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## A review on EPDM / polyolefinic blends and composites

V.K.Abitha<sup>1,\*</sup>, A.V.Rane<sup>2</sup><sup>1</sup>Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kerala (INDIA)<sup>2</sup>Centre for Green Technology, Institute of Chemical Technology, Mumbai, Matunga (INDIA)

E-mail : abithavk@gmail.com

### ABSTRACT

EPDM polymers are the fastest growing general purpose elastomers on the market today. Blends of EPDM and other polyolefinic polymers are most commonly used ones. There has been a large improvement in the production of EPDM and PP blends and composites. The composite industry is now being improved from the micro level to the nano level. Biocomposites based on EPDM and polypropylenes are now becoming more popular than the organic based composites. EPDM and Polypropylene are not compatible with each other. Compatibilizers such as MA-g-EPDM are added in order to improve the compatibility of each other. In this review a study on various EPDM/PP blends and composites is carried out.

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### KEYWORDS

Ethylene propylene diene monomer;  
Polyolefenic;  
Compatibility;  
Blends;  
Composites;  
Grafting.

### INTRODUCTION

The scientific and commercial progress in the area of polymer blends and composites during the past two decades has been tremendous and blending can be implemented more rapidly and economically than development of new polymers. Polyolefins have been modified by the incorporation of elastomers to improve low temperature impact strength and elongation. Owing to adequate level of compatibility between polypropylene and ethylene-propylene copolymers, simple blends of these two polymers have been known for a long time. More recently, blends of a partially crosslinked thermoplastic elastomer with 5-40 parts of a Polyolefine (viz. LLDPE, PP, EPR, or PB-1) were developed for low density, foamable alloys. Composites are combinations of two or more than two materials in which one of the materials, is reinforcing phase

(fibers, sheets or particles) and the other is matrix phase (polymer, metal or ceramic)<sup>[1-3]</sup>. Blending of EPDM within the family of Polyolefin (PO) has, however, been more common. Although they are usually immiscible with each other, there exists some degree of mutual compatibility between them. The similarity of their hydrocarbon backbones and the closeness of their solubility parameters, although not adequate for miscibility, accounts for a relatively low degree of interfacial tension<sup>[3]</sup>. Compatibility between EPDM and PP can be improved by the addition of maleated compounds. The elastomeric part in the EPDM/PP blends can be crosslinked by the addition of suitable crosslinking agents such as DCP or sulphur and the corresponding vulcanizates are known as dynamic vulcanizates. EPDM polypropylene based nanocomposites and biocomposites are becoming commercialized now a day's<sup>[4]</sup>.

## EPDM/POLYOLEFINIC BLENDS

PP has good mechanical properties but lacks low temperature impact properties. Many studies have been carried out on the blends of PP and low-modulus rubbers to obtain good low-temperature properties and impact resistance. EPDM has similarity in chemical structure with polyolefinic types of thermoplastics; hence it has been most intensively tested as the rubber component of the thermoset/thermoplastic blends. Among PP/rubber blends; the PP/EPDM blend has acquired some commercial success, and finds applications in various industrial fields because the composition-dependent properties of the blends can meet the diverse requirements of industrial applications<sup>[5]</sup>. To improve the mechanical properties of blends of polypropylene (PP) and terpolymer of ethylene-propylene-diene (EPDM), a triblock copolymer, (PP-*g*-MA)-*co*-[PA-6,6]-*co*-(EPDM-*g*-MA), was synthesized by coupling reaction of maleic anhydride (MAH)-grafted PP (PP-*g*-MA), EPDM-*g*-MA, and PA-6,6. The newly prepared block copolymer brought about a physical interlocking between the blend components, and imparted a compatibilizing effect to the blends. Introducing the block copolymer to the blends up to 5 wt % lead to formation of a  $\beta$ -form crystal. The wide-angle X-ray diffractogram measured in the region of  $2\theta$  between  $10^\circ$  and  $50^\circ$  ascertained that incorporating the block copolymer gave a new peak at  $2\theta = 15.8^\circ$ . The new peak was assigned to the (300) plane spacing of the  $\beta$  hexagonal crystal structure. In addition, the block copolymer notably improved the low-temperature impact property of the PP/EPDM blends. The optimum usage level of the compatibilizer proved to be 0.5 wt %<sup>[5]</sup>. In another research vetiver grass was used as filler in polypropylene (PP) composite. Chemical treatment was done to modify fiber surface. Natural rubber (NR) and Ethylene Propylene Diene Monomer (EPDM) rubber at various contents were used as an impact modifier for the composites. The composites were prepared by using an injection molding. Rheological, morphological and mechanical properties of PP and PP composites with and without NR or EPDM were studied. Adding NR or EPDM to PP composites, a significant increase in the impact strength and elongation at break is observed in the PP composite with rubber content more than 20%

by weight. However, the tensile strength and Young's modulus of the PP composites decrease with increasing rubber contents. Nevertheless, the tensile strength and Young's modulus of the composites with rubber contents up to 10% are still higher than those of PP. Moreover, comparisons between NR and EPDM rubber on the mechanical properties of the PP composites were elucidated. The PP composites with EPDM rubber show slightly higher tensile strength and impact strength than the PP<sup>[6]</sup>. The toughness of PP/EPDM blends was measured over a wide range of temperature (25-132°C) and composition (0-26 wt % EPDM). It was found that increasing temperature and decreasing interparticle distance have equivalent effects on the brittle-tough transition of toughening PP with EPDM and the shift increases with increasing temperature. A correlation was found between temperature and critical interparticle distance. When critical interparticle distance was plotted versus  $T_g - T$ , where  $T_g$  is defined as the brittle-tough transition temperature of the matrix itself, the curves for different blend systems converge to a single master curve. The notched Izod impact strength of PP can be improved by increasing temperature or adding EPDM rubber<sup>[8]</sup>. PP homopolymers impact modified by EPDM sorts of different melt viscosities at a rate lower than 10% were subject to brittle fracture in a wide temperature range. The most efficient of the EPDM impact modifiers had melt viscosities similar to that of the starting PP under the conditions of mixing. The course of maximum load at rupture ( $F_{max}$ ) and notched impact strength as functions of temperature showed some analogies with one another as well as with dynamic mechanical storage ( $E'$ ) and with the mechanical loss factor ( $\tan \delta$ ). The brittle to ductile fracture transition depends not only on the rate of deformation and the testing temperature but also on the concentration of the elastomer and on the phase viscosity ratio of EPDM and consequently on the phase structure of the produced two phase system<sup>[9]</sup>. Dynamic vulcanizate blends of polypropylene (PP) and ethylene-propylene-diene rubber (EPDM) were filled with 5 wt% of micro-scale ceramic powder. To overcome the difficulty of particles dispersion and adhesion, the filler was modified through grafting using organic molecules. A combination of Raman data with thermo gravimetric analysis (TGA) results prove that grafting of organic

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macromolecules onto ceramic surfaces takes place. Dynamic mechanical analysis (DMA) has been performed from -100 to + 50°C; addition of the ceramic increases the storage modulus  $E_0$ , more so for modified filler. Compared to PP and thermoplastic vulcanizates (TPV), a higher thermal expansion is seen after addition of the ceramic filler, a result of creation of more free volume. The tensile modulus of the composites is about 1.2 times that of pure TPV, an increase in the rigidity clearly caused by the ceramic. Fracture surfaces show weak bonding of filler particles to the matrix. In the sample containing modified filler the tensile deformation is going through the polymer matrix. The brittleness  $B$  decreases upon surface modification of the ceramic. The highest value of  $B$  is seen for the PP unmodified ceramic while lower  $B$  values are obtained for TPV and its composites<sup>[10]</sup>. Flammability of polypropylene/ethylene propylene diene copolymer (PP/EPDM) filled with melamine phosphate (MP) and pentaerythritol phosphate (PEPA) was studied by limiting oxygen index (LOI), UL 94, and cone calorimetry. The thermal degradation of the composites was investigated using thermo gravimetric analysis (TGA) and Real-Time Fourier transform infrared spectrum (RT-FTIR), and the mechanical properties of the materials were also studied. It had been found that the PP/EPDM/PEPA/MP composites showed better flame retardancy than that of the PP/EPDM composites containing MP or PEPA. TG and RT-FTIR studies indicated that the interaction occurs among MP, PEPA, and PP/EPDM. The incorporation of the flame retardants deteriorated the mechanical properties of the materials. It was found that MP or PEPA when used alone in the PP/EPDM blends produced a little improvement in the flame retardation. The combination of MP and PEPA shows more effective flame retardation than the individual component. All composites containing both MP and PEPA had a high LOI value and TGA studies proved that the PP/EPDM/MP/PEPA composites were more thermal stable than the untreated PP/EPDM. It was observed from the RT-FTIR study that many complicated reactions would take place during the thermal degradation process of the PP/EPDM/PEPA/MP composites. Moreover, the mechanical properties of the PP/EPDM composites were deteriorated with addition of the flame retardants<sup>[11]</sup>. A novel flame retardant system composed

of nano-kaolin and nano-HAO (nano-sized hydroxyl aluminum oxalate) was used as a flame retardant for the low density polyethylene (LDPE)/ethylene propylene diene rubber (EPDM) blends. Results of fire testing showed that nano-kaolin and nano-HAO exhibited excellent synergistic effects on the flame retardancy of the LDPE/EPDM composites. When 12 wt% nano-kaolin took the place of 12 wt% nano-HAO in the composites, the LOI of the composites increased from 31.0% to 35.5% and the composites could meet the UL94V-0 standard. Through thermo gravimetric and differential thermal analysis (TGA-DTA) it was found that nano-HAO mainly affected the degradation of the experimental composites chemically. Scanning electronic microscope (SEM) and Fourier transformation infrared spectra (FTIR) of the composites on the char layer revealed that nano-kaolin mainly affected the transfer process physically by aggregating with nano-HAO and thus the synergistic effect on flame retardancy appeared. Through melt compounding method, a novel flame retardant system composed of nano-kaolin and nano-HAO was used to impart flame retardancy to LDPE/EPDM system. From the LOI tests and UL94 tests, it was found that when 12wt% nano-kaolin took the place of 12 wt% nano-HAO in the composites, the LOI was enhanced from 31.0% to 35.5%, and the composites passed the UL94V-0 standard, which proved that nano-kaolin had the synergistic effect with nano-HAO on flame retardancy in the LDPE/EPDM system. From the results of cone calorimeter tests, nano-kaolin was found to have obvious effects on decreasing of heat releasing rate (HRR) and smoke amount during the combustion<sup>[20]</sup>. Blends of isotactic polypropylene (iPP) and high density polyethylene (HDPE) with and without ethylene-propylene-diene (EPDM) terpolymer as compatibilizer systematically investigated to determine the influence of the EPDM on blends properties. The PP/HDPE blend revealed poor adhesion between PP and HDPE phases. Finer morphology was obtained by EPDM addition in PP/HDPE blends and better interfacial adhesion. Addition of HDPE to PP decreased tensile strength at break, elongation and yield stress. Decrease of tensile strength and yield stress is faster with EPDM addition in PP / HDPE blends. Elongation at break and impact strength was significantly increased with EPDM addition. The addition of EPDM in PP /

HDPE blends did not significantly change melting points of PP phase, while melting points of HDPE phase was slightly decreased in PP/HDPE/EPDM blends. The EPDM addition increased the percentage of crystallization ( $X_c$ ) of PP in PP/HDPE blends. The increase of  $X_c$  of HDPE was found in the blend with HDPE as matrix. Dynamical mechanical analysis showed glass transitions of PP and HDPE phase, as well as the relaxation transitions of their crystalline phase. By addition of EPDM glass transitions ( $T_g$ ) of HDPE and PP phases in PP/HDPE blends decreased. Storage modulus vs. temperatures curves is in the region between storage modulus/temperature curves of neat PP and HDPE. The decrease of storage modulus values at 25°C with EPDM addition in PP/HDPE blends is more pronounced. Addition of HDPE to PP decreased tensile strength at break, elongation and yield stress. Decrease of tensile strength and yield stress is faster with EPDM addition in PP/HDPE blends<sup>[13]</sup>. The miscibility between ethylene-propylene diene terpolymer (EPDM) and polypropylene (PP) was explored by means of dynamic mechanical thermal analysis, transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). It was confirmed that the EPDM/PP blends prepared in a single-screw extruder presented better mechanical properties than those prepared with an open mill. Effect on the mechanical properties was partially attributed to the improved mixing of the two components in the EPDM/PP blends prepared in the single-screw extruder, which was verified by TEM micrographs. It was found that the blends prepared with different ratios of rubber to plastic and with varied amounts of curing agents presented two  $T_g$  values, suggesting that the components of the blends were immiscible. All of the TEM micrographs were in accordance with the above conclusion. The  $T_g$  peaks of EPDM shifted in all blends, indicating a certain degree of miscibility between the two components. As the ratios of rubber to plastic and the amount of curing agents increased, the  $T_g$  peaks of the two components approached each other<sup>[15]</sup>. The effect of the rubber content on the deformation and impact behaviour of polypropylene-EPDM rubber blends was studied by R J Gayman. The blends are made on a twin screw extruder. The rubber content ranged from 0 to 40 vol. %. The tensile modulus and the yield stress decrease linearly with increasing rubber

content. The crystallinity of the PP phase as measured with differential scanning calorimetry did not change with rubber content. The fracture behaviour was studied with a notched Izod impact test and with an instrumented single edged notched tensile test at 1 mm/s and 1 m/s. The blends were studied in temperature range from -80 to 120°C. The brittle-ductile transition temperature ( $T_{bd}$ ) decreases with increasing rubber content from 85°C for pure polypropylene to -50°C for a 40 vol.% blend, a shift of 135°C. The  $T_{bd}$  with the notched Izod test and the single edged notched at 1 m/s are very comparable. The  $T_{bd}$  for the single edged notched at 1 mm/s if compared to the 1 m/s are at a 30°C lower temperature. The brittle-ductile transition at the low test speed is gradual, while at high test speeds the transition is abrupt, discontinuous. A good criterion for the onset of ductility is the crack propagation displacement<sup>[16]</sup>. Positron Annihilation Lifetime Spectroscopy (PALS) was employed to investigate the relationship between the free volume hole properties and miscibility of dynamically vulcanized ethylene propylene diene monomer (EPDM)/ polypropylene (PP) blend. PALS technique to find the free volume hole properties in the dynamically vulcanized EPDM/PP blends, it showed that the hole concentration ( $I_3$ ) and the relative fractional free volume (Fr) deviated positively from the linear additivity when the wt% of EPDM is below 50%, but deviated negatively when the wt% of EPDM is over 50%. These results demonstrated that the non crystalline regions of PP and EPDM in the blend were partially miscible. The miscibility of the blends was influenced by the weight percent and crystallinity of PP. The measurements of DMTA and mechanical property results also confirm the conclusion from the aspect of the interaction between the two phases<sup>[18]</sup>. The hyper elastic behavior of this blend has been characterized under cyclic uni-axial tensile tests. The experimental results show a significant effect of the fraction of (PP) particles (5%, 10%, 25% and 30% by weight) on the macroscopic behavior of the composite. In order to model this behavior, we first develop and implement a micromechanically based nonlinear model for hyper elastic composites. The PP phase is assumed in the form of spherical particles embedded in the EPDM matrix. For the particles volume concentrations considered in the study, the experimental results show a significant effect

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of the reinforcements. The micromechanical modeling developed combines the second order homogenization method with a Hashin–Shtrikman bound<sup>[19]</sup>. Study of ternary blends, particularly PP/EPDM/Scrap rubber tire mixtures, can be developed using Response Surface Methodology (RSM). This technique is useful to optimize components in the mixture and to obtain equations which are employed for mapping the response surface over a particular region of interest. A minimum number of experiments allow prediction of the optimal composition of PP, EPDM and SRT present in ternary compounding. Mechanical properties show sharp deterioration when SRT particles content increases in the ternary mixtures because of the poor adhesion between SRT and PP matrix. EPDM appears to span the interfaces between regions of SRT and PP, thus enhancing adhesion and compatibilization of the compound. Some tensile properties and particularly impact strength together with SEM micrographs proved this observation. Highest impact strength can be reached, for the experimental conditions used, only with a physical mixture of PP/EPDM/SRT when EPDM and SRT contents are maintained around 25%<sup>[23]</sup>. Morphology, thermal behavior and mechanical and dynamic properties of isotactic polypropylene blended with different amounts of EPDM terpolymer were investigated addition of 10% EPDM to PP resulted increase in spherulite size. DSC results indicated that addition of EPDM resulted in an increase in the rate of crystallization whereas nucleation is delayed. Izod impact strength increases as the EPDM content increases<sup>[7]</sup>. Electron beam irradiation has been used to improve the processability of polypropylene/ethylene propylene diene monomer blends in combination with fixation of morphology by inducing cross links in the dispersed EPDM phase. An optimum morphology for impact toughening has been obtained via extrusion–blending high molecular weight PP with EPDM<sup>[13]</sup>. Mechanical blends formed of 50 wt% of high-density polyethylene (HDPE) and 50 wt% of ethylene–propylene–diene-monomer (EPDM) elastomer have been loaded with 50 wt% of three different particle size of CaCO<sub>3</sub>, namely CaCO<sub>3</sub> 300, CaCO<sub>3</sub> 700, and CaCO<sub>3</sub> 2000 whereby the latter has the smallest particle size of 311, 82μm. Mechanical, physico-chemical and thermal properties were followed up as a function of irradiation dose for loaded and unloaded blends. The re-

sults obtained indicated that the values of tensile strength, tensile modulus at 50% elongation, gel fraction and decomposition temperature increase with increasing irradiation dose. On the other hand elongation at break, permanent set and swelling number were found to decrease with increasing irradiation dose. Moreover, the effect of particle size of CaCO<sub>3</sub> was observed in a limited but apparent upgrading of mechanical, Physico-chemical, and thermal properties<sup>[21]</sup>.

## EPDM/POLYOLEFINIC NANOCOMPOSITES

Nanocomposites of polypropylene (PP)/ethylene-propylene-diene rubber (EPDM) blend with montmorillonite-based organoclay were prepared in a solvent blending method. Solvent blending of PP and EPDM in a composition of 50:50 formed a two phase morphology in which EPDM appeared as dispersed phase with irregular shape. The size of dispersed phase reduced significantly to almost spherical domains by addition of the nanoclay. For better dispersion of nanoclay in the PP/EPDM blend, an antioxidant Irganox 1010 was used as compatibilizer. State of nanoclay dispersion was evaluated by X-ray diffraction (XRD), and also, by a novel method using permeability measurements data in a permeability model. The measured *d*-spacing data proved a good dispersion of nanoclay at low clay contents along with compatibilizer. The permeability model for flake-filled polymers was used to estimate the aspect ratio of nanoclay platelets in the blend nanocomposites. Oxygen and carbon dioxide barrier property of the PP/EPDM blend improved about two-fold by adding only 1.5 vol% organoclay. The degree of dispersion in PP /EPDM / nanoclay nanocomposite prepared by solvent blending was studied by XRD method. Presence of compatibilizer induced even more intercalation of nanoclay. State of nanoclay dispersion was also examined by evaluation of aspect ratios of nanoclay platelets from permeability measurements and using a permeability model. The PP /EPDM blend without organoclay showed a two-phase morphology with EPDM as dispersed phase in irregular-shaped domains. The EPDM domains turned to more spherical shape and much smaller in size as well in presence of nanoclay<sup>[23]</sup>. Polypropylene / ethylene-propylene diene monomer (EPDM)/ Cloisite 15A (75/20/5) thermoplas-

tic elastomer nanocomposite samples were prepared according to Taguchi design of experiment (Design Expert software) via direct melt intercalation by using a co-rotating twin-screw extruder to investigate the effect of processing parameters on the microstructure, rheological and mechanical properties of the nanocomposites. It was observed that higher screw speeds, lower barrel temperatures and lower feeding rates would improve the mechanical properties of the samples. This was supported by rheological measurements and microstructure observations. Comparing the XRD patterns, SEM and TEM micrographs, rheological and mechanical measurements confirmed the results suggested by Taguchi method. The effect of barrel temperature was observed to be significantly considerable on the properties of the nanocomposite<sup>[24]</sup>. The modification of the (HNT) halloysite nanotubes by  $\gamma$ -methacryloxypropyl trimethoxysilane increased the interactions with EPDM and the degree of dispersion of the HNTs within the EPDM. This increased the tensile strength and tensile modulus at 100% elongation (M100) of the nanocomposites. The thermal resistance of the nanocomposites decreased after the modification of the HNTs.  $\gamma$ -MPS interacted with Al-OH groups at the edges and inside the HNTs and Si-O groups at the surface of the HNTs. The EPDM / HNT nanocomposites were prepared by mixing 0, 5, 10 and 30 parts per hundred rubber (phr) of HNTs with EPDM on a two-roll mill. The tensile strength and tensile modulus at 100% elongation (M100) of the nanocomposites were higher than those of EPDM / unmodified HNTs (EPDM/HNT) while the elongation at break decreased a little after modification of the HNTs<sup>[25]</sup>. The films of EPDM / clay nanocomposite, EPDM conventional composite and unfilled EPDM were exposed against gamma irradiation in order to study the effect of gamma irradiation on their properties. The experimental data suggested that the gamma irradiation has a strong influence on properties of EPDM / clay nanocomposite, EPDM conventional composite and unfilled EPDM<sup>[26]</sup>. The study was conducted to determine the best ATH filled PP/EPDM formulation for wire and cable application. The preliminary results showed that PP/EPDM (60:40) blend as the optimum composition based in mechanical and MFI test. The effect of ATH loading on mechanical and MFI of PP / EPDM (60:40) was then determined.

The tensile modulus and hardness increased with increasing filler loading with a concomitant decrease in elongation at break and tensile strength. MFI decreased by increasing the ATH content. SEM illustrated that ATH was well distributed within the PP / EPDM matrix<sup>[27]</sup>. EPDM rubber and nano-SiO<sub>2</sub> particles were employed to modify PP simultaneously. Our goal was to control the distribution and dispersion of EPDM and nano-SiO<sub>2</sub> particles in PP matrix by using an appropriate processing method and adjusting the wettability of nano-SiO<sub>2</sub> particles toward PP and EPDM, so as to achieve a simultaneous enhancement of toughness and modulus of PP. With regard to this, two kinds of nano-SiO<sub>2</sub> particles (with hydrophilic or hydrophobic) to prepare PP/EPDM/SiO<sub>2</sub> ternary composites. A unique structure with the majority of EPDM particles surrounded by SiO<sub>2</sub> particles was first observed by using hydrophilic SiO<sub>2</sub> and two-step processing method, resulting in a dramatic increase of Izod impact strength as the rubber content in the range of brittle-ductile transition (15–20 wt%). The observation that poor adhesion and poor compatibility between particles and PP matrix could result in a significant increase in Izod impact strength was unusual and needed further investigation. This could be tentatively understood as a consequence of the overlap of the ‘stress volume’ between EPDM and SiO<sub>2</sub> particles due to the formation of the unique structure<sup>[31]</sup>.

The toughness and phase morphology of polypropylene / EPDM / SiO<sub>2</sub> ternary composites. Two kinds of PP (grafted without or with maleic anhydride (PP-g-MA)) and SiO<sub>2</sub> (treated with or without coupling agent) were used to control the interfacial interaction among the components. The dependence of the phase morphology on interfacial interaction and processing method was investigated. It was found that the formation of filler-network structure could be a reason for a simultaneous enhancement of toughness and modulus of PP and its formation seemed to be dependent on the work of adhesion ( $W_{AB}$ ) and processing method. As the work of adhesion ( $W_{AB}$ ) of PP/EPDM interface was much lower than that of PP/SiO<sub>2</sub> and EPDM/SiO<sub>2</sub>, and the two-step processing method was used, the formation of filler-network structure was favorable. In this case, a super toughened PP ternary composite with the Izod impact strength 2-3 times higher than PP/EPDM binary blend and 15-20 times higher than pure PP could be

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achieved<sup>[28]</sup>. Nanocomposite obtained by the addition of the organoclay to a blend of i-PP and EPDM. Wide Angle X-ray diffraction (WAXD) patterns demonstrated that the clay was intercalated in the polymers chains, which was corroborated by the techniques of TEM and oscillatory rheology. The Small Angle X-ray Scattering (SAXS) analysis demonstrated that the lamellar long period increased with the introduction of clay into the blends and decreased with the deformation, either under compression or stretching. Additionally, there was a variation in the angle of rotation  $\theta$ , of the polymer and clay's lamellas with the addition of the organic clay, and this variation had a tendency to stabilize when it took place with the amount of clay introduced due to the consequent restriction of molecular movement, also a demonstration that the uniaxial compression and stretching of the nanocomposites produced a reduction of intensity in the peaks. Under the compression deformations, the crystallinity of the nanocomposites decreased significantly, while under the stretching deformation, the crystallinity remained virtually constant due to the phenomenon of micro necking's. Furthermore, the addition of clay into the blend resulted in an increase in energy dissipation by sinusoidal deformation because of the formation of the intercalated morphology during melt processing<sup>[30]</sup>. EPDM/PP blend with compatibilizer and its nanocomposites were prepared by using Micro injection molding technique. Incorporation of EPDM within the PP matrix resulted in increase in the impact strength and fracture toughness of Virgin PP. It has been shown that on the addition of 40 wt% of EPDM and 3 wt% of  $\text{TiO}_2$ , which showed enhancement of the impact property. Incorporation of EPDM content in the Virgin PP investigates the fracture energy, fracture stress and crack initiation & propagation energies, the Brittle-Ductile transition, the fracture process changed from being a fast unstable with craze formation to a slow stable fracture showing ductile tearing. Morphological observation (SEM) showed fractured surface morphology of PP/ EPDM blend and PP/EPDM/ $\text{TiO}_2$  blend nanocomposites<sup>[30]</sup>.

### EPDM/POLYOLEFINIC FIBER COMPOSITES

Thermoplastic Elastomer (TPE) composite rein-

forced with Hibiscus Cannabinus, L fiber (Kenaf fiber, KF) was prepared via melt blending method using internal mixer at temperature  $180^\circ\text{C}$ , screw rotational speed at 40rpm for 10 min. TPE matrix is a blend of polypropylene (PP) and ethylene propylene- diene monomer (EPDM) at a ratio of 70:30. The optimum fiber loading were investigated from 0% to 20% by volume. The effect of coupling agent Maleic Anhydride Polypropylene (MAPP) on the TPE composite has been investigated. The result shown that, with increasing the Kenaf fiber content gradually increased the tensile strength and flexural strength for both treated and untreated PP/EPDM-KF composite. However, at 20% of Kenaf fiber loading, it showed decreasing in impact strength due to brittleness of the samples. From the scanning electron micrograph (SEM) it has shown that the composite, with compatibilizer promotes better interaction between TPE and Kenaf fiber<sup>[32]</sup>. In another experiment thermal and viscoelastic properties of ternary composites based on low density polyethylene (LDPE)-ethylene-propylene-diene terpolymer (EPDM) blend and high density polyethylene (HDPE)-EPDM blend reinforced with short jute fibers. For all the untreated and compatibilizer treated composites, the variation of mechanical and viscoelastic properties as a function of fiber loading (10, 20 and 30 wt %) and compatibilizer concentration (1, 2, and 3%) were evaluated. All the flexural strength, flexural modulus, impact strength, and hardness of the composites increased with increase in both fiber loading (at 3% MAPE concentration) and Maleic Anhydride Polyethylene (MAPE) dose (at 30 wt % fiber content). The maximum values of flexural properties and hardness were achieved for HDPE / EPDM / jute fiber composites, whereas LDPE / EPDM / jute fiber composites showed higher impact strength. However, the rate of improvement in mechanical properties of the LDPE/EPDM blend with incorporation of fibers and MAPE is found to be higher than that of the HDPE/EPDM system<sup>[33]</sup>. The mechanical properties and morphology of ternary composites based on PP/EPDM blends reinforced with natural flax fibers are analyzed. In order to evaluate the simultaneous effect of the incorporation of both elastomer and fibers, an experimental design based on a Doehlert Uniform Net has been employed. The tensile, flexural and impact behaviors of the composites are investigated, and the

results show that flax fibers behave as an effective reinforcing agent in these systems. In fact, a considerable increase in the studied properties in the presence of the fibers was observed. It is interesting to note that the reinforcing effect is more noticeable as the EPDM content in the blend increases. A little wettability or poor adhesion between natural flax fibers and the studied matrices has been observed by scanning electron microscope. It is assumed that the hydrophilic structure of natural fibers is not chemically compatible with hydrophobic polymer matrices. Enhancing the compatibility between both phases by developing new chemical treatments for the fiber and both thermoplastic and elastomeric matrices, in order to evaluate its effect on the properties and morphology of the composites<sup>[34]</sup>. The (SGF) Short Glass Fiber and photo-irradiation can considerably improve the mechanical properties of PP/EPDM blends, especially for the tensile strength and notched Izod impact strength. The Wide Angle X-ray Diffraction measurements substantiated the formation of  $\beta$ -type crystal of PP, which partly enhances the impact strength of dynamically photo-irradiated PP/EPDM/Short glass fiber composites. The SEM images demonstrated that photo-irradiation process increases the interface adhesion of SGF and matrix, whereas decreases the aggregation of EPDM particles and thus increases the sites for dissipation of shock or impact energy in photo-irradiated PP/EPDM/SGF composites. The melting and crystallization temperatures of the photo irradiated composites are not affected greatly by increasing the SGF content. The thermal analysis results show that the incorporation of SGF into PP/EPDM plays an important role for increasing its thermal stability<sup>[35]</sup>. The effect of both, a thermoplastic elastomer (EPDM) and short aramid fibres on polypropylene (PP) crystallization kinetics and tensile behaviour has been investigated. Aramid fibres are effective nucleating agents for PP crystallization giving rise to both an increase in rate of the crystallization process and the phenomenon of transcrystallinity with PP, which permits increasing the interaction at fibre/matrix interface and hence the mechanical behaviour of the composites. The radial growth rate of PP spherulites decreases in the presence of EPDM and fibres, and hardly varies with EPDM percentages in the matrix above 25%. Tensile strength at break shows a similar behaviour to the stiff-

ness, and the elongation at break generally increases as EPDM percentage in the matrix increases, and decreases as fibre content in the composite increases<sup>[36,38]</sup>. The effect of short aramid fibers on the mechanical behavior of polypropylene (PP) and ethylene-propylene diene (EPDM) and their blends has been investigated by means of an experimental design. The results have shown that aramid fibers are very effective reinforcing agents for composites when the continuous phase of the matrix is constituted by PP, so sensible increments in tensile modulus and strength are obtained as fiber content in the composites increases. An optimal matrix composition and fiber content has been observed that produced high abrasion resistance compounds. The addition of fibers to EPDM rich (>50%) matrices gives rise to a sensible decrease of the impact strength of this polymer. However, at PP contents above 50% in the polymer matrix, an increase of impact strength is observed at fiber percentages in the composites above 10%. The different behavior of the fibers depending on matrix type can be attributed to a better affinity of these fibers for PP matrix. Morphological studies of the composites have been carried out by scanning electron microscopy<sup>[37]</sup>.

### PROCESS FOR GRAFTING ON EPDM

The maleic anhydride modification of rubbers is of interest as a way of compatibilizing the rubber with polyamides in the formation of toughened blends. With maleic anhydride modification the rubber can react with the polyamide forming a graft copolymer bridging the polyamide-rubber interphase. In this way the interfacial tension is strongly reduced. With a lower interfacial tension a finer dispersion can be obtained. EPDM and EPR rubbers are used as the toughening phase and for this purpose, these elastomers are modified with maleic anhydride<sup>[40]</sup>. Maleic anhydride grafted ethylene propylene diene terpolymer was prepared using both solution and reactive processes. The maleation of EPDM by a solution process was carried out by taking 40g of EPDM, 4g of MA, and 0.1g of BPO dissolved in xylene respectively were added to a 1L four necked flask equipped with a reflux condenser, stirrer, thermometer, and nitrogen inlet. The reaction mixture was poured into excess acetone with stirring. After removing any

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unreacted MA contained in the reaction mixture, the precipitate was filtered. The purification procedure was then repeated and the precipitate was finally dried in a vacuum at 80°C for 24h. The reaction process was carried out in a banbury type internal mixer (HAAKE RHEOMIX600P). After 40g of EPDM was charged in the chamber and heated at 130°C for 5 minute, various amounts of MA and DCP were added and mixed with a 50rpm stirring rate for 25minute at the same temperature. After completing the reaction, the reaction mixture was precipitated by pouring it into excess acetone with stirring. After removing any unreacted MA, the product was filtered. The purification procedure was then repeated and, the precipitate was finally dried in a vacuum at 80°C for 24 h<sup>[39]</sup>.

### COMPATIBILIZATION OF EPDM/ POLYOLEFINIC POLYMERS

To improve adhesion between cellulosic fiber and polymer matrix, different approaches have been investigated, i.e., chemical modification, polymer grafting on the surface of the fibers, incorporation of compatibilizer such as maleated polymer or treatment with coupling agent. Maleated coupling agents are widely used to strengthen composites containing fillers and fiber as reinforcements. The established role of maleated polyolefin (MaPO) resulted from two main factors, economical manufacturing and the efficient interaction of maleic anhydride with the functional surface of fiber reinforcement. The use of maleated polymer and coupling agent has received considerable attention due to their effectiveness in modifying the interface by forming a link between them and hydroxyl groups of the fibers. For example, maleic anhydride-grafted polypropylene (MAPP) has shown to be a very effective compatibilizer for cellulosic- fiber filled PP composites<sup>[44,45]</sup>. Maleic anhydride-grafted-polypropylene (MAPP) was used as a compatibilizer to improve the compatibility of kaolin filled PP/EPDM composites. Results show that incorporation of MAPP increased the tensile strength and Young's modulus, but reduced the elongation at break. Scanning electron microscopy (SEM) of the tensile fracture surfaces of composites indicates that the MAPP improved the interfacial interaction between kaolin and PP/EPDM matrix<sup>[41]</sup>. In order to improve the compat-

ibility between natural fibers and polypropylene (PP) and polypropylene-ethylene propylene diene terpolymer (PP-EPDM) blends, the functionalization of both matrices with maleic anhydride (MA) is investigated in this study. The morphological observations carried out by scanning electron microscopy show that the incorporation of small amounts of functionalized polymer considerably improves the adhesion at the fiber-matrix interface. In these cases, the fibers are perfectly embedded in the matrix in relation to the composites prepared with the pure homopolymers, and a significant increase in the composite strength is also observed, particularly after the incorporation of both modified polymers (MAPP and MAEPDM). It has been proven that the addition of low proportions of maleic anhydride grafted PP and EPDM to their composites increases nucleation, favoring the PP crystallization process, which was reflected in a marked decrease in the half time of crystallization. The micrographs obtained by means of scanning electron microscopy (SEM) have shown that better adhesion at the fiber-matrix interface exists when grafted matrices are added to the composite. In fact, there were hardly any voids on the fracture surface, and the fibers were also perfectly encapsulated by the matrix, making it very difficult to distinguish them. In addition, mechanical measurements are in accordance with these observations, showing a considerable increase in the composite properties when the grafted matrices were added to the composite<sup>[42]</sup>. In another study two types of impact modifiers are added to PP namely; thermoplastic natural rubber (TPNR) and polypropylene/ethylene-propylene-diene-monomer (PP/EPDM). Both composites were produced via double melt blending method using Haake internal mixer before they were compression molded. The ratio of thermoplastic: elastomer was 70:30 for both polymer blends. Due to incompatibility between matrix and reinforcement, maleic anhydride polypropylene (MAPP) was added as in the case of treated composite. It was found that the tensile strength for TPNR is about 12% higher than the PP/EPDM matrix. The presence of Kenaf fiber (KF) and MAPP however has significantly increased the tensile strength of the PP/EPDM composite by approximately 81% while only 55% increment attained in TPNR-KF-MAPP as compared to unreinforced TPNR. Apart from that, flexural proper-

ties and impact strength are greatly improved for treated kenaf fiber composite. This shows that KF has imparted its tensile strength to the PP/EPDM system with good interaction provided by the compatibilizer agent. Scanning electron micrographs (SEMs) revealed that the improvement achieved in mechanical properties was due to the interaction between both matrix systems and kenaf fiber<sup>[43]</sup>. Physical properties of natural fiber/polyolefin composites can be greatly enhanced by Maleated Polyolefin coupling agents. Typical manufacturing processes necessitate that the molecular weight of a Maleated Polyolefin decrease as the acid number increases. Optimizing the balance of these two Maleated Polyolefin properties results in a coupler for natural fiber / Polyolefin composites which can yield 60% increase in flexural and tensile strengths<sup>[44]</sup>. A study on effect of chemical treatment using maleic anhydride-grafted polypropylene (MAPP) and 3-aminopropyltriethoxysilane (3-APE) was investigated. The performance of the MAPP and 3-APE were investigated by means of torque development, mechanical properties, thermogravimetric analysis (TGA), differential scanning Calorimetry (DSC), scanning electron microscopy morphology, and water absorption. The results revealed that the use of MAPP or 3-APE in the composites has increased the stabilization torque, tensile strength, Young's modulus, water absorption, and thermal stability of the PP/NR composites. The incorporation of MAPP in the composites shows higher stabilization torque, tensile strength, elongation at break, Young's modulus, and lower water uptake when compared with the use of 3-APE in the PP/NR composites. TGA and DSC results indicated that primary and secondary peak of DTG curve, initial degradation temperature, maximum degradation temperature, melting temperature, heat of fusion of composites, crystallinity of composite and PP increased, while total weight loss and thermal degradation rate decreased for both treated composites. The MAPP-treated Recycled news paper (RNP)-filled PP/NR composites were found to be more thermal resistance and more crystalline than 3-APE-treated filled PP/NR Recycled News Paper composites<sup>[45]</sup>.

#### **DYNAMICALLY VULCANIZED EPDM/ POLYOLEFINIC BLENDS**

Dynamically vulcanized thermoplastic olefin (TPO) based on polypropylene (PP)/ethylene propylene- diene (EPDM) loaded with zinc dimethacrylate (ZDMA) was prepared. The addition of ZDMA significantly improved the complex viscosity of the resulting material in the melt state, as determined from rheological analysis. TPO based on PP/EPDM//ZDMA has been successfully prepared through dynamic crosslinking of the rubber phase during the mixing process, using DCP as curing agent. Dynamic mechanical analysis (DMA), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed to evaluate the structure, as well as to characterize the morphology formed during dynamic vulcanization. The ZDMA improved the crosslinking of the rubber phase and resulted in crosslinked rubber particles with dimensions within 200 nm. The addition of ZDMA improved the compatibility between rubber and PP phases, which contributed to the enhanced mechanical and rheological properties. The crystallization behavior analysis indicated that the addition of ZDMA promoted the nucleation process of PP, but a higher ZDMA content showed a negative effect on the crystallinity of the PP component. Remarkable improvements in toughness and extensibility of PP/EPDM/ZDMA composites were achieved<sup>[46]</sup>. ZDMA can be functioned as a potent in situ reactive compatibilizer as well as an effective reinforcing agent in the TPV based on PP and EPDM. During peroxide induced dynamic vulcanization, the in situ compatibilizing of ZDMA acted through the reaction between the double bonds of ZDMA and the free radicals generated in both EPDM and PP chains. Meanwhile, ZDMA is polymerized and reinforced the TPVs. As a result, a peculiar nanocomposite structure that the crosslinked rubber particles were "bonded" by a transition zone which containing numerous of nano-particles with dimensions of about 20–30 nm is formed. The ZDMA reinforced EPDM particles and PP phase have a quite blurry inter phase boundary, which results in significant improvements in the rheological and mechanical properties of the resultant materials. Furthermore, increasing the PP phase in the PP/EPDM/ ZDMA TPVs leads to an increase in mechanical properties<sup>[47]</sup>. Positron Annihilation Spectroscopy was used to investigate the relationship between free volume hole properties and miscibility of dynamically vulcanized EPDM/PP blend.

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The results showed that the non crystalline region of PP and EPDM in the blend was partially miscible and the miscibility of the blend became worse when the weight percent of EPDM was <50%. This was demonstrated by DMTA and mechanical properties of the blends with various compositions<sup>[48]</sup>. Stabilizers are used to prevent the degradation of polymers and thereby, to effectively extend their useful lifetime. However, the application of stabilizers in combination with a peroxide-cure system needs special care, because the main function of these materials is to deactivate the radicals formed after the decomposition of a peroxide, resulting in a reduced crosslinking efficiency of the peroxide. In this investigation, the changes of the physical properties after ageing, of Dicumyl peroxide (DCP)/Triallyl Cyanurate (TAC) cured thermoplastic vulcanizates (TPVs) at a fixed polypropylene (PP)/EPDM ratio as well as at varied blend ratios in presence of various structurally different stabilizers are described. TMQ performs the best amongst all the stabilizers. However, it discolors the TPV-end products<sup>[49]</sup>. Dynamically Photocrosslinked polypropylene (PP)/ethylene-propylene-diene (EPDM) rubber thermoplastic elastomer was prepared by simultaneously exposing the elastomer to UV light while melt-mixing in the presence of a photo initiator as well as a crosslinking agent. The results showed that after photocrosslinking, tensile strength, modulus of elasticity, and elongation at break were improved greatly. The DSC curves showed that for each dynamically photo crosslinked PP/EPDM blend, there was a new smaller melting peak at about 152°C together with a main melting peak at about 166°C. Dynamic mechanical thermal analysis (DMTA) indicated that the compatibility between EPDM and PP was improved by dynamic photo crosslinking.<sup>[50]</sup> Comparative studies of microstructure, rheological behavior, and viscoelastic and mechanical properties were carried out as the amount of curing agent is increased for EPDM/PP blends (60 : 40). Dynamically cured EPDM/PP blend is composed of two phases (i.e., EPDM and PP phase). As the level of curing agent is increased, EPDM phase changed from dispersed phase to continuous one, and again to dispersed phase, and PP phase remained continuous phase throughout. The melt viscosity of dynamically cured EPDM/PP blend increases with increasing curing agent level, yet the difference in the viscosity

of the blends tends to drop at high shear stresses. As the amount of curing agent is increased, the dynamic modulus of the blends increases slightly,  $T_g$  of EPDM increases, and  $T_g$  of PP almost remains unchangeable. EPDM/PP blend showed enhancement in yield stress and ultimate tensile strength with the increase in curing agent levels, in the case of elongation at break; the relationship is the reverse of that expected<sup>[51]</sup>. Simple blending and dynamic vulcanization of EPDM/PE blends using the resol/SnCl<sub>2</sub> system was studied in an extruder. The melting of the PE pellets occurs just in front of and in the first kneading zone. Upon complete melting of the PE phase, the EPDM/PE blends reach very quickly their final morphology. Crosslinking of the EPDM phase to high levels occurs already when the PE phase is not yet fully molten. The higher the EPDM content, the higher the viscous dissipation, the higher the melt temperature and, consequently, the higher the crosslinking rate. For the EPDM/PE (50/50; w/w) TPV a transition from continuous via co-continuous to fully dispersed EPDM is observed, which is driven by crosslinking. Although the degree of crosslinking of the EPDM rubber is very high, this does not prevent phase inversion of the blend. The EPDM/PE interface is rather blurred, because PE crystalline lamellae are growing into the EPDM domains, probably because of the high compatibility between PE and EPDM (60 wt% of ethylene). This study shows that dynamic vulcanization in extruders proceeds quite differently from that in batch kneaders, where melting, mixing and crosslinking are separated in time. In extruders mass and heat transport, melting of the thermoplastic, morphology development (including dispersion and phase inversion), distribution and dissolution of (crosslinking) chemicals and crosslinking of the rubber do not occur as independent phenomena, but mutually and/or continuously interact<sup>[52]</sup>.

## CONCLUSION

EPDM based polyolefinic composites and blends can be prepared by various methods. The properties can of EPDM/Polyolefinic blends can be improved by the addition of nano and micro fillers. Addition of fibers into EPDM/Polyolefinic matrix can also improve the properties. The compatibilizer's essential for preparation of blends and composites can be prepared by ei-

ther solution or by reactive processes. Dynamic vulcanization has been done to vulcanize the rubber phase in the blend. EPDM/Polyolefenic/reinforcing agent composites can be used in shoe sole, mattress and some electrical insulation properties.

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