

Scrutinizing the influence of peroxide crosslinking of dynamically vulcanized EVA/TPU blends with special reference to cable sheathing applications

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ABSTRACT: A novel thermoplastic vulcanizate (TPV) based on the blends of ethylene vinyl acetate/thermoplastic polyurethane (EVA/TPU) at various blend ratios has been developed via dynamic vulcanization at 180 °C using di-(2-tert-butyl peroxy isopropyl) benzene (DTBPIB) peroxide as the cross-linking agent. Modification of the EVA/TPU blends via dynamic crosslinking significantly improves the tensile strength and modulus of the system and the improvement is more significant for EVA/TPU 50/50 and 60/40 blends. AFM study shows that crosslinked EVA particles are dispersed in the continuous TPU matrix and the dispersed EVA domain sizes are relatively smaller in EVA/TPU 50/50 and 60/40 blends leading to good mechanical properties. FTIR spectroscopy has been used to characterize the specific chemical changes occurring due to dynamic vulcanization. This TPV has excellent retention of physico-mechanical properties even after reprocessing twice and the blends also have very good thermal resistance as indicated by aging study. The samples were found to exhibit remarkable improvement in oil resistance property as compared to their uncrosslinked counterpart. The creep behavior of the blends significantly improves after dynamic crosslinking and blends with higher TPU content show better creep resistance. Volume resistivity of all the peroxide vulcanized blends is in the range of 10^{13} ohm cm, which is suitable for cable sheathing application. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43706.

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INTRODUCTION

Thermoplastic-elastomer blends (TPE), a unique class of polymer blend materials, are becoming technologically as well as commercially important because these blends offer remarkable properties where they perform like elastomers at ambient temperature but can be processed and easily recycled like thermoplastics.^{1,2} Of late, TPE's have attracted paramount attention as "green" polymer in the last few decades and thus become one of the fastest growing elastomers in rubber industries owing to their environment protection and resource saving (cost effectiveness).^{3,4} However, very often due to poor compatibility between the components, such polymer blends constitute a separate phase morphology that eventually leads to poor interfacial adhesion. Elastomer-thermoplastic blends often suffer from a few disadvantages like creep behavior on extended use specially at elevated temperature, lower elastic recovery, and poor set property, etc.^{5,6} This poor interfacial adhesion along with the performance properties can be substantially improved either using compatibilizing agent or by dynamic vulcanization; the latter being more likely.

Crosslinking of the elastomer phase is generally carried out to reduce the size of the elastomer domains, stabilizing the phase morphology and enhancing the interfacial adhesion between the two phases. In dynamic vulcanization process, elastomers are cross-linked under dynamic conditions at a high shear rate and at higher temperature while simultaneous blending with thermoplastic material above their melting temperature is being carried out. These cross-linked elastomers usually remain dispersed in the continuous thermoplastic matrix although the elastomer content exceeds the thermoplastic content in the TPV, which in turn, is highly desired for excellent softness, elasticity and ease of processing.⁷⁻¹⁰ The improvement in properties of the rubber-plastic blends resulting from dynamic crosslinking are reduced permanent set, improved ultimate mechanical properties, greater resistance to attack by chemicals and solvents, improved high temperature utility, greater stability of phase morphology way to produce new thermoplastic vulcanizate (TPV) which have properties as good or even in some cases, better than those of the individual polymers.¹¹

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Table I. Characteristics of the Raw Materials

Material	Tensile strength (MPa)	Elongation at break (EB %)	Modulus at 100% (MPa)	Modulus at 200% (MPa)	Modulus at 300% (MPa)	Melting point (°C)*	Glass transition temperature (°C)*
EVA	16.9 ± 0.4	1061 ± 48	3.0 ± 0.3	3.5 ± 0.3	4.0 ± 0.3	78.06	-27.70
TPU	35.1 ± 1.1	805 ± 32	5.9 ± 0.3	8.7 ± 0.2	11.5 ± 0.4	166.6	-37.76

*Glass transition temperature (T_g) and Melting point (T_m) has been obtained from DSC (Differential Scanning Calorimetry) measurements

The process of dynamic vulcanization was first reported by Gessler and Haslett in 1962 and subsequently further work by Fisher on polypropylene (PP)/ethylene propylene diene rubber (EPDM) TPVs with peroxide as the crosslinking agent, led to the commercialization of “Uniroyal TPR” thermoplastic rubber in 1973.^{12,13} Later various authors like Coran *et al.*, Katbab *et al.*, and Abdou-Sabet and Fath described qualitatively the correlation between the evolution of the two-phase blend morphology and the crosslinking reaction conversion on the elastomer phase during the tailoring of a TPV.^{8,14–16} Naskar and coworkers extensively studied the influence of different peroxides including multifunctional coagents in PP/EPDM blends and PP/ethylene octene copolymer (EOC) blends.^{17–19} Influence of dynamic vulcanization on a large number of elastomer-thermoplastic blends such as poly vinyl chloride (PVC)/epoxidized natural rubber (ENR),²⁰ nitrile butadiene rubber (NBR)/PP,²¹ EOC/silicone rubber (PDMS),²² polyamide 12 (PA12)/PDMS,²³ natural rubber (NR)/PP,²⁴ poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] triblock copolymer (S-EB-S)/solution-polymerized styrene butadiene rubber (S-SBR),²⁵ and PA12/ethylene acrylic elastomer (AEM)²⁶ have also been studied by various group of researchers. Final properties of the TPVs depend mainly on their morphology and the crosslink density in the elastomer phase. Interrelationships of morphology, properties, and processing characteristics of dynamically vulcanized blends have been critically reviewed by Karger-Kocsis.¹⁰ Since EVA does not crosslink by means of sulfur, the common chemical method for crosslinking EVA, is to cure them radically by means of peroxide.²⁷ Wu and coworkers developed EVA/ternary Polyamide blends through dynamic vulcanization with Dicumyl peroxide and studied their morphology, mechanical, and oil resistance properties in details.²⁸ Dynamically crosslinked styrene butadiene rubber/EVA blends have also been reported to produce thermoplastic moldable shoe-sole.²⁹ Dynamic mechanical properties of EVA/PP TPEs have been studied by Thomas *et al.* with special reference to the effects of blend ratio, dynamic crosslinking of the elastomer phase and temperature.³⁰ Naskar *et al.* successfully developed cable insulation and fire resistant low smoke (FRLS) sheathing compounds from peroxide crosslinked EVA/ENGAGE™ Polyolefin Elastomer blends and characterized the blends in details.³¹ Xinyan and coworkers studied the mechanical, morphological, and oil resistance properties of dynamically vulcanized blend of 75: 25 TPU and ethylene-vinyl acetate copolymer rubber (having very high, i.e., 70 wt % VA content) via DCP (dicumyl peroxide) and BIPB [bis(tert-butyl peroxy isopropyl)-benzene].³² A high performance TPV based on NR/TPU has been prepared via dynamic vulcanization using sulfur by

Vennmann and coworkers.³³ Pichaiyut *et al.* reported that dynamic vulcanization caused enhancement of mechanical, thermal and rheological properties, and improved the elasticity and stress relaxation behavior of the ENR/TPU blends.³⁴

In our previous work, a novel blend based on EVA and TPU had been prepared at various blend ratios via melt mixing technique. The effect of morphology and blend composition on physical-mechanical and thermal properties was investigated in details.³⁵ It was found that the tensile strength and elongation reduces with increasing TPU but addition of higher TPU content improves the modulus and oil resistance property of the blend system. To overcome these deficiencies and for achieving optimum performance properties with usage of minimum TPU, an attempt has been made here to induce crosslinking in the EVA/TPU blend system in presence of small amount of peroxide. This work describes the methods to develop a useful peroxide crosslinked EVA/TPU blends with 50–80 wt % EVA (EVA containing 28% vinyl acetate content). The amount of TPU was also kept low since TPU is relatively more expensive than many other polymers. The physico-mechanical, thermal, dynamic mechanical properties, and morphological variation have been studied in details. Oil resistance and volume resistance properties of the blend system suggest that the blend may find potential application in electrical and automobile industries, etc.

EXPERIMENTAL

Materials

Thermoplastic Polyurethane (TPU) Desmopan 385 S, composed of 4,4'-diphenylmethane diisocyanate hard segment and polyester based soft segment was procured from Bayer Chemicals, India. The density of TPU is 1.2 g/cm³ with a Shore-A hardness of 84. The melt flow index (MFI) for TPU is 33.90 g/10 min at 190 °C (1.2 kg load) and melting temperature is around 170 °C. Ethylene vinyl acetate copolymer (EVA) containing 28% vinyl acetate, grade Elvax 265, with a melt flow index (MFI) of 3 g/10 min at 190 °C (2.6 kg load) and a density of 0.95 g/cm³, was obtained from Dupont, India. An organic peroxide namely Perkadox14–40BD [di(2-tert butyl peroxy isopropyl)benzene (DTBPIB)] (supplied by Akzo Nobel, The Netherland) is used as the cross-linking agent for EVA. At a temperature of 146 °C, the “half-life” time of peroxide is 1 h (half-life time was determined using a dilute solution of peroxide in monochlorobenzene). The physico-mechanical and thermal characteristics of the pure polymers are reported in Table I.

Preparation of Blends

Dynamic vulcanization of EVA/TPU blends were carried out in Haake Rheomix OS (Germany) 600 internal mixer, having a

Table II. Sample Designations with Composition

Sample designation	EVA (wt %)	TPU (wt %)	DTBPIP (phr) ^a
ET80P1	80	20	1
ET70P0.5	70	30	0.5
ET70P1	70	30	1
ET70P2	70	30	2
ET60P1	60	40	1
ET50P1	50	50	1

^aphr, parts per hundred polymer.

mixing chamber volume of 85 cm³. At first EVA was added to the mixing chamber at 90 °C under 60 rpm rotor speed and allowed to melt for 2 min. Further, peroxide was added with EVA to prepare a curative master batch and mixing continued for another 4 min and then the peroxide mixed EVA master batch was taken out of the chamber.

To achieve dynamically crosslinked blends, TPU was first added at 180 °C and it was allowed to melt for 2 min. After 2 min, the premixed EVA curative master batch was added to the molten TPU and thereby dynamic vulcanization was carried out under high shear rate of 70 rpm during its intimate mixing with TPU. Then the molten mass so obtained was taken out of the chamber and sheeted under hot conditions in an open mill set at a close nip gap of 2 mm at room temperature. The sheets obtained from the two roll mill were compression molded between Teflon sheets for 4 min at 190 °C at a pressure of 5 MPa in an electrically heated hydraulic press (Moore Hydraulic Press, England). The moulded sheets were cooled under pressure to maintain the overall dimensional stability of the moulded articles. Table II shows the various blends prepared for this study having different blend ratio of EVA and TPU.

CHARACTERIZATION OF BLENDS

Mechanical Tests

Tensile test was carried out using a universal testing machine Hounsfield H10KS at room temperature at a crosshead speed of 200 mm/min. The tensile specimens were punched from the moulded sheets using ASTM Die-C as per ASTM D 412. Three measurements were taken for each samples and an average of results was reported as the resultant value.

Tension Set Test

For tension set measurement, the dumbbell specimens were extended up to 100% in the tensile direction at a rate of 200 mm/min and kept at that position for 10 min at room temperature. It was then relaxed back to unstressed condition and the percentage change in dimension in tensile direction was measured after 15 min and reported as tension set.

$$\text{Tension set (\%)} = \left(\frac{\text{Change in length}}{\text{Original length}} \right) \times 100 \% \quad (1)$$

Hardness Test

Hardness of the samples was measured in Shore-D scale as per ASTM D2240 standard at room temperature using Shore-D

hardness-testing machine (Bowers Mertoology, UK) as per ASTM D2240 standard at room temperature. The hardness value is determined by the penetration of the Durometer indenter foot into the sample.

Differential Scanning Calorimetry

Differential Scanning Calorimetry studies of the samples were carried out using a DSC Q2000 (TA Instruments) in an inert atmosphere (N₂ atmosphere) at a heating and cooling rate of 10 K/min. The experiment was conducted from −80 °C to 230 °C for all the samples. The glass transition temperatures (*T_g*) and melting behavior of the samples were observed from the second heating run of Differential Scanning Calorimetry (DSC) plot. The data of second heating cycle was used to eliminate thermal history.

Morphological Study

SEM Analysis. Surface morphology of the blends was examined using JEOL JSM 5800 Digital Scanning Electron Microscope (SEM). The accelerating potential 20 kV was used for the analysis of sample. All the blends were cryofractured in liquid nitrogen to avoid any possibility of phase deformation during cracking process. The cryofractured surface of the blends was etched in tetrahydrofuran (THF) solvent for 1 day to remove TPU phase of the blends. The etched surface after adequate drying for 24 h at room temperature was gold sputtered and then observed under SEM.

Atomic Force Microscopy. Intermittent tapping mode atomic force microscopy, ACAFM, (Agilent 5500 Scanning Probe Microscope) was used to study the phase image and height image of TPVs thin films which are prepared by compression molding at 180 °C at a pressure of 5 MPa for 4 min. The resonance frequency of the tip was 146–236 kHz and the force constant was 48 N/m.

FTIR Spectroscopy

FT-IR spectra on the thin films of the polymer blends before and after peroxide crosslinking were recorded using a Perkin-Elmer Frontier spectrometer in ATR mode at room temperature over the range of 4000–400 cm^{−1}.

Thermogravimetric Analysis

Thermogravimetric analyses (TGA) and derivative thermogravimetry (DTG) of the neat components as well as EVA/TPU blends were measured using a thermogravimetric analyzer (Mettler-Tolledo AG, Switzerland). The sample weight was 8–10 mg and the heating rate was 10 K/min. Tests were performed from ambient temperature to 700 °C under N₂ atmosphere.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical analysis (DMA) of the samples were carried out using a dynamic mechanical analyzer, Eplexor 150N DMTA (Gabo Qualimeter, Ahlden, Germany). Tests were carried out at a frequency of 10 Hz under a static strain of 0.50% and a dynamic strain of 0.001% over a temperature range of −100 °C to 80 °C. The samples were first cooled to −100 °C and then subsequently heated at a rate of 2 K/min. The temperature corresponding to the peak in tan δ versus temperature plot was taken as the *T_g*.

Oil Swelling Study

The test specimens were immersed in ASTM 3 oil at room temperature for 7 days. After the required period of time the specimens were removed from the oil, quickly dipped in acetone, and blotted lightly with a clean blotting paper to eliminate the excess oil on the specimen surfaces and the final mass was taken. For every single composition three specimens were tested and their average values have been reported. Swelling percent was measured as follows:

$$\text{swell (\%)} = \frac{M_2 - M_1}{M_1} \times 100\% \quad (2)$$

Where, M_1 = initial mass of specimen in air and M_2 = mass of specimen in air after immersion

The percentage error in the oil swelling was found to be more or less $\pm 1.5\%$.

Thermal Aging Study

Test samples were heated at 50 °C and 100 °C in an air-circulating oven for 72 h. After being cooled down and conditioned at room temperature, the dimensions of each specimen were measured. The tensile properties of these samples were determined according to ASTM D412-87 using an Instron Universal Testing Machine at a crosshead speed of 200 mm/min.

Crosslink Density Study

Crosslink densities of the various blends were calculated from the modulus values using the kinetic theory of elasticity using the following equation.³⁶

$$\nu = \frac{\sigma}{(\lambda - \frac{1}{\lambda^2})RT} \quad (3)$$

Where, ν is the crosslink density (CLD), σ is the modulus (100%), λ is the extension ratio (2 in case of 100% elongation), R the gas constant, and T the absolute temperature during test (here, 298 K).

Reprocessability Studies

To evaluate the reprocessability, all the moulded TPV specimens (used while testing) were milled and then cut into small pieces. Then the samples were introduced into the mixing chamber and remixed at a temperature of about 180 °C at 60 rpm for 5 min. Finally, the molten mass was retrieved and sheeted out on a cold two roll mill at room temperature. The sheet was then compression molded in a compression molding hydraulic press at 180 °C at a pressure of 5 MPa for 4 min to obtain tensile sheets of about 2 mm thickness. Dumbbell specimens were punched out of these tensile sheets, and the tensile test was performed in a UTM 10HK at room temperature at a crosshead speed of 200 mm per minute as per ASTM D412.

Creep Study

The creep experiments were carried out with the help of the DMA instrument using the tension mode. The samples were subjected to a constant stress of 0.5 MPa, and the resulting strain and its recovery were recorded at 30 °C. In addition to the test at 30 °C, the creep experiments were also carried out at 30 °C, 40 °C, and 50 °C and the corresponding values of strain and recovery were recorded. Compliance $D(t)$ was calculated from the stress and strain data using the following equation.³⁷

$$D(t) = \frac{\epsilon_t}{\sigma_0} \quad (4)$$

Volume Resistivity Test

Volume resistivity of the samples (dimension $10 \times 10 \text{ cm}^2$) has been measured in a Hewlett Packard 4339B (manufactured by Agilent Technology, Japan) high resistance meter at room temperature (30 °C) with an applied voltage of 500 V. Volume resistivity has been calculated using the following formula and measured as per ASTM D-257-66. The specimen was placed in the resistivity cell, clamped between electrodes and guard ring, for the specified time and applied voltage.

$$\text{Volume resistivity } (\Omega \text{ cm}) = \frac{A \times R}{t} \quad (5)$$

Where, A = the area of upper electrode (19.6 cm^2), R = the resistance (in ohm) between upper and lower electrode, and t = the thickness (in cm) of the test specimen

RESULTS AND DISCUSSION

Physico-Mechanical Properties

In our previous paper, it was found that for uncrosslinked EVA/TPU blend system only 80/20 EVA/TPU blend showed slight increase (4% increase) in the tensile strength than that of neat EVA (16.9 MPa) and as the TPU content in the EVA/TPU blend increases from 30 wt % to 50 wt %, tensile strength (T.S.) gradually decreases from 12.2 to 9.3 MPa.³⁵ However, dynamic crosslinking with peroxide causes significant improvement in the tensile properties of the EVA/TPU blends. For achieving good physico-mechanical properties it is necessary to reach an optimum level of crosslinking. To find out the effect of peroxide crosslinking on neat EVA, various amounts of DTBPIP (0.5 to 2 phr) were added to the pure polymer and the physico-mechanical properties were evaluated. It was found that the tensile strength of pure EVA increases from 18.7 to 21.9 MPa as the amount of peroxide increases from 0.5 to 1 phr. But, with further addition of peroxide (1.5 phr), the T.S. marginally improves to 22.5 MPa and at 2 phr peroxide concentration; the tensile strength reduces slightly to 21.2 MPa. However, the % elongation at break (EB %) continuously decreases from 828 to 660% with increase in peroxide content from 0.5 to 2.0 phr. At higher peroxide dosage beyond 1.5 phr, possibly excessive crosslinking or some chain scission may be the reason for such reduction in tensile properties. When DTBPIP is added to EVA, two processes will compete with each other. One is the crosslinking of the amorphous and partly crystalline regions of EVA; and the next is the chain scission of the main chain. Although both processes occur simultaneously, it is presumed that at lower to medium DTBPIP doses, the crosslinking becomes predominant and at higher doses chain scission of the EVA chains become more pronounced.²⁷ To get better idea about the optimum peroxide dosage, different amount of peroxide (0.5, 1, and 1.5 phr) was added in the EVA/TPU 70/30 blend and the corresponding tensile properties has been noted and summarized in Table III. The results clearly reveal that with incorporation of only 0.5 phr peroxide the T.S. increases from 12.2 to 13.8 MPa (13.1% higher than the uncrosslinked blend). As the peroxide content further increases to 1 phr, the T.S. also increases to 17.5 MPa with an improvement of 43.4% as

Table III. Mechanical Properties of the ET70 Blends with Varying Amounts of Peroxide

Sample designation	Tensile strength (MPa)	EB %	Modulus at 100% (MPa)	Modulus at 200% (MPa)	Modulus at 300% (MPa)
ET 70	12.2 ± 0.6	832 ± 25	3.5 ± 0.3	4.0 ± 0.2	4.5 ± 0.2
ET70P0.5	13.1 ± 0.7	675 ± 12	3.6 ± 0.3	4.5 ± 0.3	5.9 ± 0.3
ET70P1	17.5 ± 0.3	554 ± 34	3.7 ± 0.2	5.9 ± 0.3	8.7 ± 0.2
ET70P2	16.3 ± 0.4	417 ± 48	4.0 ± 0.3	6.8 ± 0.4	9.4 ± 0.4

compared to the neat blend. However, with further increase of peroxide to 2 phr causes the tensile strength to reduce to 16.3 MPa. Moreover, the elongation property of the blend continuously reduces from 832 to 417% with the rise in peroxide content. It is due to fact that, at higher peroxide dosage the crosslinked rubber networks become more dense and tighter and consequently flexibility of the rubber is diminished due to restriction in structural reorganization during elongation. Therefore, analyzing the above results it has been concluded that 1 phr peroxide concentration can be used as optimum dose for the subsequent research to get the best combination of T.S. an elongation.

However, no significant improvement in tensile properties has been found after addition of 1 phr peroxide with the pure TPU. There is some possibility that the peroxide could also distribute in the TPU phase and take part in crosslinking of the TPU phase to some extent. It would reduce the overall mechanical properties of EVA/TPU blends. To reduce that possibility phase mixing procedure was adopted as explained earlier in the experimental section. Thus, here crosslinking occurs predominately in the EVA phase, which finally affects the final phase morphology and the ultimate mechanical properties.

Physico-mechanical properties like tensile strength, elongation, modulus at various strain and hardness of the various EVA/TPU blends before and dynamic crosslinking are shown in Table IV. From Figure 1 it has been clearly observed that for all the blends tensile strength improves after dynamic crosslinking. It is found that with only 1 phr peroxide T.S. increases from 10.4 to 19.8 for ET60P1 blend and for ET50P1 blend T.S. changes from 9.5 to 20.7 MPa as compared to uncrosslinked blend. Such a remarkable improvement in the tensile strength for the blends with lower rubber fraction is explained as follows. At the same peroxide content EVA phase in the ET60P1 and ET50P1 blends gets crosslinked to greater extent as compared to the ET80P1 blends. Consequently it results in higher crosslink density and better physico-mechanical properties.^{26,38} Thus, the problem of lower tensile strength of the EVA/TPU blend system can be solved by phase mixing and subsequent dynamic vulcanization of the blend system with small amounts of peroxide. Although, the elongation at break for the crosslinked blends becomes somewhat lower (varies from 523% to 625%) than that of the uncrosslinked blends but their elastic property is still quite good for many applications. However, in case of ET50P1 the elongation at break slightly improves because for uncrosslinked 50/50 EVA/TPU blend elongation property was much lower due to poorer compatibility between

the components but after dynamic crosslinking elongation increases due to somewhat better compatibility and the cross-linked rubber particles can also be strained to comparatively larger extensions before failure. Table IV also demonstrates the variation in modulus at various blend ratios after peroxide crosslinking and it is observed that there is huge improvement of modulus at 100%, 200%, and 300% after dynamic crosslinking for all the blends. It is also found that with a decrease in the EVA content in the blend, modulus value also slightly goes up. Since the modulus depends directly on the degree of crosslinking, the increase in crosslink density also reflected in such an improvement in the modulus after dynamic vulcanization.

Hardness Test

Hardness is usually referred to the local deformation and the change in hardness value after dynamic crosslinking has been reported in Table IV. In all the cases hardness value becomes higher after peroxide crosslinking. The hardness of the blends varies from 30 to 33 in shore D scale and the above result clearly suggests that all the samples show better resistance to local deformation after crosslinking due to the crosslink formation in EVA phase.

Tension Set Test

The results of tension set test for all the sample are also given in Table IV. It is a well-known fact that the lower the set % value, the better is the elastic recovery and from Table IV it is found that for all the blends tension set value of both the

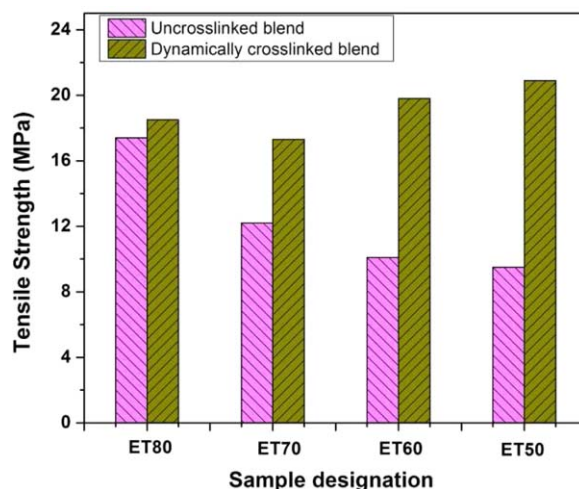


Figure 1. Variation of tensile strength of the different blends before and after dynamic vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Mechanical Properties of the Dynamically Crosslinked Peroxide Crosslinked EVA/TPU Blends

Sample designation	Tensile strength (MPa)	EB %	Modulus at 100% (MPa)	Modulus at 200% (MPa)	Modulus at 300% (MPa)	Tension set (%)	Hardness (Shore D)
ET 80	17.6 ± 0.4	1067 ± 45	3.3 ± 0.2	3.9 ± 0.3	4.3 ± 0.2	17	25
ET 70	12.2 ± 0.6	832 ± 25	3.5 ± 0.3	4.0 ± 0.2	4.5 ± 0.2	18	25
ET 60	10.4 ± 0.7	722 ± 37	3.7 ± 0.3	4.1 ± 0.3	4.6 ± 0.3	20	29
ET 50	9.5 ± 0.5	494 ± 15	3.9 ± 0.2	4.7 ± 0.2	5.7 ± 0.3	20	31
ET80P1	18.5 ± 0.5	523 ± 55	3.5 ± 0.2	5.8 ± 0.2	8.5 ± 0.2	11	30
ET70P1	17.6 ± 0.6	554 ± 30	3.7 ± 0.3	5.9 ± 0.3	8.7 ± 0.3	13	32
ET60P1	19.8 ± 0.4	612 ± 32	3.9 ± 0.3	6.0 ± 0.3	8.8 ± 0.2	14	33
ET50P1	20.7 ± 0.7	625 ± 57	4.2 ± 0.2	6.1 ± 0.2	9.0 ± 0.2	15	33

blends reduces on crosslinking. In our previous studies, it was found that pure EVA has somewhat better set property than TPU and tension set % for the EVA/TPU blends gradually increase with increasing TPU content in the blends.³⁵ Tension set value for ET80 blend decreases from 18% to 11% and for ET50 blend it reduces from 20% to 15% after peroxide crosslinking. Such improvement in the tension set property occurs mainly due to the crosslinking in the EVA phase which enhances the elastic recovery of the blend system.

DSC Studies

DSC measurements were pursued to characterize the melting and crystallization behavior of both uncrosslinked and dynamically vulcanized blends. The melting temperature (T_m), glass transition temperature (T_g), and crystallization peak temperature (T_c) for different blends were determined from the DSC heating and cooling scans and the results for the various blends before and after dynamic crosslinking with peroxide are enlisted in Table V along with the thermal properties of pure polymers. All the dynamically vulcanized blends show a single T_g in between the T_g of EVA and T_g of TPU indicating technological compatibility.³⁹ In our previous work, it was already shown that the theoretical T_g and the experimental T_g (calculated using Fox equation) for the uncrosslinked blends are very close.³⁵ It has

been found that for all the crosslinked blends, the T_g value marginally increases (Figure S1, Supporting Information) with respect to the corresponding uncrosslinked blends mainly due to the formation of three dimensional network in EVA phase and such crosslinked network restrict the segmental mobility of polymer chains leading to slight increase in T_g . However, there is a significant fall in T_m after dynamic crosslinking and for all the crosslinked blends the melting temperature corresponding to EVA melting decreases by almost 7 K. In general, T_m depends on specific interfacial energy of lamella, thickness of lamella, melt enthalpy, and equilibrium melt temperature.⁴⁰ The lowering of T_m after dynamic vulcanization can be associated with the effect of change in molecular structure due to crosslinking, which in turn destroy the ordered structure of the polymer to some extent and consequently the crystallization process is slightly affected due to variation in the aforementioned parameters. The crystallization peak temperature (T_c), as reported in Table V, reveals that the T_c corresponding to EVA phase also shifts to lower temperature by 5–6 K due to lower degree of chain alignment resulting from predominant crosslinking which hinders the growth of the crystals. Further, lower molecular mass of polymer, which might arise from the chain breakdown, lead to high mobility of polymer chain. Hence, during cooling scan, more under cooling is required for crystallization process.⁴¹

Table V. DSC Data of Various Samples

Sample designation	Glass transition temperature, T_g (°C)	Melting temperature, T_m (°C)	Crystallization temperature, T_c (°C)
EVA	-27.7	78.0	54.9
TPU	-37.7	166.6	82.1
ET 80	-29.1	77.0	55.0
ET 70	-31.0	77.6	55.0
ET 60	-31.8	77.5	55.8
ET 50	-32.9	77.1	56.0
ET80P1	-28.8	69.4	50.3
ET70P1	-29.3	70.2	50.1
ET60P1	-30.7	69.9	50.0
ET50P1	-31.5	70.2	49.9

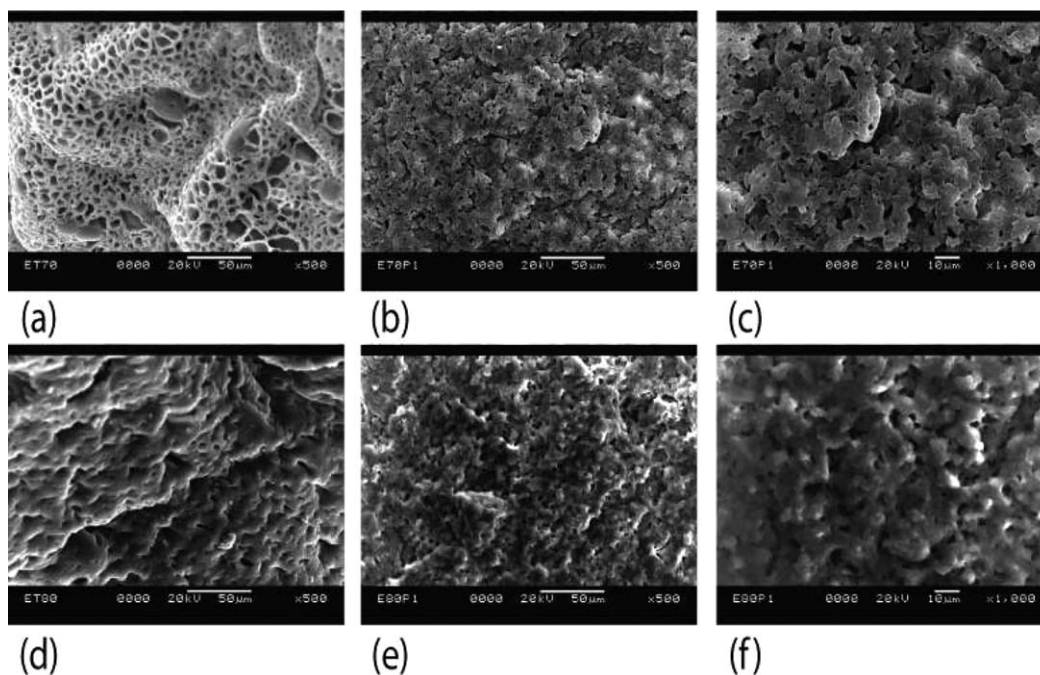


Figure 2. SEM photomicrographs of ET70P1 (a) before crosslinking, (b) after crosslinking at 500 \times magnification (c) at 1000 \times magnification and ET80P1 (d) before crosslinking, (e) after crosslinking at 500 \times magnification (f) after crosslinking at 1000 \times magnification.

Morphology

SEM Analysis. SEM study has been pursued with the cryogenically fractured and etched samples in JEOL JSM 5800. The cryofractured samples were etched by tetrahydrofuran for 24 h to preferentially remove the TPU phase. Figures 2(a–c) and 2(d–f) represents the SEM photomicrographs of E70 blends and E80 blends before and after dynamic vulcanization, respectively.

These SEM images reveal that there is significant change in morphology in the peroxide crosslinked blends than their uncrosslinked counterparts. It has been found that two phase morphology is visible for all the various blends and TPU phase can be extracted by solvent etching even after dynamic crosslinking which indicate that the TPU phase is not effectively crosslinked by peroxide, otherwise extraction of TPU phase

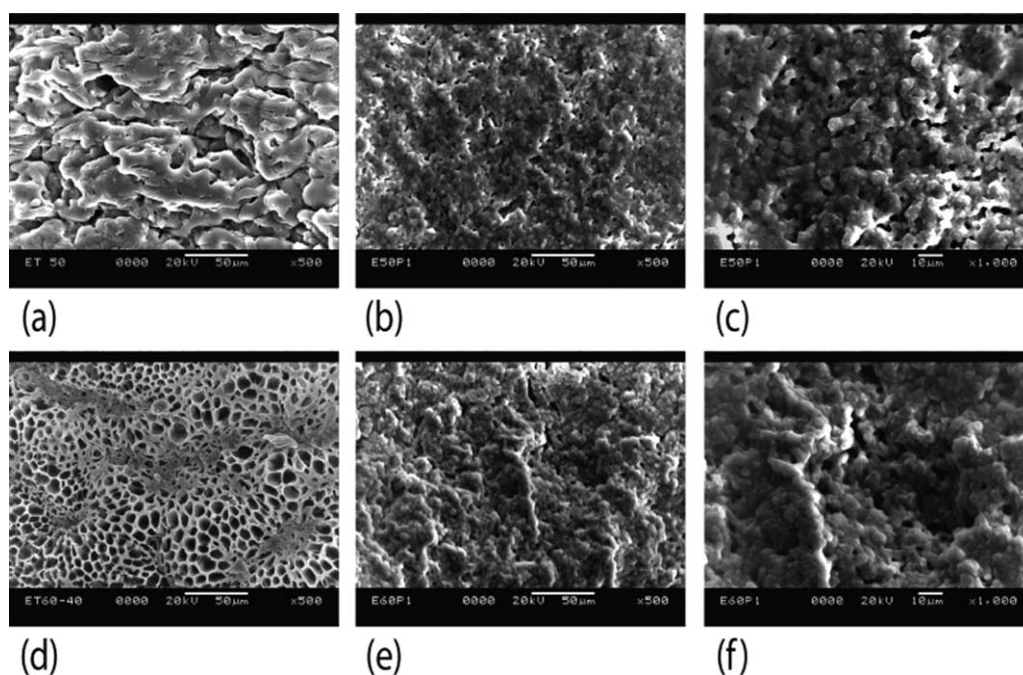


Figure 3. SEM photomicrographs of ET50P1 (a) before curing, (b) after curing at 500 \times magnification (c) at 1000 \times magnification and ET60P1 (d) before curing, (e) after curing at 500 \times magnification (f) after curing at 1000 \times magnification.

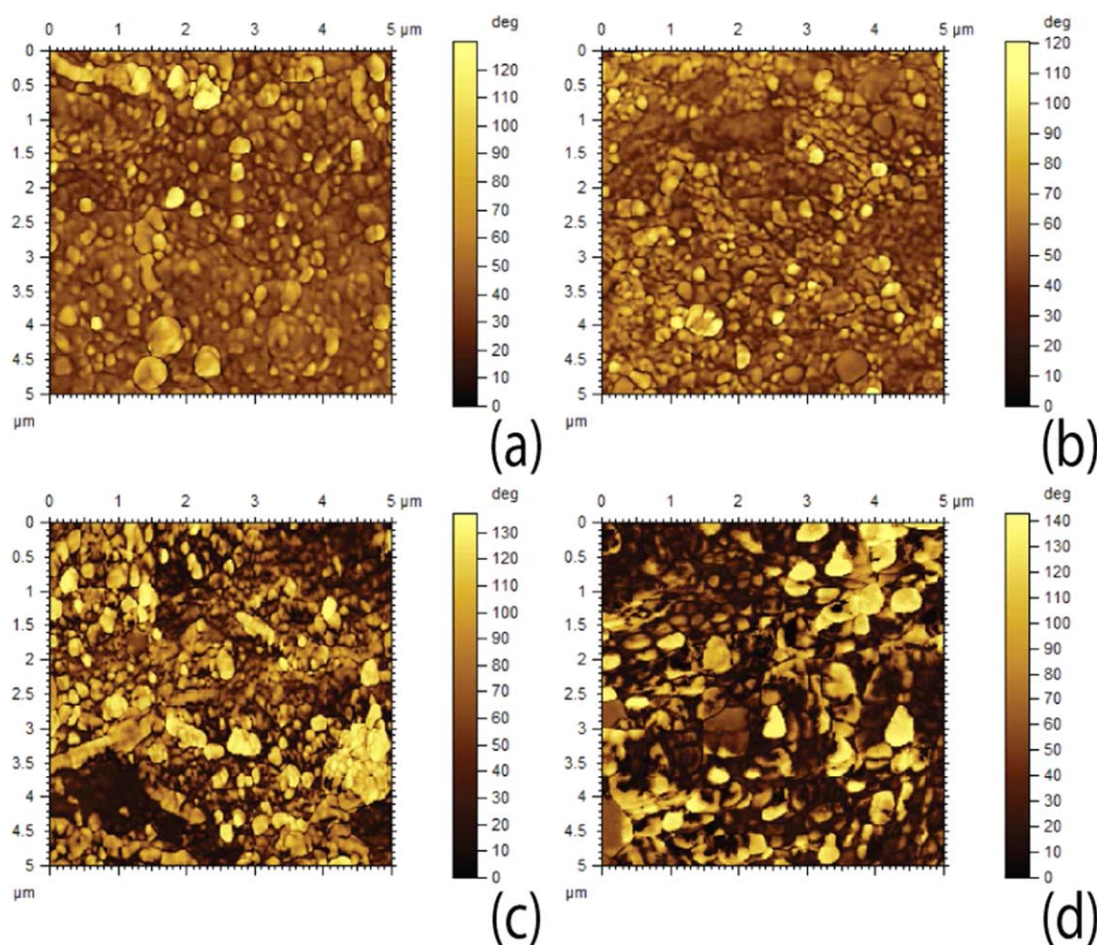


Figure 4. AFM photomicrographs of (a) ET50P1, (b) ET60P1, (c) E7T0P1, and (d) ET80P1 blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

would have been very difficult in the crosslinked blend system.⁴² Similar variation of morphology has also been observed for E60 and E50 blends as depicted in Figure 3(a–f), respectively. However, the uncrosslinked blends show larger voids of TPU after THF etching (suggesting greater incompatibility and lower interfacial adhesion) whereas in the peroxide crosslinked blends the removal of TPU phase is quite restricted. It can be suggested that some interfacial crosslinks formed between EVA and TPU phase may become the reason for inhibition in easy extraction of TPU to some extent. Such morphology also indicates better interfacial adhesion between the two components, which lead to improved compatibility and better physico-mechanical properties for the peroxide crosslinked blends. Improvement in compatibility via dynamic crosslinking has also been reported by other researchers.⁴³

Atomic Force Microscopy. To get a better insight about the final phase morphology of the dynamically crosslinked EVA/TPU blends further investigation has been conducted by AFM, a powerful characterization technique for analyzing the surface morphology of polymer blends. Figure 4 (a–d) demonstrates the phase images of the peroxide crosslinked blends at different blend ratios. The light-yellow region in the AFM images represents the crosslinked EVA domain and the dark brown region indicates the TPU phase.^{38,44,45} The microstructure of TPVs

including the shape and size of rubber phase and their distribution in the matrix plays significant role in determining the final mechanical properties and processability of the crosslinked blend system.² Previously several researchers have reported that in case of dynamic crosslinking, the crosslinked rubber particle exists as dispersed phase in thermoplastic elastomer matrix even when the rubber fraction remains as major component. It happens due to the fact that while dynamic crosslinking, when majority of the rubber fraction gets crosslinked, the viscosity of the rubber phase would become increasingly higher which in turn increases the stress in the material. Further, during the dynamic crosslinking due to the shearing action this larger rubber phase breaks down into smaller nanosized droplets that get dispersed in the thermoplastic matrix.³ Here, from the AFM photomicrographs it has been clearly observed that in E50P1 and E60P1 blend (with increasing TPU content in the blend) the average domain diameter of the crosslinked rubber phase become smaller as compared to E80P1 and E70P1 blends. Such phenomenon may be due to the variation in degree of crosslinking in EVA phase in various blends.⁴⁶ When the amount of EVA is lesser (E50P1), the amount of DTBPIP is sufficient to crosslink the EVA phase more effectively and this results in higher crosslink density for the E50P1 and E60P1 vulcanizates. However, when the amount of EVA increases (E80P1), the same

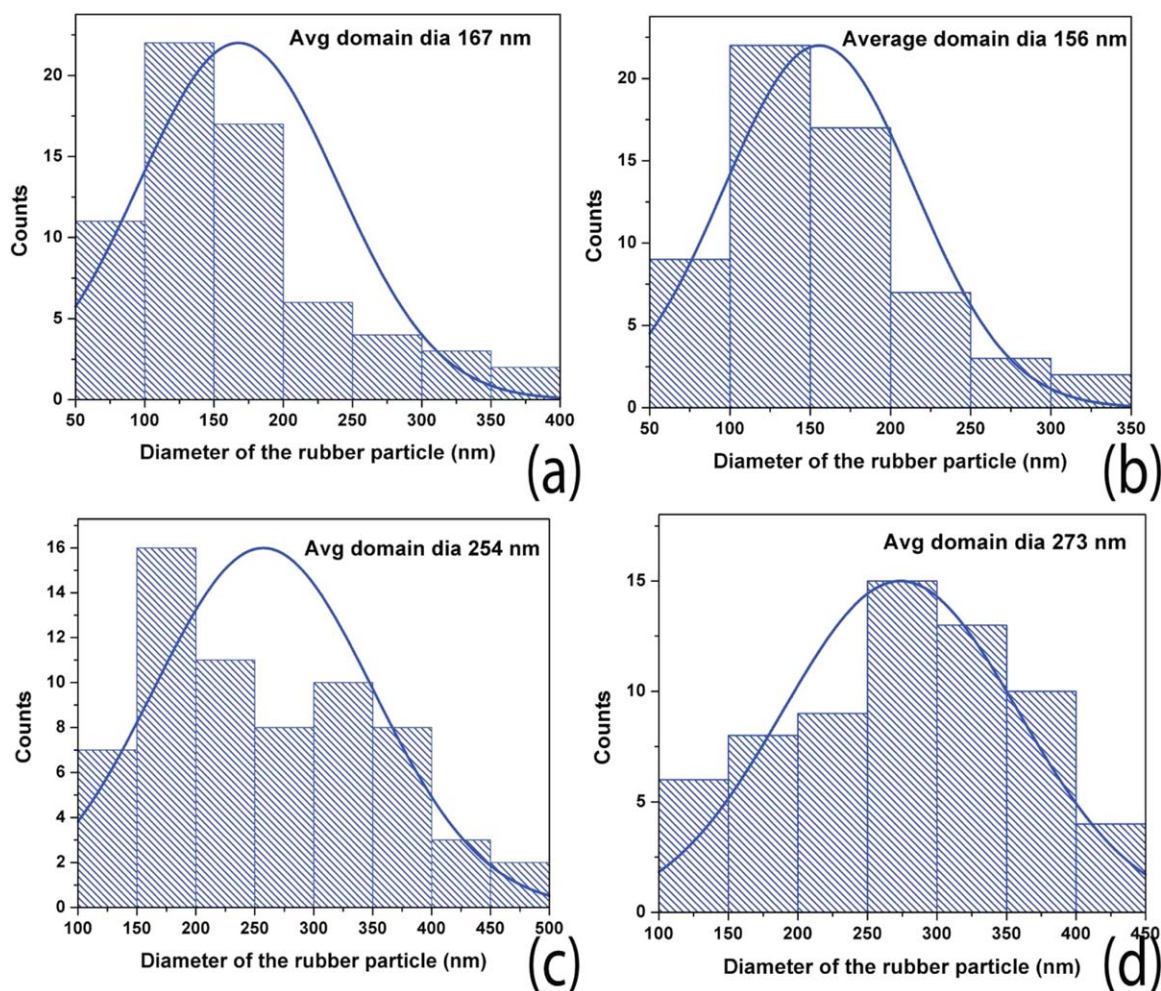


Figure 5. Rubber domain size distribution of (a) ET50P1, (b) ET60P1, (c) ET70P1, and (d) ET80P1 blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount of DTBPIP (1 phr) is not sufficient enough to crosslink the EVA phase fully and the extent of crosslinking reduces leading to lower crosslink density. Hence for E70P1 and E80P1 vulcanizates, there is a possibility that the uncrosslinked EVA rubber particle has a tendency to get coalesced to form aggregates as seen in the AFM images of E80P1 and E70P1 vulcanizates. It may be the reason behind the larger average crosslinked rubber domain diameter of E80P1 and E70P1 vulcanizates (around 250–300 nm) as obtained from Figure 5. This larger EVA domain may act as stress concentration points and lead to comparatively poorer mechanical properties.²² However, for E50P1 and E60P1 vulcanizates, the EVA phase having higher degree of crosslinking may become immobilized and would not coalesce further.^{47,48} As a consequence the average domain diameter of crosslinked EVA in E60P1 and E50P1 are in the range of around 180–200 nm which is comparatively lower.

FTIR Spectroscopy

FTIR spectroscopy has been used to characterize the specific chemical changes that might take place due to dynamic vulcanization of EVA/TPU blends. Figure 6(a) represents the FTIR spectra of the various blends before and after crosslinking in the

region of 2600–4000 cm^{-1} . It has been found that for all the virgin blends there is a broad intense peak at around 3390 cm^{-1} due to N-H stretching vibrations of urethane groups of TPU.^{49,50} However, in the FTIR spectra of all the dynamically crosslinked blends the intensity of N-H stretching vibration reduces and the peak also shifts slightly towards lower wave no of 3337 cm^{-1} which indicates that there might be intramolecular (within TPU) and interfacial crosslinking to some extent via TPU urethane bond.⁵¹ Additionally, two strong peaks can be seen at 2910 and 2847 cm^{-1} corresponding to the symmetric and asymmetric C-H stretching vibrations of $-\text{CH}_2$ groups. It is found that in case of all the peroxide crosslinked blends there is a reduction in the intensity of C-H stretching vibration and similarly, the intensity of C-H bending peak at 1460 cm^{-1} and C-H stretching peak at 1240 cm^{-1} also slightly decreases after dynamic vulcanization as seen in Figure 6(b) which demonstrates the FTIR spectra in the region of 1000 to 1800 cm^{-1} . Such lowering in C-H stretching and bending peak intensity may be associated with the hydrogen abstraction and resulting crosslink formation in the EVA phase.^{52,53} It is also to be mentioned that in the dynamically vulcanized EVA/TPU blends, another small peak appears at 1170 cm^{-1} which can be ascribed

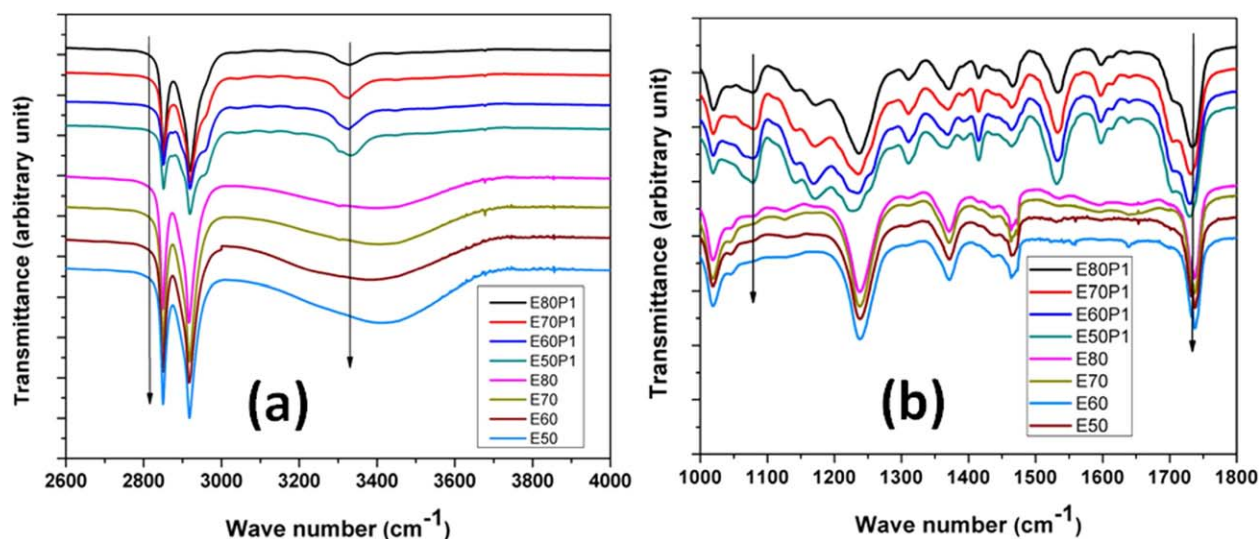


Figure 6. FTIR spectra of the various blends before and after dynamic curing in the range (a) 2600–4000 cm^{-1} and (b) 1000–1800 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the formation of crosslinked C-N bond between EVA and TPU as a result of some interfacial interaction during dynamic crosslinking.^{53,54} The participation of C=O-N-H group of TPU and $-\text{CH}_2$ group of EVA in the formation of crosslinked C-N bond can be also supported from the considerable reduction in the intensity of N-H stretching vibration as mentioned earlier. Similar type of C-N bond formation also occurs in case of electron beam induced crosslinking of EVA/TPU system also.⁵³

Thermogravimetric Analysis

TGA is an effective way to measure the thermal stability of the polymer blend systems. The quantitative data of the thermal analysis for all the blends and neat polymers are summarized in Table VI. In our previous work, it was found that EVA is thermally somewhat more stable than TPU and with addition of increasing amount of TPU, the thermal stability of the blends reduces.³⁵ However the TGA results clearly show that all the peroxide crosslinked blends have very good thermal stability which is even better than neat EVA in some cases. The 5%

decomposition temperature (T_5), 50% degradation temperature (T_{50}) and the maximum decomposition temperature of the blends shifts towards higher temperature after dynamic vulcanization (Figure S2, Supporting Information). For ET80P1, ET70P1, ET60P1, and ET50P1 the 5% decomposition temperature was 334.1 °C, 336.8 °C, 332.0 °C, and 333.7 °C, respectively, which is increased by 11 K, 13 K, 15 K, and 16 K, respectively, on dynamic crosslinking as compared to the uncrosslinked blend. It has been also observed that the maximum decomposition temperature also rise by 13–14 K for all the crosslinked EVA/TPU blends. Such improvement in thermal stability is mainly associated with the formation of more compact crosslinked networks which makes the blend thermally more stable against the formation of gaseous products on heating and postpones the weight loss procedure.⁵⁵

Dynamic Mechanical Analysis

DMA is widely used for studying the visco-elastic behavior of various polymer blends. Since the dynamic mechanical

Table VI. TGA and DTG Data of EVA/TPU Blends before and after Dynamic Crosslinking

Sample designation	Temperature corresponding to 5% decomposition T_{95} (°C)	Temperature corresponding to 50% decomposition T_{50} (°C)	Maximum decomposition temperature, T_{max} (°C)
EVA	332.2	457.4	470.1
TPU	315.4	392.6	409.5
ET80	323.2	447.3	467.2
ET70	322.1	443.2	466.8
ET60	318.0	422.5	466.1
ET50	317.3	414.8	465.3
ET80P1	334.1	452.1	481.1
ET70P1	336.8	453.4	479.5
ET60P1	333.7	438.5	480.4
ET50P1	332.0	426.7	478.2

Table VII. Dynamic Mechanical Properties of Different Blends Irradiated at Various Doses

Sample designation	$\tan \delta$ peak temperature ($^{\circ}\text{C}$)	Storage modulus at -60°C (MPa)	Storage modulus at 25°C (MPa)	Loss modulus peak temperature ($^{\circ}\text{C}$)
EVA	-14.61	1430	22.6	-26.2
TPU	-29.02	2745	49.5	-40.2
ET80	-15.86	1532	19.5	-28.8
ET70	-16.68	1645	24.2	-33.3
ET60	-16.95	2040	30.6	-34.2
ET50	-17.45	2151	31.0	-35.3
ET80P1	-14.91	1747	23.7	-27.4
ET70P1	-15.65	2037	28.7	-30.3
ET60P1	-16.10	2314	32.4	-30.8
ET50P1	-16.62	2363	33.1	-31.5

properties of polymers are highly dependent on the material structure, the molecular level changes that occur in a polymer under the application of a sinusoidal stress is often reflected in dynamic mechanical measurements.²⁵ The temperature dependence of damping factor ($\tan \delta$) of different EVA/TPU blends before and after dynamic crosslinking over a temperature range from -80°C to $+60^{\circ}\text{C}$ has been investigated to determine their relevant stiffness and damping characteristics for various applications. Table VII demonstrates the variation of storage modulus (E') with peroxide crosslinking at two different temperatures. It has been found that for all the crosslinked blends the storage modulus value is higher than that of their uncrosslinked blends. For ET80, the E' value steadily increase from 1532 MPa to 1747 MPa at -60°C whereas for ET50 the E' value changes from 2151 MPa to 2363 MPa. Similar trend in storage modulus value has also been observed at ambient temperature. This increase in storage modulus can be associated with the crosslinking in EVA phase which in turn improves the interfacial adhesion and impart stiffness to the blends. The glass transition temperature (the position of $\tan \delta$ max peak corresponds to T_g) of the peroxide crosslinked blends slightly shifts to higher temperature but the change is only marginal. This minor change in T_g value may be due to some restriction in molecular motion imposed by the crosslinks formation in elastomeric phase. The variation of loss modulus peak temperature is also reported in Table VII. It can be clearly observed that after crosslinking the loss modulus peak also shifts to higher temperature by 2–3 K which may be the result of some restriction in viscous energy dissipation due to more elastic cross-linked network structure formation.

Oil Swelling Study

Oil resistance property is very important for many applications like hose and tube, cable sheathing etc. which has the chances to remain exposed to external environment. Oil resistance properties of the blends (before and after dynamic crosslinking) have been measured by immersing the samples in ASTM oil 3 at room temperature for 7 days. EVA does not show good resistance in ASTM oil 3. However, in our previous report, it has been shown that oil resistance property of the blend gradually improves with addition of TPU.³⁵ Figure 7 demonstrates that

the oil swelling of different EVA/TPU blends before and after dynamic cross-linking and it clearly indicates that all the cross-linked blends show significant improvement in oil resistance property as compared to their uncrosslinked counterparts. It has been found that oil swell % is 31.5 for ET80P1, while it reduced to 12.5 for ET50P1. Thus, after peroxide cross-linking the oil swelling reduces by 22%, 46%, 56%, and 30% for 80/20, 70/30, 60/40, and 50/50 EVA/TPU blends, respectively. Such improvement in oil resistance property after dynamic crosslinking can be attributed to the increasing probability of three dimensional network formation and increasing degree of cross-linking density (CLD) which in turn resist the penetration of oil into the blend to cause swelling. However, it is to be noted that similar improvement in oil resistance property could not be achieved even after the cross-linking of neat EVA and for EVA cross-linked with 1 phr peroxide the oil swell % is found to be 39% which is quite high. Therefore, it is found that this EVA/TPU blend after dynamic cross-linking with only 1 phr peroxide provides excellent oil resistance in ASTM oil 3.

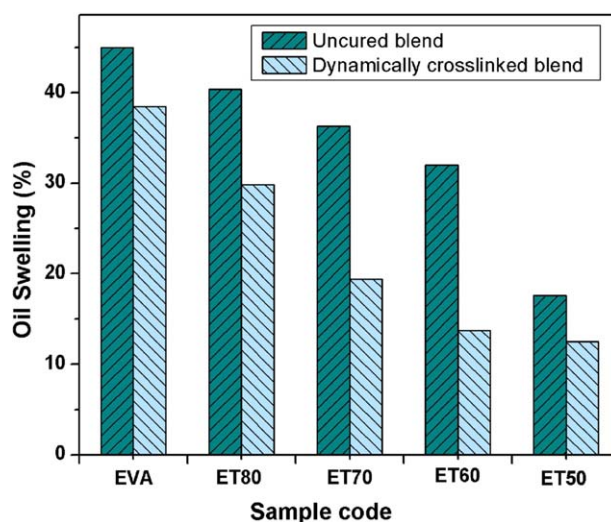


Figure 7. Variation in oil swelling of the EVA/TPU blends after peroxide crosslinking. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

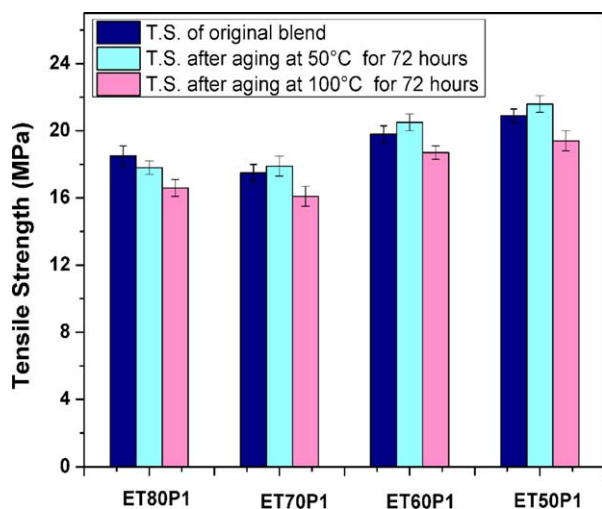


Figure 8. Change in T.S. of various blends before and after aging at 50 °C and 100 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Air Aging Study

Along with good mechanical properties of the blends it is also very important to have good heat aging properties for satisfactory performance during service conditions. Most of the TPV show very good retention of properties even after aging and have good resistance to heat. Aging studies was carried out at 50 °C and 100 °C for 72 h and mechanical properties of EVA/TPU blends before and after aging at two different temperatures have been shown in Figures 8–10 (Table S1 Supporting Information). It was observed that after 72 h of aging at 50 °C, there is marginal improvement in tensile strength and modulus at 100% strain also goes up whereas the elongation at break slightly reduces. Such increase in tensile strength and modulus may happen due to some additional crosslink formation during thermal aging at 50 °C.³⁶ Although it is noted that the tensile strength, modulus and elongation at break slightly reduces after

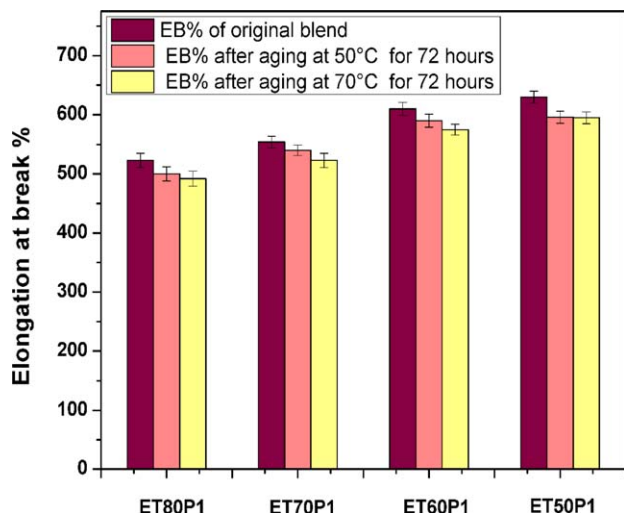


Figure 9. Change in EB % of various blends before and after aging at 50 °C and 100 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

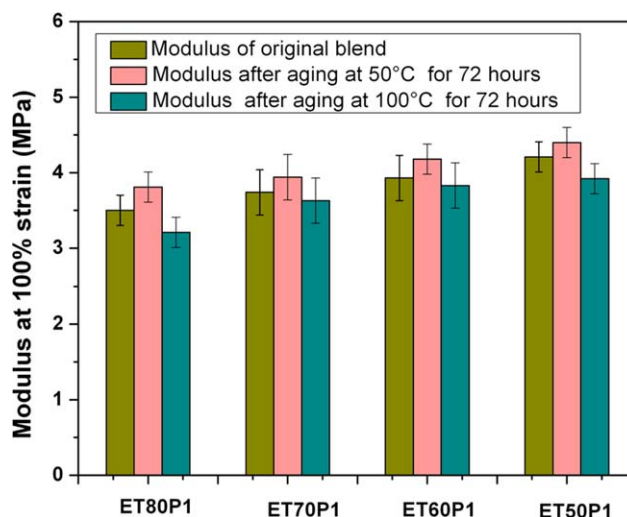


Figure 10. Change in modulus at 100% strain for various blends before and after aging at 50 °C and 100 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aging at 100 °C for 72 h for all the samples. While the percentage retention of tensile strength is 93.7%, 94.4%, 92.0%, and 89.7% for E50, E60, E70, and E80 blends, respectively, elongation at break retains its property by ~93% for all the blends. This is likely because of some disintegration and rupture of crosslinks at elevated temperatures. Therefore, the aging study clearly reveals that the tensile properties of dynamically crosslinked EVA/TPU blends are not much affected by heat and all the blends show very good retention of mechanical properties suggesting good thermal resistance which, is mainly due to the strong C-C linkages formed during peroxide crosslinking.

Crosslinking Density Determination

The extent of crosslinking of the elastomer phase in the crosslinked blends can be studied from the modulus value (at 100% strain) using kinetic theory of elasticity.^{19,36} It is a well known fact that the modulus depends directly on the number of closed loops in the network. The variation in Crosslinking density (CLD) of the TPV's with aging at two different temperatures has been given in Table VIII. It has been found that at 50 °C the crosslink density slightly increases than the un-aged blends due to some additional crosslink formation. Although, reduction in CLD value for all the TPV's at 100 °C indicates degradation of the crosslinked structure to some extent at elevated temperature. From the above results it is also observed that the crosslink density gradually increases with increasing TPU content and ET50P1 shows the highest CLD value among these blends. This result can be explained on the basis that as the EVA content reduces in the blend, the same amount of peroxide leads to higher extent of crosslinking in the lower rubber fraction and the crosslinked network become denser and consequently the CLD value becomes higher.

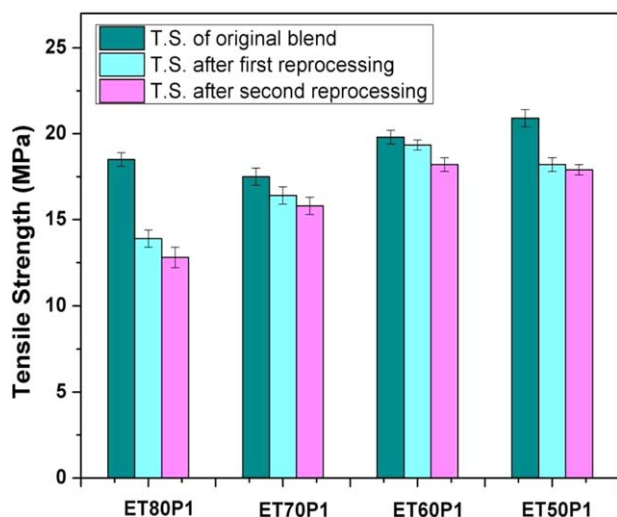
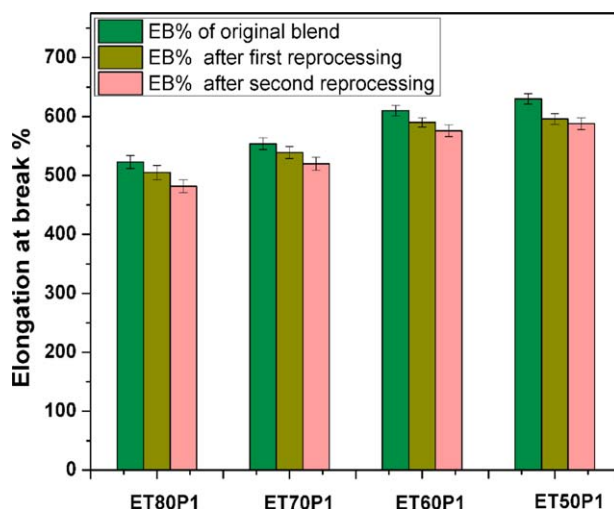
Reprocessing

One of the most interesting aspects regarding TPVs over conventional vulcanized elastomer is the capability of recycling the material even after vulcanization without significant

Table VIII. Crosslink Density of the Various Blends before and after Aging

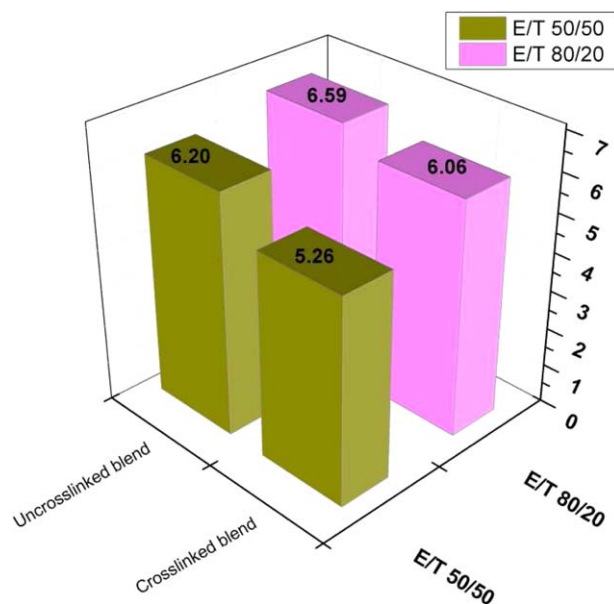
Sample designation	Crosslink density (10 ⁻⁴ mol/cc)		
	Before aging	After aging at 50 °C	After aging at 100 °C
ET80P1	8.07	8.78	7.40
ET70P1	8.62	9.08	8.37
ET60P1	9.06	9.64	8.83
ET50P1	9.70	9.91	9.06

deterioration in the physico-mechanical properties. To investigate the reprocessing ability of dynamically crosslinked EVA/TPU blends, they have been successfully reprocessed two times and the mechanical property after each cycle has been measured and compared with that of the virgin TPVs (Figures 11 and 12). The blends having more amount of TPU show better reprocessability and lower reduction in physical properties which may be because of higher thermoplastic elastomer component helps in the ease of processing of the compound. It has been observed that tensile strength and elongation at break only slightly reduces even after second recycle. The tensile strength, after second recycle, reduces by 10.84%, 8.17%, 12.7%, and 22.1% while elongation at break reduces by only 4.4%, 4.6%, 5.6%, and 10.6% for ET50, ET60, ET70, and ET80, respectively. Whereas for dynamically vulcanized ET50P1, ET60P1, ET70P1, and ET80P1 the reduction in tensile strength, after second reprocessing is by 14.7%, 10.8%, 16.0%, and 30.8% and elongation at break decreases by 6.6%, 5.5%, 6.1%, and 7.8% only (Table S2 Supporting Information). Thus, it is found that uncrosslinked blends have slightly better retention of mechanical properties than that of crosslinked TPVs due to ease of processability of TPE. However, even after peroxide crosslinking, the overall retention of mechanical prop-

**Figure 11.** Change in T.S. of various blends after two times reprocessing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 12.** Change in EB % of various blends after two times reprocessing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

erties is quiet good for reusing the material again. These results are practically very important from a technical point of view because it allows reusing the material several times without adversely affecting their mechanical properties. Moreover, such a reuse of the material entails delay in discarding the material which can be advantageous from environmental point of view also.

Creep Studies. Literature reveals that very few studies had been pursued on the creep behavior of TPU and EVA so far. All polymers being viscoelastic material show creep behavior on application of constant stress. Creep is a time dependent phenomenon which is quiet important for the material's application requiring long term durability and reliability. The stress-strain curves are modeled by Kelvin and Voigt as³⁷

**Figure 13.** Comparison of creep compliance for 50/50 and 80/20 EVA/TPU blends before and after peroxide crosslinking. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

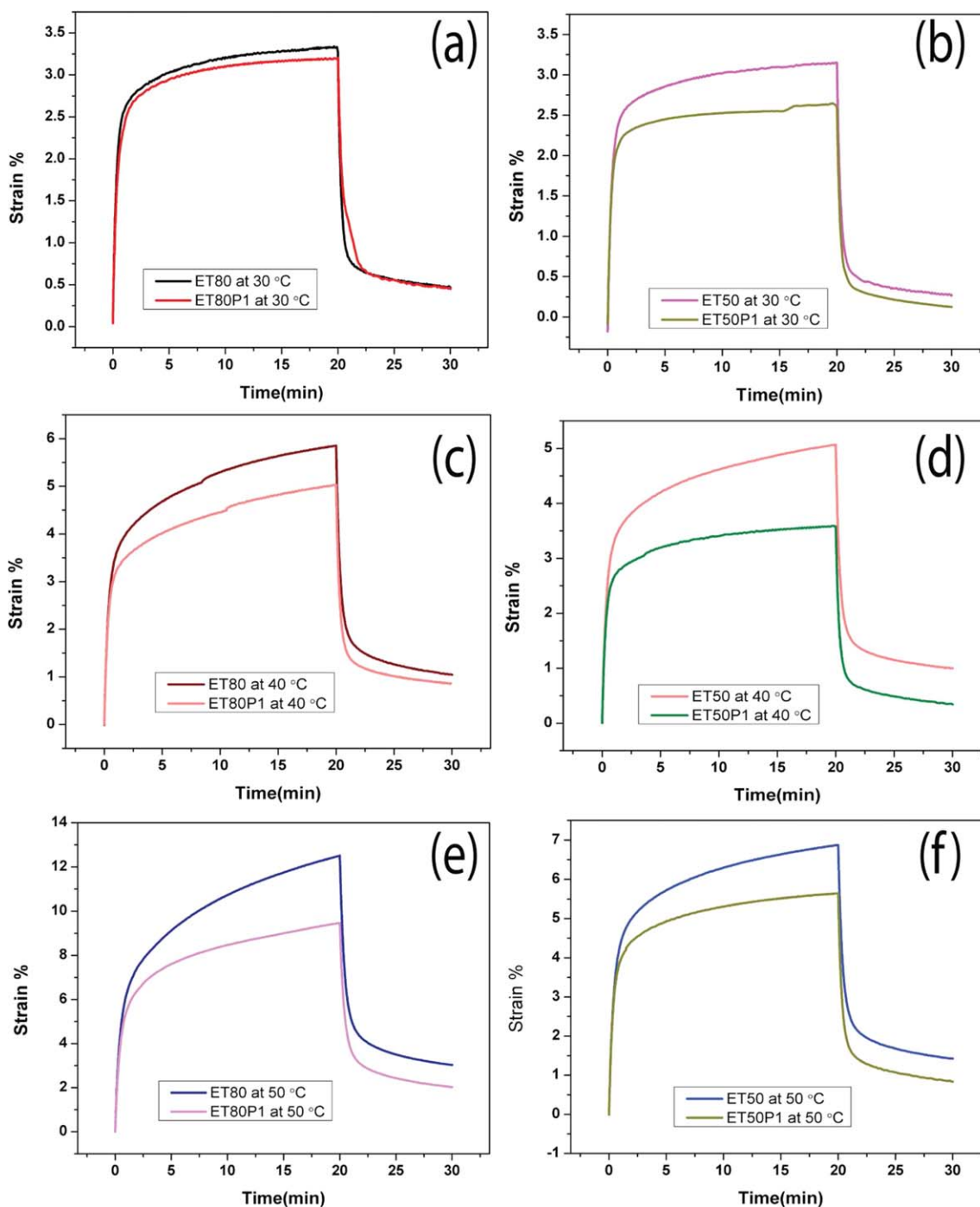


Figure 14. Comparison of strain versus time curves for (a) 80/20 EVA/TPU blend before and after crosslinking at 30 °C, (b) 50/50 EVA/TPU blend before and after crosslinking at 30 °C, (c) 80/20 EVA/TPU blend before and after crosslinking at 40 °C, (d) 50/50 EVA/TPU blend before and after crosslinking at 40 °C, (e) 80/20 EVA/TPU blend before and after crosslinking at 50 °C, (f) 50/50 EVA/TPU blend before and after crosslinking at 50 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$J(t) = J_0 + \sum_{i=2}^n J_i \left[1 - \exp\left(-\frac{t}{\tau_i}\right) \right] \quad (6)$$

Where $J(t)$ and J_0 are the creep compliance after time t after instantaneous creep compliance and J_i and τ_i are the constant characteristics of the system.

Because of the elastic nature of the material, they at first exhibit instantaneous deformation as constant stress is applied and thereafter it is followed by a stable increase in strain with respect to time. Again on removal of stress there occur a sudden fall in strain and a smooth decrease in strain which may be the

Table IX. Variation in Primary and Secondary Creep of the Blends at Three Different Temperatures

Sample	Temperature (°C)	Primary creep	Secondary creep	Percentage increase (%)
E80	30	2.81	3.31	17.79
	40	4.04	5.84	44.55
	50	7.96	12.41	55.90
E80P1	30	2.60	3.04	15.15
	40	3.63	5.02	38.29
	50	6.81	9.48	39.20
E50	30	2.75	3.12	13.81
	40	3.66	5.06	38.25
	50	5.04	6.87	36.31
E50P1	30	2.36	2.64	11.86
	40	2.91	3.57	22.68
	50	4.42	5.64	27.60

result of elastic recovery of the material.^{25,56} Figure 14(a,b) demonstrate the strain time plot of EVA/TPU blends at two different blend ratios (80/20 and 50/50 EVA/TPU) and illustrates the effect of peroxide crosslinking on the creep response of the blend system at room temperature 30 °C under a constant stress of 0.5 MPa. The plots clearly show a good coherence with the characteristic strain time plot for viscoelastic polymeric materials and both the blends exhibits a primary creep with relatively high strain rate and a secondary creep due to the steady state attainment.²² It has been observed that there is a significant change in strain response for both the EVA/TPU blends before and after the dynamic crosslinking and in both the cases the primary and secondary creep values are lower than that of their uncrosslinked blends. It is also quiet clear from the plot that the improvement in creep resistance is more prominent for the EVA/TPU 50/50 blend. This result suggests that crosslinking in the rubber phase led to better dimensional stability and lowered the primary and secondary creep as compared to the uncrosslinked blend.

Creep Compliance. A comparative analysis of creep compliance for the EVA/TPU blends before and after peroxide crosslinking is given in Figure 13. The Figure clearly shows that the creep compliance value for all the blends decreases after dynamic crosslinking. However, it has also been found that such reduction in creep compliance is found to be more prominent for 50/50 EVA/TPU blend as compared to the 80/20 EVA/TPU

blend. It is possibly due to higher amount of crosslinking in the EVA phase which provides better creep resistance for the blend system and presence of more TPU content also contribute to make the 50/50 blend dimensionally more stable.

Effect of Temperature on Creep Properties. Temperature has an important role in determining creep response of the polymer samples. It is clearly observed that at lower temperature (30 °C) the difference between the primary and secondary creep is relatively low for both crosslinked and uncrosslinked blends (Table IX). It is visibly apparent from the plots (Figure 14) that with the increase in temperature both the value of primary and secondary creep increases which indicates the temperature-activated softening of the polymer matrix as a result of reduction of stiffness of the entangled polymer network and enhanced ease in the segmental mobility of the polymer chains.⁵⁷ It is also interesting to note that for 80/20 EVA/TPU blend system (for the blend containing more EVA content), the percent difference between the primary and secondary creep is more as compared to the uncrosslinked blends at all temperatures. As the temperature increases from 30 °C to 50 °C the difference between the primary and secondary creep for ET80 blend increases from 17.79% to 55.9% but after peroxide crosslinking the difference becomes only 38.3% and 39.2%. However, for ET50 blend this difference increases from 13.81% to 36.31% as the temperature rises from 30 °C to 50 °C; whereas in case of ET50P1 the difference reduces to 11.86% and 27.60%. It is to be mentioned that since the melting point for neat EVA is around 76 °C, the creep effect become much higher for ET80 blends as the temperature reaches 50 °C. However, the creep resistance improves significantly after the peroxide crosslinking for the 80/20 EVA/TPU blend (ET80P1) as evident from the results. It can also be mentioned that with an increase in temperature the strain recovery for all the samples gradually diminishes but for both the blends the strain recovery is better after peroxide crosslinking.

Electrical Properties

For successful application of the peroxide crosslinked EVA/TPU blend material in cable industry, electrical resistivity study is

Table X. Variation in Volume Resistance with Blend Composition

Sample	Volume resistance (ohm cm)
EVA	4.24×10^{15}
TPU	6.45×10^{11}
ET80P1	7.45×10^{13}
ET70P1	5.16×10^{13}
ET60P1	4.62×10^{13}
ET50P1	1.05×10^{13}

very important as all cable insulation and sheathing material must have sufficient ability to restrict the leakage of electrical current during service. Table X summarizes the variation of volume resistance of the crosslinked EVA/TPU blends with blend composition. It has been found that neat EVA has volume resistance of 4.24×10^{15} ohm cm while for pure TPU it is only 6.45×10^{11} ohm cm. Table X shows that for the peroxide crosslinked EVA/TPU blends the volume resistivity varies from 7.45×10^{13} to 1.05×10^{13} ohm cm. The minimum volume resistance required for satisfactory use of a material as cable sheath is 10^8 ohm cm.⁵⁸ Therefore, from the electrical test it can be concluded that this blend material has volume resistance well above the required range and is suitable for cable sheath application. The high value of electrical resistivity can be associated with the crosslinked structure formation via dynamic crosslinking where the numerous crosslinking points may be considered to act as barrels to cause restriction in the electrical charge movement between polymer chains.⁵⁹ It is also to be mentioned that since neat EVA has better electrical resistance than TPU, the electrical resistance of the blends gradually reduces with increasing TPU content.

CONCLUSIONS

In summary, the influence of peroxide crosslinking on dynamically vulcanized EVA/TPU blends at various blend ratios has been investigated where all the vulcanized blends show higher physico-mechanical properties as compared to the corresponding un-vulcanized blends. Interestingly, while the 80/20 EVA/TPU blend causes a marginal increase in the tensile strength by 5.1% on addition of 1 phr DTBPIP, 50/50 EVA/TPU blend shows drastic increase by 117.9% under similar condition. This drastic enhancement is may be due to the higher extent of crosslinking and relatively smaller size of dispersed EVA domain in the later compared to the former leading to good physico-mechanical properties. The air aging study reveals that for all the TPVs, retention in T.S. is above 88% and elongation reduces by only 6–7% even after aging at 100 °C for 72 h. 50/50 EVA/TPU blend shows better creep resistance at all temperatures as compared to 80/20 EVA/TPU blend. Oil resistance property of the blends show remarkable improvement after dynamic crosslinking, and the oil swell % reduces with increasing TPU content. The volume resistivity of all the peroxide crosslinked blends lie in the range of 10^{13} ohm cm which is suitable to use this material in cable sheathing application and the electrical resistance of the blends become slightly lower at higher TPU content. This dynamically crosslinked EVA/TPU blends are also capable of reprocessing without much deterioration in physical properties. Considering all the improvement in physico-mechanical, thermal, dynamic mechanical, oil resistance and electrical properties, the dynamically vulcanized 60/40 EVA/TPU blend with 1 phr peroxide has been found to be an excellent economically viable (compared to 50/50 EVA/TPU blend) reprocessable material for technological applications especially in cable and automotive industries.

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