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Study of Mechanical, Thermal and Micro structural Properties of EPDM/Polypropylene/Nano clay Composites with Variable Compatibilizer Dosage

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Abstract

Thermoplastic elastomers are a special class of polymeric materials that combine the properties of thermo plasticity during processing and rubber-like behaviour in service. They can be processed in conventional plastic processing equipment, such as twin screw extruders, internal batch mixers, extruders and injection moulding machine, but exhibit vulcanized rubber like ultimate properties (i.e. long-range reversible extensibility) immediately on cooling. Dynamically vulcanized thermoplastic nanocomposites (TPV - NC) based on melt intercalated hybrid ethylene-propylene diene rubber (EPDM)/maleic anhydride (MA) grafting and polypropylene (PP) with nanoclay were prepared. Nanoclay acts as a nucleating agent for polypropylene crystallization; they also form physical interlocking between EPDM/Polypropylene blends which serve the function of compatibalization along with EPDM – g – Maleic anhydride. Results from X-ray diffraction, transmission electron microscopy (TEM), thermo gravimetric analysis and mechanical properties, reflect upon the microstructure developed during dynamic cross linking. The nanoclay forms intercalated and exfoliated structures in the EPDM/PP / EPDM-g-MA nanoclay hybrid thermoplastic vulcanizates. The EPDM/PP TPV nanocomposites show a matrix-disperse type of morphology in which the cross linked EPDM particles appear in the form of agglomerates covered by a layer of PP nanoclay composites. This has been assigned to the formation of a nanoclay network structure by the layer of nano composite PP covered EPDM rubber particles.

Keywords- Nanoclay, Dynamic vulcanizates, Thermoplastic nanocomposites, Intercalated, Exfoliated

1. Introduction

Rubber when used to plasticize a thermoplastic is accomplished by dispersing microscopic particles of rubber, into thermoplastic which is a continuous phase, where dispersed rubber acts as a minute shock absorbers and enhances the toughness of the thermoplastic along with mechanical strength and offers a wide range of physical properties and applications [1]. EPDM and PP have similarity in structure due to presence of common polypropylene structure. In spite of structural similarity however EPDM is not compatible with PP. The EPDM phase exists as separate particles in PP matrix due to stratification, segregation and phase inversion. The incompatibility of the EPDM/PP blend is signified by poor interphase adhesion, to improve the compatibility of the EPDM/PP blend, various compatibilizers have been prepared and incorporated into the EPDM/PP blend [2]. Filler addition is the simplest way to modify the properties of the base materials. Addition of filler at an optimum level increases the physical properties of the blend but excess addition of filler acts as diluents and causes degradation in properties of the blend formed [3]. Filler increases the physical properties, but some of the properties of the filler, like particle size, shape, volume fraction and surface are to be considered while selecting filler for a particular application. Considering the particle size of the filler, for smaller particle size of the filler, increase in the physical properties is observed. Incorporation of smaller particle size filler is very difficult and takes more time than coarse fillers but its dispersion is easy. If coarse filler is used in a blend between EPDM rubber and Polypropylene, it leads to formation of large filler agglomerates, which influences the mechanical response of the blend, hence nano size filler have been used in our study. We have used Nanoclay, as Nanoclay is compatibilizing filler which reduces the interlayer attractions along with it also allows the diffusion as well as accommodation of polymeric chain into interlayer spaces. Nanoclay is used to obtain an effective dispersion and exfoliation of the layered silicates into polymer to provide high aspect ratio, particles for mechanical reinforcement, improved barrier properties, increased modulus, dimensional stability, increased strength, heat resistance and decreased permeability [4]. Structurally nanoclay has hydrophilic functional group present on its surface, while the EPDM and Polypropylene are hydrophobic and hence comapatibilizer are used which improves the polymer filler interaction thereby increasing the physical properties of the blend as well as the processing capability of the blend.

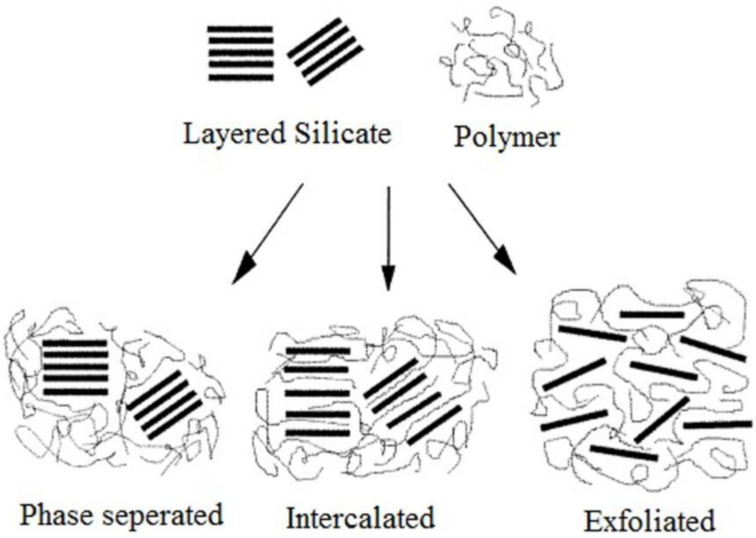


Figure 1: Structure of composites from the interaction of Layered silicate and Polymer matrix [5]

The structure of nanocomposites depends on the structure of nanoclay particles in the polymer blend matrix, which are usually classified as intercalated or exfoliated (figure 1). In the intercalated state, the nano clay is dispersed as lamellar structures and polymer chains penetrate between the silicate layers of clay. Exfoliated structure characterizes itself by a complete delamination of nanoclay particles and individual silicate layers are dispersed throughout the polymer blend matrix which leads to improvement in mechanical properties. This work gives a comparative study of the blends with 90/10, 80/20, 70/30, 60/40, 50/50 of EPDM/PP and the blend with optimum mechanical properties was selected for preparation of nanocomposites. Further with variable compatibilizer dosage its effect on the mechanical properties, thermal properties, barrier properties and microstructure of EPDM/Polypropylene/Nanoclay composites are reported.

2. Materials and methods

2.1. Materials

The Polypropylene (PP) used in this study was supplied by Reliance Industries Ltd. Ethylene Propylene Diene Monomer Rubber (EPDM) was obtained from DSM Elastomers, Netherlands. Maleic anhydride (MA) was obtained from the Aldrich Chemical Company. Nanoclay was procured from Sisco Research Laboratories, Dicumyl Peroxide (DCP) and Triallyl Cyanurate (TAC) was obtained by Arkema Inc, EPDM grafted Maleic Anhydride was prepared by reactive process.

2.2. Optimization of EPDM: PP blend ratio

Blends of EPDM /PP were prepared by melt blending process. The formulations for blend preparation as well as the result obtained are given in Table 1.The materials are melt mixed in Brabender Plasticorder at 180°C and at a speed of 50rpm for 10 minutes, thereafter the molten mass was taken out and while hot, passed through two-roll mill for sheeting. The 2mm sheet was then cut and press moulded in a hydraulic press at 180°C, under specified pressure. The sheet was then cooled down to room temperature still under pressure. The test specimens were die-cut from the compression molded sheet and used for measuring mechanical properties after 24 hours of conditioning at room temperature.

Table 1: Formulation of EPDM/PP blend ratio, along with the mechanical properties values for optimization of blend ratio (‘**E**’ refers to EPDM content and **digit** refers to loading of EPDM, phr – parts per hundred rubber)

Batch no	E90	E80	E70	E60
EPDM (phr)	90	80	70	60
PP (phr)	10	20	30	40
Mechanical Properties				
Tensile strength(MPa)	2.5	2.7	3.2	3.7
Elongation at break%	220	200	170	145
50%modulus(MPa)	2.1	2.4	2.7	3.2
100%modulus(MPa)	2.3	2.5	3.0	3.7
Tear strength (Kg/cm)	21	20	22	23
Hardness (shore A)	65	63	60	54

On the basis of optimum mechanical properties obtained we can select 60:40 blend ratio of EPDM: PP for the preparation of ternary nanocomposites.

2.2. Preparation of EPDM-grafted-Maleic Anhydride

Brabender was used for the reactive compatibalization i.e. grafting of Maleic Anhydride on EPDM. EPDM was charged in the chamber and heated at 130°C for 5 minutes, Maleic anhydride and Dicumyl peroxide were added and mixed at the same temperature. After completing the reaction, the reaction mixture was dissolved in Xylene, and then the product was precipitated by pouring it into excess acetone with stirring. After removing unreacted Maleic Anhydride, the product was filtered. The purification procedure was repeated and, the precipitate was finally dried in a vacuum at 80°C for 24 hours [6].

2.3. Preparation of Ternary Nanocomposites

Polypropylene nanoclay masterbatch was prepared in a Brabender Plasti-Corder, having a mixing chamber volume of 350 cm^3 at a temperature of 180°C and rotor speed of 80 rpm. The fill factor of the chamber was maintained at 0.80.The prepared Polypropylene nanoclay masterbatch was then melt blended with prepared EPDM-g-MA at 180°C. At final stages of mixing cross-linking agent Triallyl Cyanurate was added to affect dynamic vulcanization. Immediately after mixing, the molten mass was taken out from the mixer and while still hot, passed through the cold two-roll mill to chill it and sheet it to about 2 mm thick. The sheet was then cut and press moulded for 5 minutes in a hydraulic press at 190°C, under 5 MPa pressure. The sheet was then cooled down to room temperature still under pressure. The test specimens were die-cut from the compression molded sheet and used for measuring mechanical properties after 24 hours of conditioning at room temperature. Similarly the other batches with varying comapatibilizer dosage were carried out to prepare ternary nanocomposites.

Table 2: Formulation for 60:40 EPDM: Polypropylene with variable dosage of Compatibilizer (‘**C**’ refers to Compatibilizer and **digit** refers to loading of Compatibilizer)

BATCH NO →		C0	C2	C4	C6	C8	C10
INGRED	EPDM	60	60	60	60	60	60
	PP	40	40	40	40	40	40
	Maleic Anhydride	0	2	4	6	8	10
	Nanoclay	0	2	4	6	8	10
	DCP	2.5	2.5	2.5	2.5	2.5	2.5

IENTS (*)	TAC	1	1	1	1	1	1

In the above formulation you will observe that the Maleic Anhydride and Nanoclay are taken in same ratio, because maleic anhydride will only act as a compatibilizer between EPDM and PP (interphase compatibalization) and nanoclay acts as a nucleating agent for polypropylene crystallization; they also form physical interlocking between EPDM/Polypropylene blends which serve the function of compatibalization along with EPDM – g – Maleic anhydride. Hence both Maleic anhydride and nanoclay both are considered as compatibilizers (* - parts per hundred rubber)

3. Results and discussion

3.1. Mechanical Properties

The mechanical properties such as tensile strength, modulus, hardness, tear strength and elongation at break of EPDM/Polypropylene/nanoclay nanocomposites are mentioned in Table 3 as a function of nanoclay and Maleic Anhydride loading which are incorporated at the same levels. It is seen that increasing Maleic Anhydride and nanoclay levels in the blend matrix improve the tensile strength of EPDM/Polypropylene ternary nanocomposites upto 8 phr beyond which it decreases (figure 2). The enhanced tensile strength and moduli of ternary nanocomposites are attributed to the reinforcement phenomenon due to interfacial interaction between the blend matrices and dispersed nanoclay galleries. Crosslinking between EPDM molecules causes further compactness in the clay galleries thus enhancing strength properties. Higher elastic modulus as well as tensile strength of the Ternary nanocomposites as compared to EPDM/Polypropylene blend (without nanoclay) has been observed (figure 3 & 4). The hardness rapidly increases with nanoclay loading (figure 5) where as tear strength show marginal improvement.

Table 3: Physical Properties of 60:40 EPDM: Polypropylene Ternary Nanocomposites, (‘**C**’ refers to Compatibilizer and **digit** refers to loading of Compatibilizer)

BATCH NO →		C0	C2	C4	C6	C8	C10
PROPERTIES	Tensile strength(MPa)	3.7	4.3	4.8	5.4	4.8	4.5
	Elongation at break%	145	135	125	115	135	130
	50%modulus(MPa)	3.2	3.6	4.0	4.4	4.7	5.2
	100%modulus(MPa)	3.7	4.3	4.4	4.8	5.3	5.4
	Tear strength (Kg/cm)	23	25	24	25	29.5	30
	Hardness (shore A)	54	56	62	67	68	70

Graphical Representation: Effect of the variable dosage of comapatibilizer

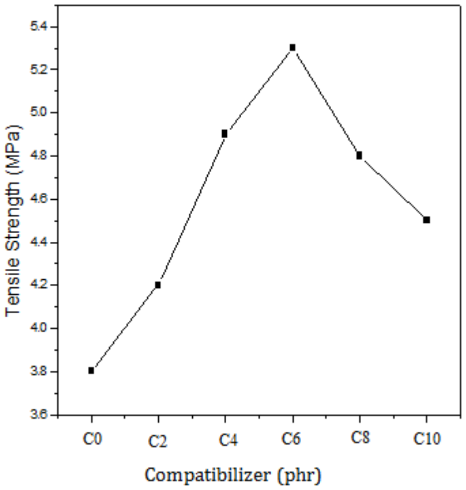


Figure 2: Tensile Strength

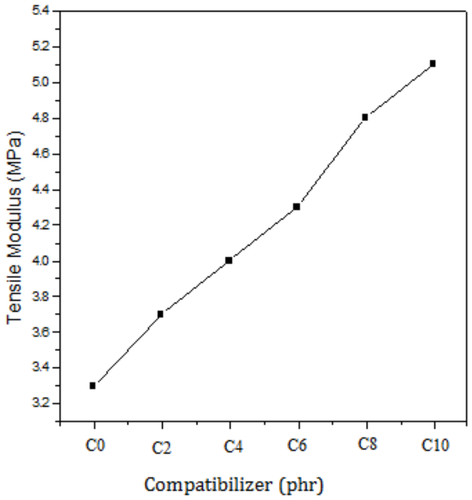


Figure 3: 50% Modulus

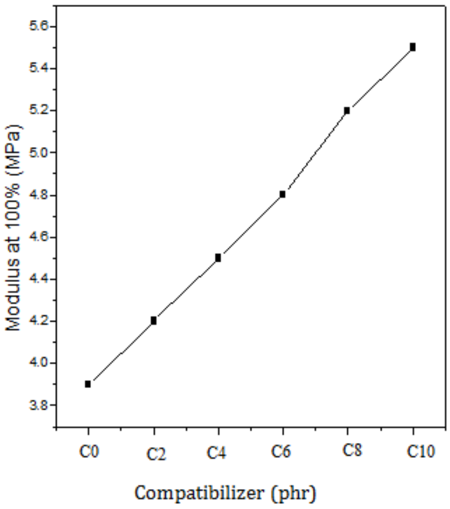


Figure 4: 100% Modulus

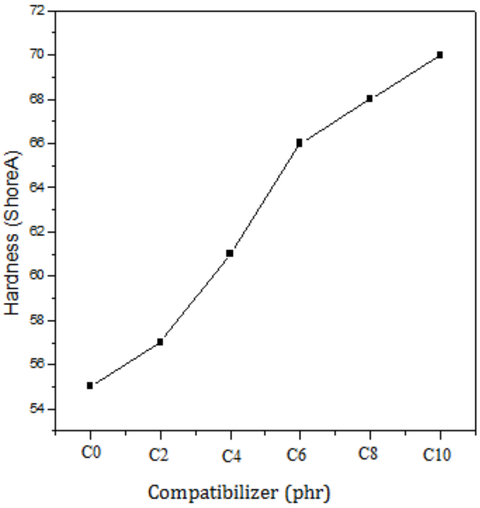


Figure 5: Hardness

3.2. Thermal Properties

3.2.1. Dynamic Mechanical Analyser

Figure 6 and 7 show the storage modulus and loss factor (tanδ) as a function of temperature of EPDM/Polypropylene/nanoclay ternary nanocomposites with variation in the dosage of compatibilizer, in the temperature range 70ºC to 200ºC. From figure 6, it is observed that the initial storage modulus (G') is higher in case of nanoclay and Maleic Anhydride dispersed ternary nanocomposites as compared to the gum vulcanizates of EPDM/Polypropylene. The storage modulus decrease with increasing temperature and reaches a plateau at higher temperature beyond 100ºC for dispersed ternary nanocomposites as well as for gum vulcanizates, ternary nanocomposite samples show a sharper fall as compared to the gum vulcanizates. From figure 7, it is marked that three major transitions occur in the damping curve, first one occurs at lower temperature of −55ºC considered to be the glass transition of EPDM (T_{g1}), another transition occurs at around 2ºC may be taken as the glass transition temperature of Polypropylene (T_{g2}) and third one occurring at a higher temperature of around 100^0C attributed to the α' – relaxation in the crystalline zone of Polypropylene. Table 4 shows tanδ $_{max}$ values at different temperature and corresponding T_g of different polymer. There is only a slight change of T_g value of EPDM upon nanoclay and Maleic Anhydride addition. Moreover, the tanδ peak maxima corresponding to EPDM decrease from 0.44 to 0.40 on incorporation of compatibilizer into it indicating a reduction in the damping behaviour of the nanocomposites, a consequence of enhanced dispersion of nanoclay and Maleic Anhydride in the polymer matrices.

Table 4: Glass transition temperatures and tanδ values of 60:40 EPDM: Polypropylene ternary nanocomposites at variable compatibilizer dosage (‘**C**’ refers to Compatibilizer and **digit** refers to loading of Compatibilizer)

PROPERTIES →		T_{g1} (°C)	Tan δ at T_{g1}	T_{g2} (°C)	Tan δ at T_{g2}
BATCH	C0	-56.3	0.44	1.4	0.12
	C6	-57.5	0.41	2.3	0.11
	C8	-58.03	0.40	3.4	0.10

Graphical Representation: Effect of the variable dosage of comapatibilizer

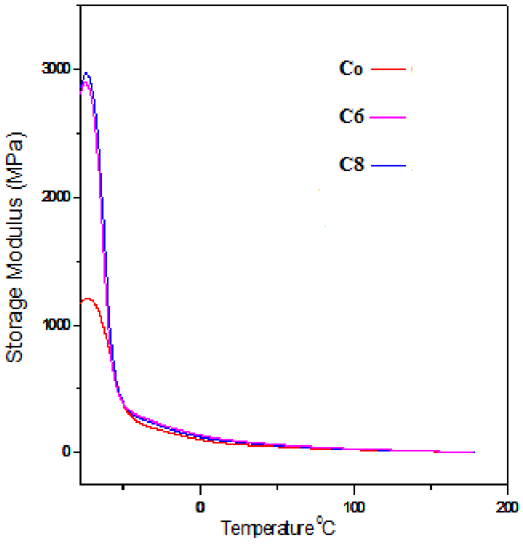


Figure 6: Storage Modulus

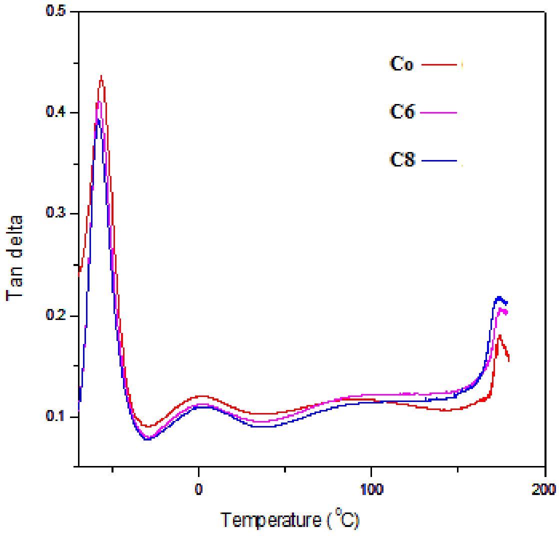


Figure 7: Tan δ (Loss Factor)

3.2.2. Thermal Gravimetric Analysis

In order to investigate the thermal stability of EPDM/Polypropylene ternary nanocomposites, TGA study was carried out. Figure 8 shows the TGA thermographs of EPDM/Polypropylene Ternary nanocomposites with variable dosage of compatibilizer. Thermographs reveal that the onset of degradation of the Ternary nanocomposites shifts towards a higher temperature on increasing concentration in the blend indicating higher thermal stability. The maximum degradation temperature (T_{max}) also increases with compatibilizer loading. The T_{max} without compatibilizer is 464ºC which increases with C2, C4, C6, C8 and C10 to 465, 467, 472, 473 and 473ºC respectively. It is also seen that the residue weight increases with compatibilizer concentration, as shown in Table 5.

Table 5: Onset of degradation, maximum degradation, and residual weight of 60:40 – EPDM/Polypropylene ternary nanocomposites at variable compatibilizer dosage, (‘**C**’ refers to Compatibilizer and **digit** refers to loading of Compatibilizer)

PROPERTIES →		T_i(ºC)	T_{max}(ºC)	Residual weight (%)
BATC	C0	388	464	1.8
	C2	404.8	465	3.1
	C4	406.7	467.2	3.7

H	C6	409	472	4.9
	C8	411	472.8	5.8
	C10	414	473	6.6

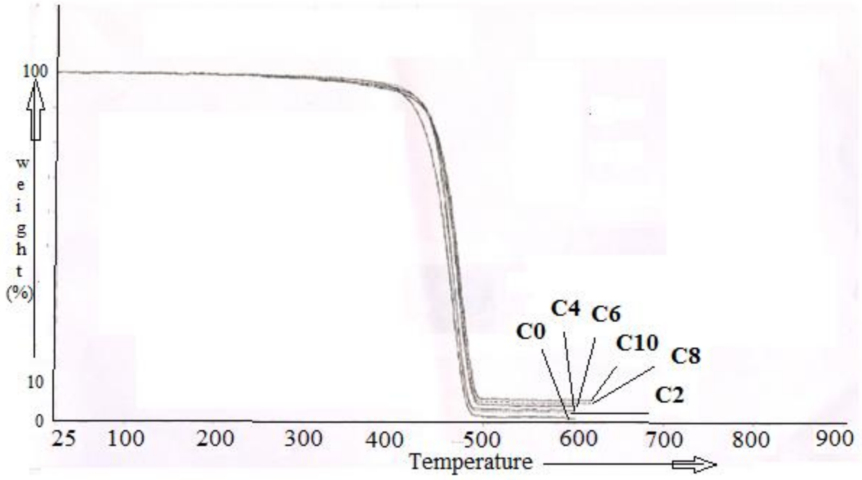


Figure 8: Thermograph of variable compatibilizer dosage in EPDM/Polypropylene composites

3.3. Microstructure Determination

3.3.1. X-Ray Diffraction

XRD measures the degree of dispersion by estimating the distance between individual silicate layers after mixing with polymer. A shift towards lower angles of the XRD peak suggests an increase in interlayer spacing or gallery space within the clay layers, which is referred to as intercalation. Figure 9 compares the X-ray diffraction (XRD) patterns of the montmorillonite clay and the ternary nanocomposites prepared. From the X-ray diffractogram, it is evident that the nanoclay exhibits a peak at around 2.52° which indicates the gallery spacing of the modified clay is (d = 35.04 A°), its calculated by using Bragg's equation (nλ = 2d sinθ), By incorporating 2phr of nanoclay into EPDM-g-MA /Polypropylene blends matrix the nanoclay peak is shifted towards lower angle i.e. approx 2.27, 2θ thus increasing the gallery gap of (d= 38.9 A°). Figure 9 shows that after 6 phr loading, there is no significant shift in the diffraction peak towards the lower angle. This indicates that insufficient polymer molecules enter between the clay galleries to affect higher intercalation i.e. to push the nanoclay galleries further apart. This may be explained due to the fact that the dynamic vulcanization of EPDM phase in the blend of EPDM/Polypropylene increases the viscosity of the blend due to networking in the amorphous rubber phases thus enhancing the shear stress imposed by the matrix during the mixing process, which facilitates a break-up process of nanoclay agglomerates. These results lead to the conclusion that more exfoliation and intercalation of the nanoclay layers is expected at low concentrations of the nanoclay in EPDM/Polypropylene/ nanoclay based Ternary nanocomposites. However, 10 phr of nanoclay in the matrix show no change in d-spacing for clay before and after dispersion in the polymer. This may be explained by realizing the fact that nanoclay-polymer nanocomposites consist of a hierarchical structure.

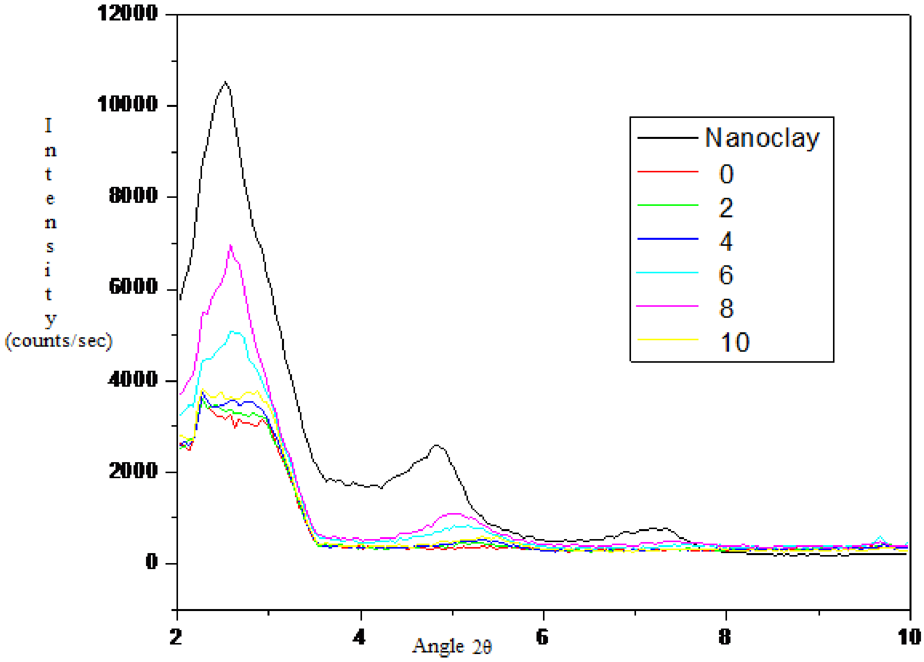


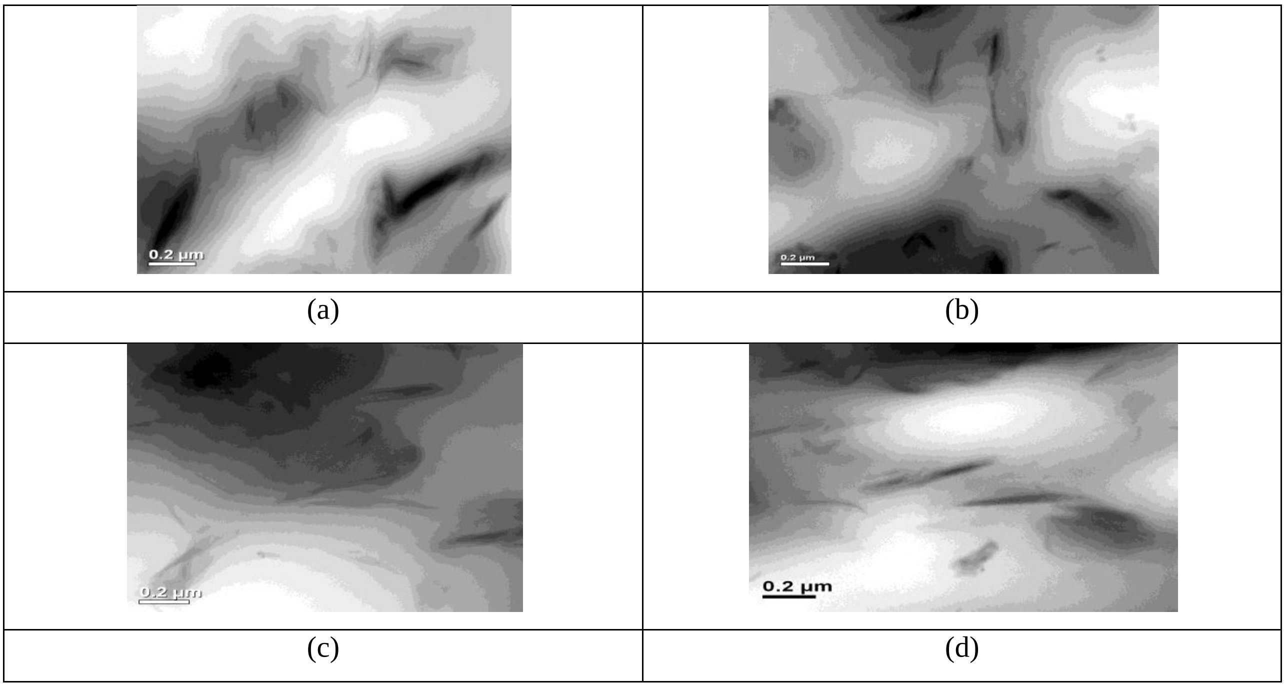
Figure 9: XRD Spectra of nanoclay and EPDM/Polypropylene/ nanoclay ternary nanocomposites at variable dosage of compatibilizer

Table 6: 2θ and d-spacing value of nanoclay and 60:40 EPDM: Polypropylene ternary nanocomposites at variable compatibilizer dosage, (‘**C**’ refers to Compatibilizer and **digit** refers to loading of Compatibilizer)

PROPERTIES →		Angle (2θ) (°)	d- Spacing (A°)
BATCH	Nanoclay	2.52	35.04
	C0	2.35	37
	C2	2.27	38.9
	C4	2.275	38.5
	C6	2.56	34.1
	C8	2.57	34.4
	C10	2.59	34.8

3.3.2. TEM Analysis

Transmissions Electron Microscopy (TEM) photomicrographs of EPDM/Polypropylene/nanoclay composites are shown in Fig 10. Figure 10 (a) shows that nanoclay galleries exist in the form of large aggregates and Figure 10 (b & d) show the nanoclay galleries in the form of exfoliated platelets for EPDM/Polypropylene (60/40) ternary nanocomposites. Also it is observed that there are small intercalated tactoids of nanoclay present in the system - Figure 10 (b & d). This suggests that upon loading nanoclay into well dispersed EPDM/Polypropylene gum vulcanizates, the aggregates begin to split as they are subjected to shearing and therefore nanoclay platelets become separated on coming in contact with the functionalized component of the blend. This gives rise to a significant proportion of exfoliated nanoclay platelets at the very early stages of compounding. Presence of exfoliated nanoclay platelets in the EPDM matrix in the early stages of mixing can contributes to matrix properties, ultimately contributing to the development blend morphology.



(a) (b)

(c) (d)

Figure 10: TEM images of EPR/PP TPV nanocomposites by (a) C2 (b) C 4 (c) C6 (d) C8

3.4. Gas Barrier Properties

The gas permeability test for the different nanoclay loaded EPDM/Polypropylene blend vulcanizates are shown in Table 6. Permeability of the gum vulcanizates and nanocomposites are denoted by P and PNc respectively. The permeability gradually reduces and the P/PNc ratio increases with nanoclay loading in the EPDM/Polypropylene gum vulcanizates. It clearly establishes the fact that gas barrier nature of the nanoclay platelets which are predominant in the Ternary nanocomposites improve with nanoclay loading. This is due to the dominance of the nanoclay platelets, which act like flakes in the matrix improving its barrier properties. Moreover, it is generally accepted that the crystalline zones are less permeable to gases than the amorphous zones [7]. Adding nanoclay to the neat polymer film is expected to improve its barrier properties due to the combination of two phenomena occurring simultaneously, Firstly decrease in the area available for diffusion, a result of impermeable flakes replacing permeable polymer and secondly increase in the distance a solute must travel to cross the film as it follows a tortuous path around the impermeable flakes. The simple mechanism by which the nanoclay can improve barrier properties lie on the nanoclay loading and the extent to which the intercalated clay platelets experience a tortuous path responsible for retarding the transport of diffusing species, such as oxygen, carbon dioxide.

Table 7: Gas permeability and aspect ratio of EPDM/Polypropylene ternary nanocomposites at variable compatibilizer dosage, (‘**C**’ refers to Compatibilizer and **digit** refers to loading of Compatibilizer)

PROPERTIES		Gas permeability, Q (m²/sPa)	P/PNc
BATCH	C0	4.6	1
	C2	4.32	1.06
	C4	4.1	1.12
	C6	3.9	1.17
	C8	3.82	1.2
	C10	3.36	1.36

Conclusion

The compatibility between nanoclays and EPDM/Polypropylene matrix is significantly improved by the addition of Maleic anhydride as a comapatibilizer. Existence of comapatibilizer induced even more intercalation of nanoclays. Increases in compatibilizer concentration significantly improved tensile strength, modulus, tear strength and hardness of ternary nanocomposites upto a certain extent. DMA study shows that tanδ that is loss factor is maximum at low temperature and decreases with increasing compatibilizer concentration, indicating less damping characteristics. Thermo gravimetric analysis (TGA) studies revealed that thermal stability of gum vulcanizates are improved in the presence of compatibilizer. XRD analysis shows clay gallery separation or d-spacing calculated from Bragg's law increases first with 2, 4 & 6 phr nanoclay, thereafter remains unchanged indicating that Ternary nanocomposites form intercalated and exfoliated structures. TEM study shows the presence of nanoclay aggregates and exfoliated structures with the little intercalation of nanoclay layers in the Ternary nanoclay composites. Gas impermeability of EPDM/Polypropylene/nanoclay Ternary nanocomposites increases with increase in nanoclay concentration upto 10 phr of nanoclay.

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