

Development of novel polar thermoplastic vulcanizates based on ethylene acrylic elastomer and polyamide 12 with special reference to heat and oil aging

Syed Mohammed Reffai Syed Ismail, Tuhin Chatterjee, Kinsuk Naskar

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

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

ABSTRACT: Thermoplastic vulcanizates (TPVs) based on ethylene acrylic elastomer (AEM) and polyamide 12 (PA12) have been developed by the dynamic vulcanization process, in which selective cross-linking of the elastomer phase (AEM) during melt mixing with the thermoplastic phase (PA12) has been carried out simultaneously. TPVs at varied blend ratios (50 : 50, 60 : 40, 70 : 30) of AEM/PA12 were prepared at 185°C at a rotor speed of 80 rpm up to 5 min of mixing. Di-(2-tert-butyl peroxy isopropyl) benzene (DTBPIB) was chosen as the suitable cross-linking peroxide to carry out the dynamic vulcanization. Morphology study reveals the development of continuous agglomerate of rubber network in case of all the TPVs took place and the average dimension of the rubber particles are in the range of 30–40 nm. TPV based on 50 : 50 AEM/PA12 shows better physicochemical properties, thermal stability, and dynamic mechanical behavior among all the TPVs. For aging test, TPVs were exposed to air, ASTM oil 2 and 3. Air aging tests were carried out in hot air oven for 72 h at 125°C, while the oil aging tests were carried out after immersion of the samples into the oils in an aging oven. After aging, there are only slight deterioration of physicochemical properties of the TPVs. Particularly in case of 50 : 50 blend of AEM/PA12, the retention of the properties even after aging was found excellent. The recyclability of these new TPVs is also found to be excellent leading to find potential application in automobiles. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42655.

KEYWORDS: cross-linking; polymer blends; thermoplastic vulcanizate

Received 7 April 2015; accepted 24 June 2015

DOI: 10.1002/app.42655

INTRODUCTION

Polyolefinic thermoplastic elastomer (TPEs), blend of elastomer and thermoplastics, belong to a specific family of polymeric alloys that offers the two main advantages of the polymeric materials: elastomeric behavior at room temperature and thermoplastic behavior at high processing temperature.¹ The dual behavior is obtained because of the two-phase structure of the materials and this characteristic makes it a suitable alternative for conventional cross-linked rubber.² Recyclability of the scraps and wastes of thermoplastic elastomers is also an added advantage.³ TPE often suffers from the following disadvantages: (a) creep behavior on extended use, (b) poor set property and lower elastic recovery, etc.⁴ To get rid of those disadvantages, thermoplastic vulcanizates (TPVs) have been developed by a dynamic vulcanization process, in which selective cross-linking of the elastomeric phase with melt mixing of the thermoplastics are carried out simultaneously.^{5,6} Simple blending offers a material with co-continuous morphology, while dynamic vulcanization enables the cross-linked elastomers to become the

dispersed phase even if the volume fraction of the elastomer is >0.5.^{1,7} Increment in elastomer viscosity during dynamic vulcanization affects the phase continuity and promotes the phase inversion which results heterophase morphology in TPVs. As a result, the major elastomeric phase becomes the dispersed one and the thermoplastic component despite being the minority also remains continuous and thus offers the ease of processing like thermoplastics.^{8,9} In 1962, Gessler and Haslett first reported the process of dynamic vulcanization and later Fischer further developed the concept through his novel work on polypropylene (PP)- and ethylene propylene diene rubber (EPDM)-based TPVs with peroxides as a cross-linking agent.^{10,11} After that, Coran and Patel extensively studied on various blend systems in which the rubber phase is dynamically cross-linked with high cross-link density.^{12,13} Influence of various peroxides and multi-functional peroxide upon PP/EPDM TPVs was successively investigated by Naskar *et al.*^{14,15} A new family of TPV based on PP and ethylene octene copolymer (EOC) has also been explored and thus gained special attention due to better toughening characteristics of EOC.^{16,17} Later on Giri *et al.* also

Table I. Characteristics of the Raw Materials

Material	Trade name	T_g (°C)	T_m (°C)	Tensile strength (MPa)	Tensile elongation at break (%)
Ethylene acrylic rubber (AEM)	Vamac DP(VDP)	-32	-	2.8	1560
Polyamide (PA12)	Rilsan® AESNO TL	55	177	68.9	330

reported a new class in this family based on LLDPE/PDMS blend system.¹⁸ A newly developed high-performance thermoplastic vulcanizates based on blends of natural rubber and thermoplastic polyurethanes has been developed by Charoen Nakason *et al.*¹⁹ The role of phase morphology on the damage initiated self-healing behavior of ionomer blends (EMNa and EMZn) has been reported by Rahman *et al.*²⁰ Recently, thermally cross-linked and sulfur-cured soft TPVs based on styrenic block copolymer S-EB-S/S-SBR blends has been reported by Dey *et al.* The microstructure change upon reprocessing has also been focused.^{21,22} Very recently, Joyeeta Dutta *et al.* studied the influence of electron beam irradiation on the morphology, physicomechanical, thermal behavior, and performance properties of EVA and TPU blends.²³ Recently, a new family of TPV based on silicone rubber (PDMS) and polyamide (PA12) has been reported by a group of researchers^{24,25} which suffers from compatibility mismatch of the two phases. Although in this case also oil-resistance property of the TPV is not mentioned in the literature. All the above-mentioned TPVs have limitation in automotive application due to their poor heat and oil resistance properties.

In this work, novel polar TPV based on ethylene acrylic dipolymer elastomer (AEM) and polyamide 12 (PA12) at a different blend ratio has been developed and characterized in detail. Both the components have excellent oil resistance properties. Especially PA12 shows outstanding resistance to alkali and acid and also it has excellent environmental stress cracking resistance at elevated temperature. However, PA12 being a thermoplastic has a glass transition temperature (T_g) higher than room temperature, which inhibits low temperature flexibility property of PA12. On the other hand, AEM has the outstanding low temperature flexibility due to its low T_g . AEM also shows very good compression set resistance property.

EXPERIMENTAL

Materials

Vamac® DP (ethylene acrylic dipolymer elastomer) (VDP) was procured from DuPont elastomer. It has a Mooney viscosity, $ML_{(1+4)}$ at 100°C of 22 and density of 1.04 g/cc at 25°C. Polyamide 12 (PA12) (Rilsan® AESNO TL) has a melt flow rate (MFI) of 0.6 g/10 min, measured at 190°C and 2.16 kg load. It has the density of 1.02 gm/cm³ at 25°C and it was procured from Arkema, France. The characteristics of these raw materials are shown in Table I. An organic peroxide namely Perkadox14-40BD {di(2-tert butyl peroxy isopropyl)benzene (DTBPIB)} (procured from Akzo Nobel, The Netherlands) is used as the cross-linking of AEM. At a temperature of 146°C, the “half-life” time of peroxide is 1 h.

Preparation of the Thermoplastic Vulcanizates (TPVs)

TPVs based on AEM and PA12 at three different blend ratio (50 : 50, 60 : 40, 70 : 30) of AEM/PA12 were prepared by batch process in an internal mixer (Haake Rheomix 600), cam-type rotor having a mixing chamber volume of 85 cm³ with a rotor speed of 80 rpm at 185°C by phase mixing method.²⁶ Before addition to the molten PA12, peroxide was premixed with AEM at 90°C at a rotor speed of 60 rpm. At first, PA12 was poured into the mixing chamber at 185°C and at 80 rpm. To carry out the reactive blending, after melting of PA12 matrix, AEM (premixed with peroxide) was added to the molten thermoplastic phase. The scheme of preparation of TPVs has been depicted in Figure 1. Finally, TPVs were developed at three different blend ratios of AEM and PA12 at a rotor speed of 80 rpm at 185°C up to 5 min of mixing. Immediately after mixing, the composition was removed from the mixer and while still molten, passed once through a cold two-roll mill to achieve a sheet of about 2 mm thickness.

Preparation of the Molded Specimen

After mixing, the sheet obtained from the two-roll mill was compression molded in a hydraulic press (Moore Presses, George E. Moore & Sons Birmingham Ltd., UK) at 185°C for 4 min under a pressure of 10 MPa to form tensile sheets of about 2 mm thickness. Keeping under pressure, the mound was allowed to cool to the ambient temperature. Dumbbell-shaped specimens were cut off from the sheets using a standard cutting die.

Testing Procedures

Curing Characteristics. Curing characteristics of only AEM rubber (without any PA12) contain selective cross-linking agent, Perkadox 14-40B, were carried out by using Monsanto Rheometer R100 (an oscillating disc rheometer, ODR) at 185°C for 30 min.

Morphology Study. Morphological study of final TPV samples and the dispersion of AEM and PA12 phase were carried out using an intermittent contact mode atomic force microscopy, AFM (Agilent 5500 Scanning Probe Microscope). The resonance frequency of the tip was 146–236 kHz, and the force constant was 48 N/m. Tip stiffness was 40 N/m and tip radius was 10 nm. To carry out the AFM study, thin films of the TPVs were prepared by compression molding at 10 MPa pressure and at 185°C for 4 min to form sheets of about 2 mm thickness.

Mechanical Properties. Tensile testing of the blends was carried out as per ASTM D 412 using a dumbbell-shaped specimen (symmetrically placed in the grips of the testing machine so that distribution of tension is uniform throughout the specimen cross-section) using a universal testing machine (Hounsfield H25KS) at a cross-head speed of 200 mm/min. As per ASTM D

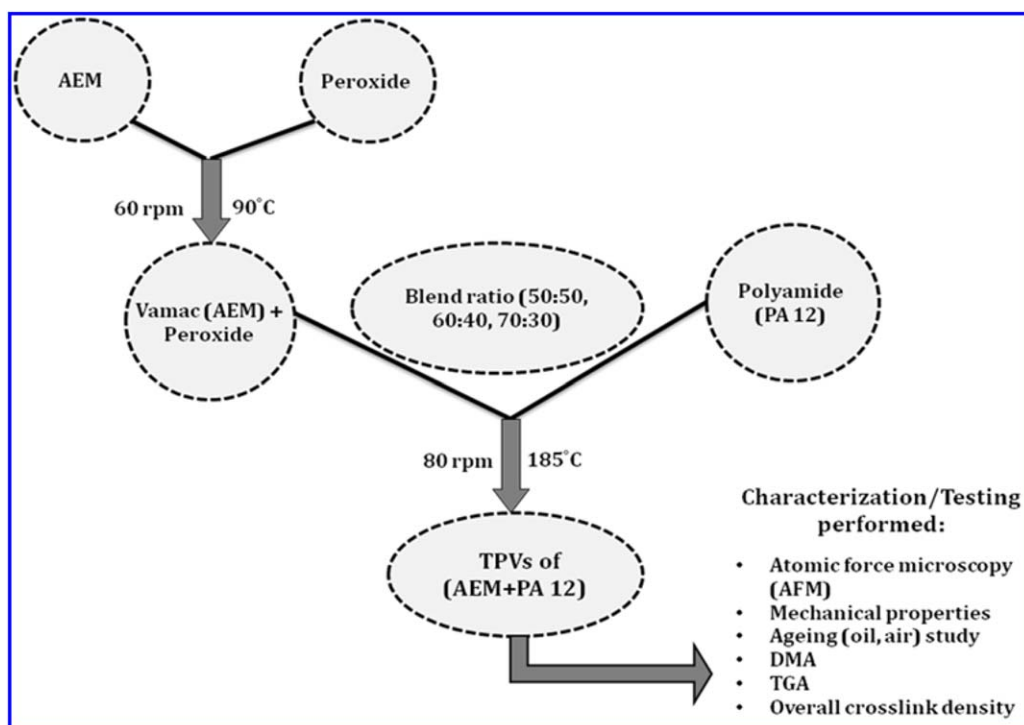


Figure 1. The scheme of preparation of TPVs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2240 hardness of the samples (minimum 6 mm of thickness) was determined using a Shore A and Shore D Durometer hardness tester. All sample testing was carried out at ambient temperature. We have used the 2-mm-thick sheet by placing three sheets, each one on top of the other.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) of the samples was performed out using a dynamic mechanical analyzer (Metravib 50 N, France). In tension mode, temperature sweep of the blends were carried out over a temperature range of -80 to $+120^{\circ}\text{C}$, at a heating rate of $2^{\circ}\text{C}/\text{min}$. During test, the samples were scanned at a frequency of 10 Hz and under static strain of 0.50% and dynamic strain of 0.10%, which was well within the linear viscoelastic region (LVR). Storage modulus (E'), loss modulus (E''), and the loss tangent ($\tan \delta$) of the blends were recorded as functions of temperature.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) of the blends of VDP/PA12 was measured by using a thermogravimetric analyzer (TGA Q5000, TA Instruments, USA) at a heating rate of 10 K/min under nitrogen atmosphere.

Aging Study. Air and oil aging tests were performed in a hot air oven and aging oven in the temperature range of 125°C for 70 h as per ASTM D 471-98. Oils used were ASTM No 2 (IRM902) medium polar and ASTM No 3 (IRM903) high polar. When the specified time was reached, the test specimens were removed from the oil and wiped with tissue paper to remove the excess oil from the sample surface. Finally, tensile properties of the specimens after aging were measured to estimate oil resistance according to ASTM D471-98. The samples were kept

at room temperature for 24 h after aging and physical properties were measured. The aging resistance is expressed as a percentage of retention in tensile properties and elongation at break.

Cross-Link Density. Equilibrium solvent swelling measurements were conducted on a small rectangular specimen in order to find out the overall cross-link density. The specimens were immersed in ethylmethylketone (MEK) for 72 h at room temperature. At the end of the immersion period, the specimens were removed from the solvent, smoothly wiped with tissue to absorb the solvent on the surface and then immediately transferred to the weighing balance to get the swollen weight of the specimens. After that the specimens were dried at 50°C for 6 h to get the deswollen weight of the specimen. From the swollen weight and deswollen of the specimen, the overall cross-link density of the blends was determined by the use of the well-known Flory–Rehner equation [eq. (2)] at room temperature:

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

where, $(\nu + \text{PA})$ = number of moles of effectively elastic chains per unit volume of AEM [mol/mL] (cross-link density) in presence of PA12. V_s = molar volume of solvent (MEK) [c.c/mol], which is 89.6 mL/mol. χ = polymer-swelling agent interaction parameter, taken as 0.0015 for both AEM and MEK at 20°C . V_r = volume fraction of rubber in the swollen network and V_r can be expressed as follows:

Table II. Physicomechanical Properties of AEM, Cross-Linked by Different Concentration of Peroxide (Standard Deviation Values for 5 Numbers of Test Specimens are Given in Parenthesis)

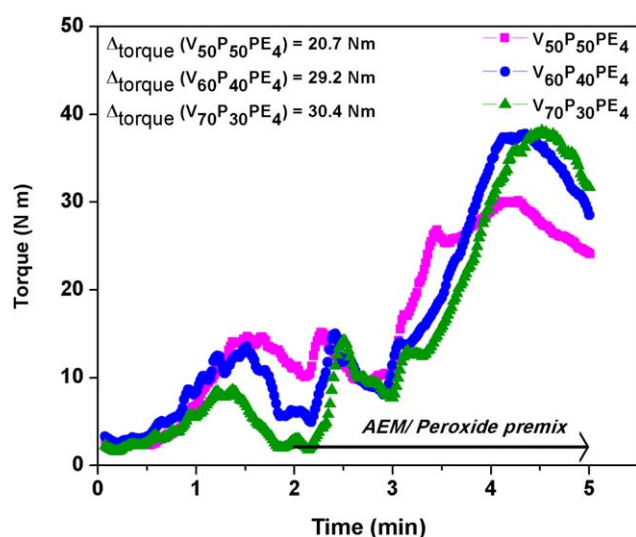
Sample code	Tensile strength [MPa]	Elongation at break [%]	Modulus [MPa] M100	Hardness [Shore A]
V ₂	5.4 (0.16)	643 (11.8)	0.4 (0.04)	37 (1.73)
V ₄	6.9 (0.10)	504 (6.11)	0.3 (0.04)	41 (1.52)
V ₆	3.8 (0.19)	206 (4.93)	0.4 (0.04)	46 (0.57)

Table III. Curing Characteristic of AEM in Presence of Perkadox 14–40BD Peroxide at 185°C

Sample code	Concentration of Perkadox 14-40BD (in phr)	Minimum torque (dN m)	Maximum torque (dN-m)	Delta torque (dN-m)	T ₉₀ (min)
V ₂	2.0	2.55	13.75	11.2	4.97
V ₄	4.0	2.63	15.60	12.97	3.68
V ₆	6.0	3.06	24.60	21.54	2.99

Table IV. Physicomechanical Properties of TPVs and TPEs (Standard Deviation Values for 5 Numbers of Test Specimens are Given in Parenthesis)

Sample code	Tensile strength [MPa]	Elongation at break [%]	Modulus [MPa] @ 100%	Hardness [Shore A]	Hardness [Shore D]
V ₅₀ P ₅₀	7.9 (0.23)	68 (2.10)	-	85 (0.5)	36 (0.57)
V ₆₀ P ₄₀	6.7 (0.56)	30 (1.53)	-	74 (1)	29 (0.7)
V ₇₀ P ₃₀	5.9 (0.72)	28 (0.90)	-	62 (0.15)	22 (0.15)
V ₅₀ P ₅₀ PE ₄	18.5 (0.45)	123 (2.03)	18.1 (0.5)	96 (1.15)	44 (0.47)
V ₆₀ P ₄₀ PE ₄	13.5 (0.58)	103 (1.21)	13.1 (0.15)	95 (0.57)	40 (1.57)
V ₇₀ P ₃₀ PE ₄	9.0 (0.75)	76 (0.95)	-	90 (0.57)	33 (1.15)

**Figure 2.** Mixing energy curves for TPVs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

where, A_r = ratio of the volume of absorbed MEK to that Vamac DP after swelling.

Recyclability Study. One of the major advantages of the TPEs and TPVs is its ability of recycling without significant deterioration of mechanical properties. In order to test the

Table V. TPV Compositions at Varied AEM/PA12 Blend Ratios at a Fixed Peroxide Concentration (4 phr)

Components	V ₅₀ P ₅₀ PE ₄	V ₆₀ P ₄₀ PE ₄	V ₇₀ P ₃₀ PE ₄
AEM (VDP)	50	60	70
PA12	50	40	30
PER 14-40B	4	4	4

V, vamac dipolymer (VDP) (AEM); P, Polyamide (PA12); PE, Perkadox 14-40BD; V50, 50 phr of AEM rubber; P50, 50 phr of PA12 plastic; PE₄, 4 phr of perkadox 14-40b peroxide.

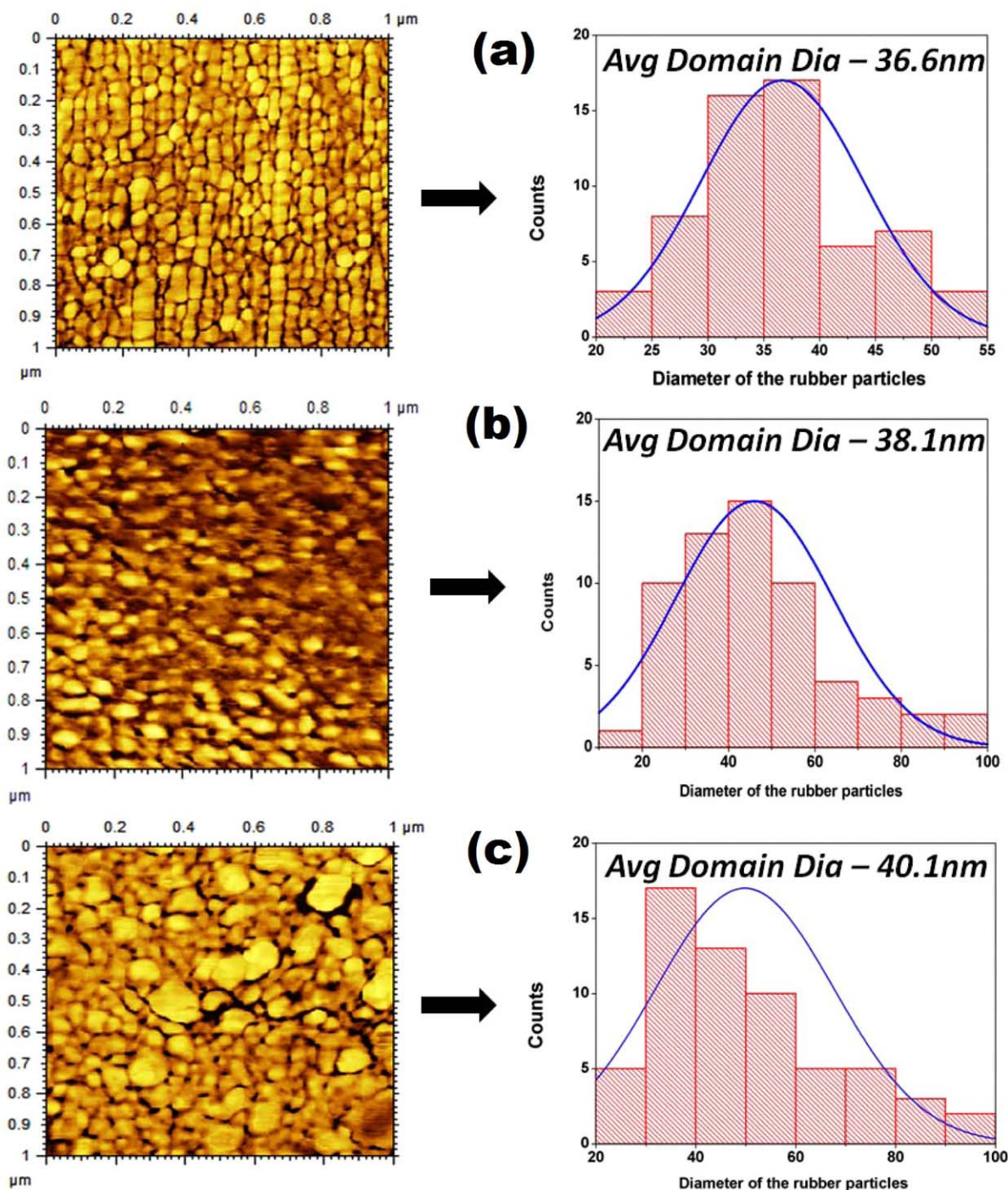


Figure 3. AFM phase images of (a) $V_{50}P_{50}PE_4$, (b) $V_{60}P_{40}PE_4$, and (c) $V_{70}P_{30}PE_4$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reprocessability of the thermoplastic elastomer composition, the molded samples were cut into small pieces and remixed in the Haake Rheomix at 185°C for 3 min and sheeted out and molded 185°C for 4 min under a pressure of 10 MPa to form tensile sheets of about 2 mm thick. Keeping under pressure, the mold was allowed to cool to the ambient temperature. Dumbbell-shaped specimens were cut off from the sheets using a standard cutting die.

RESULTS AND DISCUSSION

Curing Characteristics and Physicomechanical Properties of Cross-Linked AEM

To assess the dynamic vulcanization of AEM/PA12, it is necessary to know the curing characteristics of pure AEM gum compounds in presence of Perkadox 14-40BD peroxide. Different concentrations (2, 4, and 6 phr) of peroxide were mixed with pure AEM gum compound and curing characteristics was

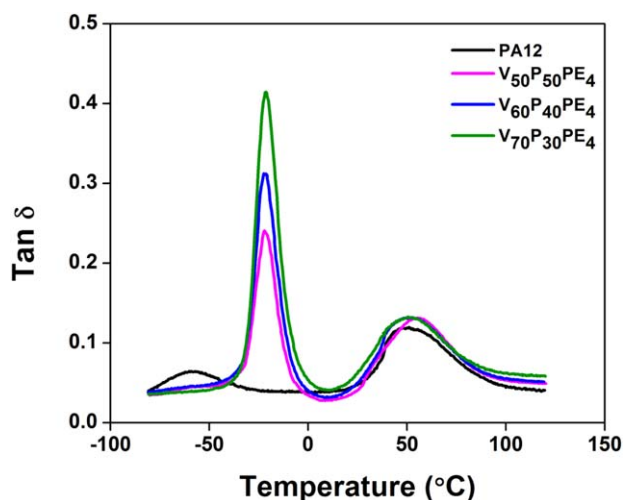


Figure 4. Tan δ versus temperature plot of the TPVs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

studied in an Oscillating Disk Rheometer (ODR) at 185°C. Optimum curing time (t_{90}), maximum torque, and delta torque (maximum–minimum torque) values of three different compounds is given in Table II. The delta torque values obtained from ODR generally correlates with the cross-linking efficiency of the peroxide, i.e., the number of moles of chemical cross-links formed per mole of peroxide. From Table III, it can be clearly seen that with increasing concentration of peroxide delta torque value also increases, which imply a higher degree of cross-links formation (in case of V_6 compound). On the other hand, with higher peroxide concentration, optimum curing time (T_{90}) for the compound gets reduced. The optimum curing time for V_2 is 4.97 min, whereas T_{90} of V_6 is only 2.99 min. There is no significant increase in delta torque value for 2–4 phr of peroxide concentration. However, it is slightly high for the 4–6 phr peroxide concentration. It is anticipated that due to formation of higher degree of cross-linking which results in higher modulus value of the material. To achieve an optimum property, there should be an optimum level of cross-linking. In this regard, it can be observed from Table II that the property is deteriorating with 6 phr peroxide concentration though the delta torque shows high delta torque value. On the other hand, 4 phr of peroxide concentration displays better properties as because the system reached an optimum cure. Nevertheless, the scenario of the physicochemical properties of the peroxide cross-linked AEM compound is different. The physicochemical properties of peroxide cross-linked AEM compound is given in Table IV. From Table IV, it can be observed that with higher degree of cross-link formation, elongation at break of the AEM

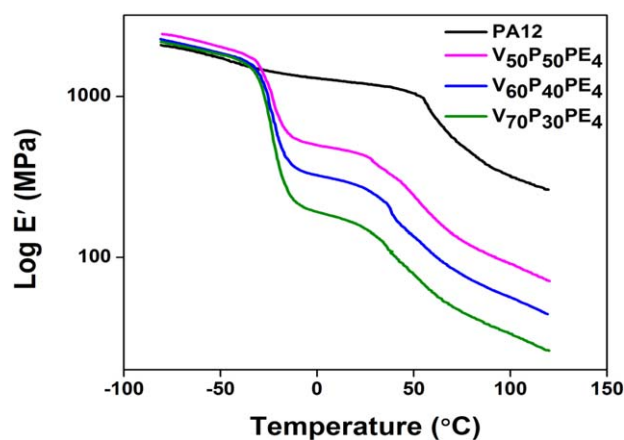


Figure 5. Storage modulus versus temperature plot of the TPVs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compound reduces. V_2 compound shows elongation at break of 643% and it drastically reduces to 206% for V_6 compound. Thus, considering both the curing characteristics and physico-mechanical properties of the AEM compounds, 4 phr peroxide was chosen as an optimum concentration of peroxide for the development of TPVs in the next step of the investigation.

Mixing Curve

Mixing energy curves during the process of dynamic vulcanization is shown in Figure 2. Increment of torque values during mixing of polymer inside the mixing chamber is a complex combination of shear and elongational flow. All the mixing curves (torque–time plots) consist of two peaks: the first peak corresponds to the rise of viscosity value due to resistance pretended on the rotor by the unmolten polymer (PA12) followed by a viscosity decrease due to the complete melting of PA12 and the addition of peroxide premixed AEM phase upon the molten PA12 phase implies the rise of the second peak because of the rise of viscosity. From $V_{50}P_{50}PE_4$ to $V_{70}P_{30}PE_4$, with a decrease of PA12 content (from 50 parts to 30 parts) torque value reduces from 15.8 to 8.7 Nm while the opposite scenario was noticed after addition of peroxide mixed AEM phase. $V_{70}P_{30}PE_4$ blend containing 70 parts of rubber shows maximum torque value of 30.4 Nm after dynamic vulcanization while maximum torque value is 20.7 Nm after dynamic vulcanization in case of $V_{50}P_{50}PE_4$ blend (Table V).

Morphology Study

Morphology plays a very important role in TPV to predict its solid-state properties. It is also important that at the end of dynamic vulcanization, typical TPV-like morphology should be

Table VI. Storage Modulus (E') and $\tan \delta$ Values of TPVs

Sample code	E' (MPa) at -31°C	E' (MPa) at 23°C	$\tan \delta$ at -21°C	$\tan \delta$ at 50°C
PA12	–	1219	–	0.119
$V_{50}P_{50}PE_4$	1672	434	0.239	0.126
$V_{60}P_{40}PE_4$	1479	272	0.312	0.131
$V_{70}P_{30}PE_4$	1375	154	0.415	0.132

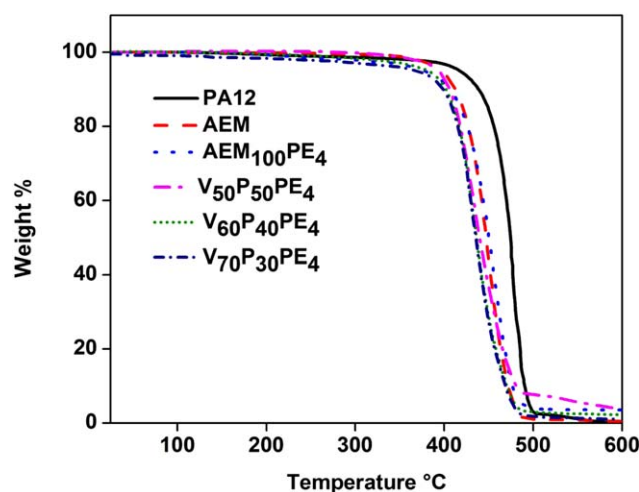


Figure 6. TGA thermograms of different TPVs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formed. To get an insight regarding the developed morphology after dynamic vulcanization, atomic force microscopy (AFM) has been carried out. Figure 3(a–c) shows the phase images of the three TPVs respectively. The light-yellow regions in the phase images indicate presence of cross-linked rubber particles and dark-brown region represents the PA12 phase.²⁷ Previously it was reported by many researchers that TPV contains micron-sized rubber particles dispersed in continuous thermoplastic matrix phase.^{28,29} From the phase image, it is clearly seen the formation of continuous agglomerate of rubber network in case of all the three TPVs and it is also evident that the average diameter of rubber particles are in the range of 30–40 nm. On the other hand, a few regions can still be seen where formation of nanodomain are confirmed in all the three TPVs. However, as we move from higher rubber fraction to lower rubber fraction (70–50 parts), the rubber nanoparticles are distinctly identifiable by the image of V₅₀P₅₀PE₄. Therefore, it can be concluded that the development of continuous agglomerate dictates the ultimate mechanical properties for V₅₀P₅₀PE₄, whereas the higher rubber fraction causes severe network disruption, which may lead to low mechanical properties for V₇₀P₃₀PE₄.²⁷

Physicomechanical Properties

From Table IV, it can be observed that V₅₀P₅₀PE₄ TPV, containing the highest fraction of PA12 among all the other TPVs give

the best result in term of tensile strength, hardness, and elongation at break. With decreasing PA12 content from 50 parts to 30 parts, mechanical properties and hardness of the TPVs become inferior. Therefore, V₅₀P₅₀PE₄ TPV shows the tensile strength of 18.5 MPa and elongation at break of 123%, whereas tensile strength of 9 MPa and elongation at break of 76% only was noticed in case of V₇₀P₃₀PE₄ TPV. Shore D hardness of V₅₀P₅₀PE₄ is 44; which is 33 for V₇₀P₃₀PE₄ TPV. Such improvement in mechanical properties from V₇₀P₃₀PE₄ TPV to V₅₀P₅₀PE₄ TPV may be of two reasons³⁰ (a) higher PA12 fraction (plastic phase) or (b) higher degree of cross-linking in the AEM rubber phase.

Dynamic Mechanical Analysis (DMA)

Tan δ (ratio of loss modulus to the storage modulus) peak from DMA is often used as a measure of the glass transition temperature (T_g). Tan δ versus temperature plot of the blends has been shown in Figure 4. It indicates that the glass transition temperature peak for AEM appears at around 21°C. From Figure 4, it can be clearly noticed that with the increase of AEM content, tan δ values of the blends at the transition region increases, as given in Table VI. Higher the AEM content, higher the rubber fractions exposed to dynamic transition, which leads to the higher tan δ values (higher dissipation of energy) at the transition region. The availability of the rubber molecules to the dynamic transition becomes lower with gradual addition of plastic phase (from 30 parts to 50 parts) into the blends. This is due to the immobilization of the rubber molecules which comes close to the plastic phase and as a result that rubber molecules cannot contribute to the dynamic transition which implies lower dissipation of energy (lower tan δ values).²⁷ Another peak in tan δ plot was observed near about 50°C, which corresponds to the glass transition peak of polyamide (PA12). From the figure, it can be seen that for higher plastic containing TPV (V₅₀P₅₀PE₄), the tan δ peak has been shifted slightly which may be of extensive intermolecular hydrogen bonding. Storage modulus of the three TPVs is shown in Figure 5. Considering the storage modulus, it can be argued that at lower temperature, storage modulus (E') is more or less same. V₅₀P₅₀PE₄ is showing little bit of higher E' value compared to the other two. It is well known that all the TPVs are in glassy state below glass transition temperature (T_g). After T_g , it shows glass-to-rubber transition state and it is called rubbery plateau. Length of the rubbery plateau region is based on the rubber content or we can say based on the composition, the E' values vary. As a

Table VII. TGA Data of Neat Polymers and Their TPVs

Sample designation	Temperature corresponding to 5% decomposition T_{95} (°C)	Temperature corresponding to 50% decomposition T_{50} (°C)	Maximum decomposition temperature, T_{max} (°C)
PA12	416	474	501
AEM	396	447	491
AEM ₁₀₀ PE ₄	379	450	492
V ₅₀ P ₅₀ PE ₄	392	439	489
V ₆₀ P ₄₀ PE ₄	381	436	487
V ₇₀ P ₃₀ PE ₄	366	434	481

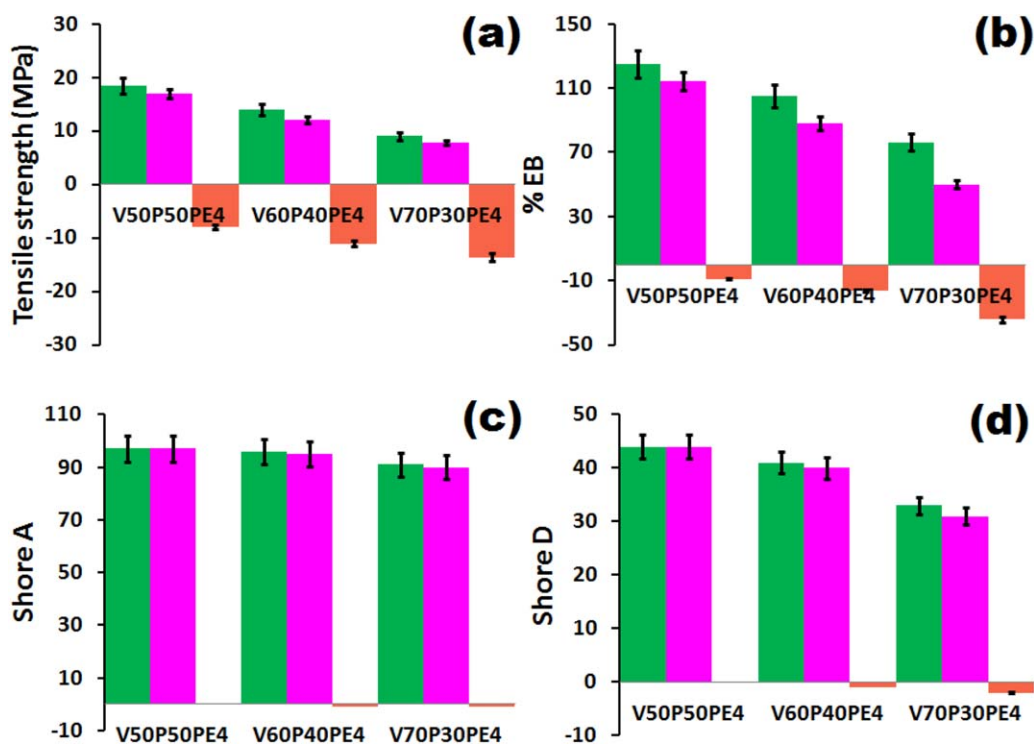


Figure 7. Change of (a) tensile strength, (b) elongation at break and hardness, (c) Shore A, and (d) Shore D of the TPVs due to heat aging (72 h at 125°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

result, V50P50PE4 TPV containing 50 phr AEM rubber and 50 phr PA12 shows highest E' value, whereas V70P30PE4 TPV containing 70 phr AEM rubber and 30 phr PA12 shows the lowest value of E' . In all the TPVs, the rubber phase are cross-linked

and PA12 are continuous matrix phase but the composition varies which results in difference in E' value. At higher temperature, TPVs get soften which implies the decrease in E' value. Even at lower temperature also, the storage modulus of

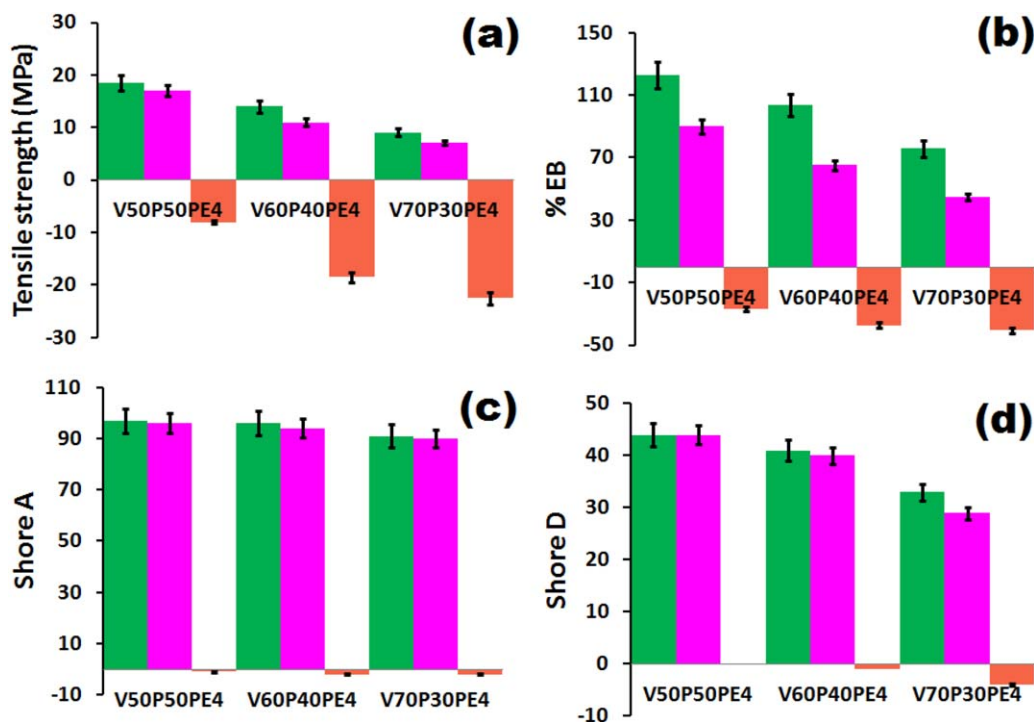


Figure 8. Change of (a) tensile strength, (b) elongation at break and hardness, (c) Shore A, and (d) Shore D of the TPVs due to ASTM Oil No II aging (72 h at 125°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

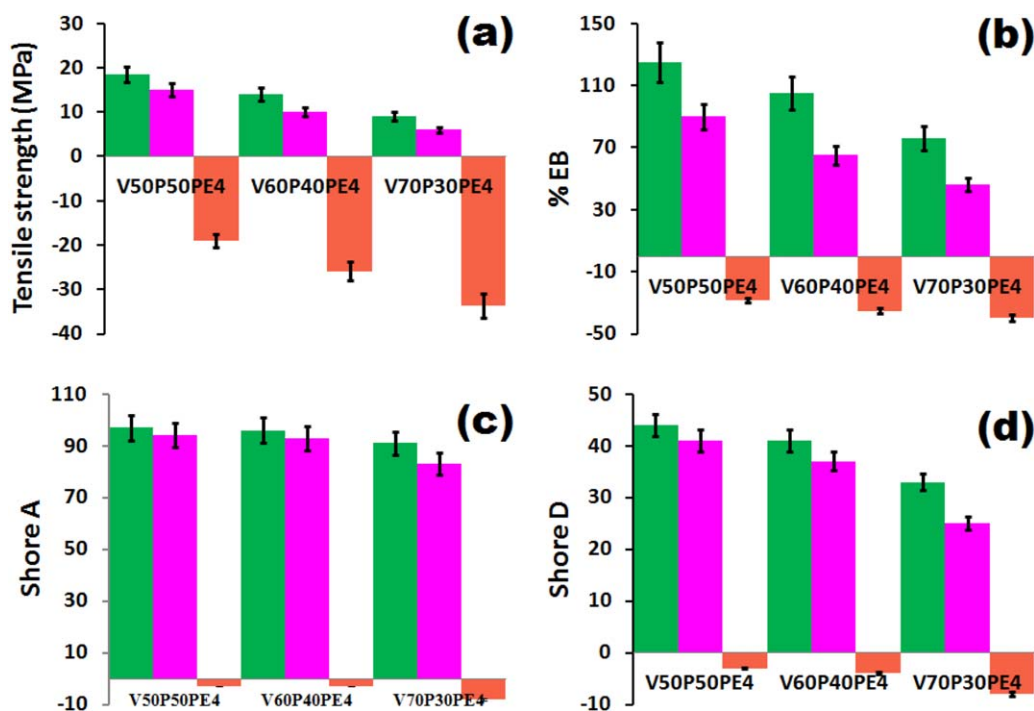


Figure 9. Change of (a) tensile strength, (b) elongation at break and hardness, (c) Shore A, and (d) Shore D of the TPVs due to ASTM Oil No III aging (72 h at 125°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$V_{50}P_{50}PE_4$ TPV is higher because of the presence of higher PA12 phase. Sharp decrease in storage modulus value for all the TPVs has been observed during glass-to-rubber transition region. In the rubbery plateau region (-10 to $+35^\circ\text{C}$) also, the storage modulus value of the $V_{50}P_{50}PE_4$ TPV is the highest because of higher PA12 content and this trend was continued throughout the remaining temperature range.

Thermogravimetric Analysis

TGA plots of AEM, PA12, and their TPVs are shown in Figure 6 and the quantitative data are summarized in Table VII. Due to the presence of strong intermolecular hydrogen bonding, pure PA12 shows the higher initiation temperature corresponding to 5% about 416°C with temperature corresponding to maximum decomposition (T_{max}) value at 501°C . On the other hand, pure AEM (ethylene acrylic elastomer) shows the temperature corresponding to 5% about 396°C and the T_{max} at 491°C due to its polar nature, which implies the dipole–dipole interaction. From the figure, it can be seen that all the TPVs exhibit low thermal stability than that of the virgin components. This may be due to the blending of two components, which hampers the extensive intermolecular hydrogen bonding of PA12 on one side and on the other side destroys the dipole–dipole interaction presence in AEM. However, the thermal stability of $V_{50}P_{50}PE_4$ TPV is the highest among all due to the presence of higher fraction of PA12 and $V_{70}P_{30}PE_4$ TPV shows the lowest thermal stability. Initial decomposition temperature of $V_{50}P_{50}PE_4$ is 392°C and this is 366°C only in case of $V_{70}P_{30}PE_4$. Therefore, the above results imply that TPV containing higher fraction of PA12 component shows superior thermal stability than the other TPVs.

Heat and Oil Resistance Properties of the TPVs

Figure 7 shows the heat aging properties of AEM/PA12 TPVs. It can be seen that even after heat aging at 125°C for 72 h also, there is no such change in the physicochemical properties of the TPVs. Most of the TPVs show very good retention of properties even after aging, and this indicates good resistance to heat aging. Peroxide curing provides strong C–C linkages as cross-links in the rubber phase (AEM), and this is reflected in the better aging behavior. Apart from higher fraction of polyamide (PA12) also improves the aging characteristics of the TPVs. As a result, TPV containing higher fraction of PA12 shows better heat aging properties rather than lower PA12 containing TPV. Percentage retention of tensile strength, elongation at break, and hardness, Shore (A and D) of the blends after being dipped in

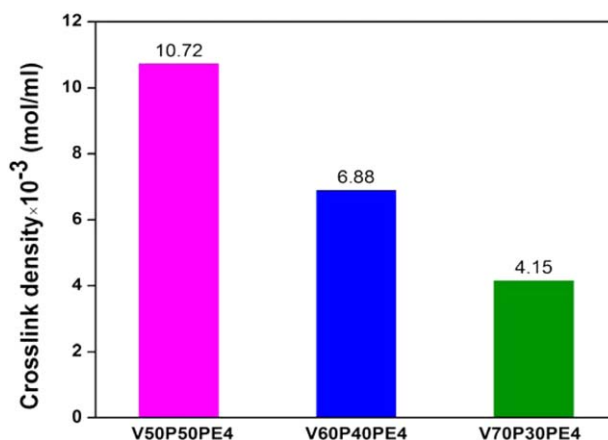


Figure 10. Overall cross-link density of the TPVs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

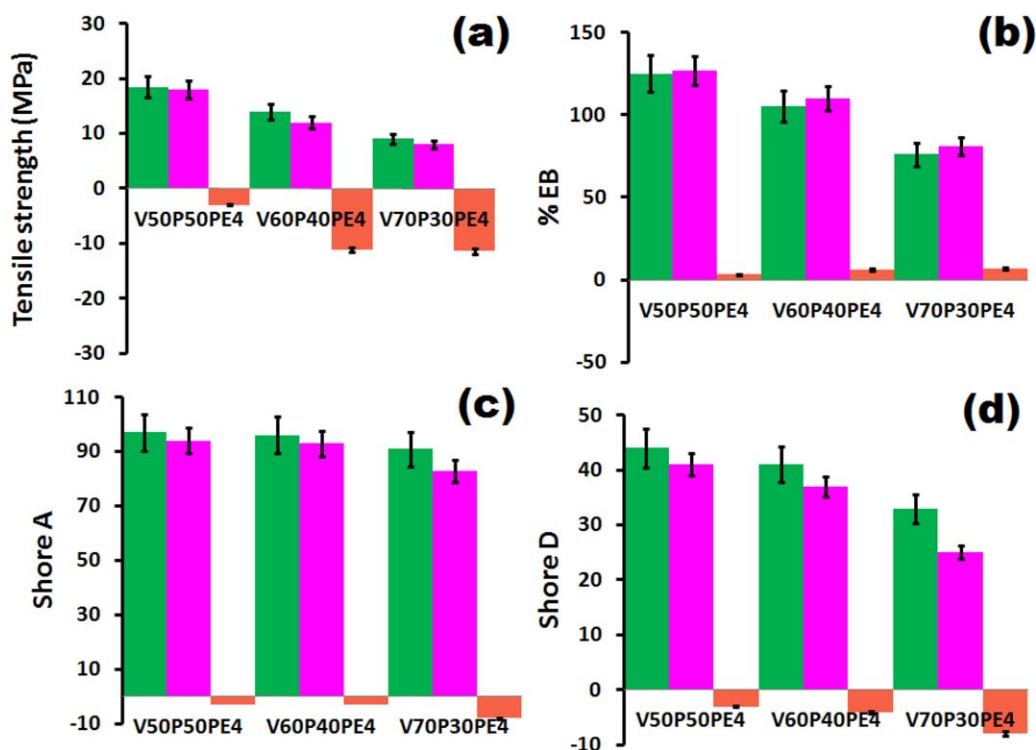


Figure 11. Change of (a) tensile strength, (b) elongation at break and hardness, (c) Shore A, and (d) Shore D of the TPVs due to recycling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrocarbon oil at 125°C at 72 h in an ASTM oil no 2 (medium polar) and in ASTM oil no 3 (high polar) are shown in Figures 8 and 9. Specialty rubber exhibits better oil resistance properties due to its polar character. Presence of polar group in AEM imposed polarity which is responsible for the oil resistance behavior of AEM. On the other hand, PA12 is also polar in nature, which also imparts oil resistance characteristics to PA12. After immersion in ASTM oil no 2 and 3, it can be clearly observed that the changes in physicochemical properties and hardness of the TPVs is marginal. Especially 50 : 50 dynamically cured blend shows only slight change in properties like tensile strength, elongation at break, and hardness point of view compared to other 60 : 40 and 70 : 30 blends. The above results imply that the 50 : 50 dynamically cured blends have excellent oil resistance and heat resistance properties. It reveals that at high temperature, in presence of oil, degradation of AEM has been taken place in higher extent whereas PA12 phase shows better thermal stability than AEM itself. Therefore, higher AEM containing TPV shows poor resistance to oil aging than the TPV containing low amount of AEM.

Overall Cross-Link Density

Cross-linking density plays a very important role in determining ultimate properties in rubber vulcanizates. Figure 10 demonstrates the overall cross-link density value of the TPVs in presence of PA12. From Figure 10, it can be clearly noticed that with increase of the rubber phase at a fixed peroxide concentration, the degree of cross-linking in the rubber phase decreases. Therefore, V₅₀P₅₀PE₄ TPV shows the highest overall crosslink density value of 10.72×10^{-4} mol/mL, whereas V₆₀P₄₀PE₄ TPV

shows 6.88×10^{-4} mol/mL and V₇₀P₃₀PE₄ TPV shows 4.15×10^{-4} mol/mL. From these results, it can be stated that the highest overall cross-link density of 50 : 50 blend results better mechanical behavior, dynamic mechanical properties, thermal stability, and oil resistance properties also.

Recyclability Study

The recyclability/reprocessability test is the one of the vital one in the field of thermoplastic elastomer and thermoplastic vulcanizates. Figure 11 shows the tensile strength, elongation at break, shore A and D hardness values for various systems before and after recycling. After one time recycling, all the TPVs show a minor decrease in the mechanical properties like change of tensile strength, elongation at break, and hardness. Maximum changes in properties were exhibited by the TPV containing the highest fraction of rubber and it can be seen that with increase of rubber content in the TPVs, tensile strength gradually reduces whereas elongation at break increases after recycling. As a result, V₇₀P₃₀PE₄ TPV shows the highest reduction in tensile strength and highest increment in elongation at break also among all the TPVs. This may happen due to the fact that after recycling the TPVs, the rubber phase gets softer much more than the plastic (PA12) phase. The softer rubber phase will provide higher elongation but lower tensile strength. Therefore, V₇₀P₃₀PE₄ TPV which contains 70 phr of AEM shows the highest increment in elongation at break and also shows the highest reduction in tensile strength after recyclability test. On the other hand, V₅₀P₅₀PE₄ TPV results small reduction in tensile strength and also little bit increment in elongation at break because of presence of lowest rubber fraction among all the TPVs.

CONCLUSIONS

Novel heat and oil resistant thermoplastic vulcanizates based on blends of ethylene acrylic elastomer and polyamide 12 have been developed. Dynamic vulcanization was carried out in presence of Perkadox 14-40B peroxide. Considering the curing characteristics and mechanical properties, 4 phr of peroxide was chosen as an optimum concentration of the cross-linking agent for TPV preparation. Continuous agglomeration of cross-linked rubber particles (nanodomains) has been observed from AFM studies for all the three TPVs. V₅₀P₅₀PE₄ TPV (containing 50/50 parts of AEM/PA12). Among all three TPVs shows better physico-mechanical properties, dynamic mechanical behavior, and thermal stability which was ascribed due to presence of highest fraction of plastic content and also due to the highest degree of cross-linking in the AEM phase. Air aging and oil aging tests of the TPVs also reveal superior properties of V₅₀P₅₀PE₄ TPV among the all other TPVs, which also implies that highest level of plastic content and highest degree of cross-linking in case of V₅₀P₅₀PE₄ TPV. It reveals that at high temperature, in presence of oil, degradation of AEM has been taken place in higher extent whereas PA12 phase shows greater resistance to oil than AEM itself. Therefore, 70 phr of AEM containing TPV shows poor resistance to oil aging than the TPV containing 50 phr of AEM. Thus, it can be concluded that V₅₀P₅₀PE₄ TPV is the superior one from all relevant point of view. The recyclability of these TPVs is also found excellent and these newly developed reprocessable TPVs may find potential application in automobiles.

ACKNOWLEDGMENTS

The authors are grateful to and thank the Council for Scientific and Industrial Research (CSIR), New Delhi, India for financial assistance for this project. Also thanks to Dr. R. Rajesh Babu (Apollo Tyres, Advance Tyre Research) Chennai for his suggestion.

REFERENCES

1. Holden, G.; Legge, N. R.; Schroeders, H. E. *Thermoplastic Elastomer: A Comprehensive Review*; Hanser: Munich, **1987**.
2. Paul, D. R.; Barlow, J. W. *J. Sci.-Rev. Macromol. Chem.* **1980**, *C18*, 109.
3. Utracki, L. A.; Favis, B. D. *Polymer Alloys and Blends-Thermodynamics and rheology*; Hanser: Munich, **1990**.
4. Paul, D. R.; Sperling, L. H.; eds, *Adv. Chem. Ser. No. 211: Multicomponent Polymer Materials*; American Chemical Society: Washington, DC, **1986**.
5. Karger-Kocsis, J. In *Polymer Blends and Alloys*; Shonaike G. O.; Simon G. P., Eds.; Marcel Dekker: New York, **1993**; p 125.
6. Abdou-Sabet, S.; Puydak, R. C.; Rader, C. P. *Rubber Chem. Technol.* **1996**, *69*, 476.
7. Metelkin, V. I.; Blekht, V. S. *Kolloid, Z. H.* **1984**, *46*, 476.
8. Utracki, L. A. *J. Rheol.* **1991**, *35*, 1615.
9. Ellul, M. D.; Tsou, A. H.; Hu, W. G. *Polymer* **2004**, *45*, 3351.
10. Gessler, A. M.; Haslett, W. H. Process for preparing a vulcanised blend of crystalline polypropylene and chlorinated butyl rubber. U.S. Patent 3037954, **1962**.
11. Fisher, W. K. Thermoplastic blend of partially cured monolefin copolymer rubber and polyolefin plastic. U.S. Patent 3862106, **1973**.
12. Coran, A. Y.; Patel, R. *Rubber Chem. Technol.* **1980**, *53*, 141.
13. Coran, A. Y.; Das, B.; Patel, R. P. Thermoplastic vulcanizates of olefin rubber and polyolefin resin. U.S. Patent 4130535, **1978**.
14. Naskar, K.; Noordermeer, J. W. M. *Rubber Chem. Technol.* **2003**, *76*, 1001.
15. Naskar, K.; Noordermeer, J. W. M. *Rubber Chem. Technol.* **2004**, *77*, 955.
16. Babu, R. R.; Singha, N. K.; Naskar, K. *Express Polym. Lett.* **2010**, *4*, 197.
17. Babu, R. R.; Gohs, U.; Naskar, K.; Mondal, M.; Wagenknecht, U.; Heinrich, G. *Macromol. Mater. Eng.* **2012**, *297*, 659.
18. Giri, R.; Naskar, K.; Nando, G. B. *Rubber Fibres Plast. Int.* **2011**, *6*, 97.
19. Kalkornsurapranee, E.; Nakason, C.; Kummerlowe, C.; Vennemann, N. *J. Appl. Polym. Sci.* **2013**, *128*, 2358.
20. Rahman, M. A.; Spagnoli, G.; Grande, A. M.; Landro, L. D. *Macromol. Mater. Eng.* **2013**, *298*, 1350.
21. Dey, P.; Naskar, K.; Nando, G. B.; Dash, B.; Nair, S.; Unnikrishnan, G. *RSC Adv.* **2014**, *4*, 35879.
22. Dey, P.; Naskar, K.; Nando, G. B.; Dash, B.; Nair, S.; Unnikrishnan, G. *J. Appl. Polym. Sci.* **2014**, *131*, 41182.
23. Dutta, J.; Chatterjee, T.; Dhara, G.; Naskar, K. *RSC Adv.* **2015**, *5*, 41563.
24. Mani, S.; Cassagnau, P.; Bousmina, M.; Chaumont, P. *Macromol. Mater. Eng.* **2011**, *296*, 909.
25. Chatterjee, T.; Wiessner, S.; Naskar, K.; Heinrich, G. *eXPRESS Polym. Lett.* **2013**, *8*, 220.
26. Babu, R. R.; Singha, N. K.; Naskar, K. *Polym. Eng. Sci.* **2010**, *50*, 455.
27. Dey, P.; Naskar, K.; Nando, G. B.; Dash, B.; Nair, S.; Unnikrishnan, G. *Mater. Today Commun.* **2014**, *1*, 19.
28. Coran, A. Y.; Patel, R. *Rubber Chem. Technol.* **1980**, *53*, 141.
29. l'Abée, R. M. A.; Van Duin, M.; Spoelstra, A. B.; Goossens, J. G. P. *Soft Matter* **2010**, *6*, 1758.
30. Selvakumar, M.; Mahendran, A.; Bhagabati, P.; Anandhan, S. *Adv. Polym. Technol.* **2015**, *34*, 34.