

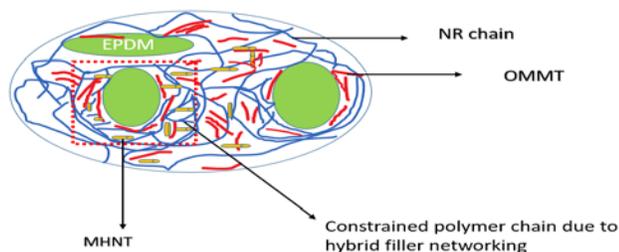
Synergistic effect of hybrid fillers on transport behavior of NR/EPDM blends

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ABSTRACT



Organically modified nanoclay (OMMT), silane modified halloysite nanotube (MHNT) and a hybrid of both modified nanoclay and halloysite nanotube were added to natural rubber (NR) and ethylene propylene diene rubber (EPDM) blend (60NR:40EPDM) matrix. The addition of these nanofillers affected the morphology and transport behaviour of the matrix considerably. The combinations of OMMT with MHNT having tubular morphology have shown specific result in synergistic behavior of solvent diffusion. The effect of nature of solvent and size of solvent molecule on the transport behavior of NR/EPDM blend nanocomposites in the presence of hybrid fillers were conducted. The cross-link density measurement and morphology analysis by TEM analysis confirms the filler networks and entrapped polymer chain segment. The quantity of immobilized polymer chain due to filler network formation has been determined by dynamic mechanical analysis and a nice connection was settled between the transport characteristics and polymer chain confinement. The analysis of swelling coefficients and diffusion parameters confirmed the excellent barrier property of NR/EPDM matrix filled with dual filler. The mode of transport through the rubber blend nanocomposites remained anomalous. Peppas-Sahlin model is well fitted with results.

Keywords: morphology, synergism, solvent diffusion, reinforcement, cross-link density

INTRODUCTION

Now a days rubber/clay nanocomposites are of great interest because of its gas barrier properties and excellent mechanical properties^{1,2} especially polymer filled with silicates having layered structure. Matrix filled with nanofillers prevent the interpenetration of solvents and gases which make it applicable in many fields. The

rate of solvent diffusion through polymer matrix is controlled by factors such as polymer structure, its cross link density, type of cross-linking, penetrant size, presence of fillers, temperature, and polymer morphology at the interface. Thus transport behavior of solvents and gases through polymer membrane is very important because of its innumerable applications.³ The permeant diffusion through the polymeric material is significantly reduced by the tortuous path created by the platelet particles of layered silicates. Thus the presence of layered silicates in polymeric matrix increases barrier properties. Dufresene and co-workers⁴ investigated the swelling behavior of NR filled with mazy starch nanocrystals. They found that as the starch content increases, the absorption rate decreases. Ahmad et al.⁵ observed that as filler loading increases swelling properties of NR /LDPE (low density polyethylene) blends decreases. Hanna et al.⁶ studied NR/NBR (nitrile rubber) with different mixing method and found that solubility parameter

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difference between blend nanocomposite and solvents also affects transport properties of elastomeric blends.

Recently researchers are interested in using environment friendly, low cost and low weight reinforcement fillers in the polymeric membrane. HNT's are such type of nanofillers which has the same chemical composition as that of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$. Because of the tubular morphology, low density of hydroxyl functional group on the surface which reduces its surface energy makes it a good reinforcement nanoparticle for NR, NBR, EPDM etc.^{7,8,9} Now days, an increasing interest is for using hybrid system of different fillers in elastomeric system. Many hybrid system involves nanofillers such as nanoclay, CNT, nanographite with nanodimensional CB, SiO_2 etc. were studied.^{10,11} Very recently, Aleksandra et al.¹² reported the dispersion of EOMt in presence of MWCNT in NR and suggested that synergism caused between two nanofillers only when EOMt (organically expanded OMMT) is used above a particular amount. The present work is based on the idea to use benefits of hybrid system of different fillers, especially difference in the size and shape of fillers (OMMT and MHNT) in order to obtain a novel elastomeric system to reduce the solvent permeation. HNT exhibits high level of biocompatibility and very low cytotoxicity makes it a good candidate for household and medical application. The present study discusses synergistic the effect of nanofillers on transport properties of NR/EPDM, two nonpolar and incompatible rubbers. Often blends of NR/EPDM are used in outdoor application. Thus the transport studies in NR/EPDM blend nanocomposites are of much interest. In the present work we have studied the sorption of commonly using laboratory solvents through 60/40 NR/EPDM blends filled with organically modified nanoclay (OMMT), silane modified halloysite nanotube (MHNT) and hybrid of OMMT and MHNT. The present work is the first attempt to analyze the transport properties of NR/EPDM blends in the presence of hybrid fillers where the filler network formation immobilizes the polymer chain. Till now, in our knowledge no reports have been made on the transport characteristic of NR/EPDM with hybrid nanofillers of OMMT and MHNT.

EXPERIMENTAL SECTION

2.1. Materials

Natural rubber (NR) ISNR-5 was supplied by Rubber board Kottayam, India having Mw - 7.8×10^5 g/mol and Mooney viscosity 65 ML (1+4) 100°C. Ethylene propylene Diene monomer rubber, EPDM (KEP 270) with ethylene content 57% is an ethylidene norbornene (ENB) type monomer with 4.5% and a Mooney viscosity 71 ML (1+4) 125°C, was supplied by Maharashtra polymer products, Mumbai. The organically modified (35-40% dimethyldialkylamine) MMT (montmorillonite), 1.44p used in this present study was provided by Sigma Aldrich, USA. Halloysite nanotube was also purchased from Sigma Aldrich, USA. The typical surface area of this halloysite was 64 m²/g, pore volume of 1.26-1.34 mL/g, refractive index 1.54 and specific gravity 2.53g/cm³. The surface modification of the halloysite nanotubes were done using 3-(Trimethoxysilyl) propylmethacrylate (γ -MPS) supplied by Sigma Aldrich. The solvents and other reagents of laboratory grade were used for this study.

2.2. Preparation of blend nanocomposites

Blend nanocomposite of NR/EPDM (60/40)¹³ were prepared by direct mixing in an open two roll mill (laboratory size). Firstly, NR was masticated for 5 minutes followed by the addition of EPDM. Both rubbers together masticated for 5 more minutes. After this vulcanization ingredient were added. Five minutes after adding the vulcanization agents, nanofillers and finally sulphur were added. After reaching 20 minutes the nanocomposites were removed. Throughout the process of nanocomposite preparation time was kept for 20 minutes and maintained temperature at 60°C.

Table 1. Composition of prepared nanocomposites

Ingredients(phr)	N60	N60H ₃	N60H ₅	N60H ₇	N60M ₃	N60M ₅	N60H ₇ M ₃	N60H ₇ M ₅
NR	60	60	60	60	60	60	60	60
EPDM	40	40	40	40	40	40	40	40
Silane modified Halloysite nanotube	0	3	5	7	0	0	7	7
Modified Nanoclay	0	0	0	0	3	5	3	5
ZnO	5	5	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2	2	2
MBTS	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
CBS	1.5	1.5	1.5	1.5	1.2	1.2	1.2	1.5
Sulphur	2	2	2	2	2	2	2	2

The NR/EPDM blends were compounded according to ASTM D 3182. The amount of curatives used for the mixing process for all compositions studied were; ZnO-5phr, stearic acid-2 phr, MBTS-0.2 phr, CBS-1.5 phr for and sulfur-2 phr. After mixing, the rubber compositions were molded in hydraulic press to optimum cure using molding conditions. It was cured under a pressure of about 120 bar at 150°C. The formulation of different mixes is given in Table 1.

CHARACTERIZATIONS

3.1. Procedure for sorption experiment

Cured samples of 2mm thickness were cut into round shape were used for sorption studies. Uniform sized round cut samples of nanocomposites were weighed. It was then put into diffusion bottle containing approximately 20ml of solvent. The whole experiment was done at room temp. At regular intervals of time, the samples were taken away from the sample bottle and adhered solvent from the surface were completely removed. The samples were weighed again using electronic balance. The experiments were repeated several times until the attainment of equilibrium.

(a) Determination of the percentage uptake ($Q_t(\%)$): The mol% uptake of solvent by the polymeric matrix are expressed in terms of $Q_t(\%)$ and it was calculated by using Equation (1).

$$Q_t\% = \frac{(M_t - M_0)}{M_0} \times 100 \dots (1)$$

Where M_t is the mass of sample at time 't' and M_0 is the initial mass of sample, M_w is the molecular mass of the solvent. The diffusion curves were plotted as percentage mol uptake of solvent ($Q_t\%$) versus square root of time \sqrt{t} .

(b) Diffusion coefficient (D): The extent of diffusion through a polymeric matrix can be expressed in terms of Diffusion coefficient which is a kinetic parameter.¹⁴ Diffusion process mainly depends on the polymer segmental mobility. The Diffusion coefficient of a solvent molecule through a polymer membrane can be calculated by using the Equation (2) which is based on Fick's second law.¹⁵

$$D = \pi \left(\frac{h\theta}{4Q_\infty} \right)^2 \dots \dots \dots (2)$$

Where θ the slope of is initial linear portion of the sorption curve before the attainment of the 50% equilibrium uptake and Q_∞ is the equilibrium sorption value

(c) **Sorption coefficient (S):** The penetration of solvent into a polymer depends on diffusion as well as on sorption. The sorption coefficient hence calculated using the Equation (3),

$$S = M_\infty / M_0 \dots \dots \dots (3)$$

Where, M_∞ is the mass of the solvent at equilibrium swelling and M_0 is the initial polymer mass.

(d) **Permeation coefficient (P):** The permeability or permeation coefficient (P) of a penetrant in a polymer membrane depends on the diffusivity as well as solubility or sorption of the solvent in the polymer membrane. The permeability of organic solvents¹⁶ was obtained using the following Equation (4).

$$P = D \times S \dots \dots \dots (4)$$

The values of transport coefficients such as Diffusion coefficient (D), Sorption coefficient (S) and Permeation coefficient.

(e) **Swelling Parameters:** The extent of swelling by the polymeric matrix can also be expressed in terms of swelling parameters such as swelling coefficient and swelling index.¹⁷ The swelling coefficient and swelling index can be calculated using the Equations (5) & (6) respectively.

$$\text{Swelling coefficient } \beta = \left[\frac{M_\infty - M_0}{M_0} \right] \times \rho_s \dots (5)$$

Where M_0 and M_∞ are mass of the sample before and after swelling, ρ_s is the density of the solvent.

$$\text{Swelling index } \% = \left[\frac{M_\infty - M_0}{M_0} \right] \times 100 \dots \dots (6)$$

3.2. Morphological analysis. The morphology of the composites was analyzed by TEM (JEM-2100HRTEM). The cryocut specimens prepared using an ultra-microtome (Leica, Ultra cut UCT) were placed on 300 mesh Cu grids (35 mm diameter) and

were analyzed. The transmission electron microscope was operated at an accelerating voltage of 200 kV.

3.3. Dynamic Mechanical Analysis. Dynamic mechanical properties were measured using dynamic mechanical analyser (TA instrument Q800-US) over a temperature range of -80 to +80 °C at a heating rate of 1°C per minute.

RESULTS AND DISCUSSION

4.1. Morphology of hybrid nanocomposites

The dispersion of organically treated fillers in the blend matrix can be well understood from the transmission electron micrograph. Figure 1 (a) & (b) indicates the dispersion of organically modified nanoclay (3phr) and silane modified halloysite nanotube (7phr) in 60/40 NR/EPDM blend matrix. From the figure it is clear that OMMT layers are well intercalated than MHNT fillers.

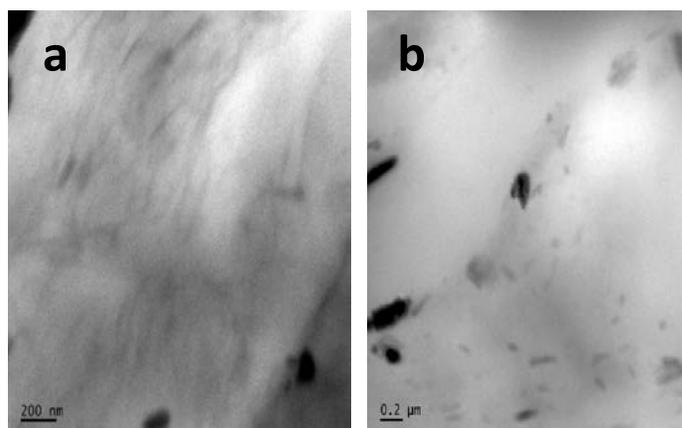


Figure 1. Transmission electron micrograph of 60/40 NR/EPDM blend in presence of (a) 3phr OMMT (b) 7phr MHNT.

Filler dispersion in different weight ratio of OMMT and MHNT in 60/40 NR/EPDM blends by TEM is shown in Figure 1 (a) & (b). The dispersion of the halloysite nanotubes and nanoclays are clearly visible in the TEM micrographs. It can also be seen that MHNT fillers occurs between OMMT layers. Thus an effective networking is formed between the fillers.

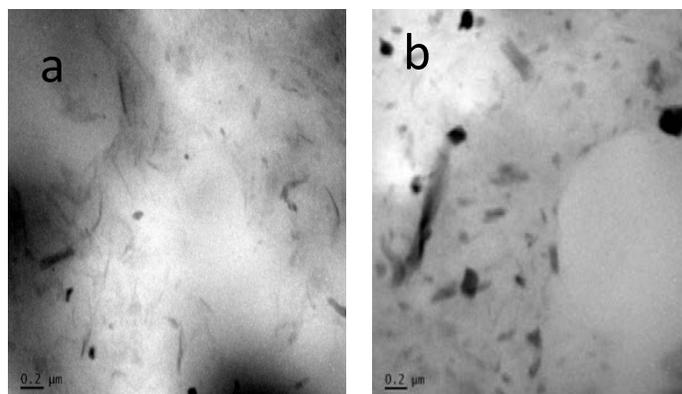


Figure 2. Transmission electron micrograph of 60/40 NR/EPDM blends in presence of (a) MHNT:OMMT(7:3 wt%) [N60H7M3] (b) MHNT:OMMT(7:5 wt%) [N60H7M5]

As pointed out by Josmin *et al.*¹⁸ both fillers are organically modified at the surface and the interaction between the modifiers on the surface of two fillers take part in network formation. Interestingly, the filler localization is more concentrated in the NR matrix and interface and this is quite visible in the Figure 2 (a) & (b). Thus the modification of the interface of the blend due to the variation in surface energy of both the fillers is easily achieved and the blend separation is quite visible. This morphological architecture will change overall property of the blend nanocomposites i.e., the structural networking formation by both the organically modified nanomaterials and interface modification of blends through the hybrid fillers made the blend matrix as a diverse feature rich matrix.

The high resolution TEM images indicated that the dispersion of both the MHNTs and nanoclay in an intercalated manner. The polymer chains are squeezed through the highly separated HNT tubes through organic modification and the organically modified nanoclays through the chemo-mechanical process adopted for the preparation of the blend nanocomposites. The variation in the surface energy of two nanofillers in the blend matrix helps to direct the proper orientation at the interfaces of the blend matrix i.e., the synergism helps to develop more concentration of nanofillers towards the interfaces of the blend matrix. TEM images of N60H7M3 in different magnification is given in Figure 3 to understand the hybrid filler networking effect.

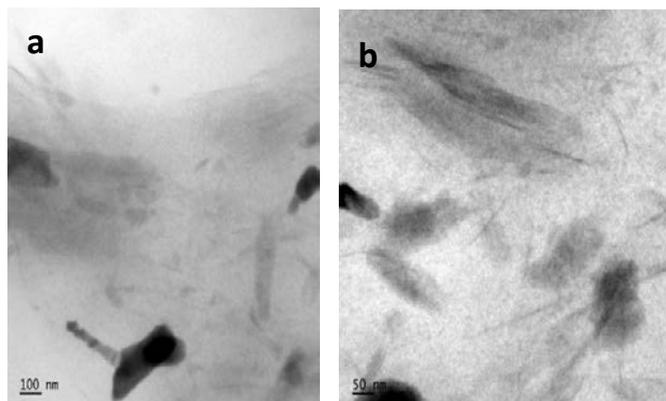


Figure 3. Transmission electron micrograph of N60H7M3 in different magnifications

The Van der Waal's force of attraction between alkyl group of alkyl modified montmorillonite and alkyl part of γ -methacryloxypropyltrimethoxy silane of halloysite nanotube prompted the fillers to take part in effective network formation. When modified halloysite nanotube and organomontmorillonite were used in 7:3 wt.% ratio hybrid filler networking occurred in an effective manner, i.e. there was optimal weight ratio between hybridizing fillers as reported by Leung *et al.*¹⁹ A schematic representation of such type of interaction is given in Figure 4.

4.2. Diffusion characteristics

4.2.1. Effect of filler loading

The swelling behavior of vulcanized rubber blends is significantly affected by the nature of the polymer, surface area,

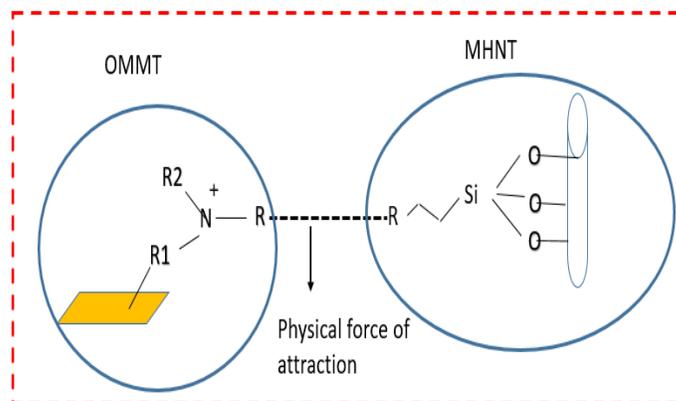


Figure 4. Schematic representation of the interaction between alkyl groups of dialkyldimethylamine modified nanoclay and 3-(Trimethoxysilyl) propylmethacrylate (γ -MPS) modified halloysite nanotube

and amount of filler. The solvent diffusion through N60 blends in presence of silane-modified halloysite nanotube (MHNT) and organically modified nanoclay (OMMT) and their hybrids are shown in the Figure 5 (a, b & c). The addition of nanofillers such as MHNT and OMMT brings out substantial changes in the solvent sorption behavior of the matrix. When the filler loading increases the rate of diffusion decreases. In the case of the OMMT filled N60 blend, the maximum reduction occurs when 5phr OMMT was used. But, MHNT filled N60 showed maximum reduction up to 7phr and above that the addition of filler has little influence. This may be due to the low density of -OH groups on the surface of MHNT lowering surface energy and thereby reducing filler-filler aggregation. MHNT filled N60 blend showed higher Q_{∞} compared to OMMT filled N60 blends. This may be due to the intertubular diffusion of all the polymers and curatives through the hollow nanotube. It limits the intercalated structure and hence shows the higher Q_{∞} values. The addition of both fillers restricts the long-range movement of the polymer molecule, preventing the solvent uptake. Moreover, the presence of fillers increases the tortuous path for solvent, and up taking the quantity of solvent is reduced. The addition of OMMT and MHNT to the matrix also reduces the available free volume in the composites again lessening the solvent transport through the matrix.

Comparing the solvent uptake of N60 blend with single filler and their hybrid (MHNT and OMMT), it is evident that the sorption of solvent is very low in the presence of hybrid fillers. The formation of local filler-filler networking between MHNT and OMMT, which increases the tortuous path for the solvent through the matrix. As described earlier, the morphological analyses by TEM reveal that in the case of nanoclay and MHNT filled system, the filler is mostly concentrated in the NR phase and at the interface. The presence of intercalated clay in the NR phase exhibited good polymer-filler interaction. But in the hybrid system, both fillers are well dispersed in the presence of each other by the way of synergism and this interrupted filler from forming agglomerates. This intercalated and exfoliated morphology of the blend nanocomposite hinders the movement of the penetrant molecule through the hybrid filled N60

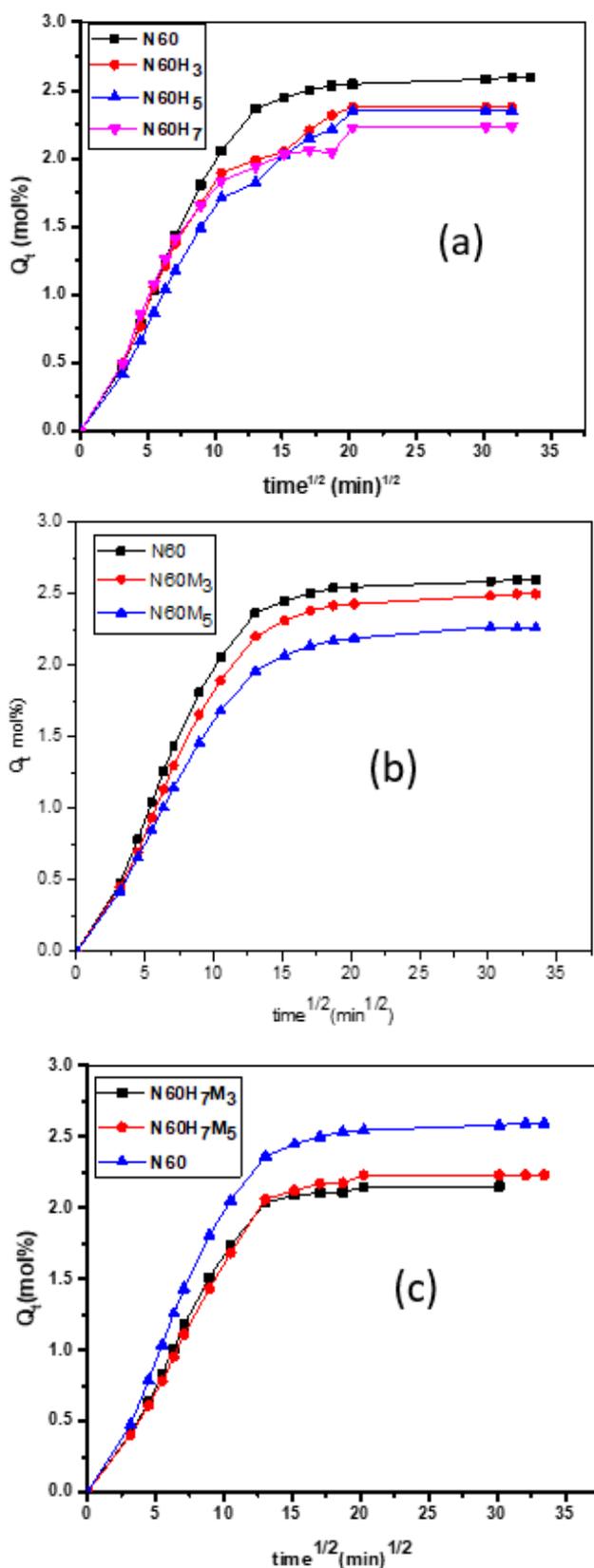


Figure 5. (a) The solvent diffusion behavior of NR/EPDM(N60) blend matrix with (a). MHNT, (b). OMMT & (c). Hybrid filler.

blends. The formation of filler networking is also supported by TEM images. Strong adhesion between NR/EPDM-MHNT-OMMT is also responsible for the reduced segmental motion. This reduced the transport of solvent through the matrix in the presence of hybrid fillers. Among the matrixes N60H₇M₃ showed the lowest solvent uptake. On the other hand, when 5phr OMMT was added to N60H₇ matrix, the clay layers undergo agglomeration and prevented the filler network formation. This enhanced the solvent permeation through N60HM5 matrix. A schematic representation of the tortuous path provided by hybrid filler networking is given in Figure 6.

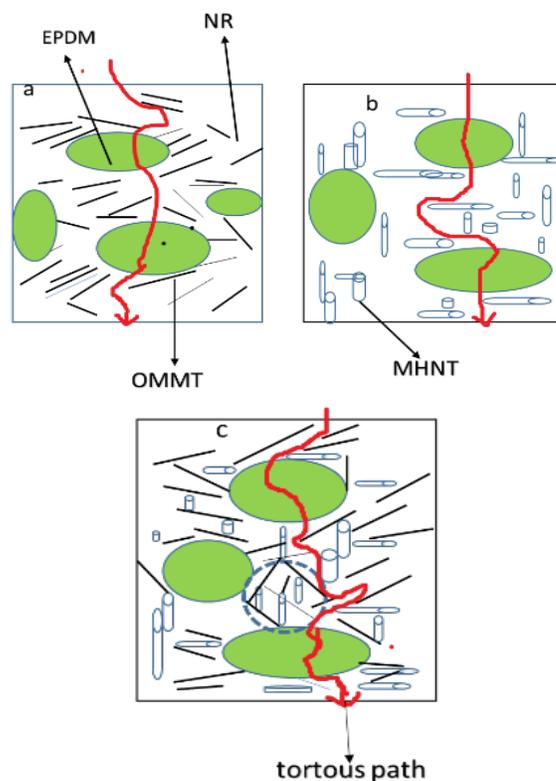


Figure 6. Schematic representation of tortuous path developed in presence of (a). modified nanoclay (OMMT), (b). modified hallosite nanotube(MHNT) & (c). hybrid of MHNT and OMMT (7:3 wt.% ratio)

4.2.2. Effect of nature of solvent

The nature and molecular size of penetrant also affect the transport of solvents through the polymeric matrix. To study this effect, four different solvents were selected among them two belongs to aliphatic series (n-hexane and n-heptane) and two belongs to aromatic series (toluene and xylene). Transport of these solvents through N60 blend nanocomposite with single filler and hybrid filler shown in Figure 7 (a & b). In the case of both aliphatic and aromatic solvents a systematic trend for the diffusion of solvents through composites were observed. Among toluene and xylene, xylene showed the lowest uptake. The high molecular weight and molar volume of xylene caused its lowest uptake in the nanocomposites. In the case of aliphatic solvents, n-heptane showed the lowest uptake compared to n-hexane. As the penetrant

size increases, a reduced interaction occurs between the polymer and solvent and as result solvent uptake is reduced. Systematic trend in penetrant size was observed.

Due to higher molar volume, aliphatic solvents have reduced tendency to penetrate through the polymeric matrix compared to aromatic solvents. Thus low solvent diffusion values of aliphatic solvents when compared to aromatic solvents are due to their higher molar volume.²⁰

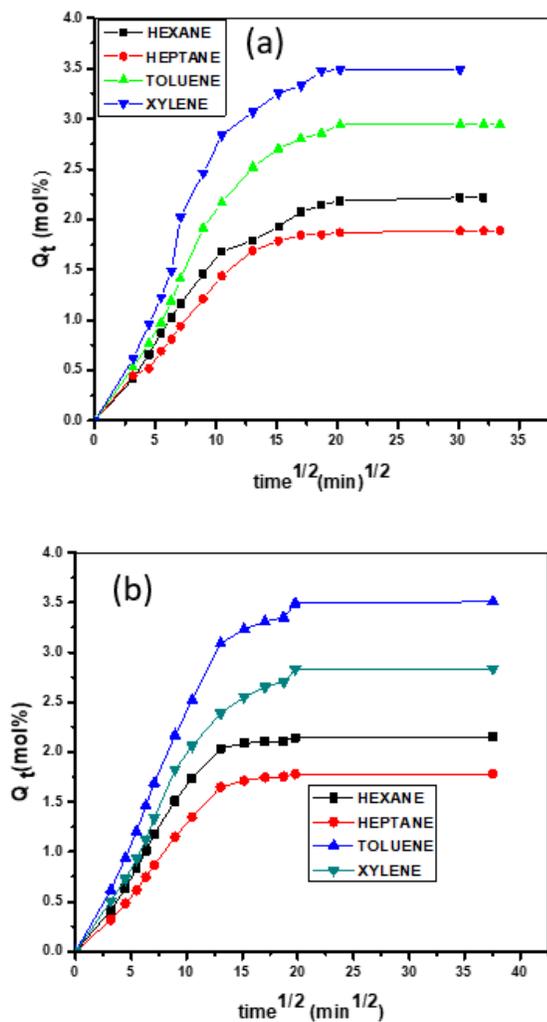


Figure 7. Mol% uptake of NR/EPDM(N60) blend nanocomposites with (a). HNT and (b). hybrid filler in different solvents.

The dependence of penetrant size on diffusion has been reported by many researchers.^{21,22} According to them as the size of penetrant increases the diffusion of it through the polymer system decreases. Free volume theory²³ gives a better explanation for the dependence of penetrant size on the rate of diffusion. According to this theory the rate of diffusion of solvent molecule greatly depends on the ease with which the polymer chain can interchange its position with the solvent molecule. As the penetrant size increases the exchange become less especially in the nanocomposites and this leads to a reduced solvent uptake. The high activation energy needed for the larger penetrant molecule to penetrate is another reason for lower

solvent uptake.²⁴ Instead of these factors sorption of solvents through the polymer matrix also depends upon the solubility parameter difference between polymer blend system and solvent used.

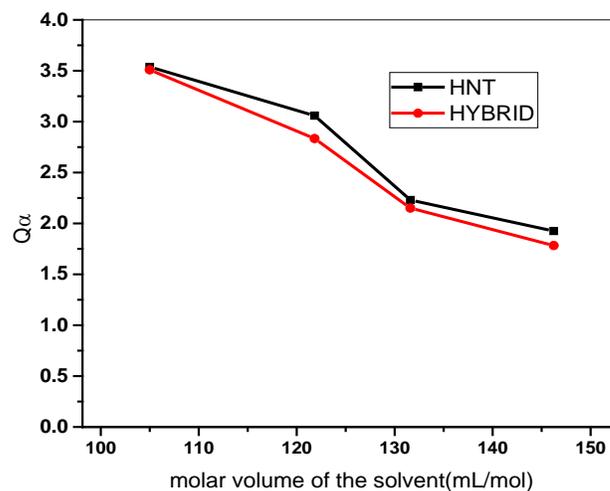


Figure 8. Effect of molar volume on the percentage uptake of solvents through nanocomposites

Swelling of polymer in solvent will be reduced when a large difference in solubility parameter of polymer blends and solvent exist. The effect of molar volume on Q_∞ values of N60 blends in presence of conventional and hybrid filler is shown in Figure 8.

4.3. Transport coefficients and swelling parameters

The diffusion of solvent through the polymer depends on the free volume within the polymer and the polymer chain segmental mobility. The presence of nanofiller will lower the availability of free space and constrain the movement of polymer chain. It can be observed that as the addition of filler increases diffusion coefficient decreases. This is due to the better polymer–filler interaction. When MHNT added to N60 blends D values decreases for each solvent which is in agreement with the results reported by various researchers.²⁵ In the case of hybrid system, the value of diffusion coefficient is too much reduced compared to gum samples and also N60 blends filled with the conventional fillers. This may be due to the formation of a local filler networking between MHNT-OMMT which increases the tortuous path for the solvent. Thus in the presence of hybrid fillers both fillers disperse very well in the rubber matrix and its occurrence at the interface creates a tortuous path for the solvent transport. It can be concluded that the increased solvent resistance of N60H₇M₃ nanocomposite was mainly due to the contribution from the synergistic effect of hybrid filler than from the individual fillers. Also, the above results confirm that the synergistic effect of hybrid fillers was adequate only when these fillers are in a particular concentration. Sorption coefficient S , is calculated using the equation $S = M_\infty / M_0$. The incorporation of 7wt% MHNT and 3wt% OMMT to N60 blend increased filler dispersion and lowered the sorption coefficient.

Table 2. The calculated diffusion parameters based on the Equation (2), (3) and (4)

Solvent	Sample	Diffusion coefficient D(cm ² /s ⁻¹)	Sorption coefficient,S	Permeation coefficientP(cm ² /s ⁻¹)
Hexane	N60	2.38	2.23	5.30
	N60H ₃	2.12	2.04	4.32
	N60H ₅	2.06	2.01	4.14
	N60H ₇	1.97	1.91	3.76
	N60M ₃	2.04	2.14	4.36
	N60M ₅	1.78	2.06	3.66
	N60H ₇ M ₃	0.92	1.83	1.68
	N60H ₇ M ₅	0.98	1.91	1.87
Xylene	N60	3.58	3.44	12.31
	N0H ₃	3.49	3.44	12.01
	N60H ₅	3.30	3.39	11.18
	N60H ₇	3.06	3.24	9.91
	N60M ₃	3.22	3.28	10.56
	N60M ₅	2.51	3.20	8.03
	N60H ₇ M ₃	1.77	3.004	5.31
	N60H ₇ M ₅	1.87	3.17	5.92

The permeation coefficient values also support the synergistic effect caused by hybrid fillers. This is due to the better dispersion of both fillers in the matrix and its occurrence at the interface creates a tortuous path for the permeation of solvent molecules. The dispersion of OMMT in the matrix is a dynamic process, which means that dispersion and agglomeration of OMMT layers happen simultaneously. In the presence of MHNT agglomeration of OMMT is prevented and most of the clay migrates towards the NR phase, and at the interface of NR and EPDM. The presence of dispersed fillers in the NR phase and at the interface of the NR and EPDM phase hinders the movement of solvent molecules.

Various diffusion parameters such as diffusion coefficient (D), sorption coefficient (S), permeation coefficient (P), swelling coefficient and swelling index of N60 blend nanocomposites are summarized in the Table 2. Values of swelling coefficient and swelling index found to be decreases with increase in filler loading. This is due to the hindered path offered by fillers to the penetrant molecules. This can be clearly seen in the Table 2. In all solvents N60 blends with hybrid filler possess lowest swelling parameters.

4.5. Transport Mechanism

The mode of transport of solvents through the polymeric matrix is studied by the Equation (7),

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \dots\dots\dots (7)$$

Where k, indicates the interaction between polymer and the penetrant and ‘n’ represents the mode of transport, Q_t and Q_∞ are the mol % sorption at time ‘t’ and at equilibrium respectively.

Table 3. Calculated swelling coefficient and swelling index(%) based on the Equation (5), and 6)

Solvent	Sample	Swelling coefficient	Swelling index(%)
Hexane	N60	3.40	223.16
	N60H ₃	3.11	204
	N60H ₅	3.080	201
	N60H ₇	2.92	191
	N60M ₃	3.27	214
	N60M ₅	3.14	206
	N60H ₇ M ₃	1.83	183
	N60H ₇ M ₅	2.9	191
Xylene	N60	4.02	344
	N0H ₃	4.00	344
	N60H ₅	3.93	339
	N60H ₇	3.76	324
	N60M ₃	3.81	328
	N60M ₅	3.81	320
	N60H ₇ M ₃	3.004	300
	N60H ₇ M ₅	3.68	317

The value of ‘n’ and k are determined by regression analysis of the linear portion of plots of log(Q_t/Q_∞) against log t. When the rate of diffusion of solvent molecule is lower than that of rate of relaxation of polymer chain, the mechanism of transport is known as Fickian, for which n=0.5. ²⁶ For non-Fickian mode of transport, where the chain relaxation is slower than the liquid penetration the value of n is, n=1. The sorption is anomalous, non-Fickian when the value of n lies between 0.5 and 1. The lower value of n than zero indicates that the permeation of solvent is lesser than the polymer chain relaxation process. ²⁷ This situation is known as ‘Less – Fickian’ or ‘Pseudo-Fickian. The values of ‘n’ and K for N60 blend nanocomposites were obtained from the plot of log (Q_t/Q_∞) against log ‘t’ are shown in Table 4.

Here the value of n varies from 0.59 to 0.97, which shows that solvent transport is anomalous. The k value is the indication of the interaction of the polymer with the solvent. As the filler loading increases, generally, the k value decreases, showing less interaction of the polymer with the solvent. But in our system, the k value of the MHNT filled system is more than the gum sample. As MHNT loading increases k value gradually decreases. In the case of MMT-filled N60 blend nanocomposites, the k value decreases as per

Table 4. Values of n and K of N60 blend nanocomposites

Sample	n	K x10 ⁻¹ (min ⁻¹)
N60	0.68	0.56
N60H ₃	0.64	1.41
N60H ₅	0.63	1.4
N60H ₇	0.72	1.0
N60M ₃	0.63	0.42
N60M ₅	0.59	0.38
N60H ₇ M ₃	0.76	1.00
N60H ₇ M ₅	0.97	0.67

expectation. It shows a better interaction of OMMT with N60 blends. Due to the tubular morphology of MHNT, some of the solvent molecules can readily ooze out through the tube and so more solvent can enter the system consequently swelling increases at lower loading. When 3 phr OMMT added to MHNT filled N60 blend nanocomposites value of k is not affected. With the addition of 5phr OMMT, the value of k reduces too much. It indicates the addition of OMMT to the MHNT filled system increases the polymer–filler interaction. The k values of N60/MHNT/OMMT blend nanocomposites are found to be more than the gum sample. Only by taking this value, we cannot predict that the filler interaction is not good in the case of hybrid filler nanocomposites. Many reports pointed out that this fact is true for pure polymer systems, but this may not be accurate for blend nanocomposites.²⁸

4.6. Molar mass and Cross link density

Molecular mass (M_c) between two successive crosslinks can be calculated by using the Equation (8)

$$M_c = \frac{-\rho_r V_s (\phi_{rf})}{\ln(1-\phi_{rf}) + \phi_{rf} + \chi_{rf} \phi_{rf}^2} \dots\dots\dots (8)$$

Where ρ_r is the density of the rubber, V_s is the molar volume of solvent used φ_{rf} is the volume fraction of rubber in the swollen material φ_{rf} is given by the Equation (9) by Ellis and welding.²⁹

$$\phi_{rf} = \frac{\frac{(d-fw)}{\rho_p}}{\left(\frac{d-fw}{\rho_p}\right) + \frac{As}{\rho_s}} \dots\dots\dots (9)$$

Where d is the deswollen weight, f the volume fraction of the filler, ‘w’ is the initial weight of the sample, ρ_p and ρ_s are the density of polymer and the solvent respectively. A_s is the amount of solvent absorbed. χ is the interaction parameter between polymer and solvent. It was calculated from Hilderbrand Equation (10).³⁰

$$X = \beta + \frac{V_s(\delta_s - \delta_p)^2}{RT} \dots\dots\dots (10)$$

Where β is the lattice constant, V_s is the molar volume, R is the universal gas constant, T is absolute temperature, δ_s and δ_p are

solubility parameters of solvent and polymer respectively. The cross-link density can be calculated from the Equation (11).

$$\text{Cross link density } \nu_c = \frac{1}{2M_c} \dots\dots\dots(11)$$

Values obtained for ν_c and M_c are given in the Table 5. The values clearly show that with the addition of nanofillers in the N60 blend, ν_c increases. In the case of N60 /OMMT blend nanocomposites maximum value of crosslink -density is obtained with the addition of 5 phr clay. At the same time, MHNT filled blend nanocomposite ν_c values are lower than that of the MMT filled matrix. The increase in cross-link density with the addition of nanoclay is due to the better reinforcement clay with the polymer. This interaction between the clay and polymer reduces the penetration of solvent molecules. At higher concentrations, clay agglomerates and reduces the interaction between clay and polymer. N60 blends with hybrid filler showed increased crosslink -density than the binary blend nanocomposites which again supports the synergistic effect caused by the hybrid fillers.

Affine limit model M_c (aff) and phantom network model M_c (ph) suggested by Guth and James to compare the molecular mass formed between the crosslinks in the polymer matrix and are given in Equations 12 and 13 respectively.^{31,32} The transport phenomena through the polymer membrane can be better understood through the study of the deformation of the polymeric network during swelling.

$$M_c(aff) = \frac{P_p V (\phi_{2m})^{1/3} (\phi_{2c})^{2/3} (1 - \frac{\mu}{\nu} \phi_{2m}^{1/3})}{-\ln(1-\phi_{2m}) + \phi_{2m} + \chi \phi_{2m}^2} \dots\dots (12)$$

$$M_c(ph) = \frac{(1 - \frac{2}{\chi}) \rho_p V \phi_{2c}^{2/3} \phi_{2m}^{1/3}}{-[\ln(1-\phi) + \phi_{2m} + \chi \phi_{2m}^2]} \dots\dots\dots(13)$$

Where μ, and ν are the number of effective chains and junctions.³³ φ_{2c}, the polymer volume fraction during cross linking, where the chain may move freely through one another, and χ is the junction functionality.³⁴ The calculated values are given in Table 5 along with the experimental values.

Table 5. Values of molecular mass M_c(exp), M_c (aff) and M_c (ph)

Sample	M _c (Exp) g/cm ⁻³	Cross link density (ν _c x 10 ⁻⁴) mol/cc ⁻¹	M _c (Aff) g/cm ⁻³	M _c (Ph) g/cm ⁻³
N60	1253.86	3.99	752.11	569.66
N60M ₃	1109.7	4.50	602.13	457.3
N60M ₅	867.38	5.76	434.95	334.65
N60H ₃	1124.42	4.4	735.8	315.7
N60H ₅	1125.3	4.44	725.8	250.37
N60H ₇	1112.24	4.5	734.47	212.58
N60H ₇ M ₃	746.94	6.9	559.84	322.96
N60H ₇ M ₅	771.22	6.4	585.22	355.26

It can be seen that the M_c values of affine model showed moderate agreement with the experimental values rather than with

the phantom model. Here, the chain can move freely through one another, i.e. junction points fluctuate over time around their mean position without any hindrance from the neighboring molecules.

4.7. Kinetics of sorption

The interpenetration of solvent through the polymer matrix induces structural disturbances in them. This promote kinetic behavior in polymer matrix. Segmental mobility and availability of free volume within the polymer matrix influences the kinetics of sorption of solvent through the polymer matrix. So transport of solvents through polymer membrane can be considered as a rate controlled kinetic process and it can be studied by applying first order kinetic equation which is given as in Equation (14).³⁵

$$K_1 t = 2.303 \log \left(\frac{C_\infty}{C_\infty - C_t} \right)$$

Or

$$\log (C_\infty - C_t) = \log C_\infty - \frac{K_1 t}{2.303} \dots\dots\dots(14)$$

Where K_1 is the first order rate constant, C_t and C_∞ represents the concentration at time 't' and at equilibrium. Plot of $\log (C_\infty - C_t)$ against for different filler loading is given in Figure 9.

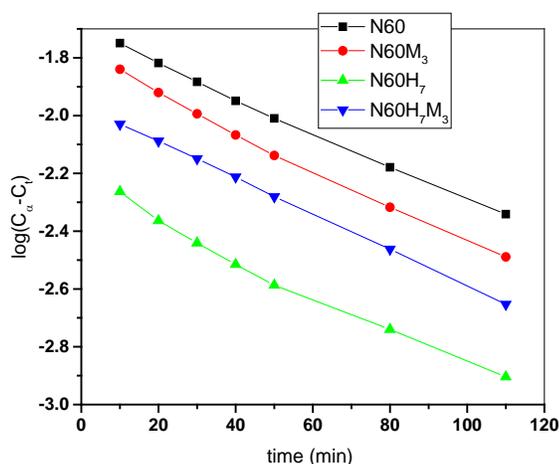


Figure 9. Plot of $\log (C_\infty - C_t)$ versus time for N60 blend nanocomposites in n-hexane

From the slope of the plot, we can calculate the values of 'k' and are given in Table 6. The rate constant represents the speed with which a solvent molecule penetrates the polymer. As the filler loading increases in N60 blend system, the rate of swelling decreases and hence the k values decreases. This is due to increased filler interaction with the matrix. The rate constant values also decrease with increasing penetrant size. In the case of hybrid filler N60 system k value did not show an expected lower value than nanoclay filled system, as the value of k represents the quantitative measure of speed with which polymer uptakes the solvent. Thus synergistic behavior of hybrid filler is not observed in the k values, which was also observed in k values (interaction parameter). But all other results confirm the synergistic behavior of hybrid filler with increase of filler weight ratio showing better interaction of hybrid filler with the polymer matrix.

Table 6. Rate constants of N60 blend nanocomposites in presence of n-hexane as solvent

Sample	Rate constant k x10 ² min ⁻¹
N60	1.57
N60M ₃	1.3
N60H ₇	1.54
N60H ₇ M ₃	1.40

4.8. Comparison with theory

Usually the mode of transport of solvent through polymer matrix were analysed by comparing the experimental results with theoretical models. Here Peppas-Sahlin equation was selected for predicting the diffusion behavior of solvents through NR/EPDM blend nanocomposites. According to Peppas- Sahlin model of diffusion the process of diffusion through the polymer matrix take place by two process, i.e. diffusion into the swollen polymer and matrix relaxation.³⁶

According to Peppas Sahlin

$$M_t/M_\infty = K_f t^m + K_r t^{2m} \dots\dots\dots(15)$$

where M_t/M_∞ is the fraction of solvent released at time t, K_f is the diffusion Fickian contribution coefficient and m is purely Fickian diffusion exponent.

Table 7. Peppas-Sahlin parameters obtained by fitting the Equation 15.

Sample	k_f	k_r	m	R ²
N60	0.00882	-0.00181	0.5006	0.9813
N60H ₃	0.1047	-0.00262	0.4648	0.9860
N60H ₅	0.0749	-0.00133	0.5138	0.9923
N60H ₇	0.1349	-0.0044	0.4243	0.9893
N60M ₃	0.0782	-0.00143	0.5162	0.9850
N60M ₅	0.0775	-0.0014	0.5147	0.9886
N60H ₇ M ₃	0.0846	-0.0016	0.5117	0.9779
N60H ₇ M ₅	0.0687	-0.0011	0.5421	0.9835

When $K_f > K_r$, the release is mainly controlled by diffusion, and when $K_r > K_f$, the diffusion is mostly due to matrix swelling. When $K_f = K_r$, the diffusion is a combination of diffusion and polymer relaxation. Experimental and Peppas-Sahlin model fitting values are plotted in Figure.10. and parameters obtained are given in Table 7. From the figure, it is clear that the peppas-Sahlin model is fitted well for the experimental values, which can be confirmed from values of R², which is the correlation coefficient. This value gives an idea of the extent of the fitting. These results indicate that the diffusion process is regarded as a combination of diffusion into the swollen polymer and the polymer relaxation process. The hybrid filler system shows values of k_f between that of binary blend

nanocomposites. Values of k_f also change with filler addition but not showing a particular trend.

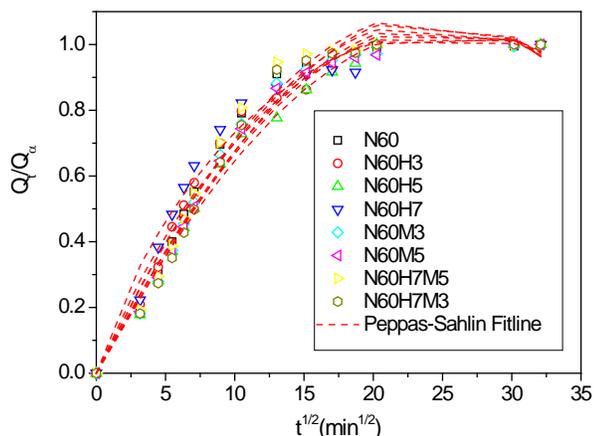


Figure 10. Peppas-Sahlin fitting of diffusion curves

4.9 Dynamic Mechanical Thermal Analysis

Figure 11 shows storage modulus and loss modulus as a function of temperature for unfilled blend, N60M3, N60H7 and N60H7M3 composites. It is clear that N60H7 composite with nanoclay (3phr) addition exhibited higher storage modulus and loss modulus than the neat blend matrix and other nanocomposites.

Here HNT along with nanoclay showed a remarkable synergistic effect in enhancing the storage modulus of NR/EPDM blend. The hybrid architecture developed by the hydrophobic interaction of modifiers of nanofillers with the polymer matrix aided the load transferring through the hybrid nanofiller.^{37,38} It is also seen from the figure that the hybrid nanocomposite showed reduced damping ($\tan\delta_{max}$) in comparison to the unfilled blend matrix and other blend nanocomposites. This indicates a strong interface in the presence of hybrid filler which dissipates a smaller part of deformational energy through the interface. The glass transition temperature (T_g) of all the nanocomposites shifted a little towards lower temperature. Allaoui et. al.,³⁹ showed that the T_g of CNT filled epoxy is lower than that of gum rubber and explained that it may be due to the lower curing rate of rubber. With other polymers like glass-like polymers, liquid-like polymer in the presence of MWCNT showed a decrease in the T_g value.⁴⁰ The decrease in T_g values of the N60 blend nanocomposite might be due to the plasticizing effect of organic surfactants or extra volume that is created by organic surfactants at the polymer filler interface. In all the cases single T_g was observed due to the overlapping of T_g 's of NR and EPDM phases in the blend. Same observation has been reported in several other studies.^{41,42}

The effective polymer/filler interaction leads to the formation of a constrained polymer layer around the filler surface. When the polymer chain is within this constrained length, the mobility of polymer chain is lost. The height of dissipation factor obtained from the dynamic mechanical analysis is useful in calculating the constrained region of polymer chain around the filler surface. $\tan\delta$ peak is reduced due to the reduction in chain mobility by the adsorption of polymer chain segment on the filler surface.

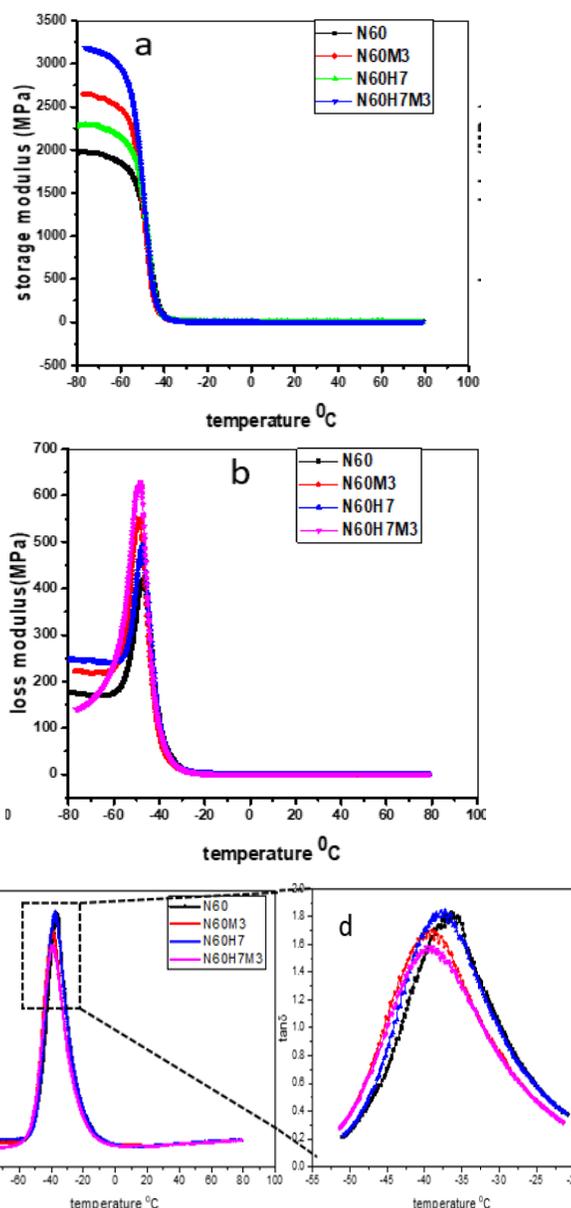


Figure 11. Storage modulus (a), Loss modulus (b) and $\tan\delta$ (c) of NR/EPDM blend nanocomposites. [(d) magnified $\tan\delta$ max curve]

The lower $\tan\delta$ of the N60 blends with hybrid filler showed reduced molecular mobility of the rubber chain in the constrained environment between the fillers. Due to the interaction of hybrid fillers with the matrix, a constrained region of polymer around the hybrid network was formed. This hybrid network arrested the segmental mobility of neighborhood chain.

The restricted mobility of polymer in the filled polymer matrix, is useful in determining the Constrained polymer volume ($Con.$) and this gives an idea about filler-matrix interaction. It can be calculated by using the equation 16.⁴³

$$Con. = \frac{[1-(1-Co)W]}{W0} \dots\dots\dots (16)$$

For rubbery system, Co assumed to be zero, W can be calculated from the plot of $\tan\delta$ using the equation (17 & 18)

$$W = \frac{\pi \tan \delta}{\pi \tan \delta + 1} \dots \dots \dots (17)$$

$$Con = \frac{1-W}{W_0} \dots \dots \dots (18)$$

The estimated constrain region is given in the Table 8

Table 8. Estimated constrain region in N60 blend nanocomposites.

Sample	Constrained region (Con.)
N60	-
N60M ₁	0.176
N60M ₃	0.185
N60M ₅	0.192
N60M ₇	0.190
N60H ₁	0.1821
N60H ₃	0.1831
N60H ₅	0.1792
N60H ₇	0.1761
N60H ₇ M ₃	0.2004

N60/MHNT/OMMT blend nanocomposites showed higher constrained volume. The OMMT occupied at the polymer filler interface lead to the immobilization of polymer chain. The addition of hybrid filler increased the constrained volume of NR phase in 60/40 NR/EPDM blend. This shows that the effective filler-filler networking formed between the hybrid fillers drastically increased the constrained polymer chain. Thus, the strong interaction of the polymer chain with the hybrid nanofillers created cross-links of the matrix.

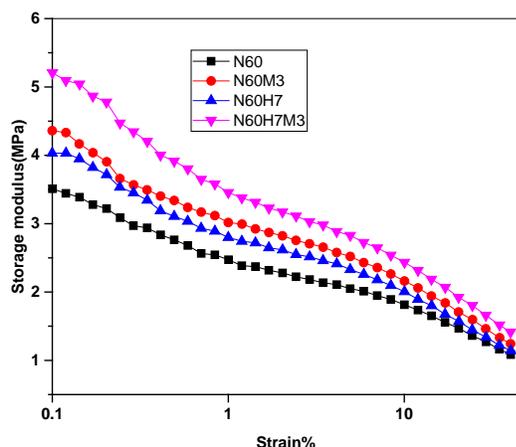


Figure 12. Storage modulus as a function of strain amplitude for unfilled NR/EPDM blend nanocomposites.

The lower Q_∞ value from Figure 5.c is in good agreement with the calculated constrained region in the hybrid nanocomposites. The correlation between Q_∞ and constrained volume shows the function of chain dynamics in the transport behaviour of hybrid nanocomposites.

The dynamic viscoelastic properties of elastomer nanocomposites also depend on the amplitude of strain that have been applied to the material. At low strain filled matrix shows higher storage modulus (E') and as the amplitude of the strain increases, storage modulus (E') decreases. This difference in storage modulus is known as Payne effect ($\Delta G = E' - E''$). Analysis of Payne effect is very useful in understanding the filler network formation in elastomer nanocomposites. The roles of HNT, OMMT and their hybrid HNT/OMMT in N60 blend nanocomposites on filler network formation could be elucidated from variation of storage modulus with amplitude of strain and is given in Figure 12.

Here hybrid nanocomposite exhibited higher $\Delta G'$ than other nanocomposites. In general Payne effect decreases with better filler dispersion. However, subramaniam et.al.⁴⁴ reported tubular nature of filler can increase filler dispersion and prevent nanoclay from aggregation through the network path formed by the hydrophobic interaction formed by the surface modifiers of both fillers in the blend matrix. This filler network formation might increase the Payne effect in dual filled blend nanocomposite.

CONCLUSION

60/40 NR/EPDM blends reinforced with hybrid nanofillers (MHNT-OMMT) have been formulated in a two-roll mill mixing method. The effect of OMMT, MHNT, and hybrid of MHNT-OMMT on the transport behavior of the N60 blend is investigated. The mol% uptake of N60 blend nanocomposites decreased with filler loading. In the case of hybrid filled blend nanocomposites, sorption of solvent is too much reduced showing the synergistic effect of hybrid fillers. An additional local filler networking formed between the fillers reduced the available path for the solvent through the matrix and the formation of this filler network is supported by the increased Payne effect in the presence of hybrid fillers. Cross-link density measurements and TEM analysis supported the above facts. The amount of immobilized polymer segment by the hybrid filler surface has been obtained from dynamic mechanical analysis and found a good correlation between diffusion characteristics and chain dynamics. The swelling coefficients, swelling index, sorption coefficients, diffusion coefficients, and permeation coefficient values were lowered by the incorporation of 7wt% MHNT and 3wt% OMMT to the N60 matrix with the presence of hybrid fillers. The mechanism of transport suggested that transport is anomalous ($n > 0.5$). The deformation of the network during swelling was studied by using the affine and phantom model. It is found that the affine model agrees well with the experimental results rather than the phantom model. Peppas-Sahlin model is used to study the diffusion behavior of blend nanocomposites in the presence of hybrid fillers and find that the model well fitted with the experimental results.

Conflict of Interest: Authors declared no conflict of interest.

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