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ORIGINAL PAPER

Phase morphology and melt rheological behavior of uncrosslinked and dynamically crosslinked polyolefin blends: role of macromolecular structure

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Abstract Thermoplastic vulcanizates (TPVs) based on polypropylene (PP) with ethylene–octene copolymer (EOC) and ethylene propylene diene rubber (EPDM) have been prepared by co-agent-assisted peroxide crosslinking system. The study was pursued to explore the influence of two dissimilar polyolefin polymers having different molecular architecture on the state and mode of dispersion of the blend components and their influence on melt rheological properties. The effects of dynamic crosslinking of the PP/EOC and PP/EPDM have been compared with special reference to the concentration of crosslinking agent and ratio of blend components. Morphological analyses show that, irrespective of blend ratio, dynamic vulcanization exhibits a dispersed phase morphology with crosslinked EOC or EPDM particles in the continuous PP matrix. It was found that viscosity ratio plays a crucial role in determining the state and mode of dispersion of blend components in the uncrosslinked system. The lower viscosity and torque values of uncrosslinked and dynamically crosslinked blends of PP/EOC in the melt state indicates that they exhibit better processing characteristics when compared to corresponding PP/EPDM blends.

Keywords Polypropylene · Ethylene–octene copolymer · Ethylene propylene diene rubber · Thermoplastic vulcanizate · Peroxide · Rheology

Introduction

Thermoplastic elastomer (TPE) combines the processing and recycling of conventional thermoplastic material in the melt state with comparable elasticity, fracture resistance of the crosslinked thermoset elastomer, or rubber in the solid state [1, 2].

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Thermoplastic vulcanizates (TPVs) belong to the much broader group in the family of TPEs. TPVs are prepared by dynamic vulcanization process, involving melt blending of elastomer and thermoplastic material, in which the elastomer part was crosslinked simultaneously [3, 4]. Principally, the micron-sized crosslinked elastomer phase is dispersed in thermoplastic matrix phase. This special morphology evolution is possible even at high composition of elastomer phase remains dispersed in the low composition of thermoplastic material. The final morphology is the key behind to retain the elasticity of elastomer phase along the ease of processing of plastic phase [4, 5].

Polyolefin blends have attracted much attention due to their easy processing, availability, wide range of properties, and cost effectiveness. Among them, polypropylene (PP)/Ethylene propylene diene rubber (EPDM) have gained much commercial interests [6]. Studies on the uncrosslinked and dynamically crosslinked PP/EPDM blends have been carried out by several authors [7–10]. Recently, ethylene alpha olefin copolymer have been used, especially ethylene–octene copolymer (EOC) in the place of EPDM. Literature shows that EOC is continuously replacing EPDM market in almost all field of application [11, 12]. Addition of EOC in PP had been shown to increase the impact resistance or notch toughness in the PP phase when compared with the conventionally used EPDM material [13]. Our previous article examined the detailed investigation on the mechanical, thermal, morphological, and rheological characteristics on the peroxide-cured PP/EOC TPVs [14–18]. Recently, comparison on PP/EOC and PP/EPDM TPVs in terms of performance properties have been studied in detail [19]. Addition of peroxide involves two major competing reactions: crosslinking in the EOC/ethylene units of EPDM and degradation or chain-scission in the PP phase. Thus, final viscoelastic characteristics of the TPVs are dependent on the balance amongst those two competing reactions. The basic understanding of the relationship between morphology and rheology of the polymer blends is of great importance and has important practical implications. Numerous studies related to the rheological properties of dynamically vulcanized blends have been reported [20–22]. The present study was aimed to infer the processing-microstructure-morphology linkages of blends comprised on PP/EOC and PP/EPDM. Oscillatory shear experiments have been used to understand the reinforcing characteristics and the relationship with particle size of crosslinked rubber phase. Rheological studies have been evaluated at the processing temperature (180 °C) in a Rubber Process Analyser (RPA-2000) in terms of strain sweep and frequency sweep. The experimental variable includes type of polymer (EOC and EPDM), blend ratio, dynamic vulcanization, and curative dosage.

Experimental

Materials

Isotactic polypropylene (PP), ethylene–octene copolymers (EOC) and ethylene propylene diene rubber (EPDM) were used as blend components. Metallocene-catalyzed ethylene–octene copolymers (Exact®) were employed in this study.

Table 1 Molecular characteristics of the polymers

Polymer/properties	PP	EOC	EPDM
Specific gravity	0.90	0.87	0.86
MFI (g/10 min)	3.0 @230 °C/2.16 kg	1.0 @190 °C/2.16 kg	–
ML (1 + 4)@125 °C	–	25	55
M_n	218,967	277,751	273,082
M_w	949,319	494,872	622,876
PDI (M_w/M_n)	4.33	1.78	2.28
Octene content	–	13%	–
ENB content	–	–	4.6
Propylene content	99.9%	–	25.4%
Zero shear viscosity @ 180 °C 40:1 L:D capillary (Pa s)	1,020	1,980	4,130
Grade	Koylene ADL (AS030N)	Exact 5171	Keltan 5508
Supplier	IPCL, India	ExxonMobil Chemical, USA	DSM Elastomers, The Netherlands

The octene content of these Exact copolymers was determined from ^{1}H-NMR measurement. The material and molecular characteristics of PP, EOC, and EPDM are given in Table 1. 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/cm^3 at 23 °C) was obtained from Akzo Nobel Chemical Company, The Netherlands. N–N′-m-phenylene dimaleimide (MPDM) (SR 525; specific gravity, 1.44 g/cm^3 at 23 °C) was obtained from Sartomer Company, USA.

Preparation of TPVs

TPVs were prepared by melt mixing of PP with EOC/EPDM (rubbery material) in a Haake Rheomix 600s with a mixing chamber volume of 85 cm^3 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 for 3 min and then rubbery material was added to the chamber and melt mixing was carried out for 5 min. Dynamic vulcanization was pursued by adding co-agent-assisted peroxide for 2 min. Mixing was continued for another 4 min to complete the vulcanization. The compositions of TPVs employed for this study are shown in Table 2. For better understanding, blend ratio are designated as X, Y, and Z for 75, 50, and 25% of PP, respectively. TPVs prepared by different rubbery materials are designated as follows: C for EOC and D for EPDM. For example, YC corresponds to the composition of 50:50 PP/EOC uncrosslinked blends and ZD for 25:75 PP/EPDM uncrosslinked blend. Dynamically vulcanized blends are designated with prefixes D2 or D4 followed by corresponding blend ratio designation. The letter D2 or D4 corresponds to the type and concentration of peroxide (Dicumyl peroxide of 2 phr (parts per hundred grams of rubber) or 4 phr). For example, D2ZC corresponds to the composition containing 2 phr of dicumyl peroxide in the 25:75 PP/EOC blend ratio. After mixing, the blends

Table 2 TPV compositions (wt%)

Polymers/designations	PP	EOC	EPDM
XC	75	25	–
YC	50	50	–
ZC	25	75	–
XD	75	–	25
YD	50	–	50
ZD	25	–	75

were removed from the chamber at hot condition and sheeted out on a two roll mill 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

Overall crosslink density

Equilibrium solvent swelling measurements were carried out on the PP/EOC TPVs to determine the crosslink density of the rubber (EOC/EPDM) in presence of PP. The crosslink density was calculated using modified Flory–Rehner equation [23] as shown below (Eq. 1). In case of TPVs, crosslinked rubber phase is embedded in the relatively less swellable matrix like PP. Crosslinked rubber phase swells against the compressive force exerted by the PP matrix. From the degree of swelling, the overall crosslink density was calculated relative to the (rubber + PP) phases and expressed as (v + PP). The latter was done in order to avoid the need to correct for a part of the PP, being extracted as amorphous PP. A circular piece of 2 mm thickness was made to swell in cyclohexane for about 48 h to achieve equilibrium swelling condition. Initial weight, swollen weight and de-swollen, or dried weight were measured and substituted in the following equation:

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

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 [cm^3/mol], χ = polymer swelling agent interaction parameter, which in this case is 0.306[24] and V_r = volume fraction of ethylene–octene copolymer in the swollen network, which can be expressed by

$$V_r = \frac{1}{A_r + 1} \tag{2}$$

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

Gel content

In order to estimate the degree of crosslinking in the EOC phase in the TPVs prepared, the samples were subjected to a series of solvent extraction. All the measurements were done according to ASTM D 2765. About 2 g of TPV sample was first extracted for 24 h in hot xylene at 80 °C to remove the uncrosslinked EOC phase and low molecular weight PP fragments. It appeared to be a qualitative estimation because of the restricted extraction of EOC phase in the presence of PP phase. The samples were completely dried after extraction and weighted. Then, the initial loss can be calculated from the Eq. 3:

$$R(\%) = \left(\frac{W_0 - W_1}{W_o}\right) \times 100 \qquad (3)$$

where R = Percentage of residue after xylene extraction at 80 °C, W_o = Initial weight of the specimen, and W_1 = weight after xylene extraction.

The dried sample was further extracted for 72 h in boiling xylene at 140 °C to completely remove the PP and soluble EOC phase. The gel content can be calculated from the Eq. 4:

$$\mathrm{Gel}(\%) = \left(\frac{W_h}{W_i} \times 100\right) \qquad (4)$$

where W_1 = weight of the sample after xylene extraction at 80 °C, W_h = weight of the sample after xylene extraction at 140 °C.

Morphology

Morphology studies were carried out using a scanning electron microscope (SEM) (JEOL JSM 5800, Japan). Molded samples of PP/EOC or PP/EPDM TPVs were cryofractured in liquid nitrogen to avoid any possibility of phase deformation during the fracture process. In case of uncrosslinked blends, the EOC or EPDM 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 and partially 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.

Rheology

Melt rheological behaviors of the TPVs were analyzed in a Rubber Process Analyzer (RPA 2000, Alpha Technologies, USA) equipped with bi-conical test fixtures. RPA 2000 deforms the sample in shear. A special direct drive motor moves the lower die sinusoidally over a range of strains and frequencies. The upper die connects with the torque transducer. The torque transducer measures the amount of torque transmitted through the sample. The torque is a complex torque because it is not in phase with the strain. The RPA 2000 reduces the complex torque (S*) into elastic torque (S') and a viscous torque (S'') by applying a Fourier Transform to the S^* signal. The RPA which in turn converts the torque values to the shear modulus values by multiplying by the appropriate die form factor and dividing by strain. All the specimens were directly loaded between the dies maintained at 180 °C. The tests were carried out in both frequency sweep and strain sweep mode.

Frequency sweep

The frequency was logarithmically increased from 0.33 to 33 Hz at a 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 to 1,200% with a constant frequency of 0.5 Hz.

Results and discussion

Overall crosslink density and gel content

Dynamic vulcanization enables the crosslinked elastomer to become the dispersed phase even in the cases where the elastomer is the majority component. Ultimate physical properties of TPVs depend upon both the extent of crosslinking and degree of dispersion in terms of rubber domain size and its distribution [1–3]. Conventionally, crosslink extent in TPVs is determined by xylene–gel method [24]. Recently, Ellul et al. measured the crosslink density value of the PP/EPDM TPVs by using solid state NMR [25]. In the present study, two methods were attempted to determine the crosslink density: cyclohexane solvent swelling and boiling xylene–gel method. Overall crosslink density (OCD) is determined by equilibrium solvent swelling measurement; the (v + PP) includes the PP-content of the blend in the OCD measurement. In case of TPVs, the crosslinked rubber phase is embedded in the relatively less swellable matrix like PP. The OCD values of uncrosslinked and dynamically crosslinked blends of PP/EOC and PP/EPDM is shown in Table 3. It is to be noted that blends with higher PP content exhibit higher OCD values. In contrast to other blend ratio, XC and XD series (75 wt% of PP) show a continuous decrease in the OCD values with increase in DCP concentration (Dynamic vulcanization). This may be due to the degradation effect on the matrix PP phase through β-chain-scission. Hence PP with low molecular weight species suffers less resistance to the swelling.

Furthermore, in order to get insight into the extent of crosslinking in the rubber (EOC/EPDM) phase, the samples were subjected to a series of solvent extraction i.e., gel content was measured in two stages. In the first stage, extracted at 80 °C by hot xylene, it is believed that this can extract uncrosslinked rubber fractions along with inherent low molecular weight PP fractions. In all the cases, dynamic vulcanization decreases the soluble fractions in the blend components, which is

Table 3 Overall crosslink density and gel content values

Compound name	PP/EOC			Compound name	PP/EPDM		
	Overall crosslink density $(v + \mathrm{PP}) \times 10^{-4}$ mol/mL	Residue after 80 °C (%)	Gel content (%)		Overall crosslink density $(v + \mathrm{PP}) \times 10^{-4}$ mol/mL	Residue after 80 °C (%)	Gel content (%)
XC	40.05	80.7	2.3	XD	46.15	70.9	1.6
D2XC	36.10	93.8	33.9	D2XD	39.21	93.9	32.8
D4XC	32.21	92.3	32.6	D4XD	32.38	92.9	31.3
YC	8.17	49.4	2.2	YD	13.92	50.5	1.7
D2YC	10.12	95.0	49.1	D2YD	16.84	96.6	55.2
D4YC	10.32	96.2	54.3	D4YD	16.21	97.5	56.6
ZC	0.38	20.8	2.2	ZD	2.91	25.7	1.5
D2ZC	2.58	93.4	66.7	D2ZD	4.92	97.5	68.3
D4ZC	3.72	96.3	73.1	D4ZD	5.94	98.5	78.8

Prefix: *D2* Dynamically vulcanized blends with 2 phr DCP: *D4* Dynamically vulcanized blends with 4 phr DCP mainly due to the crosslinking in the rubber phase. In the second stage, extraction was done at 140 °C, soluble PP fractions are removed leaving only crosslinked rubber gels. Variation in the gel content values for uncrosslinked and dynamically crosslinked blends are shown in Table 3. Irrespective of the blend components, amount of insoluble fraction increases by dynamic vulcanization. The extent of increase in gel content is more pronounced at higher rubber composition. In contrast to XC and XD series, other blend composition shows a continuous increase in gel content with increase in concentration of DCP. However, increment becomes marginal at 4 phr when compared to 2 phr concentration of DCP. It is worth noting, blends with higher rubber content show higher gel or insoluble fractions. Similar to the OCD values, PP/EPDM-based blends show higher gel content than corresponding PP/EOC-based blends. From the molecular architecture (Table 1), it is found that EPDM have broad molecular weight distribution and hence affirm with more trapped entanglements. These trapped entanglements act as physical crosslink juncture and exhibit more resistance to the swelling characteristics.

Dynamic viscoelastic properties of neat polymers

The variation of complex modulus (*G**) and complex viscosity (η*) of pristine polymers as a function of angular frequency (ω) are represented in Fig. 1. All samples exhibit a decrease in complex viscosity with increase in angular frequency, suggesting a pseudoplastic- or shear-thinning characteristics. Pseudoplasticity of the neat polymers is due to the random orientation and highly entangled state of the macro-molecules which under high shear get disentangled and become oriented resulting in a reduction of viscosity [26]. Figure 2 shows the variation of storage modulus (G') and loss modulus (G'') as a function of angular frequency (ω) for the neat polymers. Both G' and G'' increase with increase in angular frequency, suggesting that the molecular entanglements have enough time to slip and relax out the stress. It is very clear from Figs. 1 and 2 that EPDM exhibits higher viscosity

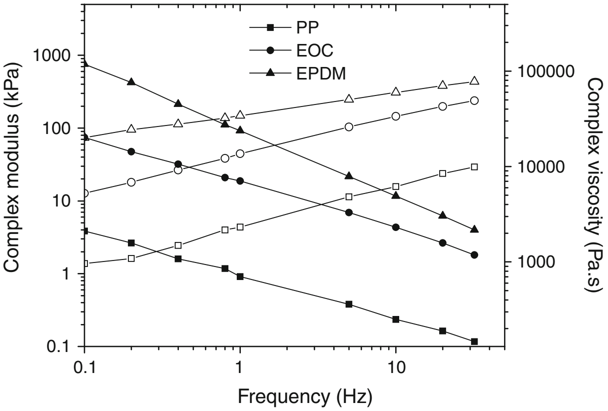

Fig. 1 Variation of complex viscosity and complex modulus as a function of frequency at 180 °C with a constant strain amplitude of 5%

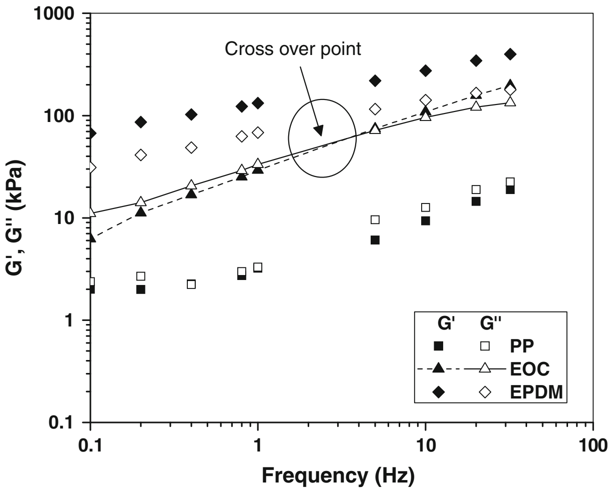

Fig. 2 Variation of storage modulus and loss modulus as a function of frequency at 180 °C with a constant strain amplitude of 5%

and elasticity in the explored frequency range followed by EOC and PP. Since PP has the compact 3_1-helix conformation which in turn have very low chain entanglement and correspondingly show more fluidity in the molten condition [27]. The longer side chains of octene monomer in EOC make more "bulky" chain conformation as compared to the more "slender" EPDM [28]. The reptation time or relaxation time (τ_r) corresponds to the reciprocal of the frequency at which $G'(\omega) = G''(\omega)$. In fact, this crossover frequency is the separation of viscous like and elastic like behavior, below which polymers will be more viscous and above which more elastic than viscous. The crossover frequency can be viewed as an indicator for polymer viscoelasticity and its inverse is a characteristic of relaxation nature of the given polymer. In case of PP, loss modulus dominates over the storage modulus, whereas EPDM shows a reverse trend, in the entire range of frequency studied. However, EOC exhibits a crossover frequency at about 3.7 Hz and corresponding τ_r at about 0.265 s. It is expected that G' and G'' of the EPDM might cross at a very low frequency and for PP at a very high frequency. When comparing EOC and EPDM, the smaller viscoelasticity of EOC i.e., shorter relaxation time may result from the absence of high molecular weight species and also due to its inherent narrow molecular weight distribution. However, it shows moderate elastic character due to its entangling tendency of long chain branches [29]. In case of EPDM, the molecular architecture is composed of broad molecular weight distribution and comparatively high molecular weight species. High molecular weight species have higher degree of chain entanglement and in turn give rise to the restriction in relaxation of polymer chains. The difference in the relaxation time between the components can be summarized as: EPDM the slowest while PP is the fastest and EOC lies in between.

Strain amplitude sweep is carried to determine the linear viscoelastic region (LVE) and to characterize the microstructural organization of the polymer. Figure 3

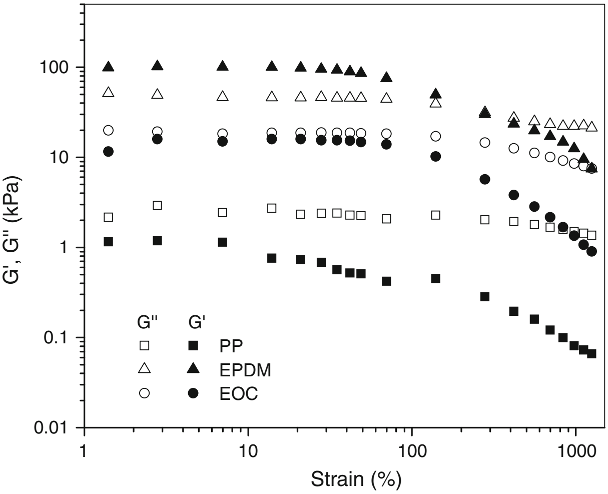

Fig. 3 Variation of storage modulus and loss modulus as a function of strain amplitude at 180 °C with a constant frequency of 1 Hz

displays the variation of G' and G'' as a function of strain amplitude (γ). As expected, both G' and G'' show a linear region followed by a non-linear region with increase in strain amplitude. It seems that G' is more sensitive to the structural changes than G'' as a function of strain amplitude. The decrease of G' with increase in deformation of neat uncrosslinked polymers is associated with the slippage of trapped chain entanglements. The molecular architecture of neat polymers is mainly composed of physical crosslinks created by trapped entanglements. The trapped entanglements can support stress for a short period of time, creating a transient network. Accordingly, in Fig. 3, the decay of modulus is related to the slippage or disentanglement of these transient networks. Moreover in the linear region, strain dependence of the G' is directly related to the molecular weight of the species [30]. A clear divergence is observed in the viscoelastic character of neat polymer as a function of strain amplitude. For PP and EOC, G'' dominates over G' in the entire strain amplitude range. But in case of EPDM, G' dominates over G'' in the low amplitude region and as the deformation increases the crossover of modulus occurs i.e., G'' dominates over G'. It is clear from the Fig. 3 that EPDM shows higher storage modulus in the low amplitude region, and more non-linear character as the deformation increases. Table 4 summarizes various rheological parameters obtained from the strain sweep and frequency sweep experiments. The extent of non-linearity is observed from the ΔG value as given in Table 4. The above rheological results suggest that the EPDM has very high molecular weight and more trapped entangled network structure. From the above rheological response, the microstructural architecture of polymer chains can be qualitatively inferred. PP has linear molecular architecture to show more viscous character, whereas EOC has long chain-branched structure with moderate elasticity and EPDM have more entangled structure to show pronounced elasticity.

Table 4 Rheological parameters and values observed from the frequency and strain sweep experiments for pristine polymers

Compound name	Frequency dependent viscoelastic properties at 180 °C			Strain dependent viscoelastic properties at 180 °C		
	η_0 (Pa s)[a]	n[b]	K[c]	G_0 (kPa)[d]	G_∞ (kPa)[e]	ΔG[f]
PP	1,075	−0.463	2.86	3.0	1.3	1.7
EOC	10,599	−0.486	3.83	16	0.9	15.1
EPDM	45,067	−0.693	4.38	101	7.5	93.5

[a] Viscosity at low shear rate (0.5 Hz)

[b] Flow behavior index

[c] Consistency index

[d] Low strain storage modulus (modulus at 2% strain)

[e] High strain storage modulus (modulus at 1200% strain)

[f] $\Delta G' = G'_\infty - G'_0$ (change in storage modulus value with strain amplitude sweep)

Morphology

In general, phase morphology of the heterogeneous polymer blends are mainly determined by viscosity ratio, blend ratio, and interfacial tension. In order to study the development of phase morphology and to predict the phase inversion region in immiscible polymer blends, a variety of empirical model equations are proposed by several authors [31, 32]. Since they are empirical, they do rely on the experimental findings. Avgeropoulus et al. [33] have developed an empirical model (Eq. 5) based on the torque ratio and the volume fractions of each phase. Jordhamo et al. [34] proposed a similar equation, where instead of the torque ratio, viscosity ratio was used (Eq. 6):

$$\frac{\phi_1}{\phi_2} \cdot \frac{T_2}{T_1} = X \tag{5}$$

$$\frac{\phi_1}{\phi_2} \cdot \frac{\eta_2}{\eta_1} = Y \tag{6}$$

which results in the following morphology variants [31]:

$X, Y > 1$	Phase 1 is continuous or matrix and phase 2 is dispersed
$X, Y < 1$	Phase 2 is continuous or matrix and phase 1 is dispersed
$X, Y = 1$	Dual phase continuity or phase inversion region

where ϕ_1, ϕ_2 are volume fractions, T_1, T_2 are torque values and η_1, η_2 are viscosity values of phase 1 and phase 2, respectively. The viscosity values are obtained from the steady shear test at 180 °C from capillary rheometer. 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 [31].

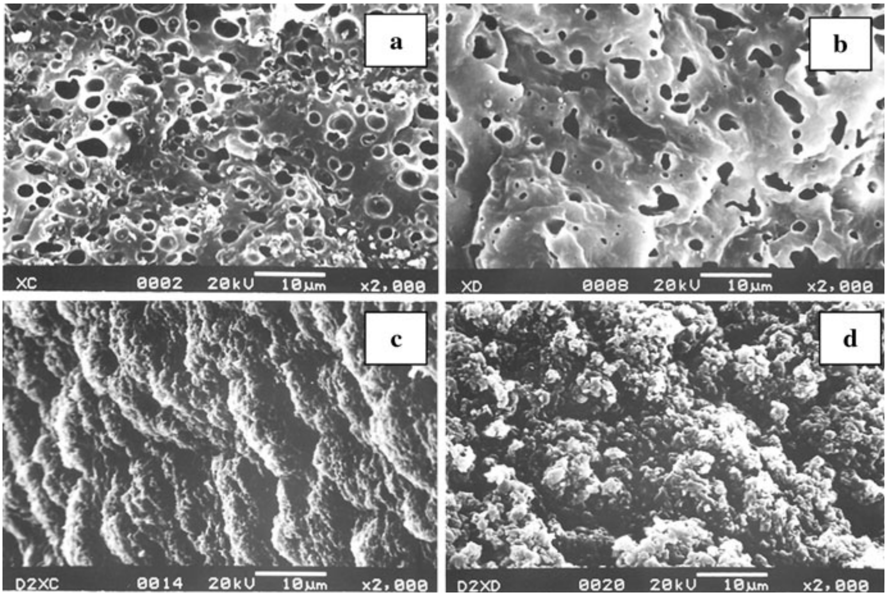

Fig. 4 SEM photomicrographs of **a** XC (75/25 PP/EOC uncrosslinked), **b** XD (75/25 PP/EPDM uncrosslinked), **c** D2XC (dynamically vulcanized; 2 phr) **d** D2XD (dynamically vulcanized; 2 phr)

Figures 4, 5, and 6 show the SEM photomicrographs of uncrosslinked and dynamically crosslinked blends of both PP/EOC- and PP/EPDM-based compounds with special reference to the effect of blend ratio. In uncrosslinked blends, rubbery phase EOC or EPDM was preferentially extracted and in dynamically crosslinked blends PP phase was preferentially extracted. Theoretical and experimental phase evolutions are summarized in Table 5.

From Fig. 4a, b, it is evident that the rubber phase (EOC or EPDM) remained as dispersed phase in continuous PP matrix. This may be due to the higher content and lower viscosity of PP phase. As seen from the Fig. 4, EOC was uniformly dispersed as spherical domains in the range of 2–3 µm, whereas EPDM exists as grossly irregular and deformed shape domains in the range of 2–4 µm in continuous PP matrix. In contrast to XD, XC shows densely dispersed particles with narrow particle size distribution. Moreover, no evidence of adhesion at the interface between PP and EOC is found. In case of XD, due to higher viscosity and inherent propylene units in EPDM (partially miscible with the PP-matrix phase in the molten stage), leads to formation of deformed and irregular shaped particles. Similar morphology was observed by Silva et al. [35] while comparing uncrosslinked PP/EOC with PP/EPDM blends. A significant difference was observed after dynamic vulcanization in both XC and XD (as shown in Fig. 4c, d). The phase morphology seems to be the dispersion of crosslinked rubber particles in the continuous PP matrix.

The increase in rubber content from the 25 to 50% (YC and YD) results in the formation of co-continuous phase morphology. Depending on the viscosity ratio,

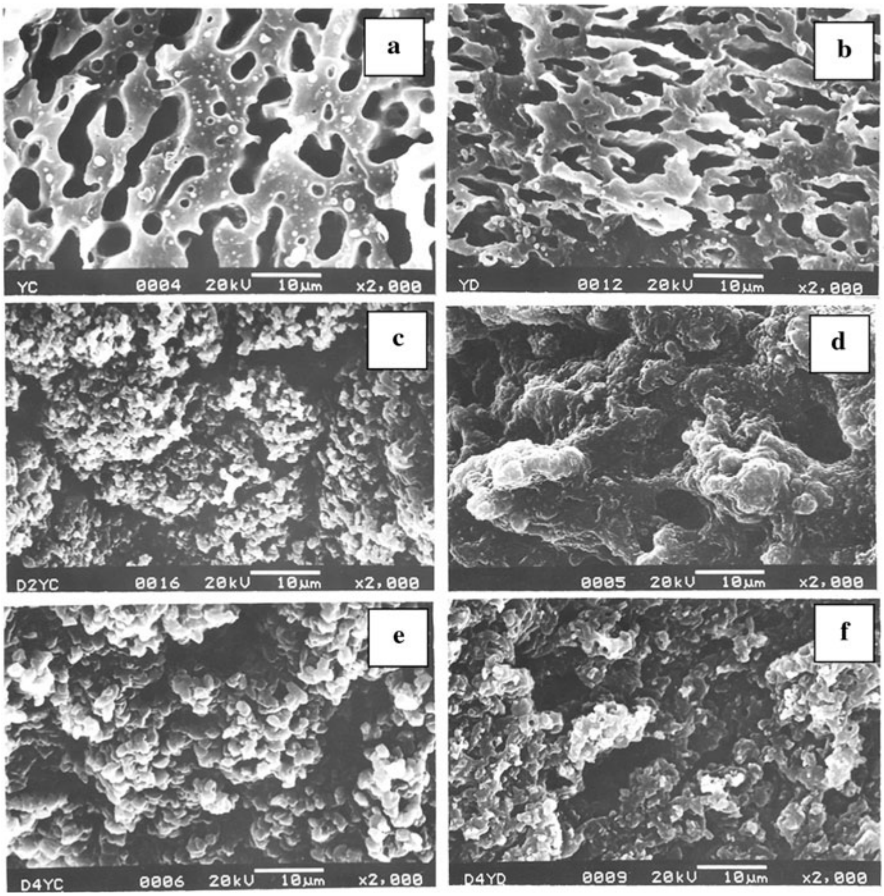

Fig. 5 SEM photomicrographs of **a** YC (50/50 PP/EOC uncrosslinked), **b** YD (50/50 PP/EPDM uncrosslinked), **c** D2YC (dynamically vulcanized; 2 phr), **d** D2YD (dynamically vulcanized; 2 phr), **e** D4YC (dynamically vulcanized; 4 phr), **f** D4YD (dynamically vulcanized; 4 phr)

various levels of co-continuity exist in the blend compounds. It is clear from the Fig. 5a, b that the PP/EOC (YC) contributes to have higher percentage of co-continuity than PP/EPDM (YD) blend. Because of higher viscosity ratio in YD, EPDM prefers to exist in dispersed phase. However by dynamic vulcanization, a complete phase transition (inversion) occurs i.e., co-continuous morphology is changed into dispersed phase morphology. The less viscous PP encapsulates the more viscous crosslinked rubber particles to minimize the mixing energy [31]. At equal curative dosage (2 phr) and compositional volume, PP/EPDM TPV shows coarser-crosslinked rubber particle size than PP/EOC TPV (Fig. 5c, d). By increasing the concentration of peroxide (4 phr) in order to increase the crosslink density of rubber phase, two opposite behaviors have been accounted in the particle size evolution for PP/EOC and PP/EPDM blend. Size of the crosslinked rubber particles increases in PP/EOC blends, whereas decreases in PP/EPDM blend as a function of peroxide concentration (Fig. 5e, f). It is well known that, PP undergoes

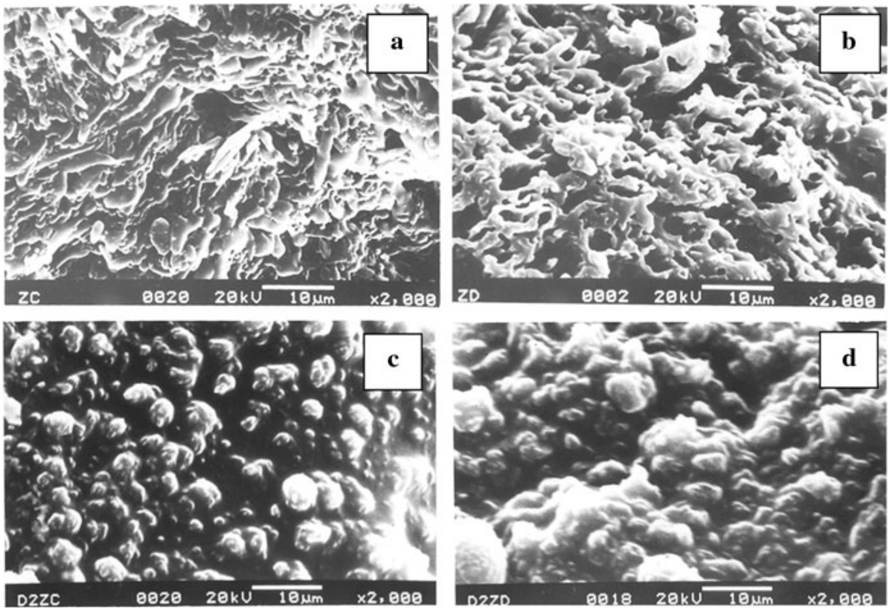

Fig. 6 SEM photomicrographs of **a** ZC (25/75 PP/EOC uncrosslinked), **b** ZD (25/75 PP/EPDM uncrosslinked), **c** D2ZC (dynamically vulcanized; 2 phr), **d** D2ZD (dynamically vulcanized; 2 phr)

chain-scission with the addition of peroxide. In case of PP/EOC blends when the concentration of peroxide increases from 2 to 4 phr, extent of degradation in the PP phase dominates over crosslinking in the EOC phase. Therefore, it becomes too difficult for a relatively very low viscosity PP matrix (low molecular weight PP) to break-up the crosslinked EOC rubber. But in case of PP/EPDM blends, in addition to the PP-matrix chain-scission, the inherent PP segments in the EPDM also undergo chain-scission which cause to form low molecular weight compound. These low molecular weight compounds have higher tendency towards fine dispersion by lowering the viscosity ratio.

In ZC and ZD (PP-25%) blends, since the rubbery component is in greater proportion than PP, the latter exists as the dispersed phase in continuous rubbery phase. As can be seen from the Fig. 6a, elongated and spherical particles of PP are dispersed in the continuous EOC matrix. In case of ZD (Fig. 6b), an intermediate morphology is formed and is quite difficult to quantify the phases in the given experimental window. However, it is expected to form dispersed phase morphology with EPDM as matrix phase. It is worth noting that after dynamic vulcanization, a complete inversion of phase morphology occurs. Dynamically vulcanized samples of ZC and ZD show crosslinked rubber (EOC or EPDM) particles dispersed in the continuous PP matrix. As a matter of fact, in the PP/EOC TPVs, the crosslinked EOC particles range from 4 to 5 µm, whereas in the PP/EPDM TPVs, the particle size is wider, coarser, and found to be in more aggregated state (5–7 µm) due to higher viscosity ratio (Fig. 6c, d). Hence, the state and mode of the dispersed phase is mainly determined by the viscosity and elasticity ratio of the blend components.

Table 5 Influence of torque ratio on the prediction of phase morphology

Compound name	Theoretical			Experimental			Inference
	X (Avgeropoulus et al. [33]) (Eq. 5)	Y (Jordhamo et al. [34]) (Eq. 6)	Prediction of morphology from model equation	Actual blend morphology obtained from SEM	Phase morphology after dynamic vulcanization	Particle size of TPVs (μm) (2 phr DCP)	
XC	10.1	12.3	EOC dispersed	EOC dispersed	EOC dispersed	0.5–1.0	No phase inversion
YC	3.4	4.1	EOC dispersed	Co-continuous	EOC dispersed	1–2	Phase inversion
ZC	1.1	1.3	Co-continuous	EOC continuous	EOC dispersed	4–5	Complete phase inversion
XD	19.5	25.8	EPDM dispersed	EPDM dispersed	EPDM dispersed	1–2	No phase inversion
YD	5.6	8.6	EPDM dispersed	Co-continuous	EPDM dispersed	3–4	Phase inversion
ZD	2.1	2.8	EPDM dispersed	EPDM continuous	EPDM dispersed	4–6	Phase inversion

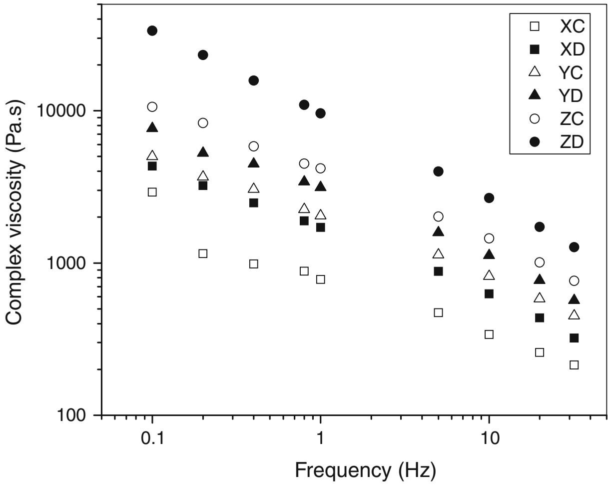

Fig. 7 Variation of complex viscosity as a function of frequency at 180 °C with a constant strain amplitude of 5%

Dynamic viscoelastic properties of uncrosslinked blends

The variation of complex viscosity (η^*) as a function of angular frequency (ω) for both PP/EOC and PP/EPDM uncrosslinked blends with varied blend ratios are shown in Fig. 7a, b, respectively. The results suggest that the rheological properties are dependent on the ratio of blend components, type of polymers and the morphology developed. All the samples exhibit a typical pseudoplastic feature in the whole range of explored frequency i.e., complex viscosity decreases with increase in shear rate or frequency. It is well established that, at low frequency the effect of flow induced molecular orientation on the viscosity and elasticity is less. Therefore, the viscoelastic response of the blends in the low frequency (low shear rate) can be used to evaluate the interfacial interaction between the components. The experimental complex viscosity values of the blend components are compared with the theoretical complex viscosity values obtained from the mixing rule (log additive model) at an angular frequency of 0.5 1/s is shown in Fig. 8. The log additive model [36] can be expressed as:

$$\log \eta = \phi_1 \log \eta_1 + \phi_2 \log \eta_2 \tag{7}$$

where η = viscosity of the blend η_1 and η_2 = viscosity of the two blend components measured at same temperature, ϕ_1 and ϕ_2 = volume fractions of the blend components.

Interestingly, both the systems (PP/EOC and PP/EPDM) exhibit a negative deviation (NDB) from the mixing rule. In general, the negative deviation is mainly associated with the incompatibility of the blend components. Indeed, it may be also due to the morphological evolution or interlayer slip or the systems approaching the phase separation [37]. A similar non-linearity i.e., negative deviation is observed

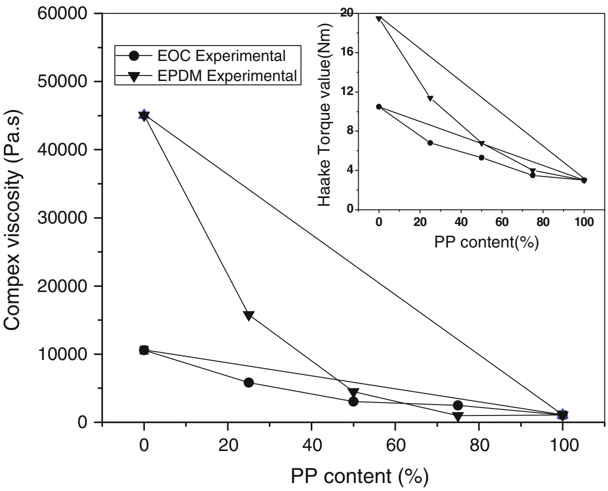

Fig. 8 Complex viscosity versus blend composition obtained from experimental and calculated using mixing rule at angular frequency of 0.5 Hz at 180 °C. *Inset graph* Stabilized torque value as obtained from Haake rheomix during mixing versus blend composition measured at 180 °C

from the stabilized torque values of the blends obtained from the Haake rheomix (shown in the inset of Fig. 8).

Frequency-dependent rheological parameters such as zero shear viscosity and Power law index parameters of the uncrosslinked blends are shown in Table 6. In general, morphology plays a vital role in determining the rheological response of the blend components. Various rheological responses observed during frequency sweep

Table 6 Rheological parameters and values observed from the frequency and strain sweep experiments for uncrosslinked blends

Compound name	Frequency dependent viscoelastic properties at 180 °C			Strain dependent viscoelastic properties at 180 °C		
	η_0 (Pa s)[a]	n[b]	K[c]	G_0 (kPa)[d]	G_∞ (kPa)[e]	ΔG[f]
XC	2,916	−0.389	2.91	1.29	0.108	1.18
YC	5,004	−0.408	3.30	3.04	0.122	2.91
ZC	10,611	−0.452	3.59	6.47	0.301	6.16
XD	4,326	−0.440	3.21	1.88	0.093	1.78
YD	7,643	−0.436	3.46	5.49	0.217	5.27
ZD	33,550	−0.563	3.87	29.45	0.734	28.70

[a] Viscosity at low shear rate (0.5 Hz)

[b] Flow behavior index

[c] Consistency index

[d] Low strain storage modulus (modulus at 2% strain)

[e] High strain storage modulus (modulus at 1200% strain)

[f] $\Delta G' = G'_\infty - G'_0$ (change in storage modulus value with strain amplitude sweep)

experiments have been examined as a function of blend ratio and correlated with the morphology developed.

1. At low elastomer content (XC and XD; 75% of PP), the rheological behavior is similar to that of neat PP. At this blend ratio, uncrosslinked rubber particles are dispersed in the continuous PP matrix. In other words, rheological properties are mainly determined by PP matrix. However, dispersed EOC or EPDM increases the viscosity and elasticity of the blends particularly in the low shear rate region. This may be attributed to the delayed response of the dispersed phase when lightly sheared.
2. At 50/50 rubber/plastic blend ratio (YC and YD; 50% of PP) blends show a co-continuous phase morphology. Hence at low frequency, the rheological response is controlled primarily by the PP phase, while at high frequency the elastomer or rubbery phase dictates the rheological response [38]. Since PP has very low relaxation time which deform first followed by the rubbery molecules.
3. At high elastomer loading (ZC and ZD; 25% of PP), PP particles are dispersed in the elastomer phase. Therefore, the rheological responses are mainly controlled by the rubbery components. However, PP particles may decrease the viscosity and elasticity of the rubbery phase.

It is worth noting that, at identical rubber/plastic blend ratio, EPDM-based blends show higher viscosity and elasticity than corresponding EOC based blends. This may be due to the higher molecular weight and more entangled microstructure of the EPDM based compound.

Figure 9a illustrates the variation of G' as a function of strain amplitude for PP/EOC and PP/EPDM uncrosslinked blends. All the samples exhibit a linear region followed by a non-linear region with increase in strain amplitude. In uncrosslinked blends, the non-linearity is mainly associated with the disentanglement or slippage of trapped and temporary entanglement network and/or debonding of the dispersed phase from the continuous matrix phase.

When comparing PP/EOC- and PP/EPDM-uncrosslinked blends, at identical blend ratios, the latter exhibit higher modulus in the low amplitude region and more

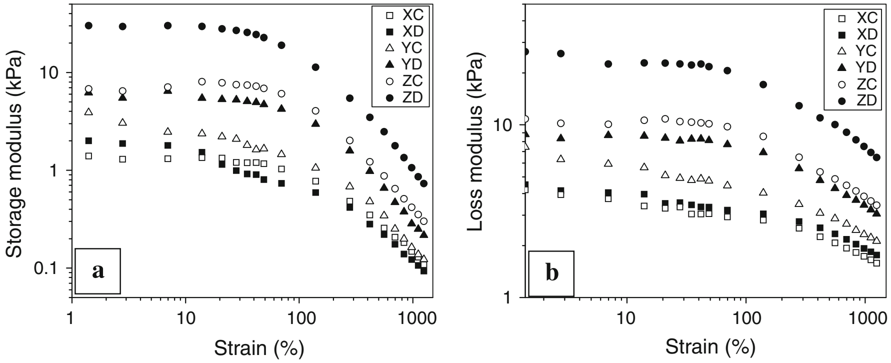

Fig. 9 Dependence of viscoelastic properties of uncrosslinked blends as a function of strain amplitude at 180 °C with a constant frequency of 1 Hz **a** storage modulus, **b** loss modulus

non-linear character. The higher modulus in the low strain region is attributed to the higher molecular weight and more trapped chain entanglement. In general, long elastomeric molecules tend to entangle with each other, forming physical crosslinks which include temporary and trapped entanglements. The presence of natural physical entanglements at their characteristics network density would cause an increase in number of effective crosslink points per molecule and correspondingly improve the modulus and set properties. Both G' and G'' follow the similar trend with strain amplitude, i.e., they decrease with increase in strain amplitude (deformation) (Fig. 9b).

Dynamic viscoelastic properties of dynamically crosslinked blends

Principally dynamic vulcanization leads to the formation of stabilized phase morphology with the uniform dispersion of crosslinked rubber particles in the continuous thermoplastic matrix. Different rheological parameters have been observed in frequency and strain sweep experiments and the results are tabulated in Table 7. The reinforcing characteristics and its relation with the morphology developed for peroxide cured PP/EOC TPVs was extensively discussed in our earlier communication [17]. It has been previously postulated that the rheology and viscoelastic properties of TPVs can be compared to that of filled polymer systems [39, 40]. Variation of η^* as a function of ω for PP/EOC and PP/EPDM is shown in Fig. 10a. It is very clear from the results that the blends with higher rubber content (50 and 75% of rubber content) show a sharp increase in viscosity and elasticity, which lead to exhibit a yield stress value at low shear rate range. This may be

Table 7 Rheological parameters and values observed from the frequency and strain sweep experiments for dynamically crosslinked blends

Compound name	Frequency dependent viscoelastic properties at 180 °C			Strain dependent viscoelastic properties at 180 °C		
	η_0 (Pa s)[a]	n[b]	K[c]	G_0 (kPa)[d]	G_∞ (kPa)[e]	ΔG[f]
D2XC	5,743	−0.6119	3.05	3.408	0.029	3.37
D2YC	51,688	−0.7996	3.88	40.86	0.487	40.37
D2ZC	18,4000	−0.8556	4.40	136.7	2.611	134.08
D2XD	2,069	−0.3997	2.73	1.602	0.041	1.56
D2YD	50,109	−0.7619	3.89	38.42	0.432	38.00
D2ZD	35,5000	−0.9001	4.64	255.30	3.129	252.18
D4YC	39,191	−0.7512	3.81	27.37	0.432	26.93
D4YD	44,321	−0.7877	3.81	32.91	0.389	32.52

[a] Viscosity at low shear rate (0.5 Hz)

[b] Flow behavior index

[c] Consistency index

[d] Low strain storage modulus (modulus at 2% strain)

[e] High strain storage modulus (modulus at 1200% strain)

[f] $\Delta G' = G'_\infty - G'_0$ (change in storage modulus value with strain amplitude sweep)

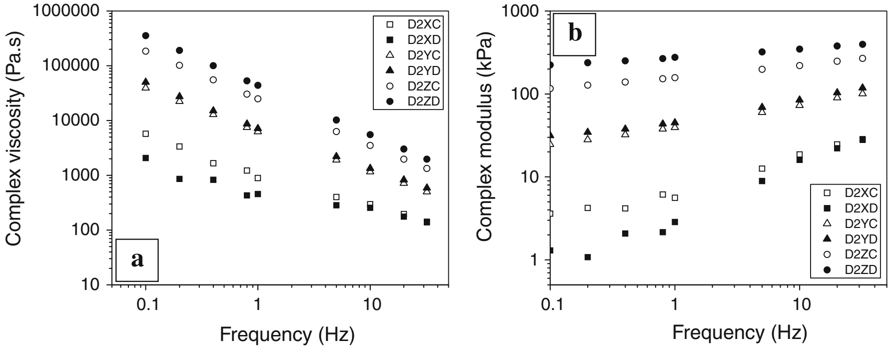

Fig. 10 Dependence of dynamic functions for various dynamically crosslinked blends as a function of frequency at 180 °C with a constant strain amplitude of 5% **a** complex viscosity, **b** complex modulus

attributed to the formation of three-dimensional network structure formed by the cured rubber particles. These particles are dispersed in the continuous matrix in the form of aggregates and/or agglomerates. These crosslinked particles are adsorbed or attached via joint shell mechanism or segmental interdiffusion mechanism [41]. Furthermore, irrespective of the different systems, dynamically vulcanized blends show more shear-thinning characteristics, which may be associated with the collapse or deformation of the secondary network structure.

Figure 10b shows the dependence of the G^* as a function of ω. In contrast to uncrosslinked blends, dynamically vulcanized blends show viscoelastic solid-like behavior; variation of storage modulus is almost independent of frequency, particularly at higher rubber/plastic ratio. When compared to uncrosslinked blends, TPVs with lower content of rubber phase (XC and XD) exhibit decrease of dynamic functions throughout the entire frequency range studied. Since the amount of PP is more, degradation in the PP phase overrides the effect of crosslinking in the EOC or EPDM phase with the addition of peroxide. As the peroxide dosage increases from 0 to 4 phr, in contrast to the blends with lower rubbery component (XC and XD), ZC and ZD (higher rubber component) show a continuous increase in the dynamic functions. At 50/50 blend ratio of PP/rubber (EOC or EPDM), dynamic functions initially increase and then start decreasing with increase in peroxide dosage. In case of PP/EOC TPVs, the decrease in dynamic function is mainly due to the evolution of morphology. It can be seen from the Fig. 5e, f that D4YC shows coarser particle size in comparison to D2YC. PP/EOC-based blends show more pronounced increase in dynamic functions than PP/EPDM blends during dynamic vulcanization. It is expected that, propylene units of EPDM rubber undergo chain-scission reaction and consequently decrease the dynamic functions.

Figure 11a, b illustrates the variation of G' and G'' as a function of strain amplitude. In general, both the modulus values (G' and G'') increase by the process of dynamic vulcanization, except in the blend having lower rubber content (XC and XD). Both the moduli show a linear region followed by the non-linear region as a function of strain amplitude. It is worth nothing that, TPVs with higher rubber content show more pronounced drop in storage modulus. Furthermore, it was

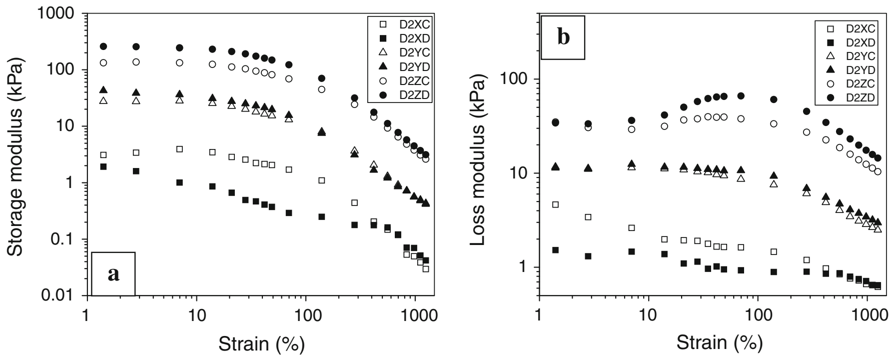

Fig. 11 Dependence of viscoelastic properties of various dynamically crosslinked blends as a function of strain amplitude at 180 °C with a constant frequency of 1 Hz **a** Storage modulus, **b** loss modulus

observed that, deviation from the linear viscoelastic behavior of PP/EPDM TPVs starts at lower strain amplitude range than PP/EOC TPVs at a particular (identical) blend ratio. In general, the non linearity of TPVs is associated with the disintegration and debonding of secondary structure formed by the crosslinked rubber particles. In case of PP/EPDM TPVs, the disintegration of aggregates and/or agglomerates of crosslinked rubber particles coupled with the breakdown or deformation of physical crosslinks in the rubbery phase (i.e., temporary and trapped entanglements in the EPDM molecular architecture). This has been reflected to show a remarkable loss maximum region (in the plot of G'' vs. strain amplitude) at the critical strain amplitude region. The strain-dependent behavior of the TPVs can be analogically compared to the so called Payne effect observed in the filled rubber systems. According to Payne, the loss maximum is associated with the rate of network breakdown and reformation which in turn related to the internal friction of the filled vulcanizates [30]. In general, G' is related to the secondary network which subsists during dynamic deformation, whereas G'' is related to the breakdown and reformation of secondary network. Therefore, the dynamic behavior of the TPVs is primarily governed by the state and mode of three dimensional network formation coupled with the deforming characteristics of the inherent physical crosslinks (temporary and trapped entanglements) in the dispersed rubbery domains.

Conclusions

The morphology of PP/EOC and PP/EPDM blends indicate a two phase morphology in which the rubber phase is dispersed in continuous PP matrix at lower rubber/plastic blend ratio and followed by phase inversion with increase in rubber/plastic blend ratio. The 50/50 composition of rubber/plastic shows co-continuous phase morphology. However, after dynamic vulcanization all the samples exhibit a dispersed phase morphology in which crosslinked rubber particles are dispersed in continuous PP matrix. The dispersion characteristics of the dispersed crosslinked rubber phase is mainly influenced by the melt viscosity ratio, shear rate, curative dosage, and the rubber content. Rheological properties of the blend (both PP/EOC and PP/EPDM) can be described as a weighted contribution of the properties of two individual phase and the dynamic functions are found to be negatively deviated from the log additive model. In contrast to the lower rubber/plastic ratio; dynamic vulcanization abruptly increases the dynamic functions for the blends with higher rubber content. This may be associated with the formation of three dimensional network structure formed by crosslinked rubber particles. Degradation in the PP phase dominates if the rubber content is less and the crosslinking tendency predominates at higher rubber/plastic blend ratio and correspondingly reflected in the melt viscoelastic properties. RPA stain sweep and frequency sweep of TPVs indirectly reflect the phase structure.

In short, PP/EOC shows better processing characteristics and mechanical properties which may be due to better interfacial interaction and unique molecular microstructure of the EOC phase. In addition EOC are supplied in free pellets which allows for both batch and continuous production of TPVs. Therefore, peroxide-cured PP/EOC TPVs combine better processing characteristics with superior performance in the solid state. Hence, peroxide-cured PP/EOC can be considered as a potential alternative to the conventional peroxide cured PP/EPDM TPVs.

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