nature of dispersed phase, SEM photomicrographs of the TPVs without (control) and with 20 mequiv concentration of MPDM (DM20) are shown in Figure 3 (in which PP matrix phase was preferentially extracted). Although, the particle size decreases with the addition of coagent (MPDM), difference in the particle size with varying the coagent type is not very clear (not shown) in the given experimental window. As the particle size decreases, the tendency to form localized network structure or agglomerated structure among the particles increases due to closed proximity of the particles. The presence of localized crosslinked EOC domains embedded in the PP matrix by joint shell mechanism or segmental interdiffusion mechanism has been proposed.^{6,7,13} The morphological analyzes

could not give a clear variation and distribution in particle size. Therefore, the evolution of network structure formed by crosslinked rubber particles could be investigated in detail by nonlinear shear experiments.

Rheological properties

Strain dependence of viscoelastic behavior

The strain dependent rheological properties of 50/100 PP/EOC TPVs prepared by three different coagents are represented in Figure 4. Dynamically vulcanized blends show significant increase in dynamic modulus and viscosity values (dynamic functions) than unvulcanized blend. As expected, coagent assisted dynamic vulcanization further increased the dynamic functions than the control (TPV without any coagent).

In a filled elastomer system, with increasing strain amplitude at a constant frequency, dynamic storage modulus decreases, commonly termed as "Payne

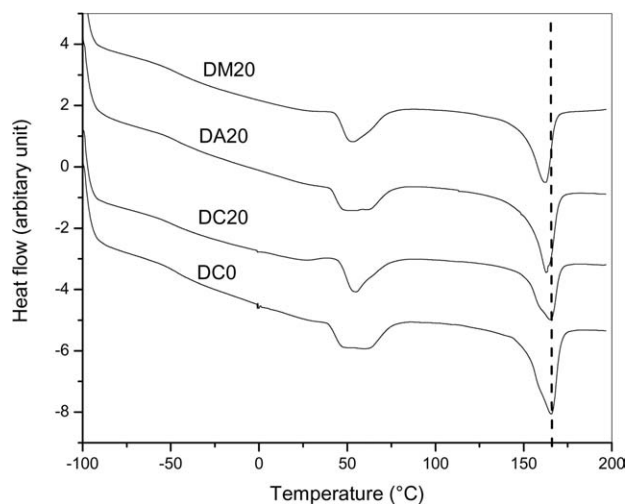


Figure 2 DSC thermograms of dynamically crosslinked blends without and with 20 mequiv concentration of different coagents.

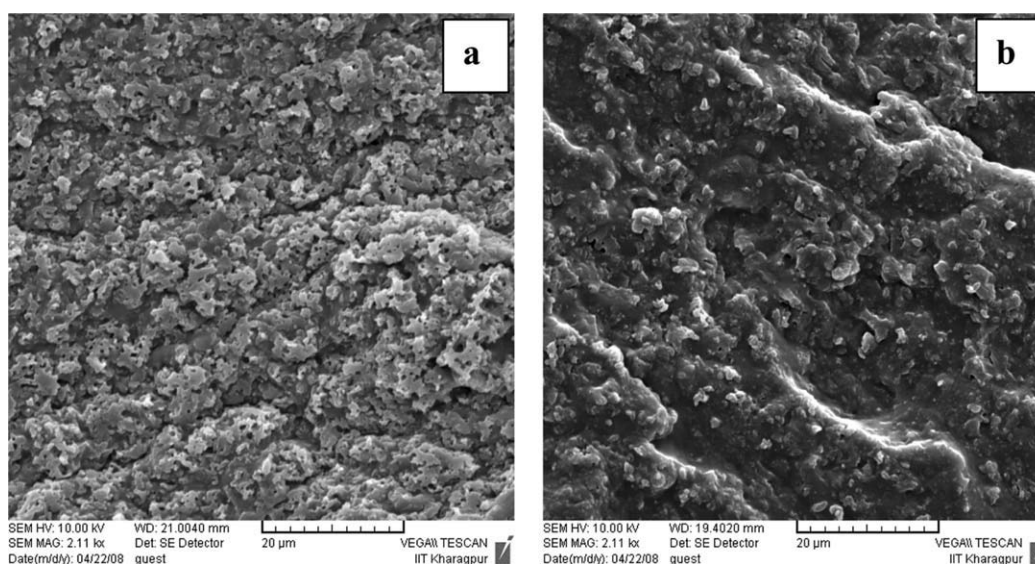


Figure 3 SEM photomicrographs of dynamically vulcanized PP/EOC TPVs. (a) Control (without coagent); (b) 20 mequiv concentration of MPDM.

effect.” The decrease in dynamic functions is related to the disintegration of secondary structures.²¹ TPVs show more progressive nonlinear behavior i.e., decrease of dynamic functions with increasing strain amplitude. [Fig. 4(a)]. In TPVs, the secondary structure corresponds to the agglomeration and/or aggregation of crosslinked EOC particles dispersed in the continuous PP matrix.²² Indeed the nonlinearity in TPVs may also relate to the debonding and rebonding of EOC dispersed phase from the PP matrix phase. In case of uncrosslinked blend, the nonlinearity at high strain is due to both disintegration of entanglement network and debonding of molecules of PP anchored in EOC matrix phase. The critical strain amplitude (γ_c), where the nonlinearity starts is related to the nature of the secondary network structure formed by

the dispersed phase. The variations in the strain dependent viscoelastic property between the coagents are mainly related to the state and mode of formation of the secondary network domains dispersed in the continuous PP phase. Among the coagents, MPDM shows increased dynamic functions and more nonlinear behavior followed by TAC and TMPTA (Table III). From the morphological analyzes presented in our earlier paper,⁷ MPDM-based TPV is found to exhibit smaller crosslinked particles and less phase heterogeneity. Therefore, it is expected that, smaller particles can impart greater storage modulus and more nonlinear behavior. These may be attributed to the two plausible effects: first, reduction of particle size by improving the interfacial interaction tends to increase both modulus and viscosity values. Second,

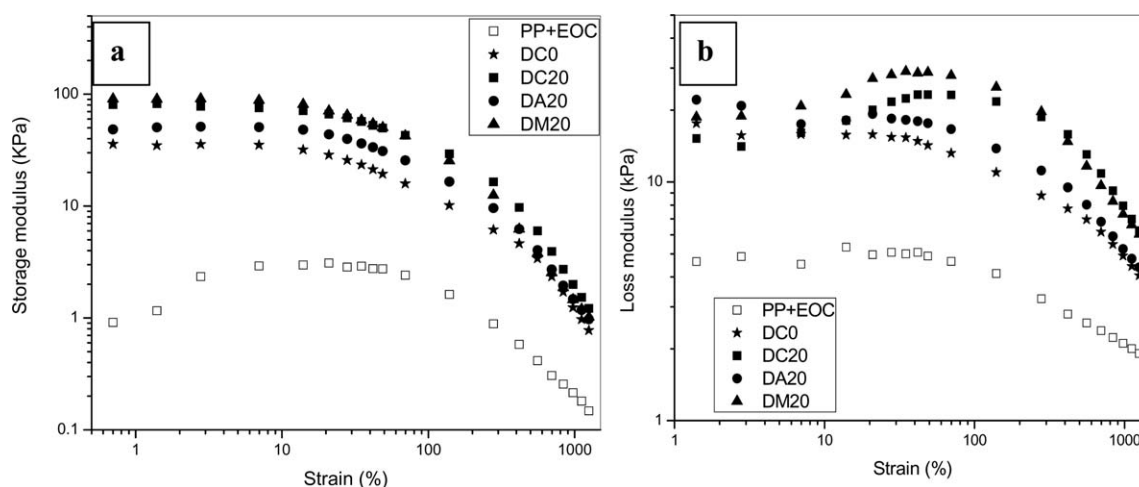


Figure 4 Variation of dynamic function as a function of strain amplitude for uncrosslinked and dynamically crosslinked blends at 180°C. (a) Storage modulus, (b) loss modulus.

TABLE III
Rheological Parameters and Values Observed from the Strain Sweep Experiments

Compound name	First run				Second run				Third run			
	G_0^a	G_∞^b	γ_c^c	$\tan \delta = 1^d$	G_0	G_∞	γ_c	$\tan \delta = 1$	G_0	G_∞	γ_c	$\tan \delta = 1$
DC0	34.8	0.773	15.2	110	33.6	0.659	7.2	61	32.1	0.650	6.3	54
DC20	82.6	1.212	6.1	203	63.3	1.052	5.4	88	62.5	1.021	4.8	80
DA20	50.2	0.972	5.7	198	41.8	0.932	5.1	66	40.2	0.921	4.5	62
DM20	92.3	1.023	5.3	146	90.3	0.941	4.8	101	89.4	0.931	4.1	92

Note: Average of three measurements were reported.

^a Low-strain storage modulus (modulus at 2% strain) (kPa).

^b High-strain storage modulus (modulus at 1200% strain) (kPa).

^c Critical strain amplitude (strain at 90% G_0 ; 0.9 G_0) (%).

^d Strain amplitude at $G' = G''$ (crossover point) (%)

these small particles have higher tendency to agglomerate or aggregate, which results in more nonlinear behavior. In other words, it can be stated that presence of secondary clusters or network domains increases the viscosity and in turn enhance the viscoelastic nonlinearity.

The strain dependence of loss modulus (G'') with and with coagent is presented in Figure 4(b). Evidently loss modulus also increased with the coagent addition throughout the strain level studied. G'' shows a well defined peak at the critical strain amplitude region. It may be related to the energy dissipation produced by the breakdown and reformation of secondary network formed by crosslinked EOC domains.²³ TPVs exhibit more elastic behavior at low strain region i.e., $G' > G''$, with increasing deformation TPVs become progressively more viscous and two curve intersect at $G' = G''$ ($\tan \delta = 1$) and the corresponding strain amplitude is mentioned in the Table III. Among the various coagents used, MPDM-based TPVs show higher dynamic modulus and more nonlinear behavior. However, interpretation of results of increase in dynamic functions and the nonlinearity still remains a topic of debate.

Frequency dependence of viscoelastic behavior

Dynamic frequency sweep tests were conducted in linear viscoelastic region to further understand the network formation and microstructural changes in detail. Polymers are of non-Newtonian nature and their viscosity decrease with increasing shear rate. Figure 5(a,b) shows the logarithmic plot of dependence of complex viscosity (η^*) and complex modulus (G^*) as a function of frequency (ω). MPDM-based TPV (DM20) exhibits higher η^* and G^* over the entire frequency range. It can be seen that, the viscosity is highly sensitive with significant drop at higher shear rate. Formation of aggregated and/or agglomerated structure of dispersed phase may be responsible for the high initial value of complex viscosity.²⁴ The tendency of G^* vs. ω plot to attain plateau state (viscoelastic solid like behavior) in the low frequency region indicating the presence of three-dimensional network structure formed by cross-linked particles which hindrance the relaxation process of the TPVs. The value of shear thinning value (n value) can be determined from the slope of straight line obtained in the low frequency region in the $\log(\eta^*)$ vs. $\log(\omega)$ plot (Table IV). The value of

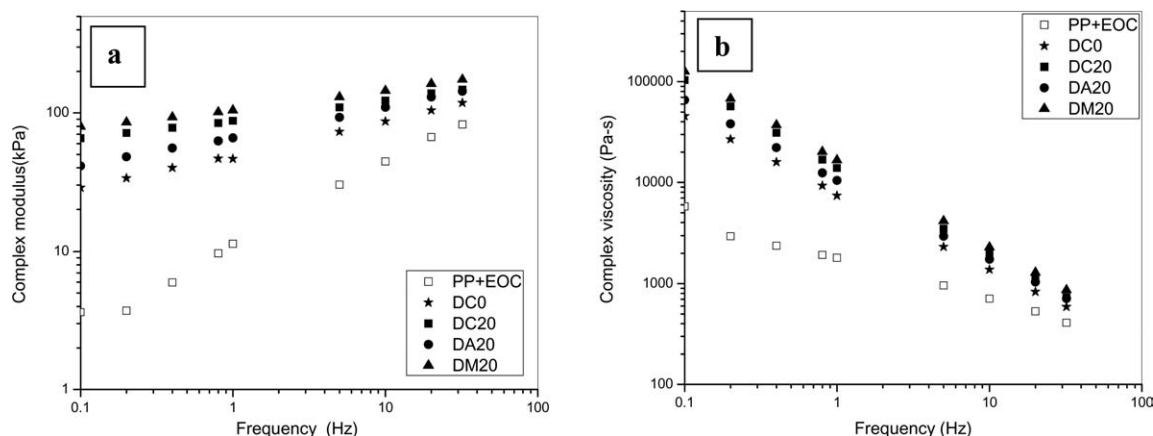


Figure 5 Variations of dynamic functions (G^* and η^*) as a function of angular frequency. (a) Complex modulus (G^*) and (b) Complex viscosity (η^*).

TABLE IV
Rheological Parameters and Values Observed from the Frequency Sweep Experiments

Compound name	First run			Second run			Third run		
	G_0^a	η_0^b	n^c	G_0	η_0	n	G_0	η_0	n
DC0	28.6	45620	-0.7519	26.1	41638	-0.7246	25.8	40524	-0.7132
DC20	57.1	104000	-0.8583	48.0	83879	-0.8250	47.0	80268	-0.8136
DA20	33.8	65718	-0.7843	31.8	57737	-0.7639	30.6	56812	-0.7542
DM20	71.8	127000	-0.8627	60.6	108000	-0.8378	60.0	101246	-0.8216

Note: Average of three measurements is reported.

^a Complex modulus at low frequency (0.05 Hz) (kPa).

^b Zero shear viscosity (complex viscosity at low frequency) (Pa s).

^c Shear thinning component (slope of the straight line obtained by plotting $\log(\eta^*)$ and $\log(\omega)$ between the frequency 0.1 and 10.0 Hz.

n increased drastically from the dynamically vulcanized blends. As the frequency increases, the network structure that tends to deform and exhibit higher shear thinning behavior. MPDM-based TPV shows higher negative n value due to the existence of the smaller particle size. Similar results have been observed for PP/EOC TPVs having smaller particle size.²³ It is expected that, MPDM acts as a booster for peroxide as well as compatibilizer for the blend components. The formation of *in situ* graft copolymers reside at the interface and consequently reduce the particle size of the crosslinked EOC phase. In other words, interfacial tension decreases with an increase in interfacial graft copolymer formation to form small crosslinked particles. As the particle size decreases, more number of polymer chains get adsorbed on the surface of the crosslinked EOC domains and average distance between the dispersed particle-particle could decrease. These lead towards physical jamming, which acts as energy barrier against the relaxation of system. These have been reflected to increase both modulus and viscosity values in the strain and frequency sweep tests.

Modulus recovery

Another important aspect to understand the mechanism of reinforcement in TPVs is restoration of module following the large strain amplitude disruption. The evolution of the secondary structure could be investigated by the nonlinear shear experiments. The sequence of test (given in experimental section) employed in this study to understand the modulus recovery kinetics has been already reported by the same authors²³ and Osman et al.²⁵ Figure 6 shows the comparative subsequent strain sweep test performed immediately after a relaxation time of 2 min and a frequency sweep (for clarity only control and MPDM-based TPVs are shown in Fig. 6). Irrespective of coagents used, initial storage modulus marginally decreased, onset of nonlinearity starts in the lower amplitude region and the magnitude of loss maximum

decreased and shifted to the lower amplitude region. These evolutions are associated with the nonreversible deformation of the network structure, the so called Mullins effect. The rheological properties associated with the strain sweep test for all the three runs or sweeps are shown in the Table III. It is worth noting that, almost more than 95% of the initial storage modulus value is reformed or regained within the given interval (2 min) and/or displacement of the physical adsorption tendency together with rearrangement favoring the strained state network chains. Furthermore, most of the stress softening effect is observed in the 2nd run and only very minor changes observed in the 3rd run. The nonlinear dynamic behavior of the TPVs can be visualized by two main mechanisms: one based on the concept of direct contact mode of the particles and the other by the indirect contact mode i.e., polymer chains adsorbed on the surface of crosslinked domains. The observed repetitive dynamic strain sweep results of the TPVs can be evaluated in terms of particle-particle and particle-matrix interaction. In case of particulate filled polymers (calcium carbonate

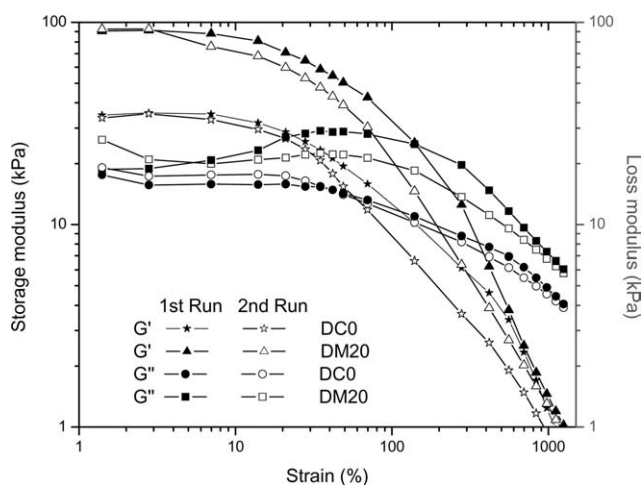


Figure 6 Storage and loss modulus of TPVs plotted as a function of strain amplitude. (Full symbol represents for first run and open symbol for second measurement after relaxation and frequency sweep).

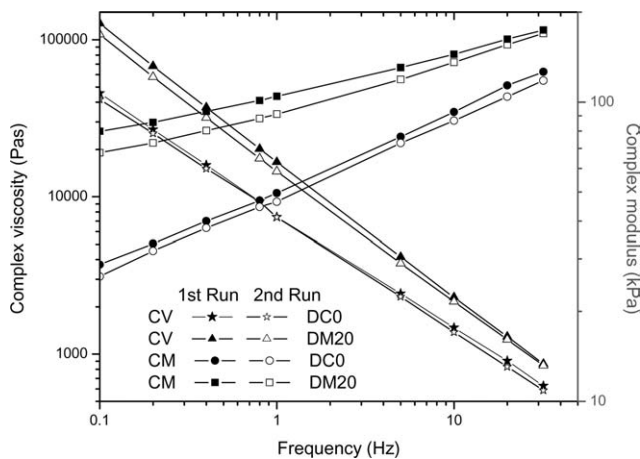


Figure 7 Dependence of viscoelastic property as a function of angular frequency. (Full symbols for first frequency sweep and open symbols for second sweep after a strain amplitude sweep and a relaxation time of 2 min).

filled polyethylene²⁵) with high degree of interaggregated, particle–particle interaction is more pronounced to give higher initial modulus value in the first strain sweep. The second strain sweep results to give, a drastic decrease in the initial modulus value and the onset of nonlinearity shifted to the higher amplitude region. However, in case of TPVs, the reverse is found to evolve i.e., initial storage modulus regained to large extent and onset of nonlinearity shifted to lower amplitude region. These rheological responses confirm that the network structure formed by the crosslinked EOC domains was dominated by the indirect contact mode or joint shell mechanism (higher particle–matrix interaction).

The kinetics of breakdown and the recovery of the structural configuration can be studied by subsequent frequency sweep after a large amplitude perturbation. In all the cases, marginal reduction in the dynamic functions is observed only in the low frequency range

(Fig. 7). Rheological properties associated with the frequency sweep for all the three runs are shown in the Table IV. However, in all the runs, MPDM-based TPVs show higher dynamic functions in the entire range of frequency studied. These suggest that, the secondary network is not significantly affected by the deformation imposed by the strain sweep or the deformation regained in the given interval (2 min). The aforementioned observation suggests that, the secondary network structure has energetically elastic network characteristics. The repetitive dynamic rheological results of TPVs observed earlier show striking similarity to that of carbon black-filled elastomer systems.²³

Stress relaxation measurements

Stress relaxation test is often considered as the simplest and fastest way to quantify the viscoelastic response of polymeric materials.²⁶ A constant step strain is applied and the resulting decay in stress is measured as a function of time. When the rate of relaxation is fast, there exists a higher viscous nature of the compound relative to its elastic nature. Le et al.¹⁶ studied the stress relaxation behavior of various TPEs and TPVs and concluded that the relaxing behavior of TPV is an interplay of viscoelastic, elastic and plastic deformation of blend components. In general, the mechanism of viscoelastic relaxation in TPVs includes configurational changes in the individual polymer chains of blend components, attachment and reattachment of crosslinked domains in the matrix and the relaxation at the interface which depends on the degree of interfacial interaction.

Linear plot of (G_t/G_0) versus $\log t$ of dynamically vulcanized blends without and with coagents of three different types are shown in the Figure 8(a,b), where G_t is the modulus at time t and G_0 is the modulus at time $t = 0$. During stress relaxation test, decay in

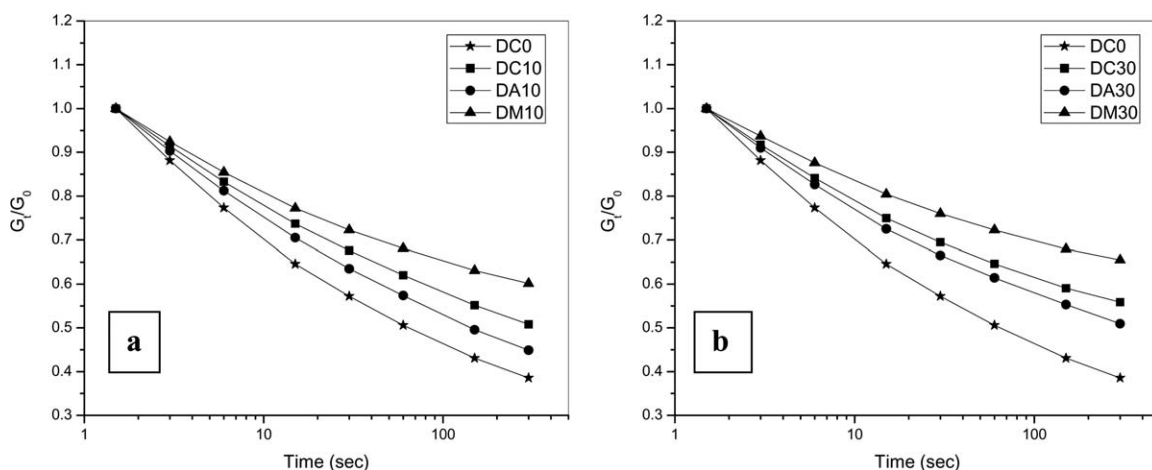


Figure 8 Stress relaxation of peroxide cured PP/EOC TPVs without and with different coagents. (a) 10 mequiv concentration and (b) 30 mequiv concentration of different coagents.

TABLE V
Stress Relaxation Data of Various Samples

Compound name	Initial modulus (kPa)	Slope (–ive)	Intercept (dNm)	Time to 50% decay (sec)	Residual Modulus (kPa)
DC0	532	0.179	59.2	0.18	205
DC10	658	0.127	76.6	0.72	334
DC30	726	0.110	83.5	0.91	405
DA10	477	0.152	55.3	0.52	214
DA30	718	0.122	81.3	0.56	365
DM10	1009	0.094	116.4	1.50	607
DM30	1139	0.078	133.2	3.80	746

stress is very fast in the beginning and it gradually slowed down with time. The initial modulus, residual modulus (modulus at 100 sec), slope (steepness of the decay), intercept, time at 50% drop in initial modulus is listed in the Table V. Irrespective of different coagents used, as the concentration of coagent increases from 0 to 30 mequiv, both initial and residual modulus increase and rate of relaxation decreases gradually. However, more substantial improvement in the elastic recovery property is observed at the lower concentration (10 mequiv) of coagent [Fig. 8(a)] in comparison with the higher loading of coagent (30 mequiv) [Fig. 8(b)]. These were reflected in the intercept and the slope value (negative value), respectively. Lower the rate of relaxation (lower the slope value), better is the elastic recovery property. Among the various coagents taken, MPDM is found to provide the lowest rate of relaxation and TMPTA is the fastest [Fig. 8(a,b)]. Significant improvement is observed for MPDM-based TPVs in terms of modulus and stress decay. These results are in line with the rheological response of the TPVs in both strain sweep and frequency sweep mode. MPDM acts as a booster for peroxide as well as compatibilizer for the blend components. Because of enhanced interfacial interaction, slippage at the interface is greatly reduced and consequently rate of relaxation decreases.

Capillary rheometer

In addition to the viscoelastic characteristics of individual polymer, interfacial interaction and morphology developed plays a vital role in determining the flow properties of polymer blends.^{8,27} The flow behavior of the polymer system can be well quantified by the Power-law model. Power law constants, flow behavior index (n) and consistency index (k) values were determined by the linear fit of the log–log plot of apparent shear viscosity and apparent shear rate²⁸ (Fig. 9). The effect of temperature, type of coagent and their concentration on n and k values are summarized in Table VI. In all the cases, the values of n are less than unity and lie within 0.60–0.65, indicating the non-Newtonian behavior or pseudoplastic nature of

the TPVs. Information regarding the temperature sensitivity on the flow characteristics is essential to determine the optimum processing temperature. It is well known that pseudoplasticity increases (n value decreases) and viscosity decreases (k value decreases) with an increase in processing temperature at all shear rates.²⁸ Higher the temperature, more thermal energy supplied to the polymer segments that may cause the easy alignment of polymer chains in the direction of flow. Irrespective of the different coagents used, n and k values increase with increase in concentration of coagent. These suggest that, addition of coagents increase the viscosity at low shear rate region which may be due to the resistance imposed by the shearing away of the dispersed phase in the flow direction. As mentioned previously, coagents employed not only enhance the crosslink density of the dispersed phase but also aid in the interfacial interaction between the dispersed phase and the matrix phase. However, different coagents show dissimilar flow behaviors as a function of coagent concentration. In case of TAC aided peroxide cured PP/EOC TPVs, increase in concentration of TAC causes to increase the k value and decrease the n value. i.e., DC30 shows higher viscosity at low shear rate region and lower viscosity at higher shear rate with respect

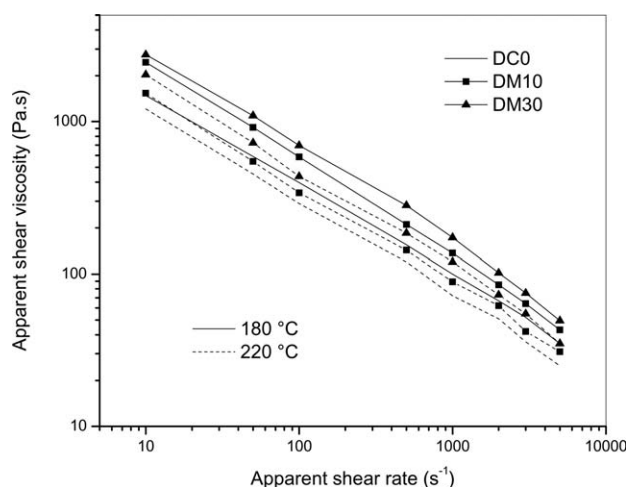


Figure 9 Log–log plot of apparent shear viscosity versus apparent shear rate for control and MPDM-based TPVs.

TABLE VI
Flow Behavior Index (n) and Consistency Index (k) at 180, 200, and 220°C for Various Coagents Added Peroxide Cured PP/EOC TPVs

Compound name	Flow behavior index (n)			Consistency Index (k ; kPa s)		
	180°C	200°C	220°C	180°C	200°C	220°C
DC0	0.607	0.596	0.591	6.02	5.88	5.05
DC10	0.645	0.623	0.615	11.57	8.31	6.53
DC30	0.632	0.621	0.605	11.74	10.00	8.77
DA10	0.635	0.602	0.589	11.44	6.45	5.46
DA30	0.636	0.596	0.590	11.48	6.30	5.55
DM10	0.651	0.625	0.620	12.22	8.94	7.16
DM30	0.660	0.656	0.650	12.88	10.23	8.97

to DC10. The crossover of G' and G'' (crossover point) is observed at around 500 s^{-1} . There appears no remarkable difference in the flow behavior of TMPTA-based PP/EOC TPVs as a function of concentration of TMPTA (n and k values do not follow a particular trend). In case of MPDM-based TPVs, viscosity was increased throughout the shear rate range with increase in concentration of MPDM. In our earlier publication, the authors reported the use of MPDM as an effective coagent and compatibilizer for the peroxide cured PP/EOC TPVs.⁷ Furthermore, the particle size considerably reduced upon the addition of MPDM. The graft copolymers formed at the interface improves the adhesion between the two components which in turn effectively transfer the stress from the matrix to the dispersed phase.

The melt viscosity and the elasticity are the two opposing factors that determine the overall processability of polymers melts. Because of the viscoelastic characteristics of the polymer melts, when emerging from the capillary dies, the oriented segments try to reorient and re-entangle. As a result, extrudates

show (die) swelling, melt fracture, wavy fracture and shark skins etc.²⁸ Figure 10(a,b) shows the photograph of extruded samples at the shear rate of 1000 s^{-1} and at 200°C for the TPVs prepared by three different coagents at two different concentrations. It is quite clear from Figure 10, in contrast to the TAC-based TPVs, MPDM-based TPVs show comparatively smoother extrudate at identical concentration. It is worth noting that, TAC at 30 mequiv concentration shows severely distorted and melt fracture characteristics. In our previous publication,⁷ it was shown that TAC at higher concentration undergoes homopolymerization or cyclopolymerization which overrides the other positive effects imparted by the coagent in peroxide cured PP/EOC TPVs. On the contrary, MPDM-based TPVs show comparatively smoother extrusion characteristics at all concentration levels, which is evident due to the formation of more compatibilized and/or formation of smaller dispersed particle size.

The extrudate of the MPDM-based TPVs, was relatively smooth at lower shear rate and lesser surface

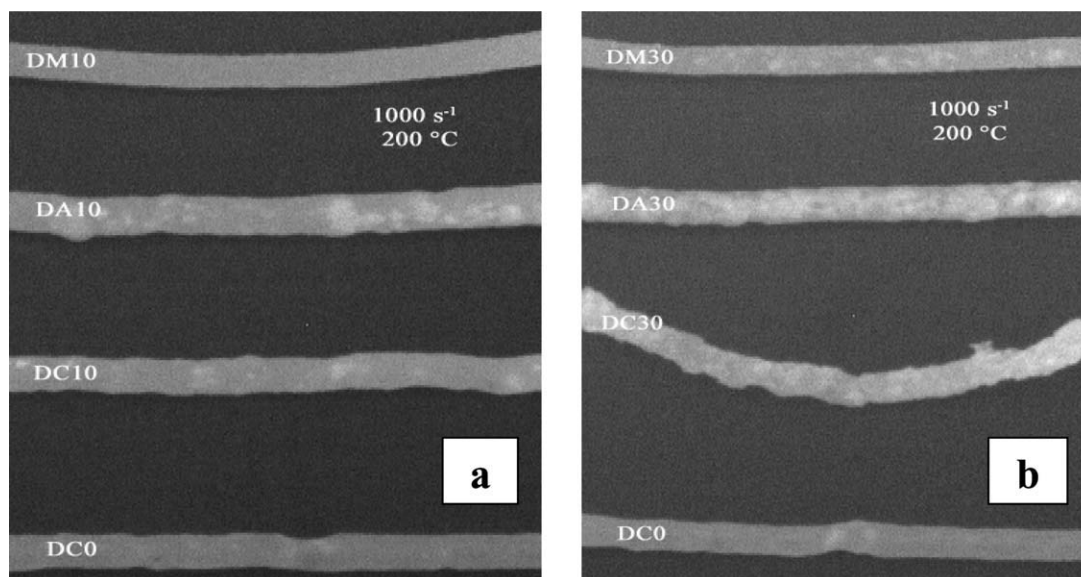


Figure 10 Photographs of the extrudates at 200°C , at 1000 s^{-1} for various coagents containing PP/EOC TPVs at different concentrations (a) 10 mequiv and (b) 30 mequiv.

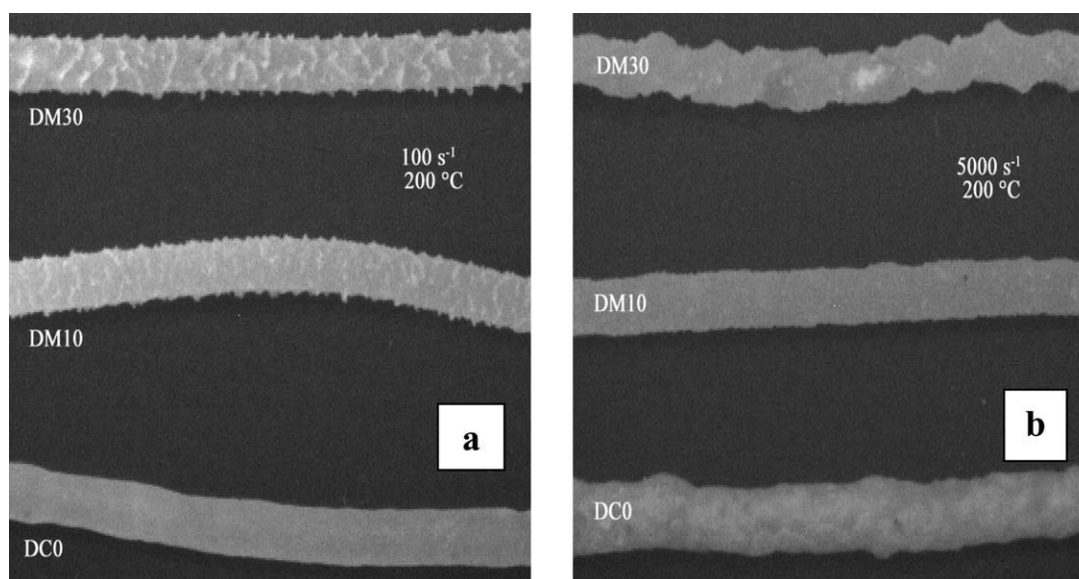


Figure 11 Photographs of the extrudates at 200°C and at different shear rates for MPDPM-based TPVs (a) 100 s⁻¹ and (b) 5000 s⁻¹.

distortion at higher shear rate than TAC and TMPTA-based TPVs at equal concentration of coagent [Fig. 11(a,b)]. DM10 shows relatively smoother extrudate even at higher shear rate than their counterpart. But DM30 shows sharkskin formation at low shear rate and more roughness is observed at higher shear rate. Sharkskin has been suggested as surfaces melt fracture, associated with the high degree of stretching in the surface layers of the melts as it emerges from the die.²⁷ Severe distortion (melt fracture) at high shear rate may be due to the higher elastic memory effect. Therefore, it can be concluded that MPDPM not only improves the surface smoothness of the extrudates but also improves the rheological and mechanical properties⁷ (even at 10 mequiv concentration) by the compatibilizing tendency in the peroxide cured PP/EOC TPVs.

CONCLUSIONS

The present investigation deals with the melting and rheological characteristics of peroxide cured PP/EOC TPVs in presence and absence of various coagents. Three different coagents such as TAC, TMPTA, and MPDPM were chosen for this investigation. Coagent assisted peroxide cured system affects the crystallizing behavior due to the various types of reactions taking place simultaneously. X_c of both EOC and PP decrease with the addition of coagent; however remains largely unaffected in case of PP. Therefore, the improvement in the mechanical properties is mainly due to the crosslinking in the EOC phase. Dynamic melt rheological properties were performed to study the viscoelastic characteristics of the TPVs. By nature, their rheological response is very similar to that of filled polymer melts.

It was found that, MPDPM-based TPVs show enhanced dynamic functions (from strain sweep and frequency sweep) and reduced rate of relaxation (from stress relaxation experiment) followed by TAC and TMPTA. Generally, increase in dynamic functions is attributed due to the improved crosslinking in the EOC phase and immobilization of the interface by compatibilizing efficiency of coagent. MPDPM-based TPVs show higher modulus in low strain amplitude region and more non-linear behavior. However, they show higher modulus in the entire range of frequency studied, it can still be processed like thermoplastic. It can be concluded from the aforementioned observations that the dual role of MPDPM i.e., as a booster for peroxide and as a reactive compatibilizer assist to improve the properties in the solid as well as in the melt state. Rheological behavior of the TPVs are mainly attributed due to the characteristics of the cluster structure formed by dispersed particles, which in turn depends on the particle size and the interaction between the dispersed particles and the matrix phase. The extrudate surface of the MPDPM-based TPVs show comparatively smoother surface than other coagents used. Amongst the various coagents, MPDPM containing TPVs show superior solid state and melt state properties. It can be concluded that, addition of MPDPM in peroxide cured PP/EOC blends turn out to give comaptibilized dynamic vulcanizates.

The authors thank Mr. S. Mushtaq for his technical assistance in rheological experiments.

References

1. Coran, A. Y. In *Thermoplastic Elastomers—A Comprehensive Review*; Legge, N. R., Holden, G., Eds.; Hanser Publisher: Munich, 1987.

2. Karger Kocsis, J. In *Polymer Blends and Alloys*; Shonaike, G. O., Simon, G. P., Eds.; Marcel Dekker: New York, 1999.
3. Naskar, K. *Rubber Chem Technol* 2007, 80, 504.
4. Naskar, K.; Noordermeer, J. W. M. *Rubber Chem Technol* 2003, 76, 1001.
5. Lai, S. M.; Chin, F. C.; Chiu, T. Y. *Eur Polym J* 2005, 41, 3031.
6. Babu, R. R.; Singha, N. K.; Naskar, K. *J Appl Polym Sci* 2009, 113, 1836.
7. Babu, R. R.; Singha, N. K.; Naskar, K. *J Appl Polym Sci* 2009, 113, 3207.
8. Harrats, S.; Thomas, S.; Groeninckx, G., Eds. *Micro and Nano Structured Multiphase Polymer Blend Systems- Phase Morphology and Interface*, CRC Press: Boca Raton, 2006.
9. Gahleitner, M. *Prog Polym Sci* 2001, 26, 895.
10. Sengers, W. G. F.; Sengupta, P.; Noordermeer, J. W. M.; Picken, S. J.; Gotsis, A. D. *Polymer* 2004, 45, 858.
11. Leblanc, J. L. *J Appl Polym Sci* 2006, 101, 4193.
12. Li, Z.; Kontopoulou, M. *Polym Eng Sci* 2009, 49, 34.
13. Katbab, A. A.; Bazgir, S.; Nazockdast, H. *J Appl Polym Sci* 2004, 92, 2000.
14. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1983, 56, 1045.
15. Corley, B.; Radusch, H. J. *J Macromol Sci Phys* 1998, 37, 265.
16. Le, H. H.; Lupke, T. H.; Pham, T.; Radusch, H. J. *Polymer* 2003, 44, 4589.
17. Dluzneski, P. R. *Rubber Chem Technol* 2001, 74, 451.
18. Costin, R. *Selection of Coagents for Use in Peroxide Cured Elastomers. Application Bulletin*; Sartomer Company: USA, 5519.
19. De Risi, F. R.; Noordermeer, J. W. M. *Rubber Chem Technol* 2007, 80, 83.
20. Stern, C.; Frick, A.; Weickert, G. *J Appl Polym Sci* 2007, 103, 519.
21. Ramier, J.; Gauthier, C.; Chazeau, L.; Stelandre, L.; Guy, L. *J Polym Sci Part B: Polym Phys* 2007, 45, 286.
22. Marinvic, T.; Susteric, Z.; Dimitrievski, I.; Veksli, Z. *Kautsch Gummi Kunstst* 1998, 51, 189.
23. Babu, R. R.; Singha, N. K.; Naskar, K. *Polym Eng Sci* 2010, 50, 455.
24. Cui, L.; Zhou, Z.; Zhang, Y.; Zhang, Y.; Zhang, X.; Zhou, W. *J Appl Polym Sci* 2007, 106, 811.
25. Osman, M. A.; Atallah, A. *Polymer* 2006, 47, 2357.
26. Dick, J. S.; Pawlowski, H. *Rubber World* 1997, 215, 21.
27. Han, C. D. In *Rheology in Polymer Processing*; Han, C. D., Ed.; Academic Press: New York, 1976.
28. Brydson, J. A. In *Flow Properties of Polymer Melts*; Brydson, J. A., Ed.; Godwin: London, 1981.