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REVIEW

Automotive applications of thermoplastic vulcanizates

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Abstract

Thermoplastic vulcanizates (TPVs) are special classes of thermoplastic elastomers, in which dynamic vulcanization of the rubber phase takes place during melt mixing with a semicrystalline thermoplastic matrix phase at elevated temperature. This review article focus on the different types of thermoplastic vulcanizates (TPVs) from various elastomer and thermoplastic blends that are suitable for the automotive applications purpose. A detailed study of the various TPVs based on polypropylene-ethylene propylene diene rubber (PP-EPDM) and polypropylene-ethylene α -olefin has been focused and their application in the automobile sector has been summarized. Most of the commercially available TPVs are PP-EPDM based. Limited applications of that TPVs in high heat and oil resistant application purposes requires new generation of TPVs. High performance TPVs or super TPVs are new generation TPVs that exhibit high heat resistance as well as excellent oil resistance property suitable for automotive under-the-hood applications. Therefore TPVs based on XNBR-PA12, HNBR-PA12 and FKM-PA6 system has also been explored in details in this study and the possibility of the use of those TPV system has been focused for the high temperature application purpose in the automobile sector where high and oil resistant application properties is the prime concern.

1 | INTRODUCTION

1.1 | Thermoplastic elastomers (TPEs) to thermoplastic vulcanizates (TPVs)

In the uncross-linked state, elastomers have restricted applications because of its low strength value, sticky behavior and higher chances of solubility in solvents. Apart from it has a higher tendency to disentanglement even under the small stress that results to viscous deformation and a permanent set. After the formation of cross-links only, it possesses the typical elastomeric properties like elasticity, flexibility, strength and solvent resistance properties that make elastomeric materials applicable for different applications such as tires, conveyor belts, seals, gaskets etc.^[1,2] One side formation of covalent cross-links restricts the motion of chain molecules and also prevents the melt processability of elastomers which is a distinct

disadvantage of the elastomeric materials rather than the thermoplastics. Other side recycling of the scrap and waste elastomeric material is also impossible. At the same time, instead of possessing better melt processability and good strength property also thermoplastic materials have a restriction for the dynamic application purpose due to low flexibility, rigidity and poor elastic behaviour.^[3]

In this aspect, thermoplastic elastomers (TPEs) are a special class of materials, which make the bridge over the gap between thermoplastics and conventional elastomers. It means TPEs combine the service properties of elastomers at room temperature with the processing properties of thermoplastics at elevated temperature. In the late 1950s, the emergence of TPEs in the field of polymer science and technology fetch a new skyline.^[4-6] Mostly the TPEs are block copolymers consisting of a soft and mobile “rubbery” blocks with a low glass transition temperature (T_g), and rigid or hard “glassy” blocks with a

high melting temperature (T_m) or high T_g . Commercially there are two main categories of TPEs:

- TPEs based on block copolymers (mainly triblock or multi-block copolymers).
- TPEs based on polymer blends.

The geometry of triblock copolymers typically consists of a soft, flexible mid-block end-capped with two rigid end-blocks, such as (styrene)-(butadiene)-(styrene) i.e., (SBS) or (styrene)-(ethylene-co-butylene)-(styrene) i.e., (SEBS). For multiblock copolymers poly(esters), poly(amides) or poly(urethanes) act as rigid or hard blocks and poly(ethers) as soft blocks.^[7-9]

The rigid blocks make the cluster together to form small domains at service temperature and that small domains act as physical cross-links between the soft blocks, which is schematically depicted in the Figure 1.

On the other hand, the physical cross-links disappear above the melting temperature of the hard blocks and the material becomes melt processable, which leads to the material with rubber-like properties at service temperature and (re)processability in the melt.^[10-13]

TPEs have the following advantages: (a) no need of vulcanization and the requirement of very little compounding, (b) recycling of the scraps without the significant deterioration of the properties, (c) easy processability like thermoplastics, (d) better quality control, (e) ease of manipulation of the properties by changing the ratios of the components. Due to the above-mentioned advantages, TPEs are gradually replacing the conventional elastomer products and many leading plastic materials in our day-to-day life.

Side by side, there are few drawbacks of TPEs and that is, (a) creep response on extended use and (b) loss of rubbery behavior at elevated temperature. As the rubber phase is not cross-linked in case of TPEs, it does not provide enough resistance to set behavior under prolonged deformation. Following this, the concept of dynamic vulcanizates or thermoplastic vulcanizates came out where the elastomeric phase is cross-linked which leads to superior elastic behavior.

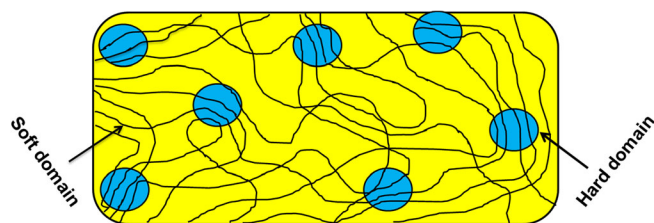


FIGURE 1 Morphology of a tri-block thermoplastic elastomers (TPEs) [Color figure can be viewed at wileyonlinelibrary.com]

1.2 | Thermoplastic vulcanizates (TPVs)

Thermoplastic vulcanizates (TPVs), a special class of thermoplastic elastomers are produced by “dynamic vulcanization” of non-miscible blends of a thermoplastic and an elastomer, that is, selective cross-linking of the elastomer phase during melt mixing with the thermoplastic.^[14-16] Simultaneous vulcanization of the rubber phase in the presence of a cross-linking agent, (maybe peroxide, diamine, sulfur-accelerator etc.) during melt blending with the thermoplastic, leads to the generation of dynamic vulcanizate that consists of dispersed cross-linked rubber particle in a continuous thermoplastic matrix phase shown in Figure 2.

Dynamic vulcanization results in an increase of the rubber viscosity, which promotes the phase inversion and offers heterophasic morphology in TPVs. Generally, the average diameter of the dispersed rubber particle varies in the range of 0.5–2.0 μm .^[17] The dispersed rubber particle enhances the elasticity of the TPVs while the thermoplastic phase explains the melt processability. It is generally accepted that one of the major advantages of the dynamically cured blends over unvulcanized blends is that the morphology is fixed on cross-linking and is not altered by subsequent melt processing. Therefore compare to the simple noncross-linked blends, TPVs exhibit more elastomer-like properties: such as lower compression set, lower stiffness, greater resistance to fatigue, better elastic recovery, higher ultimate mechanical properties, higher melt strength, enhanced resistance to heat and chemicals, improved high temperature utility.

1.3 | Concept of dynamic vulcanization and morphology development of TPVs

In the year 1962, Gessler and Haslett first reported about the dynamic vulcanization process.^[18] Following this Fischer further reported about the dynamic vulcanization process through his early work on polypropylene (PP)/ethylene propylene diene rubber (EPDM) based TPVs with peroxides as a cross-linking agent. This results in the commercialization of “Uniroyal TPR” thermoplastic rubber.^[19] Later in the year 1980, Coran and Patel extensively studied the TPVs of various blend components and that generates greater industrial attention.^[20,21] Their extensive studies upon TPVs based on PP/EPDM blends with higher cross-link density in the rubber phase leads to the commercialization of “Santoprene” TPE, by Monsanto in 1981.

Morphology development of TPVs during the dynamic vulcanization is mostly governed by the two factors and these are a) composition ratio of elastomer/thermoplastic and b) elastomer/thermoplastic viscosity

FIGURE 2 TPV development by phase inversion [Color figure can be viewed at wileyonlinelibrary.com]

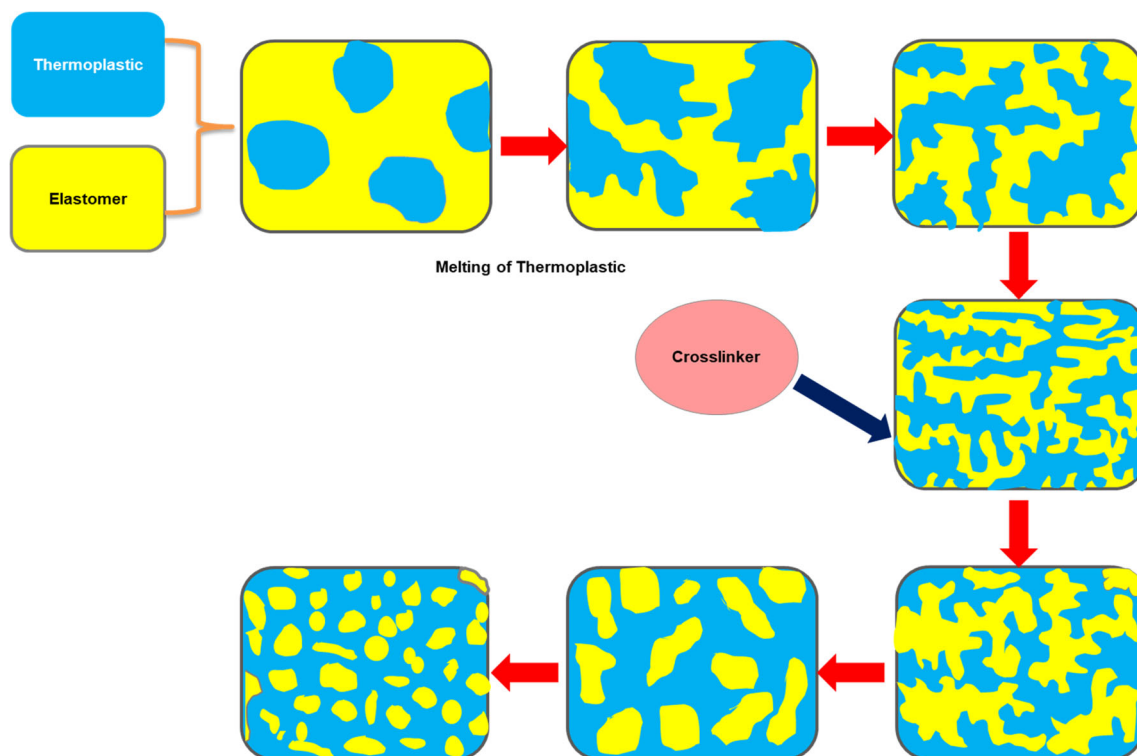
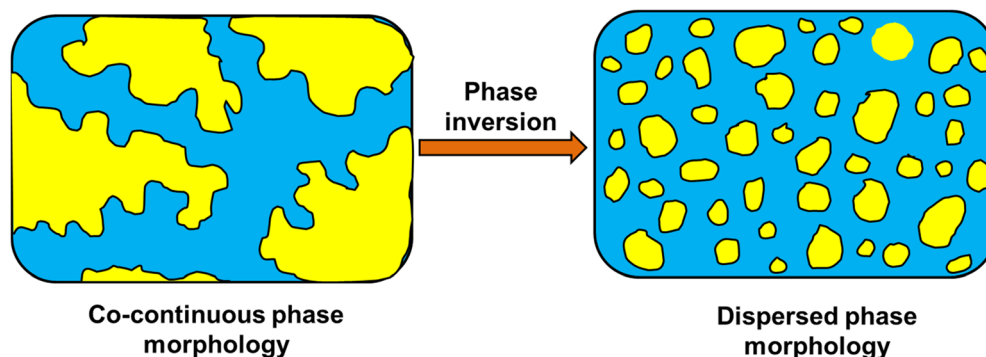


FIGURE 3 Scheme of morphology development of TPVs during dynamic vulcanization [Color figure can be viewed at wileyonlinelibrary.com]

ratio.^[22] For TPVs, scheme of morphology development has been depicted in the Figure 3.

Following the scheme of development of morphology, it can be assumed that in the starting of the mixing process the non-molten thermoplastic pellets swim in the elastomer matrix. After complete melting of the thermoplastic phase, it is assumed that the two immiscible phases get mixed intimately that results in the development of co-continuous morphology. During the mixing time the combined effect of shear and elongational forces deforms the co-continuous morphology that leads to the refinement of the co-continuous strands, that is, the strands become thinner preserving the co-continuity. Following this, cross-linking in the elastomer phase results

increment in the viscosity of the elastomer phase which leads to the simultaneous rise in shear and elongational forces acting on the system also and thus to an increased deformation of the co-continuous structure. The elastomer strands start to break up into small particles and the dispersion of the cross-linked elastomer particles takes place into the thermoplastic matrix phase only after the attainment of a certain threshold stress value. Therefore, phase inversion occurs that depicts the changes of final morphology from a thermoplastic dispersion in an elastomer matrix via a co-continuous state to a dispersed cross-linked elastomer particles to a continuous thermoplastic matrix.^[23–28] Thus the phase inversion phenomenon enables the cross-linked elastomer to become a dispersed

phase although the elastomeric component or the rubber phase is the major component with volume fractions greater than 0.5. Likewise, the dynamic vulcanization process develops the heterophasic morphology that comprises of irregularly shaped elastomer particles with a broad size distribution in the final commercial TPV. Apart from several factors like composition, viscosity ratio, interfacial tension, type of deformation, and also the rate of deformation also governs the finer particle size of the cross-linked elastomer particles. Among all this factors, the rate of deformation that is, the shear rate plays the most important role in the microstructure development of TPVs. A higher shear rate facilitates the breakdown of the rubber phase in finer particles and uniform distribution of the rubber particles.^[29]

It was reported that TPVs made of internal mixers or screw extruders possess finer rubber particles than that of the TPVs made from an open mixture. Even the twin-screw extruder exerts higher shear rate compared to the internal mixer and this results much smaller droplet of the rubber particles into the dispersed matrix phase.^[30] Sometimes injection molded TPVs appear with finer distribution of the rubber particles in nanometer level and this is due to the higher shear rate of the injection molding machine. As example Banerjee et al. reported that after injection molding the size of the rubber particles in Fluoroelastomer (FKM)/polyamide 6 (PA 6) TPVs decreased from 130–50 nm to 60–80 nm and the rubber particles were uniformly distributed in the PA 6 matrix also. They also reported that the size of the EPDM domains comes down from 1–3 μm for the compression molded PP/EPDM TPVs to 50–90 nm for the injection molded TPVs.^[31,32]

1.4 | Properties-microstructure-application of TPVs

With the same composition ratio TPVs always possess higher mechanical properties in terms of tensile strength and elastic modulus than that of the uncross-linked blends. This is attributed to the in-situ vulcanization of elastomeric phase and the phase inversion of the plastic phase from a dispersed one to a co-continuous one.^[33] Apart from mechanical properties of TPVs depend on the cross-link density of the rubber phase, the composition ratio of rubber/plastic, the size and distribution of the rubber domains, the rubber network structure, the thickness of the plastic ligaments, the compatibility between plastic and rubber phases, the additives in TPVs and the dynamic vulcanization conditions.^[34]

It was reported that an increase in plastic content in the composition ratio of rubber/plastic leads to an increase

of tensile strength value for the TPVs. At the same time, there is a decrease in the elongation at break value.^[35] It has also been reported that there is an increase of tensile strength and elongation at break value of the TPVs with increase of cross-link density in the rubber phase up to a certain extent. At higher cross-link density, the properties deteriorate.^[36] L'Abée et al. prepared TPVs with different diameter of the rubber particles, which ranged from 1 to 70 μm and it was found that a decrease in diameter led to an increase in tensile strength and elongation at break but a decrease in elastic modulus.

Another advantage of TPVs over conventional thermosetting rubbers is their reprocessability owing to their special microstructure. TPVs can be reprocessed by using common equipment for plastic processing, such as extruders and injection molding machines and it has been reported that many TPVs show good reprocessability with high stability in mechanical properties.^[37] On the other hand, due to the presence of unique microstructure the fatigue resistance property of TPVs is also high compared to the uncross-linked blends. Side by side, the unique microstructure and cross-link density of the elastic network imparts higher heat resistance and oil resistance characteristics for TPVs and this emerges its applications for high heat and oil resistant purposes.

1.5 | Rheology and processing properties of TPVs

The most advantages of TPVs over the conventional thermosetting elastomers is its melt processability. Rheological properties that indicate the processability of the TPVs have gained much attention. In the year 1982, Goettler et al. was the first to study the technical importance of the TPVs in terms of rheological characteristics using a capillary rheometer.^[38] In 1995 Han and White described the comparative rheological study of PP, PP/EPDM uncross-linked and dynamically cross-linked blends using various rheological instruments to measure steady shear flow, uniaxial extension and oscillation flow properties of the compounds.^[39] Following this, lots of study has been performed by the various research groups to get an idea about the rheological behavior of TPVs. It has been reported that due to the presence of unique microstructure the rheological behavior of TPVs is significantly different from that of the uncured blends. Presence of elastic network even imparts higher initial values of complex viscosity compared to the plastic component.

From plots of the viscosity as a function of the shear stress, a critical stress or yield stress of flow was noticed. It was reported that at a low shear stress a TPV exerts elastic behavior due to the presence of strong elastic

network of cross-linked rubber particles. At intermediate stress, it behaves like a melt of plastic filled with stiff rubber particles and in this condition, the viscosity is highly dependent upon the content of rubber particles. At high shear stress, the strong elastic network deforms and collapses and TPV behaves like a fully plastic melt.^[40–42] It was also noticed that rheological properties of TPVs were controlled by the rubber phase at low frequencies, and by the plastic matrix at high frequencies. Above all, with increase of shear stress, shear-thinning behavior was observed for all the TPV systems. It means that all the TPVs exert pseudoplastic behavior, that is, decrease in viscosity of TPVs with increasing shear stress or frequency.^[43,44]

1.6 | Production of TPVs

There are three different mixing methods by which TPVs can be prepared and these are a) phase mixing method, b) pre-blending method and c) split addition

method. Flow diagram of the three mixing methods is shown in Figure 4.

- *Pre blending method:*

In this process at first thermoplastic and elastomer is allowed to melt mixed to develop a homogeneous blend. Then at the same condition, the cross-linker is added on top of the molten mass to form the TPVs. Actually, this is the conventional method for preparing the TPVs.

- *Phase mixing method:*

In this method, at first, the cross-linker is preblended with the elastomer at low temperature to form a curative masterbatch. After that, the curative masterbatch is added to the molten thermoplastic phase at elevated temperature to carry out the dynamic vulcanization and TPV formation takes place.

- *Split addition method:*

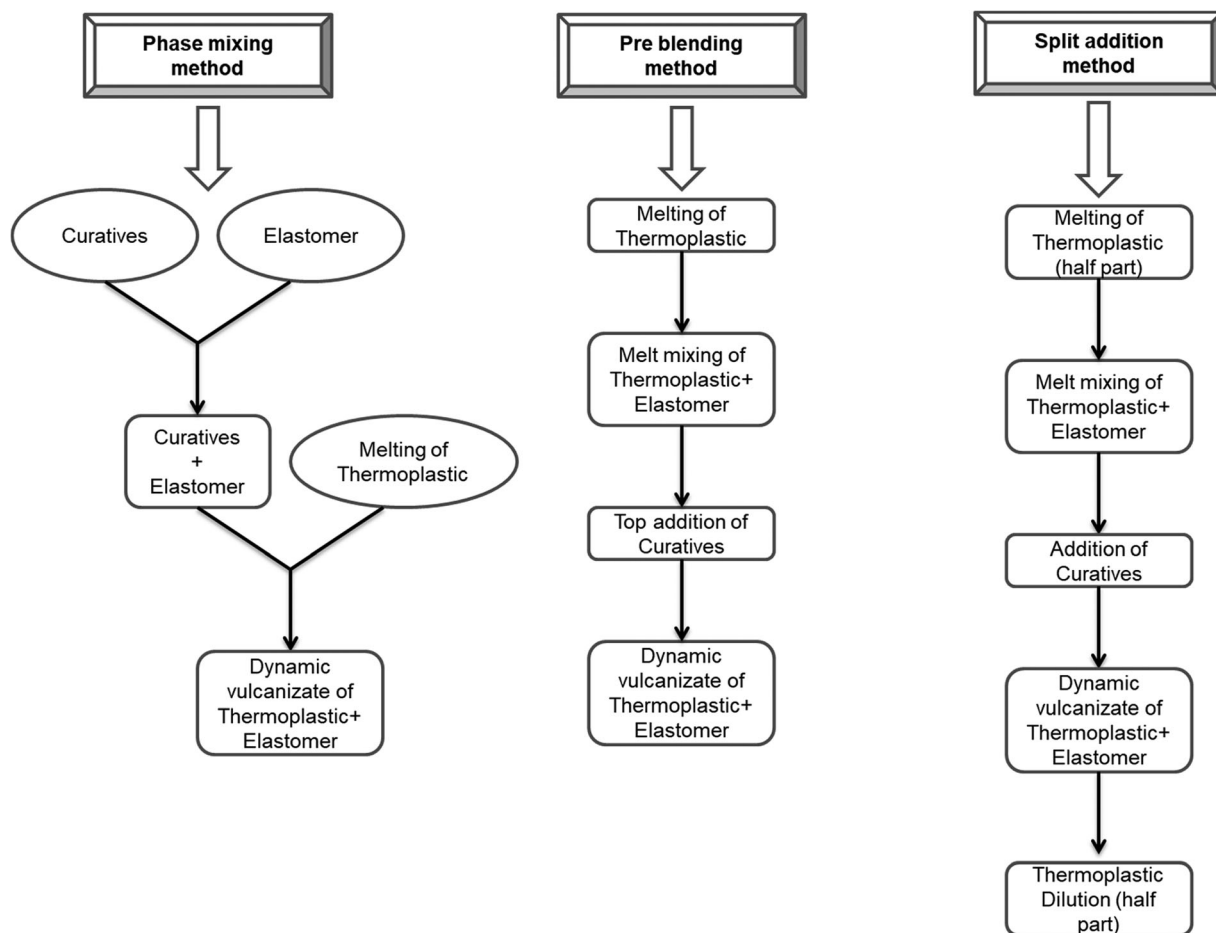


FIGURE 4 Flow diagram of the development of TPVs by different methods

At first, half part of the thermoplastic and full part of the elastomer is melt mixed at elevated temperature. Then the cross-linker is added to the molten mass under the same condition to allow the dynamic vulcanization. Once the dynamic vulcanization process gets completed, remaining half part of the thermoplastic is added to the dynamic vulcanizate and it is allowed to get melt mixed.^[45,46] Final TPVs possess poor mechanical behavior because of the poor dispersion of the thermoplastic matrix phase that is added at the last stage of mixing. Even after the increase of mixing time, there was no significant improvement in the level of dispersion of the thermoplastic matrix phase and no change in the final morphology of the TPVs also.

On the other hand, TPVs developed by phase mixing method is superior to the TPVs developed by the preblending method in various aspects such as the higher value of modulus at low strain, the higher cross-link density of the dispersed elastomeric phase. This is due to the formation of smaller rubber domains during the dynamic vulcanization for the phase mixed TPVs whereas the rubber domains are coarser for the TPVs prepared by preblending method as depicted in Figure 5 below.

Melt mixed cross-linked elastomeric particles provides the elastomeric behavior in the thermoplastic vulcanizate and thermoplastic phases provide the melt processability.^[47] Processing behavior, elastic recovery, heat resistance, resistance to oil swell is better for TPVs as compared to uncross-link blends or TPEs.^[48–50] Due to these reasons or superior properties, TPVs are getting more interest in automotive sectors.

Thus TPVs have found potential and proven applications in various areas such as mechanical rubber goods applications (gaskets, seals, convoluted bellows, flexible diaphragms, tubings, mounts, bumpers, valves, housings, glazing seals, vibration isolators, plugs, connectors, caps, oil-well injection lines), under-the-hood applications in automotive field (air conditioning hose cover, fuel line hose cover, vacuum tubing, vacuum

connectors, seals, body plugs, bushings, protective sleeves, shock isolators), industrial hose applications (industrial tubing, hydraulic [wire braided], agricultural spray, paint spray, mine hose), electrical applications (wire and cable insulation, plug, bushings, enclosures, connectors), consumer goods (sporting goods, portable kitchen appliances, business appliances).

1.7 | Biodegradability of TPVs

The degradability of TPVs in the environment like biodegradable polymers is very important issue for our daily-life. Biodegradable polymers, as promising alternatives to non-degradable ones, deserve a considerable level of attention in research and development investigations owing to their potential to protect the environment by reducing plastic waste. In the same way environment also requires degradation of TPVs after its usage to maintain the environmental sustainability. In this respect, extensive research is going on for developing a new class of TPVs with environmentally friendly properties as compared to conventional available TPVs. Considering this aspect bio-based rubber-plastic blends are a matter of concern to prepare biodegradable TPVs. Therefore, now a days bio-based TPVs, such as poly(lactic acid) (PLA)/Natural rubber (NR) TPVs, PLA/ethylene-co-vinyl acetate (EVA) TPVs and poly(butanediol-lactate-sebacate-itaconate)bioelastomer (PLBSI)/PLA TPVs are gradually coming into the focus of research.

In this review, the main objective is to focus on that TPV system that has already been potentially used in the automotive sector for the different application purpose. Else, the target is also to highlight the new TPV systems that are already in the lab scale development and to find out their potential usage in the automotive sector. Side by side, the target is also to focus the new TPV system that can be potentially used in the high heat resistant and oil resistant application purpose.

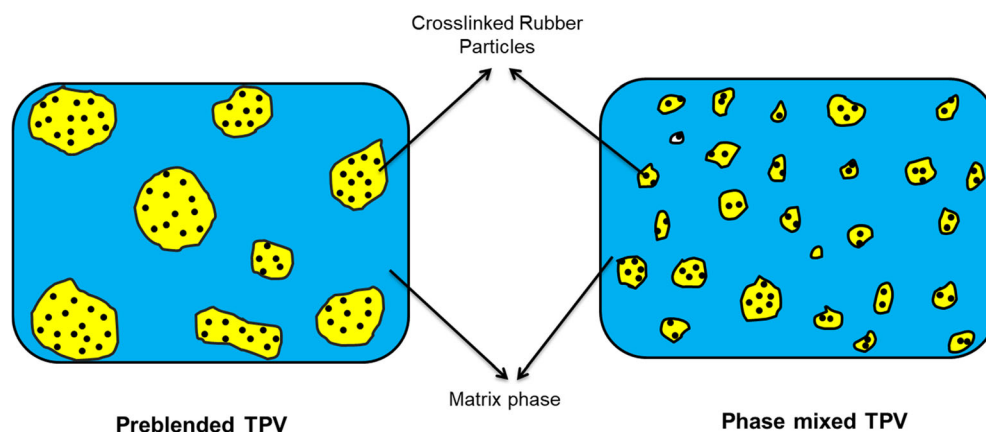


FIGURE 5 Morphology of TPVs prepared by (a) preblending method and (b) phase mixing method [Color figure can be viewed at wileyonlinelibrary.com]

2 | STATE OF THE ART: DIFFERENT TPVS

2.1 | PP/EPDM TPVs

There are different types of TPVs available in the market but among them commercially popular TPVs are typically based on PP/EPDM in which elastomeric phase is selectively cross-linked during melt mixing with PP phase at high temperature. As EPDM rubber has saturated main chain backbone so it provides excellent stability against heat, oxygen and ozone to the TPVs. Preparation of TPVs by dynamic vulcanization of EPDM rubber can be done by using different types of cross-linking agents like activated resins coagent-assisted peroxides, sulfur-accelerator system, platinum-catalyzed hydrosiloxane, vinyltrialkoxysilane/moisture, catalyzed quinonedioxime, and bisthiols etc.

2.1.1 | Phenolic resin cured TPV

Phenolic resins are usually classified into two categories namely resols and novolacs. Resols contain reactive methylol group and dimethylene-ether units. On the other hand, novolac has no reactive methylol functionalities and therefore cannot act as a cross-linking agent. Resols are widely used for cross-linking of EPDM rubber during the preparation of PP/EPDM based TPVs. Abdou-Sabet and Fath reported the improvement of rubber-like properties (compression set, oil resistance and processing characteristics) of PP/EPDM based TPVs in presence of dimethylol octyl phenol curing resin.^[51] Phenolic resin curatives containing dibenzyl-ether linkages were found much better than other phenolic resins in PP/EPDM blends. There are some disadvantages of the use of phenolic resin, which includes moisture absorption even at ambient temperature, and staining problem (dark brownish color appearance) for the final PP/EPDM based TPVs. For this reason, phenolic resins are not used in generally for the preparation of PP/EPDM based TPVs. Only esterification (acetylation, tosylation, silylation) of phenolic resin curatives eliminates the chances of staining.

2.1.2 | Sulfur cured TPV

Coran and Patel have reported sulfur-accelerator system for dynamic vulcanization of PP/EPDM and PE/EPDM blends. It was reported that with an increment of sulfur amount from 0 to 2.0 phr there is a drastic improvement of mechanical properties of PP/EPDM TPVs. Reduction in particle size during dynamic vulcanization leads to an

improvement of elongation at break (from 190% to 530%) and tensile strength (from 4.9 MPa to 24.3 MPa). However, sulfur accelerator system is not commercially applied in PP/EPDM TPVs, since PP has a high melting point and the cross-links lack in thermal and UV stability. Apart from during production and processing of PP/EPDM TPVs severe stench problem is another issue.

2.1.3 | Peroxide cured TPV

Unlike the reaction mechanism of accelerated sulfur vulcanization, the basic chemistry of peroxide decomposition and subsequent cross-link forming reactions is well established for the various unsaturated and saturated elastomer systems. There are several advantages of peroxide cross-link systems, such as simple formulation required, high temperature resistance of the vulcanizates can be achieved, rapid vulcanization happened without reversion, ability to cross-link saturated rubbers, better compression set properties (elastic recovery) of the vulcanizates even at elevated temperature.

Naskar and Noordermeer has reported the influence of different types of peroxides having different chemical structures on PP/EPDM TPVs.^[52,53] They have explored five different peroxides say: 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane (DTBPH), 2,5-dimethyl-2,5-di(tert-butylperoxy) hexyne-3 (DTBPHY), di(tert-butylperoxyisopropyl)benzene (DTBPIB), dicumyl peroxide (DCP), 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TTTP) for this study. A limited number of experiments was performed with 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TTTP) due to restricted availability.

It was found that the final mechanical properties of the TPVs are governed by the three major parameters—the solubility parameter of peroxide relative to the polymers, the decomposition mechanism of the peroxide and the kinetic aspects of the peroxide fragmentation. The closer the solubility parameter of the peroxide to that of the rubber, the higher the tensile strength and the better the compression set property. Physicomechanical properties and overall cross-link density of different peroxide cured PP/EPDM TPVs has been demonstrated in the Figure 6 below.

From the figure, it can be noticed that dicumyl peroxide (DCP) in the presence of triallyl cyanurate (TAC) as a coagent gives the overall best balance of physicomechanical and elastic recovery properties in PP/EPDM TPVs. In general, the commonly used peroxides produce volatile decomposition products, which lead to an unpleasant smell (for DCP) in the final TPVs or else it can show the blooming effect (for DTBPIB). Therefore, Naskar et al. studied the influence of multifunctional

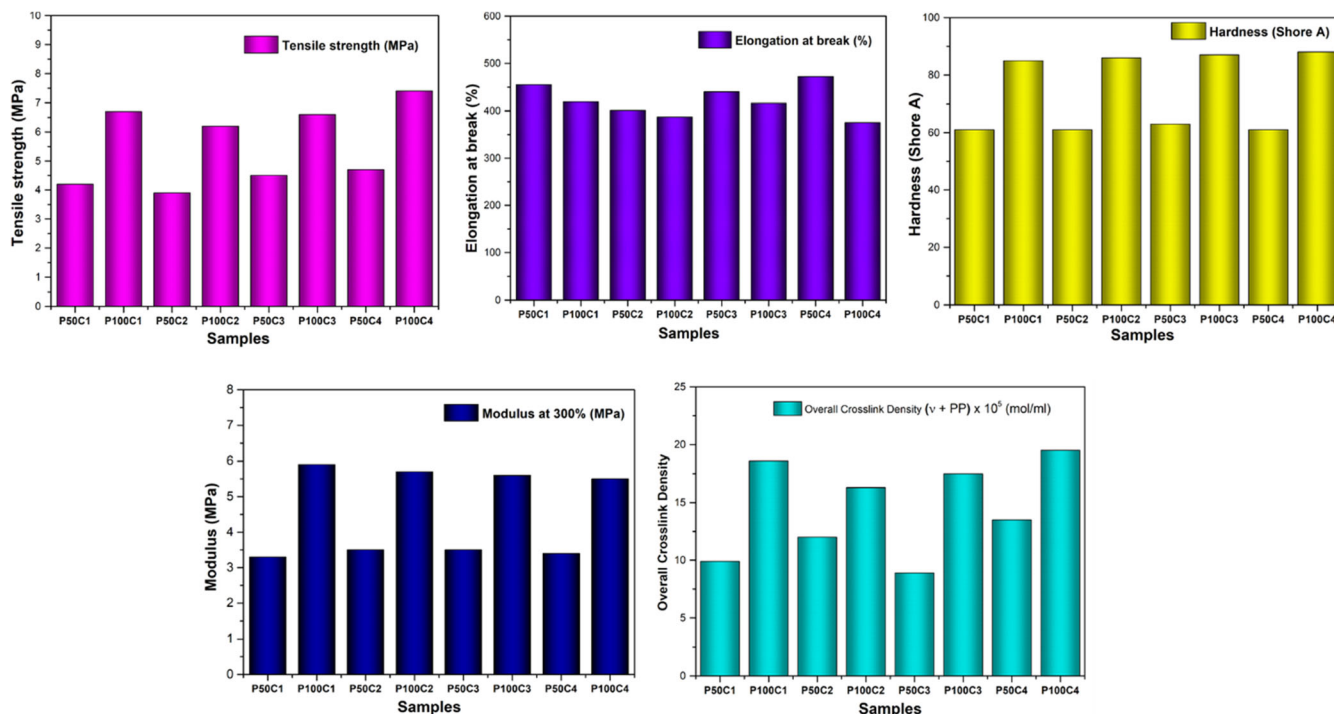


FIGURE 6 Physicomechanical properties and overall cross-link density of various peroxide cross-linked PP-EPDM TPVs. [In the figure the terms resemble, P: PP, C1: DTBPH, C2: DTBPHY, C3: DTBPIB, C4: DCP] [Color figure can be viewed at wileyonlinelibrary.com]

peroxides also to get rid of those drawbacks of the commonly used peroxides.^[54]

Kajari et al. reported the TPV based on PP matrix with polar maleated ethylene propylene rubber (m-EPM - a chemically modified EPM rubber).^[55] It was observed that incorporation of polar maleic groups results additional features for m-EPM such as moderate tensile strength and elongation at break. It also provides very high heat resistance, weather resistance and resistance to different aggressive chemicals like acid, alkali etc. In addition, it exhibits very good electrical properties, excellent fatigue resistance, good abrasion resistance and also good low temperature properties and good adhesion characteristics, especially with polar substrates. All the PP/m-EPM based TPVs were prepared in the presence of dicumyl peroxide (DCP) using m-PP as a compatibilizer. TPVs were developed in a batch process at a fixed blend ratio as well as the blend ratios were varied. Table 1 summarizes the TPV compositions with different DCP concentrations (0–3 phr) at a fixed blend ratio of PP/m-EPM.

Stress-strain properties of the PP/m-EPM based TPVs are depicted in the Figure 7 below.

From the above figure, it can be clearly observed that the tensile strength of m-EPM based TPVs varies from 3.5 to 7.3 MPa and elongation at break varies from 120 to 240%. Tensile strength and elongation reach a maximum at 2 phr of DCP concentration. This may be due to the β -chain scission of the PP thermoplastic phase at a higher

TABLE 1 TPV compositions with different DCP concentrations at a fixed PP/m-EPM blend ratio

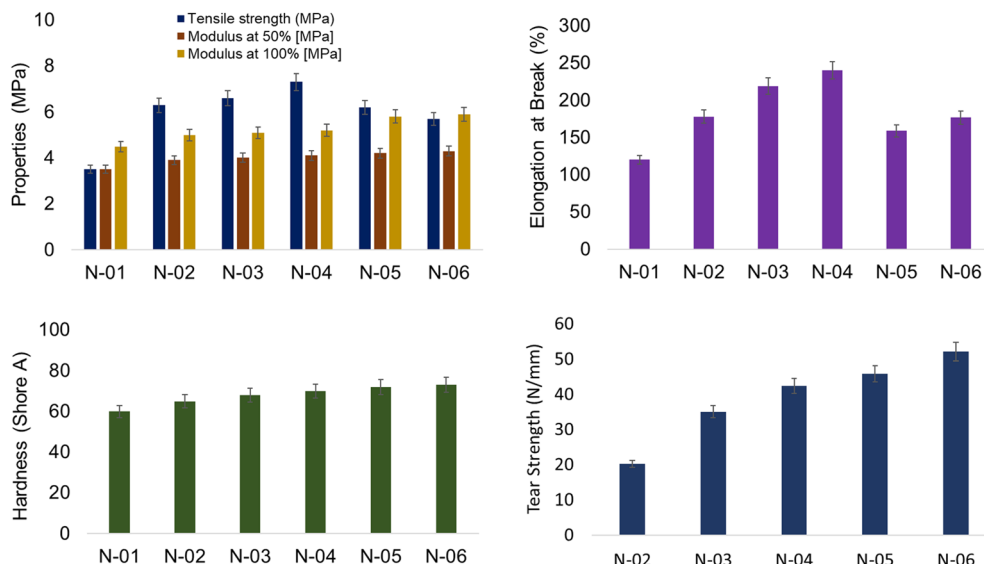
Ingredients	N-01	N-02	N-03	N-04	N-05	N-06
m-EPM	100	100	100	100	100	100
PP	60	60	60	60	60	60
m-PP	10	10	10	10	10	10
Paraffinic oil	25	25	25	25	25	25
DCP (98%)	0	1.0	1.5	2.0	2.5	3.0
TAC (50%)	0	4	4	4	4	4

concentration of peroxide. Other mechanical properties like the moduli, hardness and tear strength of TPVs have also been found to increase with increasing DCP concentration.

2.1.4 | TPVs based on electron induced reactive processing (EIREP)

To overcome the disadvantages of the peroxide cured TPVs, a new type of alternative techniques has to develop for TPVs. In this context, Dynamic vulcanization of TPVs by electron induced reactive processing (EIREP) is a unique technique where dynamic vulcanization is done by spatial and temporal precise energy through high energy electrons and chemical reaction are induced

FIGURE 7 Physicomechanical properties of PP/m-EPM based TPVs [Color figure can be viewed at wileyonlinelibrary.com]



during melt mixing. Scheme of the *EIREP* process is demonstrated in Figure 8. Naskar et al. developed electron induced reactive processed PP-EPDM TPVs.^[56] All TPVs were prepared by batch process and during the preparations absorbed dose were (25, 50, and 100 kGy), electron treatment time (15, 30, and 60 s), and electron energy (0.6 and 1.5 MeV).

It was reported that for 1.5 MeV electron energy and 60 s electron treatments with absorbed dose from 25 to 50 kGy tensile strength, elongation at break and E-modulus of the TPVs were significantly improved. For untreated sample tensile strength was only 4.7 ± 0.1 MPa and elongation at break was $46 \pm 5\%$ and at 50 kGy tensile strength was 9.2 ± 0.3 MPa and elongation at break was $298 \pm 35\%$. But after increasing the dose to 100 kGy tensile strength slightly increases 9.8 ± 0.2 MPa but elongation at break remains the same ($282 \pm 28\%$). It was also reported for the experimental data at 1.5 MeV electron energy and 100 kGy radiation dose that with decreasing electron treatment time from 60 s to 15 s tensile strength and elongation at break were further improved whereas *E* modulus remained constant at a level of 178 ± 2 MPa. Thus, it was conveyed that electron treatment time influences the dose rate as well as absorbed dose per rotation is an additional parameters controlling the stress-strain behavior of the PP/EPDM TPVs.

2.2 | TPVs based on PP/ethylene α -olefin (EOC)

Ethylene- α -olefins or polyolefin elastomers or plastomers (POEs) are a relatively new class of polymers that have emerged as a leading material for automotive interior and exterior application purposes, wires and cables,

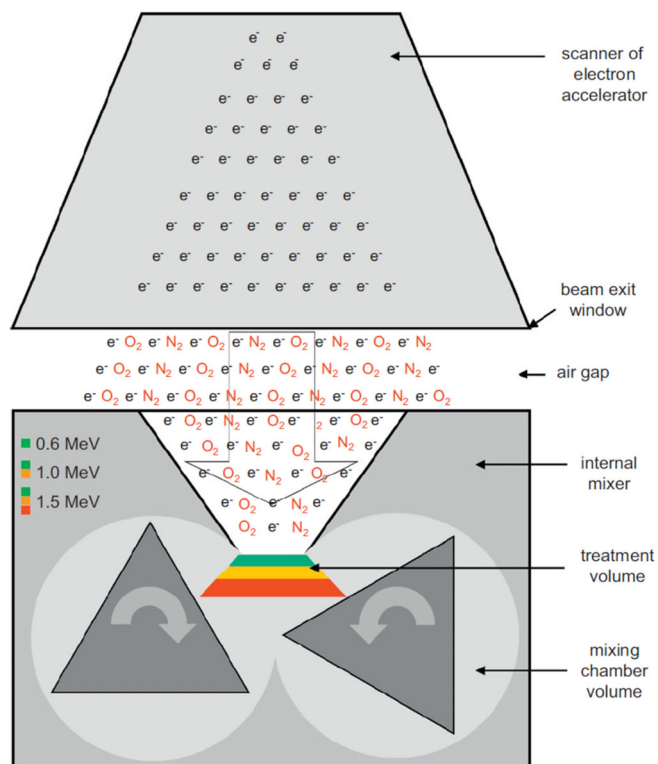


FIGURE 8 Schematic representation of the *EIREP* setup: coupling of an electron accelerator with an internal mixer [Color figure can be viewed at wileyonlinelibrary.com]

extruded and molded goods, film applications, medical goods, adhesives, footwear, foams and so on. Due to uniform comonomer distribution (intra and inter molecular), it achieves low-density products and the physical properties belong between plastic and elastomeric behavior. Babu et al. has developed TPVs based on PP/EOC system and explored different mechanical and rheological features of these systems.^[49,57–60] As phenolic resin is

TABLE 2 PP/EOC based TPV composition (phr) at a fixed blend ratio

Component	Amount (phr)
EOC	100.0
PP	50.0
Peroxide	X
Co-agent (TAC)	2.0

ineffective for this system due to the absence of double bond that forms the cross-link, a detailed investigation has been made on peroxide cured TPVs of PP/EOC system. To prepare peroxide cured PP/EOC based TPVs, structurally different peroxides with different conc. with a fixed blend ratio of PP/EOC has been studied. Peroxide cured TPV composition based on PP/EOC blend is shown in Table 2.

Here three structurally different peroxides—dicumyl peroxide (DCP), tert-butyl cumyl Peroxide (TBCP) and Di-(2-tert butyl peroxy isopropyl) benzene (DTBPIB) were explored and the peroxide concentration (X phr) was varied from 0.5–7.0 milliequivalents. Two types of EOC containing the same octene level but different molecular masses were studied to investigate the effect of molecular mass on the properties of the TPVs. Finally, it was noticed that DCP gives best properties for the PP/low molecular weight EOC TPVs and TBCP shows the best for the PP/high molecular weight EOC TPVs.

In this work, the influence of different type coagents upon different peroxide cured PP/EOC TPVs were also studied.^[61,62] Coagents are mainly reactive multifunctional vinyl monomer, reacted with reactive free radicals either by addition reaction and/or by hydrogen abstraction. Chain scission could be retarded by stabilizing the PP macroradicals by the addition reaction across the double bond in the vinyl monomer (coagent). It not only improves the end-use properties but also decreases the peroxide concentration and aids the flow characteristics during processing. TPVs were prepared by the use of three different coagents namely triallyl cyanurate (TAC), trimethylolpropane triacrylate (TMPTA) and N-N'-m-phenylene dimaleimide (MPDM). Typical recipe of PP/EOC based TPV by varying the concentration of coagents has been given in the Table 3.

Coagent concentration (Y phr) was varied from 10.0–30.0 milliequivalents. It was observed that among the various coagents used, TPVs containing N, N'-m-phenylene dimaleimide (MPDM) show the best balance of mechanical properties that is clearly shown from the Figure 9.

Even the three different mixing procedure (as mentioned in the section 1.6) have also been studied to develop the PP/EOC based TPVs. It was reported that

TABLE 3 TPV composition (phr) with varying types and concentrations of coagents at a fixed PP-EOC blend ratio

Component	Amount (phr)
EOC	100.0
PP	50.0
Peroxide (DCP)	3.38
Co-agent	Y

TPVs made by adding EOC curative master batch to the molten PP (phase mixing method) exhibit better mechanical properties and finer phase morphology than those prepared by preblending and the split addition method.

To overcome the problems for peroxide cured TPVs, similar to PP/EPDM TPVs electron induced reactive processing (*EIREP*) was applied to PP/EOC TPVs.^[63,64] Thus PP/EOC TPVs at a 50:50 weight ratio was developed in batch process and the experimental variable is exposure time (16, 32, and 64 s), while keeping absorbed dose (100 kGy) and electron energy (1.5 MeV) invariable. The samples were designated as PE-c (control), PE-16 s, PE-32 s and PE-64 s for PP/EOC blends, which were treated with an exposure time of 0, 16, 32 and 64 s, respectively. The mechanical property of PP/EOC TPVs prepared by *EIREP* at 1.5 MeV and 100 kGy in oxygen atmosphere with varying exposure time is summarized in Table 4 below.

It is evident from the table that mechanical properties increased with the decreasing exposure time. Gel content value also decreases with increase of exposure time, which can be clearly seen from the Figure 10.

The maximum value of gel content (18%) was observed for the sample irradiated at 16 s. Thus decrease in mechanical properties and lower gel content with longer electron exposure time can be related to the reduced cross-linking of EOC phase in presence of oxygen atmosphere as well as increased chain scission in both EOC and PP phases.

Apart from the above-mentioned TPVs research works has also been carried out on PP/NR based TPVs. In 2013, Mondal et al. has reported ecofriendly electron induced reactive processed PP/NR TPVs.^[65–68] But for automotive application, the TPVs are exposed at high temperature and it must be oil resistant. This is the drawback of those type of systems. To make the TPVs high temperature and oil resistant a new class of TPVs named Super TPVs has been explored and discussed in the next section.

2.3 | Super TPVs

The name Super TPV is coming from a TPV, which is made with the combination of high-performance

FIGURE 9 Tensile strength and elongation at break as a function of the concentration of different co-agents of PP-EOC based TPVs

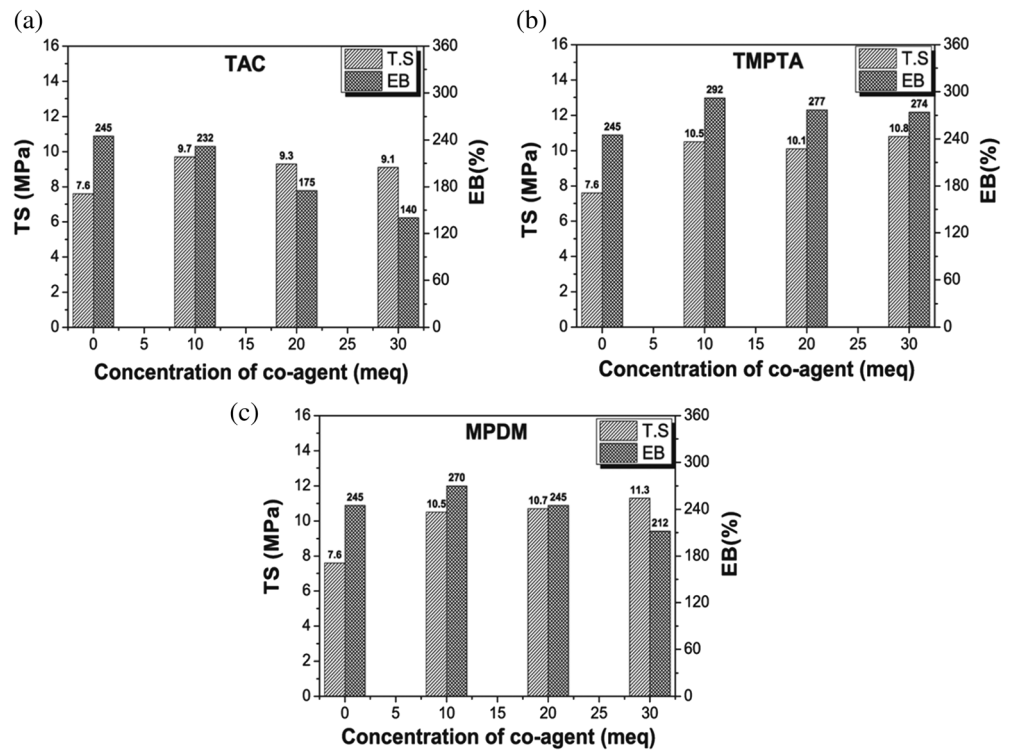


TABLE 4 Mechanical properties of PP/EOC uncross-linked and *EIReP* modified blends

Compound name	Tensile strength (MPa)	Elongation at break (%)	100% modulus (MPa)
PE-c (control)	10.8 ± 0.6	147 ± 12	10.6 ± 0.1
PE-16 s	11.0 ± 0.4	208 ± 10	10.6 ± 0.2
PE-32 s	9.4 ± 0.2	58 ± 12	—
PE-64 s	8.4 ± 0.5	23 ± 5	—

thermoplastics, and high-performance elastomer, which exhibit high heat resistance as well as excellent oil resistance property suitable for automotive applications. These type of materials (Super TPVs) are also designated as HOTs (High-temperature oil-resistant Thermoplastic Vulcanizates). These TPVs are capable to survive in very severe atmospheric conditions like heat, exposure to oil and fuel, for the application in automotive parts. Super-TPVs have inherent advantages of thermoplastic processing. In the other hand, these TPVs makes a bridge between the specialty and engineering plastics and the elastomers.

There is a wide application window of Super TPVs in automotive applications—fuel vent hose, high-performance body plugs, spark plug boots, soft-touch interiors, electrical insulation, glazing seals, electrical insulation etc. Several works has been performed in order

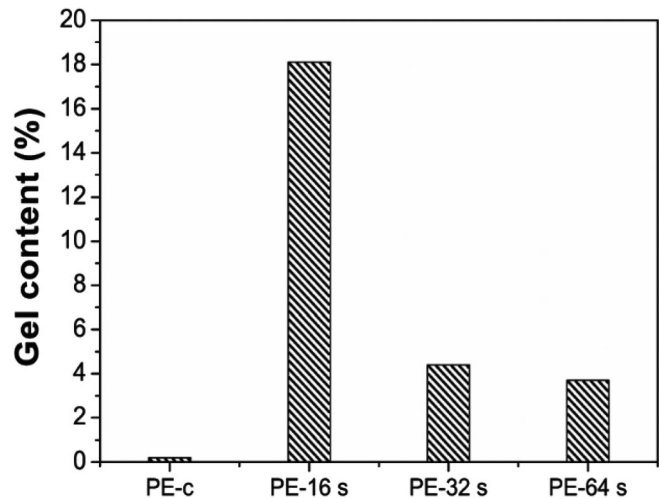


FIGURE 10 Gel content values of uncross-linked and *EIReP* modified blends

to develop the HOTs by different research groups, which has been given below.

2.3.1 | XNBR/PA12 based Super TPVs

A good amount of research has been done on this area and some are yet to explore. Chatterjee et al. have reported super-TPVs based on XNBR (Carboxylated Acrylonitrile-butadiene rubber) and PA12 (Polyamide 12) in presence of Trigonox 311 peroxide. TPVs of three

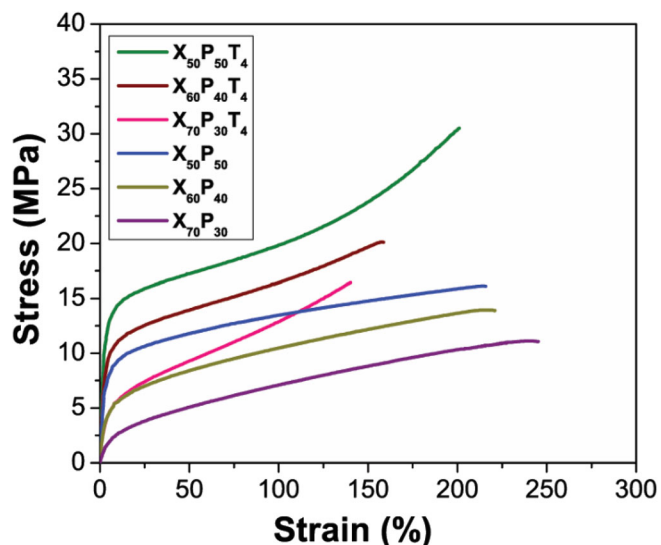


FIGURE 11 Mechanical properties of the uncross-linked blends and TPVs of XNBR/PA12 [In the figure the term resembles X_{50} : XNBR (50 wt%); P_{50} : PA12 (50 wt%); T_4 : Trigonox 301 (4 wt%)] [Color figure can be viewed at wileyonlinelibrary.com]

different blend ratio (Elastomer:Plastic = 50:50, 60:40 and 70:30) were prepared by batch mixing process in a brabender at 80 rpm at 190°C by phase mixing method.^[69,70]

Stress–strain behavior of the uncross-linked blends and TPVs of XNBR/PA12 is demonstrated in the Figure 11 below.

Considering the stress–strain curve it can be clearly demonstrated that after dynamic vulcanization there is drastic improvement in tensile strength and modulus value of the final TPVs as compared to that of the uncross-linked blend system. This clearly indicates the formation of sufficient cross-links in the XNBR rubber phase after the dynamic vulcanization. On the other side among the three different TPVs, TPV containing higher fraction of PA12 possess better results in terms of tensile strength, modulus, elongation at break point of view. As the thermoplastic PA12 content gradually reduces the stress–strain behavior also becomes inferior. This means TPV based on 50:50 blend ratio was superior in terms of stress–strain behavior compared to the other TPVs. The similar trend of result was noticed for 50:50 blend ratio for the thermogravimetric analysis, rheological study and even for the dynamic mechanical thermal analysis (DMTA) also. DMTA in terms of storage modulus (E') and $\tan\delta$ of the three different TPVs and uncross-linked blends are depicted in the Figure 12 below.

The $\tan\delta_{\max}$ peak obtained from DMTA curves and it indicates the glass transition temperature (T_g). From Figure 12, it is visible that as the XNBR content increases $\tan\delta$ value at glass transition region also increases for the

blends of different blend ratios. This is due to more rubber chain exposure for dynamic transitions which reasons higher $\tan\delta$. After the dynamic vulcanization the $\tan\delta_{\max}$ values for TPVs reduces drastically and the T_g values also shifts towards higher temperature. It indicates the formation of three dimensional network formation in XNBR rubber phase during the dynamic vulcanization. Storage modulus (E') plot of the TPVs also shows the same trend like $\tan\delta$ plot. From the E' data also it is visible that after dynamic vulcanization the T_g has shifted to the higher temperature for the TPVs compared to that of the uncross-linked blends. Higher storage modulus value of the TPVs than that of the uncross-linked blends also shows the proof of three dimensional network formation in the XNBR phase during dynamic vulcanization. Following this morphology study also reveals that dynamic vulcanization in presence of peroxide leads to selective cross-linking in the XNBR rubber phase which forms dispersed rubber domains in the continuous PA12 matrix phase as shown in the Figure 13.

The cross-linked rubber particle sizes were in the micron (μm) or submicron level. Proper dispersion and distribution of the dynamically vulcanized rubber particles lead to dispersed phase morphology that can be clearly observed from the SEM picture of TPV. Similar kind of dispersed morphology was noticed for the other TPVs.

But the most important part of this work which was reported by Chatterjee et al. is the study of the heat and oil resistant properties of the TPVs. Heat and oil resistant properties of the TPVs was checked in terms of air aging (performed in a hot air oven at a temperature of 125°C for 70 h as per ASTM D 471–98) and oil aging study (carried out at 125°C for 70 h in presence of ASTM oil No. 3 [IRM903] which is highly polar). Air aging study of the uncross-linked blends and TPVs of XNBR and PA12 is depicted in Figure 14(a, c, e) and (b, d, f) respectively.

Air aging study clearly reveals that there is only marginal deterioration of properties (like tensile strength, elongation at break, hardness) for TPVs, whereas significant deterioration of properties has been taken place for uncross-linked blend systems. Considering the figure (a and b), it can be clearly observed that after air aging tensile strength of uncross-linked blends is getting reduced to a significant amount and the reduction is highest (from 11.1 MPa to 6.7 MPa) for $X_{70}P_{30}$ uncross-linked blend. Although same trend in reduction of tensile strength value was seen for various TPVs but the reduction in tensile strength value is much less than that of the uncross-linked blends. In the similar manner, oil aging study also revealed the same picture like air aging study. Compared to uncross-linked blend, oil resistance property of the corresponding TPVs is much higher. Thus the

FIGURE 12 Storage modulus (E') vs temp. and $\tan\delta$ vs temp. Plot of uncross-linked blends and TPVs of XNBR/PA12 [Color figure can be viewed at wileyonlinelibrary.com]

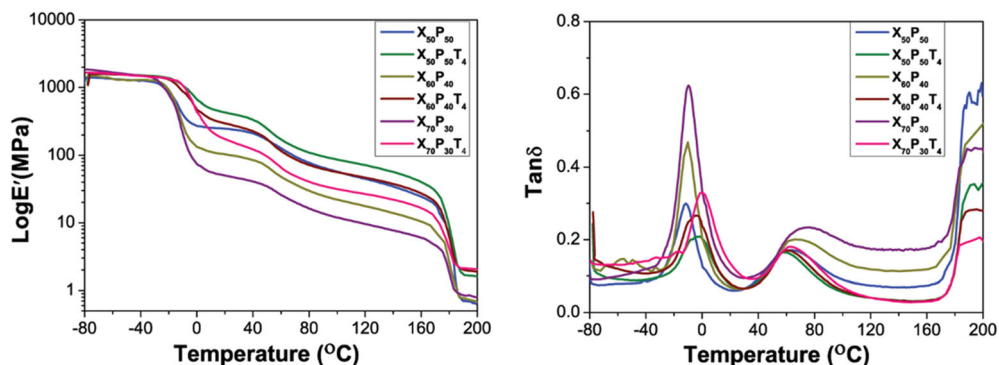
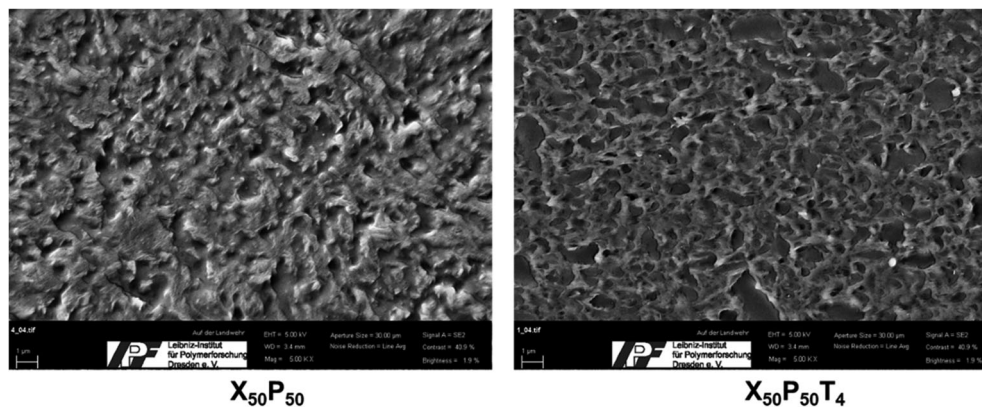


FIGURE 13 SEM photomicrographs of uncross-linked blend and TPV based on XNBR/PA12 (50:50) blend ratio



author argued that the dynamically vulcanized blend that is, the TPVs are always superior compared to the uncross-linked blend in terms of various properties. On the other hand it can also be noticed that the TPVs made of XNBR/PA12 is superior in terms of heat and oil resistant property and this TPVs can be used for high heat and oil resistant application purpose in the automobile sector.

2.3.2 | HNBR-PA12 based Super TPVs

Following the previous work based on XNBR/PA12 based TPV, Ismail et al. explored the high performance TPVs of HNBR/PA12 blend system in the year of 2016. In this study they focused on the two different TPV system, which are of HNBR/PA12 based and XHNBR/PA12 based^[71-74] and a comparative study was done. XHNBR is partially carboxylated hydrogenated acrylonitrile butadiene rubber. Stress-strain properties of the TPVs of both system has been enlisted in the Table 5 below.

Considering the table it can be stated that TPVs of XHNBR/PA12 based system is little bit superior than the TPVs of HNBR/PA12 based system. Even it was found that the tension set values of XHNBR/PA12 based TPVs was quite lower compared to that HNBR/PA12 based

TPVs. It was assumed that the superior physico-mechanical behavior of XHNBR/PA12 based TPV than that of the HNBR/PA12 based TPV was due to the better compatibility between the XHNBR rubber phase and PA12 matrix phase.

This study also reported the heat and oil resistant behavior of the HNBR/PA12 based TPVs and XHNBR/PA12 based TPVs. It was noticed that both the TPV system was good enough in terms of heat and oil resistant behavior. The presence of polar acrylonitrile group imparts the better oil resistant characteristics for the systems and on the other side hydrogenation of the polymer backbone results for the higher heat resistant behavior of the both systems. But considering the heat and oil resistant behavior of both the systems in details it was noticed that the TPVs of XHNBR/PA12 system was quite better than the TPVs of HNBR/PA12. The extra polar carboxyl group imparts more better heat and oil resistant characteristics for the XHNBR/PA12 TPV system. Thus it can be argued that both the TPVs of HNBR/PA12 and XHNBR/PA12 is quite good enough in terms heat and oil resistant behavior and it can be potentially used in the automotive sector especially for under-hood-application, where high-temperature resistance as well as high oil resistance is of prime importance.

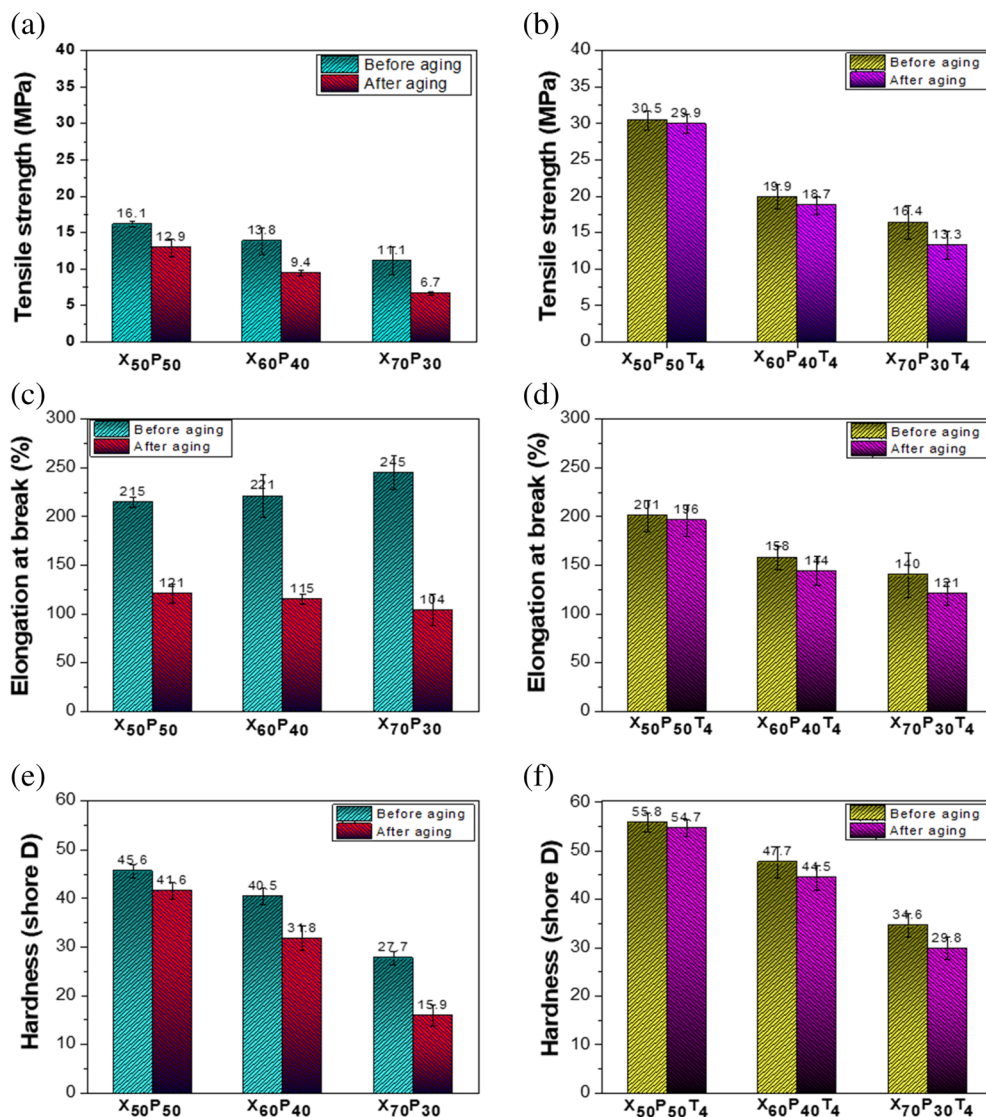


FIGURE 14 Air aging study of uncross-linked blends (a, c, e) and TPVs (b, d, f) of XNBR/PA12 [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 5 Stress-strain properties of various TPVs

Sample code	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% (MPa)
H ₅₀ P ₅₀	19.1	197	16.6
H ₆₀ P ₄₀	16.0	153	13.6
H ₇₀ P ₃₀	13.5	128	12.3
XH ₅₀ P ₅₀	22.0	206	16.9
XH ₆₀ P ₄₀	18.0	233	13.1
XH ₇₀ P ₃₀	13.4	178	10.2

Note: H: HNBR, XH: XHNBR, P: PA12 and the subscript resembles the blend ratio.

2.3.3 | Fluoroelastomer/PA6 based Super TPVs

In the year 2015, Banerjee et al. have reported the novel nanostructured polyamide 6 (PA 6)/fluoroelastomer (FKM)

based TPV system.^[75–80] They only first reported the role of injection molding in transforming the morphology. It was noticed that rubber particles in nano dimension (60–80 nm) were formed during the injection molding of the TPVs and that results the drastic improvement in physico-mechanical properties. For example, before injection molding the tensile strength and Young's modulus of FKM/PA6 TPV was 26.5 MPa and 92 MPa respectively and that values increased to 34.5 MPa and 200 MPa after injection molding. These improved tensile properties was ascribed to the fine uniform nanostructured morphology generated during injection molding. As FKM and PA6 are BOTH polar in nature and also high heat resistant so it can be argued that the TPV based on FKM/PA6 also can be potentially used for the high heat and oil resistant application purpose in the automotive sector.

Apart from in the year of 2013, Chatterjee et al. also explored a new system of TPV based on silicone rubber (PDMS) and PA12 in order to develop the high heat and

TABLE 6 TPV compositions based on m-EPM/PP

Ingredients	PHR
m-EPM	100
PP	60
m-PP	10
Paraffinic oil	25
Nanosilica	X
Si-69	1
DCP (98%)	2
TAC (50%)	4

oil resistant TPV. TPVs were prepared at a fixed ratio of 50/50 wt% of PDMS and PA12 exploring various peroxides say dicumyl peroxide (DCP), 3,3,5,7,7-pentamethyl 1,2,4-trioxepane (PMTO) and cumyl hydroperoxide (CHP).^[81,82] Although both PDMS and PA12 are highly thermally stable, the poor physicochemical behavior restricts its application for the purpose of high heat and oil resistant application purpose. The poor physicochemical behavior is only due to the lack of interfacial compatibility between the PDMS phase and PA12 matrix phase.

In the year of 2016, Ning et al. reported the new system of TPV based on ethylene-vinyl acetate (EVA) and Poly(vinylidene fluoride) (PVDF) and they also reported the superior oil resistant properties of that TPV.^[83] Apart from different polymeric blend of elastomer and plastics like acrylic rubber (ACM)/polyamide, PVDF/HNBR^[84] has been explored by several research groups in order to develop the new system of TPVs.

2.4 | Nano filled TPVs

TPV nanocomposites (TPVNs) are getting much popularity as a new category which highly demanding for industries where different types of nanofillers are acting as a reinforcing unit to the TPVs. After addition of the nanofillers to the thermoplastic matrix the modulus becomes higher while the material shows brittleness character. To achieve good impact resistant properties and modulus, elastomer is blended with the thermoplastic phase and after dynamic vulcanization the material we are getting is called thermoplastic vulcanizate nanocomposites (TPVNs).

2.4.1 | TPV nanocomposites (TPVNs) with Organoclay

Mishra et al. reported that the reinforcement of commercialized PP-EPDM TPVs (Santoprene grades) in presence

TABLE 7 Physicochemical properties of m-EPM based TPV at various Nanosilica concentrations

Properties	Nanosilica content (phr)				
	0	5	10	15	20
Tensile strength (MPa)	6.1	6.5	6.6	7.6	7.7
Elongation at break (%)	184	180	189	190	150
Modulus at 100% (MPa)	5.2	5.4	4.6	6.2	6.9
Tear strength (N/mm)	12.1	12.2	13.1	14.2	15.1

of Cloisite 20 A nanoclay and talc.^[85,86] Three TPVNs were developed by varying the clay content from 2.5% to 7.5% and 20% talc filled TPV microcomposite was also prepared by melt blending of the both the fillers with PP/EPDM based TPVs. Compared to pristine TPV, the physicochemical properties of TPVNs were improved very much. The tensile modulus of TPV/clay nanocomposite was found higher, say at 2.5% clay loading tensile modulus changed from 120 kgf.cm⁻² to 202 kgf.cm⁻² (80% higher). It was found that the tensile modulus of 5.0% Cloisite 20 A-filled TPVNs was higher than that of the 20 wt% talc-filled microcomposite.

During interaction between the Cloisite 20 A clay and polymer matrix, the intercalation of the polymer chains into the gallery of silicate layers results tremendous increment of the surface area that leads to dramatic improvement of the tensile modulus value of the TPV nanocomposites. In case of talc filled microcomposite, the surface area of interaction is less. Thus to improve the tensile modulus higher loading of talc or any other conventional filler is necessary which is not cost-effective from automotive application point of view where minimization of the material weight is the prime concern.

Incorporation of the Cloisite 20 A nanoclay also reduces the solvent uptake rate for the filled TPVs. At room temperature, the swelling rate for pristine TPV is 48% and it reduces to 22% for 7.5% cloisite 20 A-filled TPVN. With increase of filler loading, percentage reduction of solvent uptake of filled TPV system may be due to the better interaction between the filler (Cloisite 20 A) and thermoplastic vulcanizates. Better interaction between the filler and TPVs leads to the formation of either physical cross-links or bound polymer in close proximity to the reinforcing filler that restricts the solvent uptake.

Lee and Goettler in 2004 also have reported TPV nanocomposite based on Santoprene[®] 101-80, commercially available TPV.^[87] They have used two types of organically modified nanoclays such as Cloisite[®] 20A (dimethyl dihydrogenated tallow quaternary ammonium) and Cloisite[®] 30B (methyl tallow bis-2-hydroxyethyl

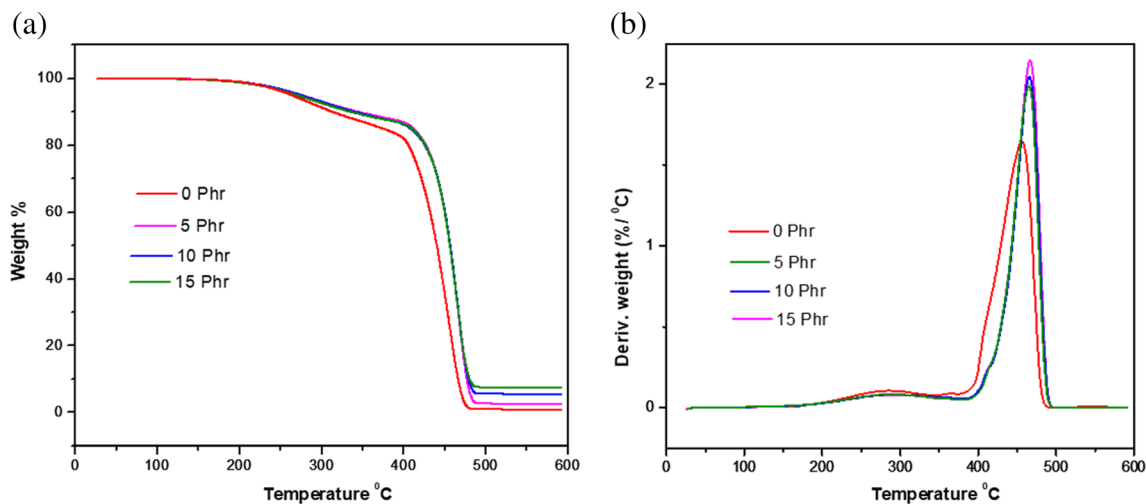


FIGURE 15 (a) TGA and (b) DTGA curves nanosilica filled TPVs at different nanosilica concentration [Color figure can be viewed at wileyonlinelibrary.com]

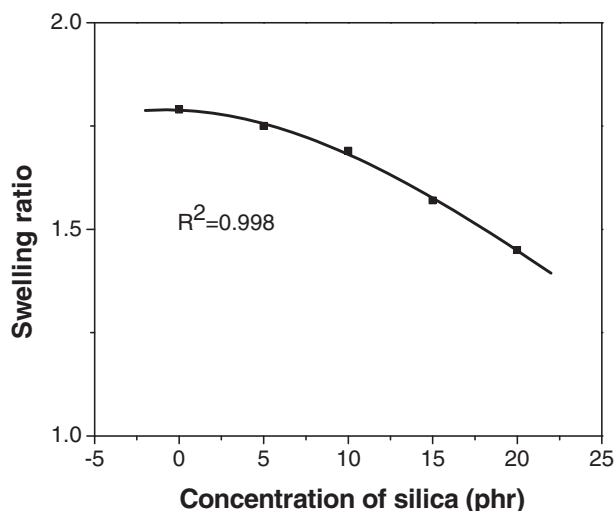


FIGURE 16 Swelling ratio of nanosilica filled TPVs as a function of nanosilica concentration

quaternary ammonium salts) in TPV. The clay loading in the TPV was 2 wt% to 8 wt%.

From the mechanical property study, it is observed that with the increase of loading of Cloisite 20A tensile modulus increases but tensile strength is decreasing gradually. Also the effect of nanoclay loading is not so much prominent for Cloisite 30B than Cloisite 20A. This is may be the strong interaction between TPV and Cloisite 20A whereas the interaction between TPV and Cloisite 30B is poor. In the TPV matrix dispersed elastomeric phase (EPDM) is dynamically vulcanized so that the layered silicates (Nanoclays) cannot penetrate into the dispersed elastomeric phases. The layered silicate can only disperse between continuous thermoplastic phases (PP) and due to compatibility mismatch between them the physicochemical properties of the

TPVNs is hampered. In the case of TPV-Cloisite 20A nanocomposite, proper dispersion of the nanoclay in the PP phases may happen while for TPV-Cloisite 30B nanocomposite may form large aggregates. As a result, TPVNs with Cloisite-20A is showing better mechanical properties than Cloisite-30B added TPVNs.

2.4.2 | Nanosilica-filled TPVs

Reinforcement of maleated EPM (m-EPM)-based TPVs has been studied using various concentrations of nanosilica by Chatterjee and Naskar.^[88] Due to the nonpolar nature of PP and the large surface area of polar nanosilica particles, it was challenging to achieve good dispersion of nanosilica in the polymer matrices. To improve the dispersion of nanosilica in PP, m-PP was used as a compatibilizer. All the TPV samples were prepared by melt mixing technique by a batch process and the TPV compositions are given below in Table 6.

As the nanosilica incorporation increased, physicochemical properties of the TPVs were improved. With increase loading (from 0 to 20 phr), there is a substantial improvement of tensile strength value (from 6.1 MPa to 7.7 MPa) and 100% modulus value (from 5.2 MPa to 6.9 MPa) for TPVNs which is very much clear from the Table 7 given below.

Addition of nanosilica also further improves the thermal stability of the TPVNs with the increasing amount of nanosilica. TGA thermograms and DTGA curves depict that the onset of degradation temperature for nanosilica filled TPVs shifts towards higher temperature as the nanosilica loading has increased with respect to the pristine TPVs have shown in Figure 15.

It was also observed that degradation temperature (T_{\max}) got increased as the amount of nanosilica increases. T_{\max} for pure TPV is 456°C; while it increases to 466°C and 468°C for TPV containing 5 phr and 20 phr nanosilica loading respectively.

Nanosilica loading also reduces the extent of swelling in terms of swelling ratio of nanofilled TPVs compare to that of the unfilled one. Swelling ratio of pure TPV is 1.79 and it reduces to 1.45 with increase of nanosilica loading upto 20 phr, which is very much clear from the Figure 16.

Thus, extent of swelling of nanosilica filled TPV get reduced, means the solvent resistance property of filled TPV system gets improved which may be due to the formation of physical cross-links in presence of nanosilica.

3 | CONCLUSIONS

After thorough study regarding TPVs, it is well established that the most commercially useful and available TPVs are based on PP/EPDM and the incorporation of nanofillers to prepare thermoplastic vulcanizate nanocomposite (TPVN) have been developed exclusively for the automotive market.

In all cases, TPVs were found improved physical properties (like tensile modulus, tensile strength), thermal properties, flame retardancy behavior, barrier properties and swelling resistance properties than the conventional rubbers and TPEs. In some cases, by incorporation of nanofillers, the properties are enhanced than the TPVs. Sometimes incorporation of the graphite improves the electrical properties also. These TPVs are finding major application in automotive sectors, especially under-the-hood applications where high temperature is the prime object, like—air brake hose, ignition coil boots, bellows, oil cooler hoses, crank case ventilation hoses etc. However, these TPVs are not well oil swelling resistant.

Although there are lots of scopes to develop new generation TPVs which can possess superior properties. TPVs based on PP/EOC blend has explored but not commercially well established. On the other hand, PP/NR, PP/NBR is getting popularity commercially in the automotive sector. There is a good replacement of the above mentioned TPVs for automotive applications named super TPVs that are high heat resistant and excellent resistant to oil and solvent swelling. In the class of Super TPVs, there is a wide variety, elastomer used HNBR, XNBR, Fluoroelastomer and as thermoplastic PA6, PA12 etc. Recently for soft touch application Silicone rubber (PDMS) based TPVs are finding popularity.

Finally, it is concluded that for some unique properties, applications of TPVs are getting much popularity in various commercial and industrial fields, especially automotive sectors, like automotive mechanical applications: convoluted bellows, flexible diaphragms, extruded profiles, tubing, gaskets, seals, mounts, bumpers, housings; for under-the-hood applications in the automotive field: air conditioning hose cover, vacuum tubing, fuel line hose cover, vacuum connectors, body plugs, seals, bushings, grommets, electrical components, convoluted bellows, steering gear boots, emission tubing, protective sleeves, shock isolators, and air ducts; sometimes synergism was also found for these type of materials. Further development of TPVs will find good potential value in several fields and the recently developed TPVs and TPV nanocomposites with excellent properties in highly petitioned.

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