IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Effect of hybrid fillers on curing characteristics and tensile properties of natural rubber/ethylene propylene diene monomer rubber blends

Manju V Nair[1], Anil Kumar S [2]

[1,2.] *Department of Chemistry, N.S.S. Hindu College, Changanassery, Kerala, PIN 686102, India*

Abstract: The main objective of the present study is to investigate the effect of hybrids of two different nanoclays, silane-modified halloysite nanotube (MHNT) and organically modified nanoclay (OMMT) on vulcanization behavior, and cure kinetics of rubber-based blends of natural rubber (NR) and ethylene propylene diene monomer rubber (EPDM). Vulcanization kinetics were analyzed by a rubber process analyzer under isothermal conditions with different temperatures starting from 140°C to 155°C. Results obtained from rheometric data such as cure time; scorch time was greatly reduced when hybrid fillers were used. To understand the curing reaction in the presence of hybrid filler, an autocatalytic model was applied. NR/EPDM blend filled with hybrid fillers of MHNT/OMMT in the ratio of 7:3 (phr) drastically improved mechanical strength. Morphology analysis by TEM and WAXD supports the intercalation of hybrid fillers in the matrix and also on the filler-filler networking formed between the fillers. Cross-link density measurements were also carried out to understand the rubber filler interaction in the presence of hybrid fillers.

Index Terms - nanocomposites, halloysite nanotube, cure kinetics, autocatalytic model, nanoclay.

I. INTRODUCTION

Studies on the vulcanized natural rubber/ethylene-propylene diene monomer rubber blends(NR/EPDM) attracted researchers' industry field extensively due to its better performance in tire application as well as remarkable enhancement in aging resistance to heat and ozone. But the incompatible nature NR/EPDM blend, due to the polarity difference and viscosity mismatch, exhibited poor mechanical properties.[1-3] In earlier times these incompatible blends were compatibilized by grafting an accelerator to EPDM or using some accelerators which have a higher solubility in the EPDM phase or by two-stage vulcanization or by reactive blending.[4-8] Nowadays nanoparticles such as clays, silica graphene, carbon nanotube, etc. were added to blends so that they can stabilize the interface of the two components in the blend matrix. These blend nanocomposites were prepared by melt mixing, solution mixing, or by using the two-roll mill mixing method. Alipour *et al.*,[9] studied NR/EPDM closite 15A nanocomposites and observed that organoclay act not only as reinforcing fillers but also as accelerators for vulcanizing NR/EPDM blends. Rahmaniar *et al.*,[10] observed that an optimum mixture of pumice and clay could improve the processability and degree of cross-linking formation in NR/EPDM blend matrixes. In another study, the effect of polyethyleneimine (PEI) wrapped graphene nanoplate and untreated graphene nanoplate (GNP) on NR/EPDM blends was investigated.[11] The studies proved that the treated GNP enhanced the filler-matrix interaction, and exhibited excellent mechanical properties compared to untreated GNP-loaded blend nanocomposites and unfilled blend matrix.

Halloysite nanotubes (HNT) is another type of naturally occurring easily available nanofiller and morphologically similar to carbon nanotube (CNT) could be used as a substitute for more expensive CNT. It has the same chemical composition as that of kaolinite, $Al_2Si_2O_5(OH)_4$. nH2O. Because of the tubular morphology, the low density of the hydroxyl functional group on the surface reduces its surface energy and makes it a better reinforcement nanoparticle. A lot of studies have been reported based on HNT/based nanocomposites.[12-16] These studies proved that in the presence of HNT's a significant improvement in thermal, mechanical, and flame retardant properties were observed.

Recently researchers are very much interested in developing hybrid reinforcement in rubber on combination of two types of nanoparticles or of nanoparticle with conventional filler such carbon black and silica. Hybrid fillers have shown to give a synergy reinforcing effect to the rubber properties and at the same time benefits from the individual fillers were retained. Many hybrid systems involve nanofillers such as nanoclay, carbon nanotube, nanographite with nanodimensional carbon black, silicon dioxide etc. [17,18]. Very recently Rooj *et al.*,[19] reported the dispersion of expanded organo-montmorillonite (EOMt) in the presence of multiwalled carbon nanotube (MWCNT) in NR. From the literature review, the addition of two fillers has a synergistic effect on increasing the electrical mechanical, and thermal properties of the polymeric matrix. Thus a judicious selection of hybrid filler material can influence the mechanical, electrical, and thermal properties of the matrix.

Often blends of NR/EPDM are used in outdoor application. EPDM is blended with NR to use in the tire sidewalls to improve resistance to cracking by ozone attack. It has also high tear resistance. The properties of any rubber dependent on the state of cure. The final state and cost of a compound depends on the energy consumed during processing and vulcanization. Therefore, the study of cure kinetics is very useful in the fabrication of a compound.

In the present work we used organically modified nanoclay (OMMT), and surface modified halloysite nanotube (MHNT) by γ-methacryloxypropyltrimethoxy silane (γ-MPS) and hybrid of OMMT (3 phr) and MHNT (7 phr) as fillers in NR/EPDM blends. Samples were prepared by two-roll mill mixing method. The vulcanization behaviour, and cure kinetics of the rubber blend nanocomposites were studied in detail.

2. Experimental part

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 an ethylene content 57%, ethylidiene 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, Bangalore. Halloysite nanotube was also purchased from Sigma Aldrich Bangalore. The typical surface area of this halloysite was 64 m^2/g, pore volume of 1.26-1.34 mL/g, refractive index 1.54 and specific gravity 2.53 g/cm^3. The surface modification of the halloysite nanotubes were done using γ-methacryloxypropyltrimethoxy silane supplied by Sigma Aldrich. The solvents and other reagents of laboratory grade were used for this study.

2.2. Preparation of nanocomposites

Blends of NR and EPDM (NR/EPDM) were prepared in a laboratory two-roll mixing mill as per ASTM designations D 3182-89. Firstly, NR is masticated for 10 minutes followed by EPDM and both are masticated together for next 10 minutes. After this curing and reinforcing agents in the order ZnO, stearic acid, accelerators, fillers and sulphur were added. In the preparation of the blend with hybrid fillers, filler in the specified ratio mixed together manually and then added. Total time of 30 minutes and roll temperature were kept constant throughout the study. The compounded sample were vulcanized in an electrically heated hydraulic press at 150^0C and at a pressure of 120kg/cm^2, till the cure time is reached. After this the sample is kept for 24hrs at room temperature and then used for further studies. The various nanocomposites such as NR/EPDM/organically modified nanoclay, NR/EPDM/modified halloysite nanotube and NR/EPDM/modified halloysite nanotube/organically modified nanoclay hybrid were prepared as per the formulation given in the Table1.

Table 1. Formulation of NR/EPDM blend nanocomposite

Materials (phr)*	N60	N60H7	N60M3	N60H1M3	N60H3M3	N60H5M3	N60H7M3
NR	60	60	60	60	60	60	60
EPDM	40	40	40	40	40	40	40
Silane Modified Halloysite nanotube	0	7	0	1	3	5	7
Modified Nanoclay	0	0	3	3	3	3	3
ZnO	5	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2	2
MBTS	0.2	0.2	0.2	0.2	0.2	0.2	0.2
CBS	1.5	1.5	1.2	1.2	1.2	1.2	1.2
Sulphur	2	2	2	2	2	2	2

* parts per hundred

2.3. Characterizations Techniques

2.3.1. Vulcanization studies

Oscillating Disc Rheometer of alpha technologies was used for determining cure characteristics of NR/EPDM blend nanocomposites at 140, 145, 150 and 155°C as stated in ASTM D 5289-93a standard. From the cure profile, cure rate index and the vulcanization kinetics was analyzed.

2.3.2 Cross-link density measurement by swelling studies.

The cross-link density the vulcanized sample was determined by swelling method. For this the samples were cut into circular shape and immersed in toluene for 72 hrs. at room temperature. The deswollen weight of the sample after drying in air for about another 72 hours. Flory - Rhener equation can be used to calculate the cross link density(ν) of the samples and it is given as equation (1) **.**

$$\vartheta = \frac{\ln[1-V_{rf}]+V_{rf}+\chi V_{rf}2}{-2\rho_r V_s V_{rf}1/3} \text{……. (1)}$$

Where ρ_r is the density of rubber ,V_s is the molar volume of the solvent, χ is the interaction parameter and V_{rf} is the volume fraction of the rubber in the swollen material.

The molecular mass between the cross links, M_c can be calculated by using the equation (2)

Cross link density $v_c = \frac{1}{2M_c}$ ……(2)

2.3.3. Transmission Electron Microscopy

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.

2.3.4 X-ray Diffraction Analysis (WAXD)

The XRD of the clay nano composites were done by using Wide Angle X-ray Scattering (WAXS). WAXS measurements were carried out on XEUSS WAXS system using a Genix micro source from Xenocs operated at 50 kV and 0.6 mA. The Cu Kα radiation (λ = 1.54 Å) was collimated with FOX2D mirror and two pairs of scatter less slits from Xenocs. The 2D-patterns were recorded on a Mar345 image plate and processed using Fit2D software. All the measurements were made in the transmission mode.

2.3.5. Tensile properties

Samples for tensile test were punched out from sheets and tests were carried out as per ASTM D412 on a instron universal testing machine at a cross head speed of 500 mm/min.

3. Results and discussion

3.1. Cure Characteristics

The cure profile given in Fig.1 illustrate the effect of hybrid filler on vulcanization behavior of N60 blend nanocomposites and the various curing parameter obtained are shown in the Table. 2

Table 2. Cure parameters obtained from cure curve of N60 blend in the presence of hybrid fillers

Sample	T_{90}(min)	Ts2 (min)	M_H (dNm)	M_L (dNm)	M_H-M_L(ΔM)	CRI=100/T_{90}-T_S2(s^{-1})
N60	8.95	4.16	9.04	0.23	8.81	20.87
N60M3	5.90	2.07	9.59	0.31	9.28	26.10
N60H7	7.84	4.50	9.06	0.22	8.84	29.94
N60H1M3	5.73	2.78	8.87	0.19	8.68	33.89
N60H3M3	4.93	2.21	9.53	0.20	9.33	36.90
N60H5M3	4.87	1.98	9.60	0.25	9.35	34.60
N60H7M3	4.76	1.84	10.65	0.26	10.39	34.24

All the samples showed reduced cure time (T_{90}) compared to pristine N60.

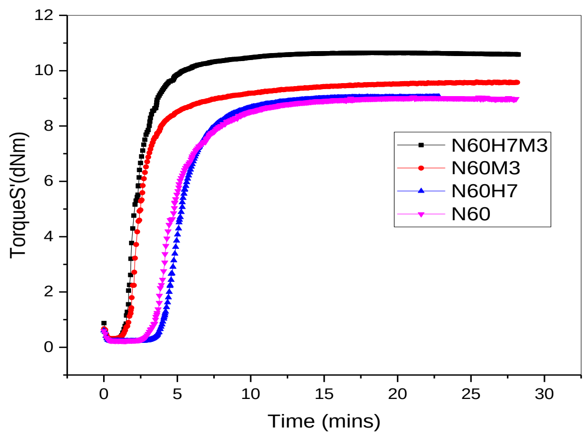

Figure 1. Cure curves of N60 blends in the presence of different fillers at 150°C.

MHNT filled matrix showed reduced vulcanization rate as indicated by cure time compared to OMMT filled matrix. In the presence of hybrid fillers T_{90} falls down and showed the lowest value when compared to N60 blend nanocomposites filled with single fillers.

During melt mixing, the shear stress produced breaks the nanotube. This reduces the aspect ratio, and render the vulcanization process at lower loading of MHNT. But as the loading of MHNT increases, more sulphurating agents are produced. This helped in forming cross-links with the rubber matrix[20]. In the presence of hybrid fillers T_{90} falls down and showed the lowest value when compared to N60 blend nanocomposites filled with single fillers. In addition to this, the addition of OMMT to MHNT filled matrix increases the dispersion of both fillers. These clay layers occupy between nanotubes and forms a local network between the surface modifiers of two nanoclays.

On adding OMMT to MHNT filled N60 matrix, the scorch time is significantly reduced due to the formation of the OMMT-MHNT bridge facilitating the vulcanization process. Like T_{90} values, the lowest scorch time is shown by the N60 matrix filled with MHNT and OMMT in the ratio of 7:3 (phr). Thus the addition of OMMT to N60MH7 reduced T_{90} and Ts2 values of the blend nanocomposites to a greater extent. Vulcanization characteristics reveal that the mixture of fillers can highly influence the curing behavior of the N60 matrix. It can be seen that the addition of MHNT has little influence on the torque value of the matrix and it is found very close to the unfilled matrix. The penetration of polymer chain and curatives into the lumen of halloysite nanotube and also the adsorption of curatives on the surface modifier of halloysite nanotube significantly reduced the curing behaviour of N60 /MHNT blend nanocomposites. On the other hand, in presence of OMMT, due to its better reinforcement with the matrix torque of the matrix increases.

With the addition of hybrid filler, due to the increased intercalation of both fillers in the matrix the polymer-filler interaction increased. The increase in torque difference (ΔM), which is the measure of cross-link density also increase in the presence of hybrid fillers. In the presence of hybrid fillers, both fillers help dispersion one another and increase the interaction with the matrix. An increase in ΔM values also supports the above fact that both matrix phases are equally cured and hence the value increased. The network formation between two nanoclays restricted chain mobility and increased the stiffness of the material. The higher ΔM value in the presence of hybrid filler supports the formation of more cross-links in the matrix. The cross-link formed in the presence of hybrid filler sensibly increased torque and this effect on cross-linking density will be discussed later in swelling measurement studies. Thus the combination of MHNT/OMMT increased the torque and vulcanizates get more reinforced. Synergic effect of hybrid fillers on vulcanization behaviour of NR /EPDM blend nanocomposite is observed here.

The cure rate index ($CRI=100/T_{90}-T_S2$), represents the rate of cure of blend nanocomposites. Here irrespective of the nature of fillers, CRI increased compared to the unfilled blend matrix. With the addition of OMMT to N60/MHNT nanocomposites, CRI get increased, but at highly loaded matrix due to the increase in viscosity, vulcanization rate is reduced.

3.3. Vulcanization kinetics

A series of mathematical expression was used for analyzing the nature of curing reaction. Here autocatalytic model[21] showed good agreement with the experimental results because the systems have reaction rate which is maximum at t > 0. In autocatalytic model maximum rate of reaction occurs at any point other than t= 0.

The model for autocatalytic reaction equation is given as below, in equation (3).

$$\frac{d\alpha}{dt} = K(T)\,(1-\alpha)^{n}\,\alpha^{m} \quad \text{....... (3)}$$

α the degree of cross-linking for cure meter study is given as in equation (4),

$$\alpha = \frac{Mt-M0}{Mh-M0} \quad \text{........(4)}$$

Where n' and m are reaction order constant, K(T) specific rate constant at T,

In autocatalytic model the rate of reaction increases as rate of conversion increases and passes through a maximum. Fig.2 shows the plot of rate of conversion ($\frac{d\alpha}{dt}$) versus the degree of conversion (α) of N60 blend nanocomposites and fitting curve for the autocatalytic model is given in the Fig.3

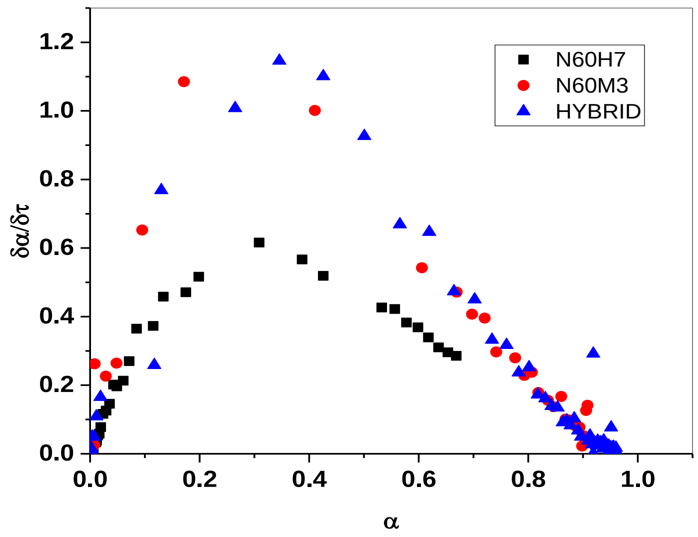

Figure 2. Comparison of reaction rate versus conversion of N60 blend with hybrid filler and single filler.

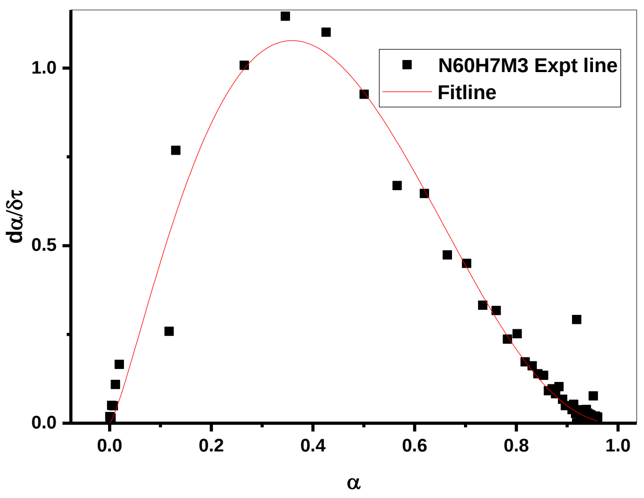

Figure 3. Fitting curve of autocatalytic model of N60 blends in the presence of hybrid filler (N60H7M3) [solid line indicating fitting line].

It is observed that the K value increases with the increase of temperature and with the addition of fillers it also increases. With the increase of temperature, viscosity decreases and more cross-links are formed between the polymer chains. But the addition of MHNT to N60 matrix, K value gets reduced than the gum sample. A lot of works in literature are available which explaining the reduction of K value with the addition of fillers[22].

The highest value of K is observed in the hybrid filled system, especially at higher temperature. This indicates that the influence of hybrid filler on curing reaction is more pronounced at higher temperature than at lower temperature. This may be due to the increased rubber-filler interaction and also due to the filler network formation. The fractional values of *m* and *n* indicate that the vulcanization process is not happening in a single step, but by various reaction steps which can occur simultaneously[23]

From the Table 3, it can be seen that *n* values are found to be higher than *m* values showing the dependency of vulcanization reaction on initial reactants of the compound[24]. *m* and *n* values increase with temperature in all the systems while at 155°C these values decrease.

Table 3. Kinetic parameters of N60 blends in presence of OMMT, MHNT and their hybrid

Sample	Temperature (℃)	K	m	n
N60	140	2.2860	0.5506	2.1725
	145	2.9460	0.7608	2.2313
	150	3.1973	1.0298	2.5107
	155	5.9082	0.5188	2.1647
N60M3	140	2.3180	0.7658	1.8214
	145	4.1790	0.8654	2.2800
	150	4.8797	1.176	2.2448
	155	6.8103	0.9028	2.0490
N60H7	140	2.1736	0.9100	1.8780
	145	2.7419	1.0300	2.6449
	150	4.4090	1.0100	2.6949
	155	4.0118	0.9600	2.0972
N60H7M3	140	2.5498	0.8330	1.4778
	145	2.8058	0.8744	2.3130
	150	7.6383	1.2589	2.7460
	155	11.1743	1.2861	2.2861

The activation energy *(Ea)* of the curing reaction was determined from the plot of ln k versus 1/T as shown in the Fig.4. The value of the activation energy is obtained from the Arrhenius plot is given in the Table 4. The presence of nanofillers significantly reduces activation energy for curing, especially in the presence of hybrid fillers.

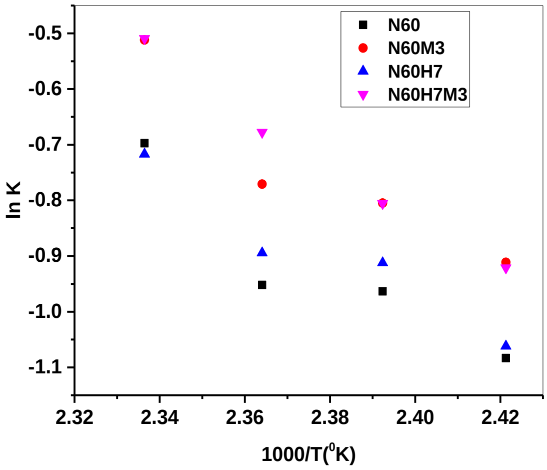

Figure 4. Arrhenius plot of N60 blends in presence of nanofillers and hybrid filler

All the filled samples had lower *Ea* than the neat blend matrix. The lowest value obtained for N60 blend with hybrid filler confirms that the presence of double phase filler increases the rate of the cure reaction.

Table 4. Value of activation energy of N60 blend nanocomposites

Sample	Activation Energy (Ea) KJ/mol
N60	92.014
N60H7	60.503
N60M3	46.049
N60H7M3	39.731

When MHNT alone used, due to the adsorption of curatives on the tubular surface delays the curing behavior, but the addition of nanoclay enhances the interaction between both fillers and occupies in between the tubes making more intercalated morphology and increases the rate of cure. Hence activation energy is reduced too much in presence of hybrid fillers.

3.2 Cross –link density measurement

The effectiveness in cross-linking in N60 blend nanocomposites were investigated by swelling measurements. From the Fig.5, it can be observed that the swelling % of NR/EPDM blend nanocomposites were reduced with filler loading irrespective of the nature of filler. The maximum reduction in swelling % was observed with hybrid filler. The presence of hybrid filler caused more cross –links and it forms networks in the blend nanocomposites. This created more tortous path for the solvent to diffuse through the blend matrix. The increase in cross-links reduced the solvent uptake.

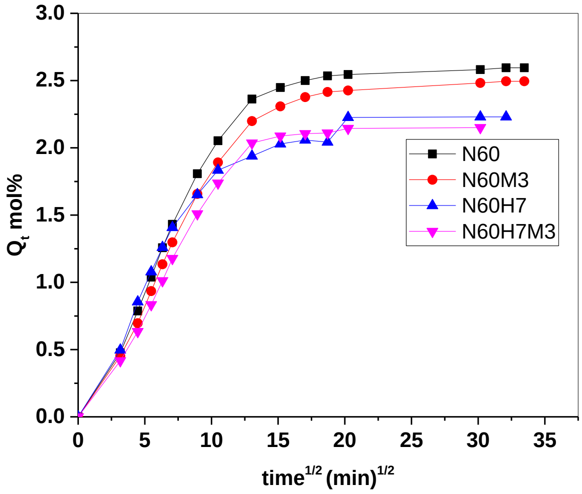

Figure 5. Swelling % of NR/EPDM blend nanocomposites

The cross-link density and molecular mass between the cross-links were calculated using Flory Rhener equation and given in Table 5. This values are in agreement with the ΔM (torque difference) values obtained from cure studies.

Table 5. Values of molecular mass and cross-link density of NR/EPDM blend nanocomposites

Sample	**M_c(Exp) g/cm^{-3}**	**Cross link density (ν_cx10^{-4}) mol/cc^{-1}**
N60	1253.86	3.99
N60M_3	1109.70	4.50
N60H_3	1124.42	4.40
N60H_5	1125.30	4.44
N60H_7	1112.24	4.50
N60H_7M_3	746.94	6.90

3.3 Morphology of hybrid nanocomposites

The dispersion of organically treated fillers in the blend matrix can be well understood from the transmission electron micrograph. Fig. 6.

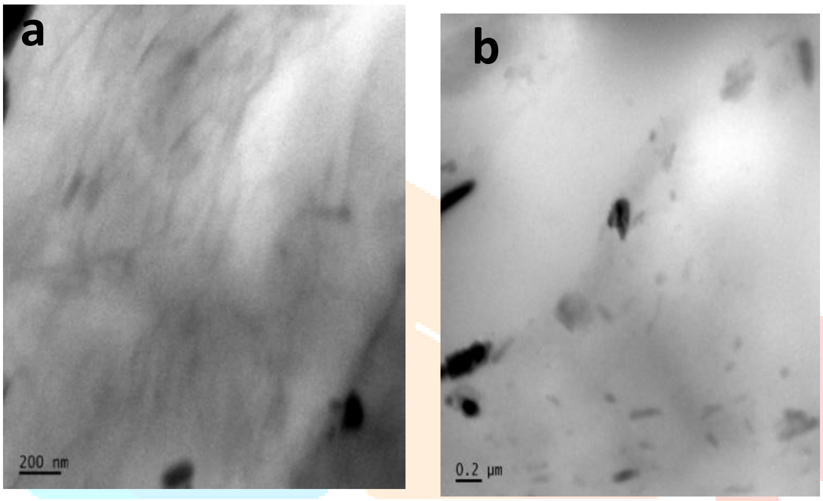

Figure 6. Transmission electron micrograph of 60/40 NR/EPDM blend in presence of (a) 3 phr OMMT (b) 7 phr MHNT.

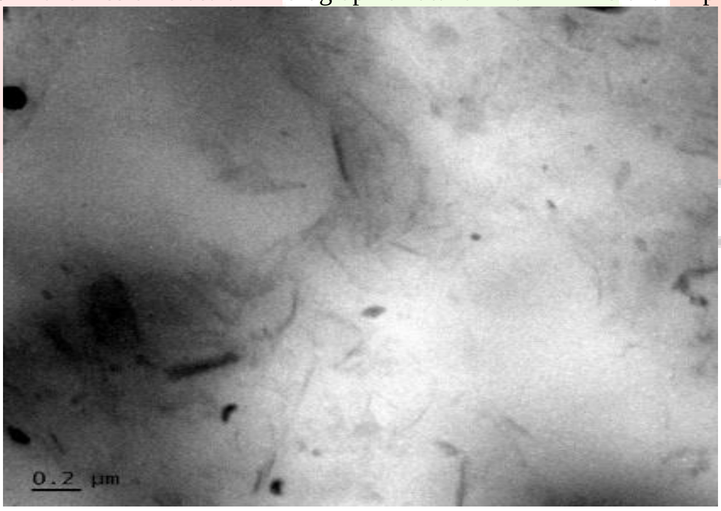

Figure 7. Transmission electron micrograph of 60/40 NR/EPDM blends in presence of MHNT:OMMT (7:3 wt%) [N60H7M3]

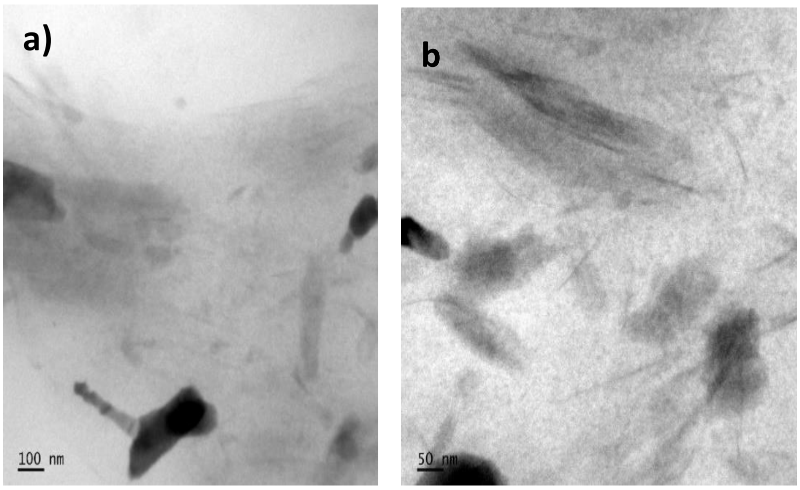

Figure 8. Transmission electron micrograph of N60H7M3 in different magnifications

The dispersion of the halloysite nanotubes and nanoclays are visible in the TEM micrographs. In the case of a hybrid filled matrix, it can be seen that MHNT fillers occur between OMMT layers as given in Fig.7 and magnified image is given in Fig.8. Thus effective networking is formed between the fillers. As pointed out by Josmin *et al.*,[25] both fillers are organically modified at the surface and the interaction between the modifiers on the surface of two fillers takes part in network formation. Interestingly, the filler localization is more concentrated in the NR matrix and interface and this is quite visible in the Fig.1. 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 the 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 a diverse feature-rich matrix. The high-resolution TEM images indicated that the dispersion of both the HNTs and nanoclay in an intercalated manner. 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. 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 effectively, i.e. there was an optimal weight ratio between hybridizing fillers as reported by Leung *et al.*[26].

3.1.1 X-ray diffraction analysis

The Fig.9 compares the XRD spectra of OMMT and MHNT with 60/40 NR/EPDM blends containing 3 phr OMMT, 7 phr MHNT and their hybrid. OMMT showed a diffraction peak at $2\theta=3.36^0$ and basal spacing d_{001} calculated according to Braggs Law is 2.62 nm. In the case of 3 phr OMMT filled nanocomposites, a diffraction peak was seen at $2\theta=2.02^0$ having a basal spacing of 4.36 nm. This shows that intercalated morphology was achieved by blends in the presence of OMMT.

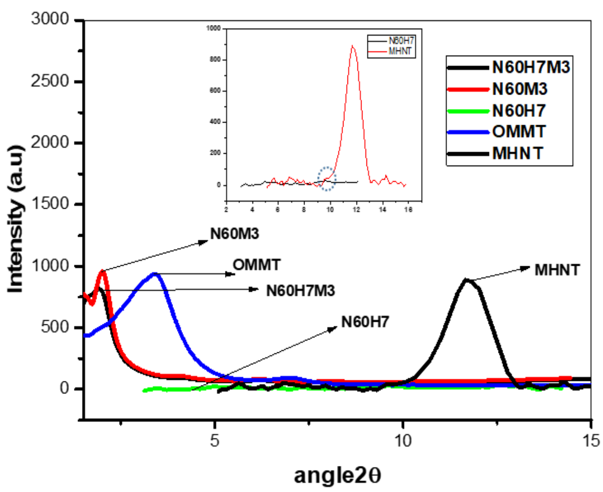

Figure 9. WAXD pattern of N60 blends filled with conventional and hybrid fillers

The modified halloysite nanotube (MHNT) shows a diffraction peak at $2\theta =11.67^0$ which corresponds to the basal spacing (d_{001}) of 0.757nm. Addition of 7 phr MHNT to N60 matrix a small peak is obtained at $2\theta=9.63^0$ with basal spacing of 0.927 nm. The spectra of hybrid filled nanocomposites shows two distinct peaks at $2\theta=1.92^0$ and 6.34^0 which corresponds to 4.5 nm and 1.39 nm distance of basal spacing, respectively. In the hybrid filled nanocomposites, clay layers get more intercalated compared to the blend nanocomposites filled only with OMMT. Thus from WAXD and TEM analysis, it can be observed that in the presence of MHNT, clay layers can be well intercalated at lower loading.

3.4. Mechanical Properties

The study of mechanical properties is very useful in establishing the reinforcing ability of nanofillers with the polymer matrix. The improvement of the physico-mechanical property of polymer matrix depends upon the strong interaction between the matrix and filler, nature of modifier, and also the size, geometry, and morphology of the filler. Literature survey supports the above fact of improvement of physico-mechanical properties of rubber nanocomposites.[27,28] In the case of hybrid filled N60 blend, the Stress-strain behaviour of N60 blend is shown in the Fig.10.

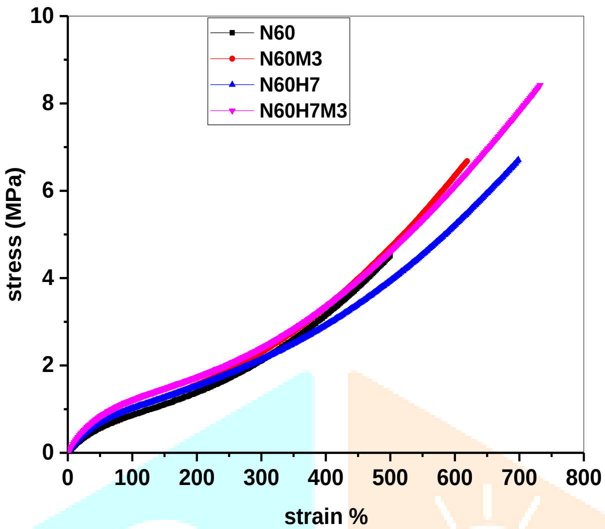

Figure 10. Stress-strain curve of N60 blends in presence of hybrid fillers

The improved performance of nanocomposites in terms of tensile strength is due to the improved interaction between NR/EPDM-OMMT-MHNT. The high aspect ratio and large surface area of HNT make strong and a little chemical interaction between OMMT and MHNT favours the formation of cross-links. Here OMMT and MHNT form a local hybrid filler network that confines the rubber chains making a more entangled structure. This is responsible for the higher performance of hybrid nanocomposites. Similar network formation was also observed in NR/CB/organoclay hybrid nanocomposites.[29] N60 with hybrid filler in the ratio (7 phr MHNT, 3 phr OMMT) increases tensile strength to 76% compared to the unfilled system and 53% (7 phr MHNT) and 18% (3 phr OMMT) compared to those containing conventional fillers. Besides the interaction, both fillers are well dispersed in the matrix.

Both of these fillers are surface modified to make hydrophobic in nature. These surface modifiers make an additional van der Waals force of attraction and increases the compatibility with the matrix. This type of interaction with the interface restricts the deformation of polymer and increases the tensile strength. The presence of OMMT in MHNT increases the interfacial interaction due to the difference in morphology of two fillers. Additional filler- filler networking due to surface interaction of two fillers increase constrained polymer phase. This synergistic interaction results in a unique structural development increases the tensile strength. The increment in tensile strength of N60 blend in presence of hybrid filler is given in Fig.11.

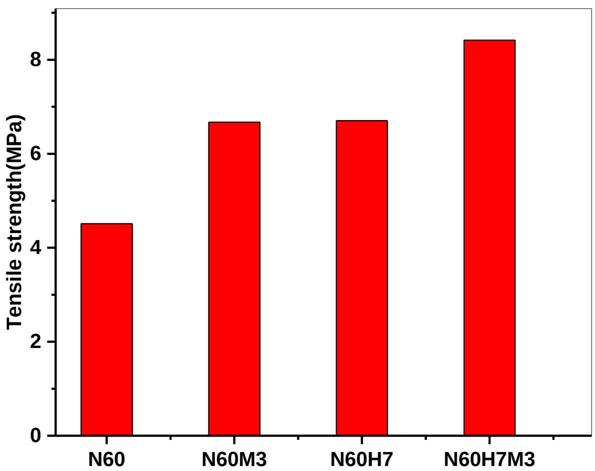

Figure 11. Tensile strength of N60 blend in presence of hybrid fillers.

100% and 300% modulus of hybrid nanocomposites is also higher than the matrix that filed with conventional fillers. This increase in modulus value is due to the strong NR/EPDM-OMMT-MHNT interfacial interaction and also due to the formation of highly intercalated structure. Modulus of the matrix depends upon the stiffness and also on its interaction with the filler. The variation of modulus of N60 blend in presence of hybrid filler is shown in Fig.12.

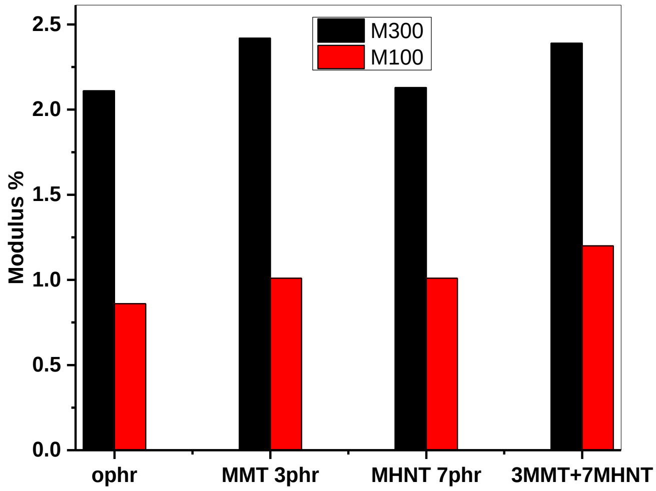

Figure 12. Variation of modulus of N60 blend in the presence of hybrid fillers

When fillers are added to the matrix reinforcement increases due to the immobilization of polymeric chain. With the addition of hybrid nanofiller to the matrix immobilization occurs due to

1. locking in of the polymer chain within filler network.
2. formation of constrained polymer chain with the filler network.

This immobilized polymer chain increases the stiffness of the matrix. It increases the modulus, which makes the matrix effective for stress transformation during mechanical deformation. Both the fillers are organically modified and have strong interaction with the NR phase and also these fillers act as a compatibilizer for the NR/EPDM matrix. Most of the clay occurs at the interface reduces the interfacial tension increases the compatibility between NR/EPDM. It is also stated by Yu *et al.*, [30] that mixing of two materials with different shapes may enhance the reinforcement effect of the composites because of the synergistic effect of hybrid fillers. In the case of MHNT filled N60 blend, lower concentration of the filler is not effective for stress transfer and shows higher modulus of elongation only at 7 phr loading. But on adding 3 phr OMMT to the same matrix immobilize a significant amount of polymer chain and increases the modulus. On the other hand, with the addition of 5 phr OMMT to the MHNT filled matrix, an agglomerated morphology is developed. Owing to the progressive filler networking with increasing filler content, a decrease in reinforcing efficiency is found when the rubber is highly filled. At lower loading of nanoclay, the well-dispersed nanostructure can reinforce the neighbouring rubber chain effectively at the interface, and increment in tensile strength occurs.

4. Conclusion

The effect of hybrid fillers on curing characteristics, curing kinetics, and morphology of 60/40 NR/EPDM blends were examined. Considerable improvement in curing rate is observed in the case of N60 blend with the use of MHNT/OMMT hybrid fillers. This is due to the increased polymer–filler interaction and well dispersion of both fillers in the matrix. Analysis of curing kinetics showed that all the systems followed the autocatalytic model. Activation energy calculated from the Arrhenius plot was found to be lower for N60 blend filled with hybrid filler again confirms that the presence of dual-phase filler increases the rate of cure reaction 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 effectively. N60 blend samples containing a combination of MHNT and OMMT showed better mechanical properties. Addition of 3 phr OMMT to N60 blend containing 7 phr MHNT showed increased tensile strength of 7.97 MPa and 100% modulus of 1.76. This value is about 19% and 74% compared to 7 phr filled MHNT. This suggests a synergistic effect between MHNT and OMMT. The filler network formation and proper dispersion of both nanofillers in the matrix especially in the NR phase and at the interphase of the polymeric blend made immobilized polymeric phase in the vicinity of nanomaterials. This filler networking trapped the polymer chain and acting as an effective center for stress transfer to the filler phase.

5. Reference

[1] P. Sae-oui, C. Sirisinha, U. Thepsuwan and P. Thapthong, Influence of accelerator type on properties of NR/EPDM blends. *Polymer Testing*, **2007**, 26(8), 1062–1067. https://doi.org/10.1016/j.polymertesting.2007.07.004.

[2] N.Z. Noriman, H. Ismail and A.A. Rashid. Characterization of styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBR) blends: The effects of epoxidized natural rubber (ENR-50) as a compatibilizer. *Polymer Testing*, **2010**, 29(2), 200-208. https://doi.org/10.1016/j.polymertesting.2009.11.002

[3] S.H. Botros and A.M. El Sayed. Swelling behavior of NR/EPDM rubber blends under compression strain. *Journal of Applied Polymer Science*, **2001**, 82 (12), 3052-3057. DOI:10.1002/app.2160

[4] A.S. Sirqueira and B.G. Soares. The effect of mercapto-and thioacetate-modified EPDM on the curing parameters and mechanical properties of natural rubber / EPDM blends. *European Polymer Journal*, **2003**, 39 (12),2283-2290.

[5] M.J. Azizli, M. Barghamadi, K. Rezacepatrt, M. Mokhtary and S. Parham. Compatibility, mechanical and rheological properties of hybrid rubber NR/EPDM-g-MA/EPDM/graphene oxide nanocomposites: Theoretical and experimental analyses, *Composite Communications*, **2020**, 22, 100442. https://doi.org/10.1016/j.coco.2020.100442

[6] S. Chattopadhyay. Compatibility studies on solution of polymer blends by viscometric and phase-separation technique *Journal of Applied Polymer Science*, **2000**, 77(4), 880-889. DOI:10.1002/(SICI)1097-4628(20000725)77:4<880::AID-APP23>3.0.CO;2-3

[7] N. Suma, R. Joseph and E. George. Improved Mechanical Properties of NR/EPDM and NR/Butyl Blends by Precuring EPDM and Butyl. *Journal of Applied Polymer Science*, **1993**, 49, 549-557.

[8] K. Sahakaro, N. Naskar, R.N. Datta and J.W.M. Noordermer. Blending of NR/BR/EPDM by reactive processing for tire sidewall applications. I. Preparation, cure characteristics and mechanical properties. *Journal of Applied Polymer Science*, **2007**, 103(4), 2358-2546.

[9] A. Alipour, G. Naderi, G.R. Bakhshandeh, H. Vali and S. Shoochi. Elastomer Nanocomposites Based on NR/EPDM/Organoclay: Morphology and Properties. International Polymer Processing, Journal of the Polymer Processing Society XXVI(1):48. **2011**. DOI:10.3139/217.2381

[10] Rahmaniar, T. Susanto, H.A. Prasetya, P. Marlina, M. Purbaya, M. Chalid and A. Hasan. The effect of pumice and clay composition in natural rubber-ethylene propylene diene monomer blends towards its curing characteristics and physic-mechanical properties. *IOP Conf. Ser.: Mater. Sci. Eng.* 980**, 2020**, 012003. doi:10.1088/1757-899X/980/1/012003.

[11] J. A. Razak, N. Mohamad, H. E. Ab Moulod, K.T. Lay, R.F Munawar, M.E. Abd Manaf, S. Ismail and M.A. Mahamood. Characterization on Thermal And Mechanical Properties of Non-Covalent Polyethyleneimine Wrapped on Graphene Nanoplatelets Within NR/EPDM Rubber Blend Nanocomposites. *Journal of Advanced Manufacturing Technology, Special issue ((TMAC) symposium*, **2017**. Vol 11, 1(1)

[12] D. Pedrazzoli, A. Pegoretti, R. Thomann, J. Kristóf, J. Karger-Kocsis. Toughening linear low-density polyethylene with halloysite nanotubes. *Polymer Composites*, **2015**, 36 (5), 869–883.

[13] N. Ning, Q. Yin, F. Luo, Q. Zhang, R. Du and Q. Fu. Crystallization behavior and mechanical properties of polypropylene/ halloysite composites. *Polymer*, **2007**, 48, 7374-7384.

[14] M. Liu, B. Guo, M. Du, Y. Lei and D. Jia. Natural inorganic nanotubes reinforced epoxy resin nanocomposites. Journal of Polymer Research, **2007**, 15(3), 205–212. DOI:10.1007/s10965-007-9160-4

[15] Przemysław Rybiński, Grażyna Janowska, Małgorzata Jóźwiak , Agnieszka Pająk. Thermal stability and flammability of butadiene–styrene rubber nanocomposites, *Journal of Thermal Analysis and Calorimetry*, **2012**, 109, 561–571. DOI 10.1007/s10973-012-2498-9

[16] Mingliang Du, Baochun Guo, Yanda Lei, Mingxian Liu, Demin Jia. Carboxylated butadiene–styrene rubber/halloysite nanotube nanocomposites: Interfacial interaction and performance, *Polymer*, **2008**, 49 (22), 4871–4876.

[17] S. Rooj, A. Das, A. K.W. Stöckelhuber, S. Wießner, D. Fischer, U. Reuter and G. Heinrich, "Expanded organoclay' assisted dispersion and simultaneous structural alterations of multiwall carbon nanotube (MWCNT) clusters in natural rubber." *Composites Science and Technology*, **2015**, 107, 36-43. https://doi.org/10.1016/j.compscitech.2014.11.018.

[18] P. Pasbakhsh, H. Ismail, M.N.A. Fauzi and A.A. Bakar, "EPDM/modified halloysite nanocomposites," *Applied Clay Science*, **2010**, 48(3), 405-413. https://doi.org/10.1016/j.clay.2010.01.015.

[19] S. Rooj, A. Das**,** V. Thakur, R.N. Mahaling, A.K. Bhowmick and G. Heinrich, **"**Preparation and properties of natural nanocomposites based on natural rubber and naturally occurring halloysite nanotubes," *Mater**ls** & Design*, **2010,** 31(4), 2151–2156. https://doi.org/10.1016/j.matdes.2009.11.009.

[20] V. Vijayalekshmi, "Studies on Natural Rubber/Clay Nanocomposites: Effect of Maleic Anhydride Grafting of Rubber," PhD Thesis, Cochin University of Science and Technology, August **2009**

[21] D.W. Green and R.H. Perry, "*Perry's chemical engineers' handbook*," 8th edn. McGraw-Hill, USA, 2007.

[22]. A. Coran, "Vulcanization. Part VII. Kinetics of Sulfur Vulcanization of Natural Rubber in Presence of Delayed-Action Accelerators," *Rubber Chemistry and Technology*, **1965**, 38 (1), 1-14. https://doi.org/10.5254/1.3535628

[23] Carmen Albano, Marianella Herna`ndez, Miren N Ichazo, Jeanette Gonza`lez and Wilmer DeSousa, "Characterization of NBR/bentonite composites: vulcanization kinetics and rheometric and mechanical properties," Polymer *Bulletin*, **2011**, 67, 653-667. https://doi.org/10.1007/s00289-010-0432-5.

[24]. Jiji Abraham, Ajesh K Zacharia, Soney C George and Sabu Thomas, "Cure characteristics of nanocomposites containing imidazolium ionic liquid modified carbon nanotubes and styrene butadiene rubber," Material *Science & Engineering International Journal*, **2018**, 2(6), 217-219.

[25] Josmin P. Jose and S. Thomas, "Alumina–clay nanoscale hybrid filler assembling in cross-linked polyethylene based nanocomposites: mechanics and thermal properties," Physical *Chemistry Chemical Physics*, **2014**, 16(28), 14730-14740. DOI: 10.1039/c4cp01532k

[26] S.N. Leung, M.O. Khan, E. Chan, H.E. Naguib, F. Dawson, V. Adinkrah and L. Hayward, "Synergistic effects of hybrid fillers on the development of thermally conductive polyphenylene sulfide composites," *Journal of Applied Polymer Science*, **2013**, 127 (5), 3293-3301. https://doi.org/10.1002/app.37941.

[27] M. Kalaee, S. Akhlaghi, A. Nouri, S. Mazinani, M. Mortezaei, M. Afshari, D. Mostafanezhad, A. Allahbakhsh, H.A. Dehaghi, A. Amirsadri and D.P. Gohari, "Effect of Nano-Sized Calcium Carbonate on Cure Kinetics and Properties of Polyester/Epoxy Blend Powder Coatings," *Progress in Organic Coatings*, **2011**, 71(2), 173-180. https://doi.org/10.1016/j.porgcoat.2011.02.006.

[28] H**.** Ismail, P. Pasbakhsh, M.N. Ahmad Fauzi and A. Abu **B**akar, " The Effect of Halloysite Nanotubes as a Novel Nanofiller on Curing Behaviour, Mechanical and Microstructural Properties of Ethylene Propylene Diene Monomer (EPDM) Nanocomposites," *Polymer-Plastics Technology and Engineering*, **2009**, 48(3), 313-323. https://doi.org/10.1080/03602550802675736**.**

[29] K. Ravikumar, K. Palanivelu, K. Ravichandran, "Vulcanization, Mechanical and Dielectric properties of Carbon black/nanoclay reinforced Natural Rubber hybrid composite," *Applied Mechanics and Materials*, **2015**, 766-767, 377-382.

[30] T. Yu, J. Lin, J. Xu, T Chen, S. Lin and X. Tian, "Novel polyacrylonitrile/Na-MMT/silica nanocomposite: Co-incorporation of two different form nano materials into polymer matrix," *Composite Science and Technology*, **2007**, 67, (15-16), 3219-3225. https://doi.org/10.1016/j.compscitech.2007.04.004.

6. ACKNOWLEDGMENT

I am extremely thankful to Prof. Dr. Sabu Thomas, School of Chemical Sciences, (Founder Director, IIUCNN) Mahatma Gandhi University, Kottayam, for his noble and motivational guidance, constructive feedback, kind support, advice with full encouragement and enthusiasm. Dr. Sabu Thomas is the true definition of a researcher and the ultimate role model for all science students. This research work would not have been possible without his support and inspiration, I am fortunate to have been a part of the Chemical science group from my M.Phil research project onwards.

.