# STUDY OF NANOCOMPOSITES WITH EMPHASIS TO HALLOYSITE NANOTUBES

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**Abstract.** The progress in field of nanocomposites formation is varied and covers different areas. Nanocomposites can be made from nanomaterials with an intention to enhance physical, thermal and other unique properties. Concomitant formed nanocomposites have properties that are superior to conventional micro scale composites and can be synthesized employing simple and inexpensive techniques. The addition of small amounts of nanomaterials in polymers have been able to alter new properties of the composite material, but results are highly dependent on the surface treatment of the nanomaterials and processing applications. It is important to determine whether nanomaterials could be integrated into nanocomposites to modify multiple desirable properties as required for a given nanocomposites. Mineral clays because of their exceptional properties have been used for nanocomposites. Materials variables have tremendous influence on the nature and properties of the final nanocomposites include the selection of clay, type of clay pre-treatment, the choice of polymer and their component and the mode in which the polymer is incorporated into the nanocomposite. Addition of Halloysite in different polymer based nanocomposites enhanced their physical, mechanical and thermal properties. In this review, we have tried to summarize the influence of Halloysite on resultant properties of various Halloysite based nanocomposites used for the pertinence in the various research fields.

## 1. INTRODUCTION

Nanocomposites have varieties of application in optical, electronic, magnetic and thermo sensitive devices. So many approaches like melt extrusion, emulsion based polymerization, entrapment, ball mill homogenisation and chemical treatments are used to prepare such nanocomposites with well-controlled structures, and diversity of templates. However, the approaches which are being used are very costly. So more optimized approach with better reproducibility are urgently needed for the fabrication of nanocomposites [1,2].

Halloysite nanotubes (HNTs) are ubiquitous in nature which occurs as silicate nanotubes in soils and weathered rocks. HNT deposits have been incurred in many geographic areas, where they are present in a variety of particle conformations and hydration states (Fig.1). HNTs have an empirical chemical formula of $Al_2Si_2O_5(OH)_4.2H_2O$, that is similar to kaolin. Typically, HNTs consists of primarily tubes of a multi-wall and hollow tubular structure with lengths typically range from 0.5 to 3.0 mm with exterior diameters ranging from 30 to 100 nm and internal diameters ranging from 15 to 30 nm [3,4].

Clays are used as fillers with polymers for the configuration of various nanocomposites but main drawback associated with these clays are their inadequate interfacial adhesion between the polymer matrix and huge polarity. So without any surface modification of the clays, resultant nanocomposite shows limited acceptability. To get the nanocomposites with high dispersion and compatibility between polymer and clay platelets is

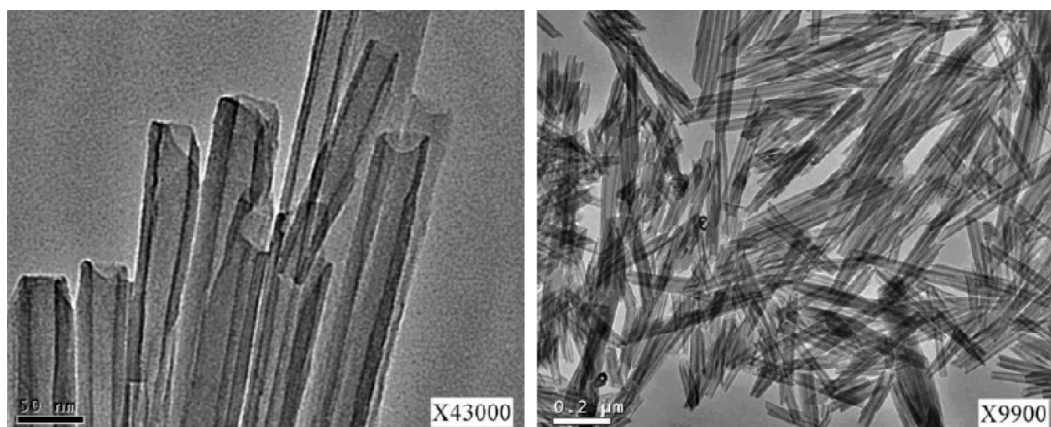Corresponding author: Deepak Rawtani, e-mail: rawtanid@gmail.com

**Fig 1.** TEM images of Halloysite nanotubes (Courtesy of Dr. Bing Zhang).

crucial. Nanocomposites based on inorganic clay minerals are being used since long but nanocomposites based on Halloysites have recently become the subject of research attention as a novel additive for enhancing the mechanical performance of polymers, particularly for strengthening and toughening epoxies [5-8].

HNTs have been demonstrated to be an ideal component for fabricating high performance polymer nanocomposites. The major advantages associated with Halloysite based nanocomposites are requirement of low filler contents to get peculiar and fascinating properties of the polymer matrix (Table 1). In comparison to the other polymer based nanocomposites, Halloysite-based nanocomposites exhibit enhanced mechanical properties, reduced gas permeability with improved thermal stability and flame retardant behaviour [1,9,10]. Halloysite is used an additive for enhancing the mechanical performance of nanocomposites as well as for strengthening and toughening of polymers or elastomers. There are many benefits associated with HNTs to use as filler in nanocomposites:

(i) HNTs are distinct nano materials with little surface charges so it require no intercalation and exfoliation compared to other nano dimensional fillers like as MMTs. They also provide ease in process-ing when amalgamated with other polymers and gives homogeneous dispersion of particles [11].

(ii) Modifications at the surface of HNTs, expand the basal spacing of HNTs by the intercalation of inorganic and organic compounds in their inter layers, which also raises the possibility to produce a homogeneous mixture of HNTs with polymers [12].

(iii) Alterations at the surface of HNTs provide good wetting and bonding of HNTs with polymers.

(iv) Similar to organically modified MMTs, rectangular expansion of basal layers provides HNTs exfoliation to individual layers [11].

(v) HNTs are composed of several siloxane groups and have only a few hydroxyl groups, which provide ability to HNTs to form hydrogen bonds and hence better dispersion potential.

(vi) Large luminal diameter of the Halloysite nanotubes provides an opportunity to accommodate different polymer molecules which can also offer polymeric composites [13].

## 2. HALLOYSITE AND POLYAMIDE 6 BASED NANOCOMPOSITES

Recently PA6 nanocomposites have drawn much attention due to their unprecedented performance compared with their micro composite counterparts.

**Table 1.** Properties of Halloysite based nano-composites.

| Improved properties | Disadvantages |
| --- | --- |
| Mechanical Properties (Tensile,Modulus,Toughness) | |
| Act as Flame retardant additives | |
| Fire retardancy (By limiting Oxygen demand) | Viscosity increase |
| Dispersion enhance | Sedimentation |
| Reinforcement | |
| Enhance interfacial interaction | |
| Chemical Resistance | |

It is well known that the physical and mechanical properties of semi crystalline polymer are, to a large degree, defined by its morphology, crystalline structure and crystallinity. There are characteristics which make HNTs an attractive material to be used in the formation of PA 6 based nanocomposites. Those are as follows:

(1) HNTs act as nucleating agent and also accelerate the crystallization. The kinetics analysis suggests that the surface free energy of PA6/HNTs nanocomposites is higher than that of neat PA6. But this increasing of the fold-surface free energy of PA6/HNTs nanocomposites is restricted to higher HNTs loading.

(2) By incorporating Halloysite nanotubes (HNTs) in PA6 nanocomposites along melt blending resultant nanocomposite has excellent physical and mechanical properties. In other approach, homogeneous dispersion of HNTs in PA 6 matrix can be achieved by processing Polyamide 6 (PA 6)/ Halloysite nanotubes (HNT) nanocomposites through melt-extrusion compounding or master batch dilution method.

(3) HNTs have profound effects on the crystallization behaviour of PA6. HNTs content significantly influence the crystallinity behaviour of the PA6/HNTs based nanocomposites and the crystallinity attains its maximum with 5 phr of HNTs content. Addition of HNTs into PA 6 matrix enhanced the crystallization temperature and degree of crystallinity, thus indicating an effective nucleation induced by the addition of HNTs.

(4) Halloysite acts as filler for polyamide 6 (PA 6) nanocomposites. It has revealed that the addition of Halloysite nanotubes favours the formation of the $\gamma$-modification for the low molar mass PA 6.

(5) In HNT's /PA6 nanocomposite, as the proportion of Halloysite increase storage modulus, the tensile modulus and the yield stress of the composites also increases.

(6) Addition of Halloysite in composites increase glass transition temperature, storage modulus, Young modulus, tensile strength and charpy impact strength without loss of ductility.

Usually Halloysite based silicate nanotubes are used in conjunction with polyamide-6 (PA 6) for reinforcement. The nanocomposites based on PA-6 and Halloysite are prepared by melt extrusion and an injection moulding process. Studies shows enhanced tensile properties as well as tensile strength is more prevalent in the organoclay nanocomposites, whereas the increse in the stor-

age modulus is more prominent in the Halloysite nanocomposites. Furthermore, compared to the thin exfoliated montmorillonite often used for polymer nanocomposites, Halloysite nanotubes have a higher intrinsic stiffness. The studies also indicate that the Halloysite nanocomposites have improved tensile properties, compared to the neat polyamide-6 and show also better thermomechanical behaviour [14-19].

## 3. HALLOYSITE AND EPOXY BASED NANOCOMPOSITES

Blending of epoxies with a certain amount of HNTs can increase fracture strength, toughness and modulus. The resultant nano composite has same thermal mechanical properties like as glass transition temperature ($T_g$). A uniform mixture of Halloysite nanotubes (HNTs) with epoxies can be attained by two methods either through ball mill homogenisation or chemical treatments. Homogenization by Ball mill or potassium acetate (PA) treatment is an effective approach to reduce the size of Halloysite particle clusters in the epoxy matrix. In chemical based approach Silane and cetyl trimethyl ammonium chloride (CTAC) treatments were given. HNTs provide not only enhanced particle dispersion within epoxies but also improved mechanical properties of the Halloysite–epoxy nanocomposites.

Halloysite has characteristically folded geometry, Phenylphosphonic acid (PPA) was used for unfolding the Halloysite. To get different levels of enfoldment and intercalaction within Halloysite, they underwent PPA treatment for altering duration. Halloysites with the unfolded and intercalated structure, were effective additives in increasing the fracture toughness of the cured epoxies without sacrificing their basic properties [20,21].

### 3.1. Halloysite for dispersion enhancement

HNT's provide the ease of processing, because HNTs are discrete nano-particles with no or little surface charge. HNT's particle produce homogeneous particle dispersion when mixed with polymers. This may eliminate the need of intercalation or exfoliation, as required by other nanoclays. Modifications at surface of HNTs may provide opportunity for intercalations of Halloysite layers with organic and inorganic compounds, contributing to layer expansion perpendicular to the base layers [21].

## 3.2. Halloysite for mechanical strength

Multiple crazing and massive shear banding are two well-accepted toughening mechanisms for nanocomposites. Although epoxy resins can be toughened effectively by rubbers via matrix banding, yet addition of rubber in epoxy resin results in a decrease in desirable properties like mechanical and physical properties including modulus, strength and thermal stability. But aim to synergise the improvement in toughness and rigidity, a micro-sized inorganic or organic modifiers can be employed in modification of brittle polymers. Thus for the enhancement of mechanical properties of the Halloysite–epoxy nanocomposites were achieved by using HNTs as filler for polymer composites [22-24].

## 4. HALLOYSITE AND ETHYLENE PROPYLENE DIENE MONOMER (EPDM) BASED NANOCOMPOSITES

Ethylene propylene diene monomer (EPDM) is unsaturated polyolefin rubbers, used for extraneous applications like as automotive sealing systems, electrical power cables, side walls of tires, roofing sheets, belting and sporting accessory as well as ablative and non conductor compounds used in solid propellant based rocket motors. This is all due to its ability to take over high loading of fillers as well as its strong standing resistance to oxygen, ozone, UV, and heat.

Recently HNTs are being used as filler for polymers to enhance the mechanical and thermal applications of the composites. HNTs because of their unique properties like tubular shape and low hydroxyl functional group density, do not require any exfoliation and they can be easily dispersed in a polymer matrix, even at high loading (>30 parts per hundred rubber (phr).EPDM/HNT based nanocomposites develop by mixing up to 100 phr (parts per hundred rubber) of HNTs with EPDM on a roll mill. The resultant nano composite obtained has significantly high tensile strength as well as high tensile modulus (at 100% elongation) (M100) and their crosslink density were also increased tremendously by increasing HNT's loading. The thermal and flammability attributes of nanocomposites enhanced, particularly at HNT loading higher than 15 phr.

Morphology of EPDM/HNT nanocomposites surface shows significant improvement. The morphological studies reveal that HNTs are homogenously dispersed within the EPDM, by the interfacial and inter-tubular interactions between HNTs and EPDM. The high HNT loading results in formation of HNTs zig-zag structures and these all factors contribute towards significant improvement in mechanical and thermal properties of EPDM/HNT nanocomposites [25,26].

## 4.1. Maleic anhydride grafted EPDM nanocomposites

Since long polymer matrices (e.g. thermoplastics, thermosets) incorporating nanofillers are used to reinforced the mechanical, thermal and physical properties. Internalization of Halloysite nanotubes (HNTs) into EPDM can increase the tensile, thermal, swelling and dynamic mechanical properties from 0 to 100 phr of HNT loading. In a similar way, incorporation of maleic anhydride via peroxide-initiated melt grafting onto EPDM further enhance the tensile properties of nanocomposites.

When maleic anhydride grafted EPDM is used as a compatibilizer in EPDM/HNT nanocomposites, resultant Nanocomposites show higher tensile qualities. Ethylene propylene diene monomer grafted with Maleic anhydride (MAH-g-EPDM) is prepared by peroxide-initiated melt grafting of MAH onto EPDM using an internal mixer at 180 C. The effect of MAH-g-EPDM compatibilizer on the interactions, and tensile and morphological properties of Halloysite nanotubes (HNTs) filled EPDM nanocomposites were influenced by two major factors. The hydrogen bonding between MAHg- EPDM and HNTs and formation of rich areas like EPDM-rich and HNT-rich, are the dominant effects on the tensile strength of the nanocomposites at low and high HNT loading, respectively. By adding MAH-g-EPDM in compatibilized nanocomposites cure time (t90), maximum torque (MH) and minimum torque (ML) get increase [26].

## 4.2. $\gamma$-Methacryloxypropyl trimethoxysilane ($\gamma$-MPS) modified EPDM nanocomposites

Halloysite nanotubes (HNTs) were modified by $\gamma$-methacryloxypropyl trimethoxysilane ($\gamma$-MPS) to ameliorate their dispersion in ethylene propylene diene monomer (EPDM). The EPDM/HNT nanocomposites are prepared by mixing different parts in per hundred rubbers (phr) of HNTs with EPDM on a roll mill. Nanocomposites with 100% elongation has higher tensile strength and tensile modulus compared to those of EPDM/unmodified

HNTs (EPDM/HNT) while after modification of HNTs, the elongation at break decreased.

SEM and TEM studies also show that EPDM modified HNTs has better dispersion. FTIR and TGA studies indicate that $\gamma$-MPS partially penetrate into the HNTs and interacted within the Si–O groups on the surfaces of the HNTs. Effect of the HNT loading on the tensile, thermal and morphological properties of EPDM nanocomposites also depicts that resultant dispersion is more uniform with even at high HNT loading (30–100 phr). In addition, HNTs is far less expensive than other clay minerals and can be mined from deposits as a raw material [27].

# 5. HALLOYSITE AND STYRENE RUBBER BASED NANOCOMPOSITES

Nanocomposites with incorporated inorganics gives better execution compared with the other polymer composites. Final acceptability of polymer nanocomposites incorporated with inorganic governs by their interfacial interactions. The type of interfacial interactions between polymer matrix and inorganic include hydrogen bonds, vander Waals force, covalent bonds and ionic bonds. There are different approaches developed to amend the interfacial interactions between various components of nanocomposites including modification of matrix. In recent time, Halloysite nanotubes (HNTs), has got an edge over reinforced polymers and then unique reinforcing effects over polymers like polyamide, natural rubber, epoxy resin, polypropylene, etc. have been demonstrated.

xSBR (carboxylated butadiene–styrene rubber) is a copolymer of styrene, butadiene and acrylic acid with many carboxyl groups in their chain which provide aid in the formation of hydrogen bonds. HNTs and xSBR based nanocomposites prepared by co-coagulation process with improve interfacial interactions via hydrogen bonding. ATR-FTIR (Attenuated total reflection Fourier transform infrared spectroscopy) and X-ray photoelectron spectroscopy (XPS) studies of xSBR /HNT nanocomposites proves the formation of hydrogen bonding between Xsbr and HNTs. It also suggests that as HNT content increase vulcanization also increase and consequently lower content of HNTs tends to delay in vulcanization of xSBR/HNT composites. The mechanical properties of materials like modulus, hardness are significantly enhanced by the inclusion of HNTs. The reasons behind this significantly enhanced effect of HNTs are correlated with co-coagulation process and strong interfacial interactions via hydrogen bonding [28].

## 5.1. Methacrylic acid (MAA) based modification

Methacrylic acid (MAA) is used with SBR/HNTs composites to obtain effective dispersion of HNTs as well as strong interfacial bonding among HNTs and styrene–butadiene rubber (SBR). Methacrylic acid (MAA), with direct blending can improve the performance of styrene–butadiene rubber (SBR)/ Halloysite nanotubes (HNTs) nanocomposites. The phenomenon behind this is either interaction between HNTs and MAA or in situ formed zinc methacrylate (ZDMA). Interfacial bonding is responsible for improved mechanical and enhanced dispersion of HNTs in rubber. The strong interfacial bonding between HNTs and rubber matrix is consequence of ZDMA and MAA intermediate linkages. ZDMA associates with SBR and HNTs via grafting or complexation phenomena. Effects of MAA content on the vulcanization behaviour, morphology and mechanical properties of the nanocomposites anticipate the mechanical altercations of MAA modified SBR/HNTs nanocomposites.

Interfacial bonding and fine dispersion on clays are two deciding factors to study the performance of the rubber/clay nanocomposite. Affinity between MAA and clays show the possibility of the formation of hydrogen bonds between clay and the acid. In accession, MAA is reactive to polymer chains such as unsaturated rubber chains or saturated polyolefins via free radical grafting. Especially, MAA is reactive to zinc oxide (ZnO) or magnesium oxide (MgO) to form unsaturated metal methacrylates which show unusual reinforcing effects for rubber compounds. In situ generated metal methacrylates were reported to reinforce rubber compounds during the compounding [29].

## 5.2. Sorbic acid (SA) based modification

MAA is corrosive in nature which limits its applicability to be used in composites, thus sorbic acid (SA) monomer is used for the modification of SBR/ HNTs nanocomposites. SA is an unsaturated carboxylic acid which contains two functional groups, that is, a carboxyl and a two conjugated carbon-carbon double bonds in each molecule.

Sorbic acid (SA) is used to enhance the performance of styrene-butadiene rubber (SBR)/Halloysite

nanotubes (HNTs) nanocomposites by direct blending. SA bonds SBR and HNTs through grafting co-polymerization/hydrogen bonding mechanism. This strong interfacial bonding between HNTs and rubber matrix causes significantly improvement in dispersion of HNTs. Incorporation of SA content influence the mechanical properties of SA modified SBR/HNTs nanocomposites. The changes in vulcanization behaviour, mechanical properties and morphology were correlated with the interaction between HNTs and SA and accompanying in largely improved dispersion of HNTs. Traditionally, except for a few self-crystallizable rubbers such as natural rubber and chloroprene rubber, most rubbers must be reinforced by fillers before practical applications for their low modulus and strength [30-32].

## 6. HALLOYSITE AND POLYPROPYLENE BASED NANOCOMPOSITES

HNTs are employed for the modification of polypropylene (PP). HNTs can be dispersed well in PP matrix in a range of 50-300 nm and have a good interfacial interaction with PP. The incorporation of HNTs within polypropylene not only enhance the crystallization temperature but also the overall crystallization rate of polypropylene to a large extent. This results in formation of constant spherules of pure polypropylene and PP/HNT composites by fast cooling of the samples [28,29].

Properties of polymer composites are largely depend on morphology as well as on crystallization behaviour. HNTs were first surface treated with methyl, tallow, bis-2-hydroxyethyl and quaternary ammonium, resultant melted master mix treated with PP. The mechanical properties were evaluated by instron and impact tests. SEM studies also revealed that HNTs could be well-dispersed in PP matrix and have a profound interfacial interaction with PP, even up to a high content of 10 wt.%. DSC data also indicated that HNTs could serve as a nucleating agent, resulting in an enhancement of the overall crystallization rate and the non-isothermal crystallization temperature of PP. This has further been confirmed by dynamic melt rheometry studies and it depicts that HNTs mainly elevate nucleation and have not much influence on the growth of PP crystallization. Nevertheless, by prompt cooling of materials, constant spherule size can be obtained for both pure PP and PP/HNT composites due to the restricted nucleation effect of HNTs on PP crystallization [32,33].

## 6.1. Water-assisted extrusion for polypropylene/ Halloysite nanocomposites

Naturally occurring Halloysite nanotubes (HNTs) used to prepare Polypropylene (PP)/HNTs nanocomposites by water-assisted extrusion process with and without the use of a PP graft-maleic anhydride (PP-g-MA) as compatibilizer. HNTs show two different effects on the thermal behaviour of PP.

A surface catalytic action of the Halloysite accelerates the thermal degradation of PP. However, this effect can be reduced with improved HNTs dispersion, meditation by entrapment mechanism of the decay products inside the lumens. Most of the layered silicates and polymer nanocomposites are prepared by this method. In order to achieve a delaminated structure of layered silicates found as stack aggregate require the use of surfactants to increase the interlayer spacing. However, this organic modification have some drawbacks like decrease of the binding energy between polymer and filler, acceleration of the thermo oxidative degradation of the polymer matrix and a reduction of the mechanical performances of the material due to the plasticizer effect of the organic modifier.

In comparison to other layered silicates material, Halloysite can be easily dispersed in a polymer matrix due to their low secondary interactions among the nanotubes via hydrogen bonds and vander Waals forces. Silane is used for organo modification of the HNTs surface to achieve a uniform dispersion of the clay nanotubes in the polymer matrix, as well as higher storage modulus. This result has been attributed to the improved interfacial adhesion between functionalized filler and matrix.

Enhancement of thermal stability and resistance to flammability of PP/HNTs nanocomposites due to a combination of several factors including presence of iron in HNTs, layer barrier properties of the nanotubes and an entrapment mechanism of the initial degradation products inside the lumen structure of the nanotubes. Sometimes PP-graft-maleic anhydride (PP-g-MA) is used as compatibilizer to improve the affinity between the hydrophilic surface of clay and the hydrophobic PP [32-34].

## 7. HALLOYSITE AND POLYSTYRENE BASED NANOCOMPOSITES

Polystyrene (PS) is low cost product with higher commercial value but its higher brittleness limit its

application to use it as high-impact modifiers for industrial purpose. Several attempts have been made to improve the toughness of polystyrene (PS) by incorporating rubber particles or inorganic particles. The addition of polybutadiene during the polymerization of styrene greatly improves the impact toughness of the resulting PS known as high-impact polystyrene (HIPS).

These high-impact polystyrene (PS) nanocomposites incorporated with individually dispersed Halloysite nanotubes (HNTs) were prepared by emulsion based polymerization of styrene in the presence of HNTs by using dispersing agent like sodium dodecyl sulfate (SDS) as the emulsifier. This emulsion polymerization induces the formation of polystyrene based nanospheres separating individual HNTs. Uniform dispersion of HNTs in PS matrix, was further confirmed by Transmission electron microscopy. This good dispersion of fillers, especially nano-sized particles in a polymer matrix, is a pre requisite for the formation of nanocomposites with high impact toughness. This in situ polymerization of styrene in the presence of surface-modified fillers is usually employed for preparation of various PS composites [35,36].

The impact strength of the Polystryrene (PS) / HNTs nanocomposites are enhanced by incorporation of HNTs in polystyrene that is little more than neat PS, commonly, the storage modulus and thermal degradation temperature of the nature rubber can significantly gain accession by the addition of HNTs. Incorporation of a small amount of HNTs also increased the strength, stiffness and elongation-at-break in polyamides.

## 8. HALLOYSITE AND PHBV (POLY-HYDROXYBUTYRATE-COHYDROXYVALERATE) BASED NANOCOMPOSITES

PHBV (Poly-hydroxy butyrate-cohydroxy valerate), a member of the PHA, has attracted the attention because of its biodegradability, biocompatibility, thermoplasticity as well as its abundance natural availability. Polyhydroxyalkanoates (PHA) comprise a class of polyesters that synthesized and accumulated as an intracellular carbon and energy storage material by many bacteria. PHBV has a high melting temperature with highly crystalline solids and large spherulitic structures. Because of its high crystallinity, PHBV is stiff and brittle, so consequently has very poor mechanical properties. Moreover, PHBV is not stable at near its melting

temperature, so results in a drastically reduction in molecular weight during the melt processing [37].

Attempts have been made to enhance the thermal stability and physical and mechanical properties of PHBV. The incorporation of nanomaterials has provided the means to enhance resulting composites performance with low filler contents. To further extend its applications, organic modifiers such as alkylammonium cations are commonly used to form organophilic montmorillonite (OMT) and thus facilitate the intercalation of MT by the polymer chains. Although PHBV/OMT nanocomposites show improved properties, some studies demonstrated that the ammonium surfactants are commonly used as clay organomodifiers, increased the thermal sensitivity of PHBV. But these nanocomposites show lack of performance due to their polymer degradation during processing [38,39].

Moreover, the higher stiffness of the HNT nanotubes compared to MT clay minerals and the high length diameter aspect ratio of the tubes can promote excellent nano reinforcement for polymer nanocomposites. Halloysite has shown interesting reinforcing characteristics, thermal stability and rheological properties in PHBV matrices. In many cases, the HNT can be incorporated within the polymer matrix even without any chemical modification [39].

## 9. HALLOYSITE AND FLUOROELASTOMER (FKM) BASED NANOCOMPOSITES

Fluoroelastomer are materials with elastic behaviour under even comparatively harsh conditions. These elastomers are also used as sealant as well as in fabricated components to afford barriers against a broad range of fluids under severe and high pressure sealing applications. Amounts of fluoroelastomers consumed per vehicle are small compared to natural and synthetic rubber within the tyres of a vehicle, but the Fluoroelastomer parts are extreme crucial for safety, reliable operation and environmental protection. Fluoroelastomers have application in number of areas such as aerospace appliances, fluidic power, chemical industries, oil field, semiconductor based fabrication and high pressure sealing for plasma [40].

Incorporation of a small amount of nano-fillers into the polymer matrix can enhance physical properties of polymer and this polymer–filler interaction was reflected in the improved mechanical and thermal properties, which was a consequence of proper dispersion of the nanotubes in the polymer

**Table 2.** Properties of Halloysite based various nanocomposites.

| Nanocomposites | Method of preparation | Physical | Mechanical | Tensile | Storage | Particle Dispersion | Thermal stability | Modules | Interfacial Interaction | Crystallization |
|---|---|---|---|---|---|---|---|---|---|---|
| HNT-PA6 | Melt extrusion/ Dilution | Enhanced | Enhanced | Enhanced | Enhanced | - | - | - | - | max. at 5phr |
| HNT-Epoxy | Ball mill/ Chemical treatment | - | Enhanced | - | - | Enhanced | - | Enhanced | - | - |
| HNT-EPDM | Ball mill | - | Enhanced | - | - | Enhanced (>30phr) | Enhanced (>15phr) | Enhanced | - | - |
| HNT-Styrene | Co-aggulation | - | Enhanced | - | - | - | - | Enhanced | Improved | - |
| HNT-Polypropylene | Chemical | - | - | - | - | Enhanced | - | - | Improved | Enhanced |
| HNT-Polystyrene | Emulsion based | - | - | Enhanced | - | Uniform | - | - | - | - |
| HNT-PHBV | Melt extrusion | Enhanced | Enhanced | - | - | - | Enhanced | - | - | - |
| HNT-Fluoroelastomer | Bis Phenol curing | Enhanced | Enhanced | - | - | - | Enhanced | - | - | - |

matrix. Fluoroelastomer nanocomposites based on Halloysite clay mineral prepared using a bis-phenol curing system resulted in formation of nanocomposites with improved dynamic mechanical properties and elevation in temperature as high as 30K of the thermal decomposition. On the other hand, incorporation of fluoroelastomers (FKM), resultant FKM–HNT nanocomposites has ultimate properties of that materials.HNT loading significantly influence the mechanical and dynamic properties of the FKM nanocomposites. HNT loading, tremendously affect the thermal stability also and at 5 phr HNT loading with increase in HNT content tends to deviate in negative direction [41,42].

## 10. CONCLUSION

The nanocomposite has multiple novel and unique properties for a different application, but those properties must not demean significantly throughout the life of the composite material. Developing these capabilities require significant research input to study the interaction behaviour of the nanomaterials and polymer matrix and determination of they are being influenced by change of temperature, moisture and mechanical stress. Thus, models of the interactions within the nanocomposite are postulated to enable development of effectual rules for mixtures. This may require a combination of expertise with numerical modelling, characterization and informatics to enable this nanocomposite with properties by design capability. Studies also suggest that degree of distribution of HNT in resultant nanocomposites is a deciding factor to assess potential decay of the nanocomposite's properties through its life.

## REFERENCES

[1] S.S. Ray and M. Okamoto // *Prog. Polym. Sci.* **28** (2003) 1539.

[2] Deepak Rawtani and Y.K. Agrawal // *Rev.Adv.Mater.Sci.* **30** (2012) 282.

[3] R.L. Parfitt and A.D. Wilson // *Catena Supplement* **7** (1985) 1.

[4] E. Joussein, S. Petit, G.J. Churchman, B.K.G. Theng, D. Righiand B. Delvaux // *Clay Minerals* **40** (2005) 383.

[5] E. Joussein, S. Petit, C.I. Fialips, P. Vieillard and R. Righi // *Clays and Clay Minerals* **54** (2006) 473.

[6] L.T. Alexander, G.T. Faust, S.B. Hendricks, H. Insley and H.F. McMurdie // *American Mineralogist* **28** (1943) 1.

[7] A. Usuki, N. Hasegawa and M. Kato // *Adv. Polym. Sci.* **179** (2005) 135.

[8] M. Alexandre and P. Dubois // *Mater Sci Eng.* **28** (2000) 1.

[9] J. Zhu, F.M. Uhl, A.B. Morganand C.A. Wilkie // *Chem Mater.* **13** (2001) 4649.

[10] P.M. Ajayan and J.M. Tour // *Nature* **447** (2007) 1066.

[11] J.W. Gilman // *Appl Clay Sci* **15** (1999) 31.

[12] C. Zilg, F. Dietsche, B. Hoffmann, C. Dietrich and R. Mulhaupt // *Macromol Symp.***169** (2001) 65.

[13] C.P. Li, J.G. Liu, X.Z. Qu, B.C. Guo and Z.Z. Yang // *J Appl Polym Sci.***110** (2008) 3638.

[14] U.A. Handge, K. Hedicke-Höchstötter and V. Altstädt // *Polymer.* **51** (2010) 2690.

[15] B. Guo, Q. Zou, Y. Lei, M. Du, M. Liu, and D. Jia // *Thermochimica Acta.* **484** (2009) 48.

[16] K. Prashantha, H. Schmitt, M.F. Lacrampe and P. Krawczak // *Composites Science and Technology* **71** (2011)1859.

[17] B. Lecouvet, J.G. Gutierrez, M. Sclavons and C. Bailly // *Polymer Degradation and Stability* **96** (2011) 226.

[18] K. Hedicke-Höchstötter, G.T. Lim and V. Altstädt // *Composites Science and Technology* **69** (2009) 330.

[19] X. Liu and Q. Wu // *Eur Polym J.* **38** (2002) 1383.

[20] Y. Ye, H. Chen, J. Wu and L. Ye // *Polymer* **48** (2007) 6426.

[21] J. Zhang, L. Ye and D. Shiqiang // *Composites Science and Technology* **69** (2009) 2497.

[22] Y. Tang, S. Deng, L. Ye, C. Yang, Q. Yu, J. Zang and C. Zhao // *Composites: Part A* **42** (2011) 345.

[23] A.J. Brunner, A. Necola, M. Rees, P. Gasser, X. Kornmann and R. Thomann // *Eng Fract Mech.* **73** (2006) 2336.

[24] G. Basara, U. Yilmazer and G. Bayram // *J Appl Polym Sci* .**98** (2005) 1081.

[25] H. Ismail, P. Pasbakhsh, M.N. Fauzi and A.A. Baker // *Polymer Testing* **27** (2008) 841.

[26] P. Pasbakhsh, H. Ismail, M.N. Fauzi and A.A. Baker // *Polymer Testing* **28** (2009) 548.

[27] P. Pasbakhsh, H. Ismail, M.N. Fauzi and A.A. Baker // *Applied Clay Science* **48** (2010) 405.

[28] M. Du, B. Guo, Y. Lei, M. Liu and D. Jia // *Polymer* **49** (2008) 4871.

[29] M. Du, B. Guo, X. Cai, Z. Jia, M. Liu and D. Jia // *e-Polymers* **130** (2008 )1.

[30] B. Guo, F. Chen, Y. Lei, X. Liu, J. Wan and D. Jia // *Applied Surface Science* **255** (2009) 7329.

[31] B. Guo, F. Chen, Y. Lei, X. Liu, J. Wan and D. Jia // *Applied Surface Science* **255** (2008) 2715.

[32] N.Y. Ning, Q.J. Yin, F. Luo, Q. Zhang, R.Du and Q. Fu // *Polymer* **48** (2007) 7374.

[33] C. Yang, P. Liu and Y. Zhao // *Electrochimica Acta* **55** (2010) 6857.

[34] B. Lecouvet, M. Sclavons, S. Bourbigot, J. Devaux and C. Bailly // *Polymer* **52** (2011) 4284.

[35] J.H. Chen, M.Z. Rong, W.H. Ruan and M.Q. Zhang // *Composites Science and Technology* **69** (2009) 252.

[36] Y. Lin, K.M. Ng, C.M. Chan, G. Sun and J. Wud // *Journal of Colloid and Interface Science* **358** (2011) 423.

[37] P. Bordes, E. Pollet, S. Bourbigot and L. Avérous // *Macromol Chem Phys.* **209** (2008)1473.

[38] P. Bordes, E. Hablot, E. Pollet and L. Avérous // *Polym Degrad Stab.* **94** (2009) 789.

[39] L.N. Carli, J.S. Crespo and R.S. Mauler // *Composites: Part A.* **42** (2011) 1601.

[40] J. Frohlich, W. Niedermeir and H.D. Luginsland // *Comp. Appl. Sci. Manuf.* **36** (2005) 449.

[41] S. Rooj, A. Das, V. Thakur, R.N. Mahaling, A.K. Bhwmick and G. Heinrich // *Materials and Design.* **31** (2010) 2151.

[42] S. Rooj, A. Das and G. Heinrich // *European Polymer Journal* **4** (2011)1746.