

Synthesis of Vinylester-Clay Nanocomposites: Influence of the Nature of Clay on Mechanical, Thermal and Barrier Properties

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Abstract: The effects of organically modified montmorillonite clay nanoparticles in neat vinyl ester resin were investigated. Organically modified MMT clay particles, Cloisite10A and Cloisite30B were dispersed into neat organic vinyl ester resin by using an ultrasonic method. Morphology of the dispersed clay particles in the nanocomposites formed during polymerization, was characterized by X-ray diffraction (XRD) spectroscopy and found that intercalated nanocomposites were formed. The thermal properties such as decomposition and glass transition temperatures, percent weight retention and $\tan \delta$ were determined by thermo gravimetric analyzer (TGA) and dynamic mechanical thermal analyzer (DMTA). A decrease in glass transition temperature was found in both vinylester/Cloisite10A and vinylester/Cloisite30B nanocomposites. The tensile, flexural and impact properties of the nanocomposites were determined by universal testing machine (UTM) and Izod impact tester. Due to the incorporation of MMT nanoparticles in vinyl ester resin an improvement in mechanical properties was observed. The effect of water absorption on nanocomposites was investigated and a significant decrease in water absorption of the vinylester nanocomposites was found.

Keywords: Vinylester resin, organically modified clay, nanocomposites, water absorption properties.

1. INTRODUCTION

Nanoreinforced composite or nanocomposites offer a great potential for novel properties because the distinct inorganic organic component properties can be combined in a single materials with a uniformity of dispersion in the nano-level. The concept of nanoreinforcement arises from the knowledge that control of structure/interaction at smallest scales. An effective exploitation of nanoreinforcement requires an understanding of nanoscale structure-property processing relationship of the nanocomposites to select the right nanocomponent and to process them properly for the target properties.

Pioneering work by researchers at Toyota led to the discovery of nanoscale polymer-clay hybrid composites for lightweight material applications [1, 2]. By replacing the hydrophilic sodium and calcium cations of native montmorillonite with more hydrophobic onium ions, they were able to initiate polymerization of caprolactam in the interlayer gallery of the montmorillonite galleries to form a nylon 6-clay nanocomposite. In recent years, this revolutionary nanocomposites chemistry has been extended into various polymer systems including epoxy [3-5], polyesters [6-8], polyurethens [9], polyimides [10], poly(ethylene oxide) [11, 12], poly(ethylene terephthalate) [13], polypropylene [14] etc.

In the field of thermoset nanocomposites, the vast majority of work reported to date has been on epoxy resin with a

variety of curing systems [15-20]. Effects of nature of interlayer exchanged cation, the cure condition and the functionality of the resin on the morphology of nanocomposite, have been investigated.

Unlike epoxy, there have been only few studies reported for vinyl ester nanocomposites [21-23]. Karger-Kocsis's group [24] reported intercalated nanocomposite using vinyl ester/epoxy interpenetrating network (VE-EP IPN) as a matrix and various commercially available organo-clay. The styrene content in the resin, high intensity ultrasonic stirring and presence of reactive group in the alkyl ammonium cation are reported to favour the exfoliation process [25]. However, no detailed analysis of interaction between molecules of a vinylester matrix and the organically modified silica sheets has been performed so far in view of water permeability; the role of individual parameter and chemical bonding aspects of chemically functionalized clay-vinyl ester nanocomposite are also yet to be extensively investigated.

Polymer nanocomposites provide improved mechanical [26, 27], thermal [28], fire resistance [29] and barrier properties [30, 31] than conventional composites. Such improvement in overall properties of nanocomposites is achieved due to high aspect ratio and high strength of these nanoscaled inorganic particles and unique morphology of the polymer/silicate clay structures. The types of nanoparticles that are mostly used include: silica particles, layered silica clays, electro-spun polymeric nanofibers and nanotubes. Polymer nanocomposites were produced either by *in situ* polymerization [32, 33] or melt intercalation of thermoplastics [34, 35]. However, full separation of the clay layers in the polymer matrix was only achieved in systems based on polyamide, polyimide and epoxy resins. This is primarily because of fairly high polarity of these prepolymers and curing agents which facilitates diffusion into the organophilic clay galleries. The presence of polar hydroxyl groups in the clay layers

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impedes non-polar species from fully entering the galleries and exfoliating the clay.

A practical problem in the synthesis of the present class of nanocomposites is to disperse an inorganic clay in an organic medium on a molecular scale. This can be addressed by treating the clay so that it becomes organophilic in nature. Clays such as montmorillonites have a remarkable ability to exchange ions. Montmorillonite (MMT) is a commonly used clay with a layered structure that is constructed of two tetrahedral sheets of silica surrounding an octahedral sheet of alumina or magnesia. The layers (with thickness of 1 nm) are stacked by weak dipole forces, while the galleries between the layers are occupied by metal cations. For the synthesis of a nanocomposites, processing of clay particle can be carried out by two stages; one is the growth of the basal (interlayer) spacing by exchanging the metal cations with an intercalating reagent (alkylammonium ions) to facilitate intercalation of polymer chains into the galleries between the clay layers and other one is the treatment of intercalated particles by a compatibilizer (a swelling agent, a functional oligomer, or a low molecular weight polymer) to improve miscibility between the organics-modified silicate layers and the host matrix.

This paper is concerned with the mechanical, thermal behavior of and moisture diffusion through a nanocomposite consisting of a vinyl ester resin matrix filled with organically modified montmorillonite clay particles. Vinyl ester exhibit many desirable quantities including mechanical properties comparable to those of epoxy resins, excellent chemical resistance and tensile strength, low viscosity (enabling room temperature infusion) and cost comparative. Vinyl ester resin are being extensively used as a matrix for glass-reinforced polymer composites employed for construction and repair of bridges and other civil, naval structures [36, 37].

2. EXPERIMENTAL

2.1. Materials

The resin used was VE-1001 epoxy vinyl ester resin (Refnol Resins & Chemicals Ltd, India) containing 45 wt.-% of dissolved styrene. A desired amount (400-500gm) of vinyl ester (VE) resin was mixed with varying amounts (2.5%, 5% and 7.5 by weight) of nanoclay particles. The curing agents for this resin were 1.5% of 6% cobalt naphthenate as a catalyst, 0.1% of N, N-dimethyl aniline as an accelerator and 1.5% methyl ethyl ketone peroxide with 9% of active oxygen as an initiator. The clays used for reinforcement in this study were commercial treated clay Cloisite10A and Cloisite30B supplied by Southern Clay Products Inc., USA. A montmorillonite clay Cloisite10A treated with benzyl (hydrogenated tallow alkyl) dimethyl quaternary ammonium chloride was used as received. The Cloisite30B clay contains methyl-2-hydroxyethyltallow alkyl quaternary ammonium ions lining the surfaces of the galleries, encouraging ingress of the monomer and hardener was used as received.

2.2. Preparation of Samples

Neat resin coupons were cast by pouring the reaction mixture into aluminium moulds. The organically treated clay was added to the liquid resin. A mechanical stirrer was used for dispersion of clay particles into polymer matrix and finally an ultrasonic tool was used to complete the dispersion.

The mixture was then degassed in a vacuum oven to remove air bubbles. Afterwards, the catalyst, initiator and accelerator were added. The mixture was allowed to cure at room temperature for 24 hours, and it was subsequently post cured in an oven for 5 hours at 90°C. The nanocomposites were formed during polymerization when the adsorbing monomer separates the clay particles into nano meter scales. The samples of vinyl ester-clay nanocomposites were prepared for investigating mechanical, thermal and water barrier properties.

2.3. X-Ray Diffraction (XRD) Spectroscopy

XRD experiments were conducted on a PANalytical (Netherlands) X-ray diffraction instrument that employed K- α radiation ($\lambda = 1.540598 \text{ \AA}$) and performed from 1.5 to 10°. The scanning rate was 0.1 deg per minute.

2.4. Tensile Strength and Tensile Modulus

An aluminum mould was fabricated in accordance with ASTM D 638 IV to prepare epoxy test specimens. The dumbbell shaped samples were prepared by casting the liquid resin with nanoclay in the mould followed by curing. The samples were 3 mm thick with a gauge length of 33 mm. Samples were measured using Hounsfield 50KN (Model 1150, UK) universal testing machine, with a 1 kN load cell at a crosshead speed of 10 mm/min. The average of the strength and modulus are reported. The tests were carried out at room temperature.

2.5. Flexural Modulus

The three point bending test was performed on rectangular shaped samples according to ASTM D790, using a universal testing machine (UTM), Hounsfield 50KN (UK). The samples are of 25 mm width, 80 mm length, 3 mm thickness. The samples were placed between the two points which are 50 mm apart i.e. the span is 50 mm and crosshead speed was 2 mm/min. The results of three samples averaged for each material.

2.6. Impact Strength

Izod impact strength of the vinyl ester and their nanocomposites samples were determined by an impact tester (Tinius Olsen, Model 892 T) according to ASTM D-256. The sample size used for the test was 63 x 13 x 9 mm³. The impact test was carried out at room temperature and impact energy was reported in J/m. The quoted result is the average of the determinations on five samples.

2.7. Dynamic Mechanical Thermal Analysis

The thermo-mechanical properties of the vinyl ester and their nanocomposites were obtained using a dynamic mechanical thermal analyzer (Qualimeter Eplexor 150N GABO, Germany). The samples were shaped using an aluminum cavity mould yielding the specimen geometry of approximately 80 x 5 x 3 mm³. Samples were sanded to obtain uniform thicknesses of ± 0.02 mm. Measurements were taken in the dual cantilever mode using a frequency of 1 Hz. Oscillation amplitude of 3mm was employed at a heating rate of 2°C/min. Three samples of each type were measured. The average and one standard deviation of the $\tan\delta$ are reported as T_g .

2.8. Thermogravimetric Analysis

TGA analysis was performed on the neat vinylester and vinylester nanocomposites using a TA1350 Series system in a nitrogen atmosphere, by placing 10 mg of sample in a crucible and heating it from 30°C to 800°C at a heating rate of 20°C/min. Nitrogen gas was allowed to flow at a sweep rate of 50 ml/min.

2.9. Water Absorption Study

Water absorption of nanocomposite sample was determined according to ASTM D471-79. Specimen of dimensions 30 X 5 X 2 mm³ were weighed and emerged in water. All specimens were polished to ensure that the surface were flat and parallel to each other, followed by the drying in vacuum oven at 90°C for 2 days. The weight of the swollen samples was recorded at various intervals. From the weight of swelled sample and the initial weight, the % weight gain was calculated.

3. RESULTS AND DISCUSSION

3.1. Structures

The most important question in this study is whether the nanocomposites are formed or not. An important characterization of nanocomposites is X-ray diffraction. The X-ray technique is often applied to identify intercalated structures through Bragg's relation:

$$\lambda = 2d \sin\theta$$

where λ corresponds to the wavelength of the X-ray radiation used ($\lambda = 1.5405 \text{ \AA}$), d corresponds to the spacing between specific diffraction lattice planes and θ is the measured diffraction angle. The d value corresponding to the (001) plane was utilized in this study.

Fig. (1) shows the XRD pattern of the vinylester-Cloisite30B (represented by VEC30B) and vinylester-

Cloisite10A (represented by VEC10A) nanocomposites systems. Pure nanoclay (Cloisite 30B) shows a broad diffraction peak at 4.82° which corresponds to the basal spacing of 1.81 nm. The vinylester nanocomposites containing 5 wt% Cloisite30B shows a main peak at 2.8° corresponding to the basal spacing 3.15 nm and one accompanying peak at 4.82°. Pure nanoclay, Cloisite10A shows a broad diffraction peak at 4.64° which corresponds to the basal spacing of 1.88 nm. The vinylester nanocomposites containing 5 wt% Cloisite10A shows a main peak at 3.15° corresponding to the basal spacing 2.79 nm along with one accompanying peak at 4.64°. The main peak is shifted towards the lower angle and the accompanying peak diminishes relatively to the main peak which confirms the formation of an intercalated structure.

3.2. Thermal Analysis

Fig. (2) shows TGA plot providing information about the thermal stability of neat vinylester and vinylester nanocomposites network containing various amounts of clay particles. The plot for the neat resin exhibits a very small weight loss which commences at 150°C, followed by a continual decrease up to 403°C which corresponds to the primary onset of decomposition (T_{dec}) temperature. The gradual weight loss up to T_{dec} possibly due to the volatilization of unreacted small molecules such as the accelerator and release of functional onium ion etc.

This study indicates that although the initial weight loss for both neat vinyl ester and VE/Cloisite30B nanocomposites commences at the same temperature, the decomposition rate for vinylester-Cloisite30B sample containing 7.5 wt% up to 400°C is comparatively higher than that of other systems. Such a behavior could be explained by the stacked silicate layers could hold accumulated heat that could be used as a heat source to accelerate the decomposition process, in conjunction with the heat flow supplied by

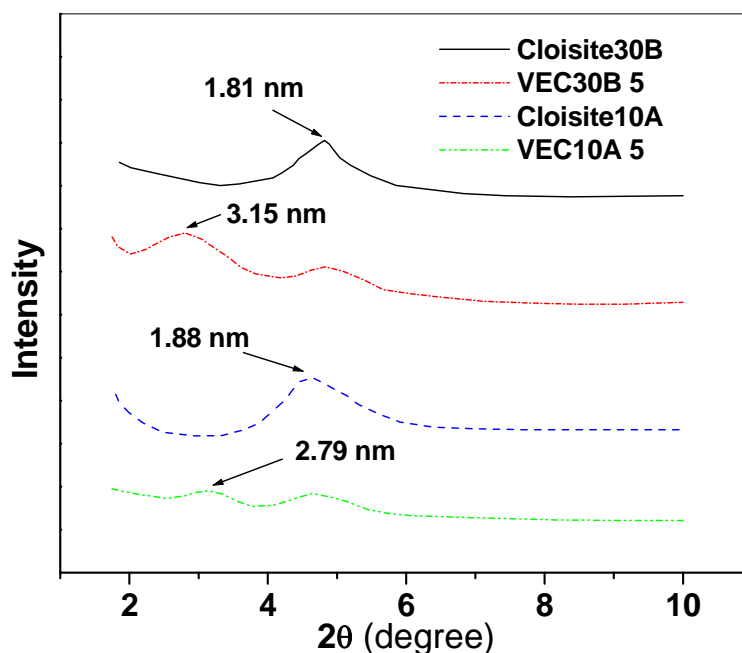


Fig. (1). XRD of Cloisite30B, Cloisite10A and 5 wt% of their vinylester nanocomposites.

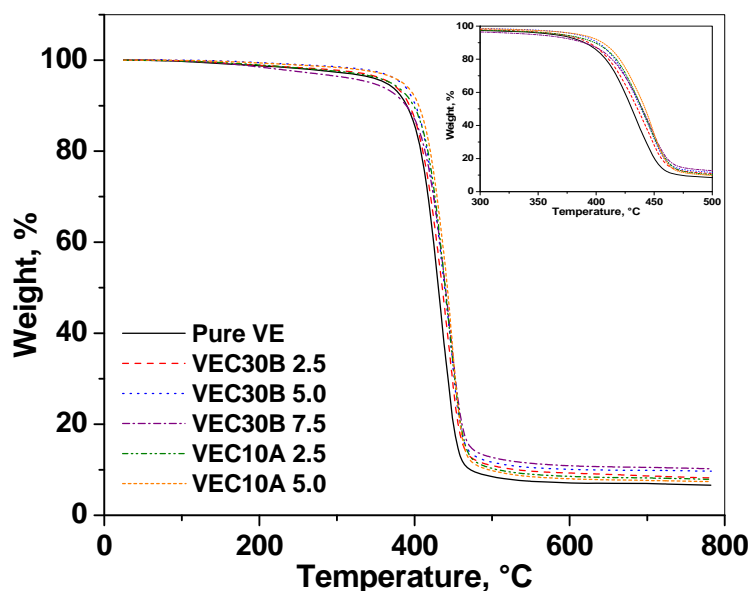


Fig. (2). TGA plot of Cloisite30B and Cloisite10A vinyl ester nanocomposites.

the outside heat source. The sample containing 5 wt% and 7.5 wt% clay provided a higher primary onset of decomposition (409°C) temperature than any other system considered in this study. Table 1 shows the on set of decomposition temperatures for various nanocomposite systems. The clay acts as a heat barrier, which enhances the overall thermal stability of the system, as well as assist in the formation of char after total thermal decomposition. It is clearly seen that mass loss of totally decomposed nanocomposites is comparatively 4 wt% less than the conventional composites. It was found that there is marginal improvement in thermal stability and clay yield for the addition of Cloisite30B clay. Similar behaviour was found in case of VE/Cloisite10A nanocomposites.

The glass transition temperature has been investigated using DMTA. The DMTA scans in the form of $\tan\delta$ vs. temperature plot for the neat VE and VE/Cloisite30B nanocomposites are shown in Fig. (3). This $\tan\delta$ primarily represents the ratio of the dissipation energy to the energy stored in the specimen during applied alternating strain cycle. It is a preferred method for studying viscoelastic behavior of poly-

mers. The shift of the $\tan\delta$ peak to lower temperature indicates a decrease in glass transition temperature, T_g for the nanocomposite. The $\tan\delta$ peak for neat VE is observed to be 133°C, whereas the same for vinyl ester-clay nanocomposites containing 5wt% Cloisite30B clay is seen to be 129°C. The $\tan\delta$ peak for vinyl ester-clay nanocomposites containing 5% Cloisite10A clay is seen to be 118°C. Table 1 shows T_g data obtained from DMTA experiments. The results show a 4°C lower glass transition temperature for VE/Cloisite30B nanocomposites whereas a 15°C lower glass transition temperature for VE/Cloisite10A nanocomposites containing 5 wt% clay particles. Reduced T_g with clay addition may be the results of a number of factors, such as changes in reaction chemistry (homopolymerization and reduced cross-link density), thermal degradation of the surface modifier, or a plasticization effect of unreacted resin or hardener monomers [38]. Chen *et al.* [39] observed a decrease in T_g and rubbery modulus and it was proposed to be related to the formation of lower density interphase consisting of the epoxy resin that is plasticized by the surfactant chains. Effect on stiffness is also reflected in the values of $\tan\delta_{\max}$. The dynamic storage

Table 1. Thermal Properties of Nanocomposites

Sample	Organically modified Montmorillonite clay, wt.%	T_g (°C)	T_{dec} (°C)	E' at 30 °C (GPa)	$\tan\delta_{\max}$
VE/Cloisite30B	0	133	403	3.72	0.95
	2.5	128	405	3.81	0.99
	5	129	409	3.86	0.93
	7.5	126	409	3.98	0.71
VE/Cloisite10A	0	133	403	3.72	0.95
	2.5	124	406	3.68	0.92
	5	118	407	4.15	0.44

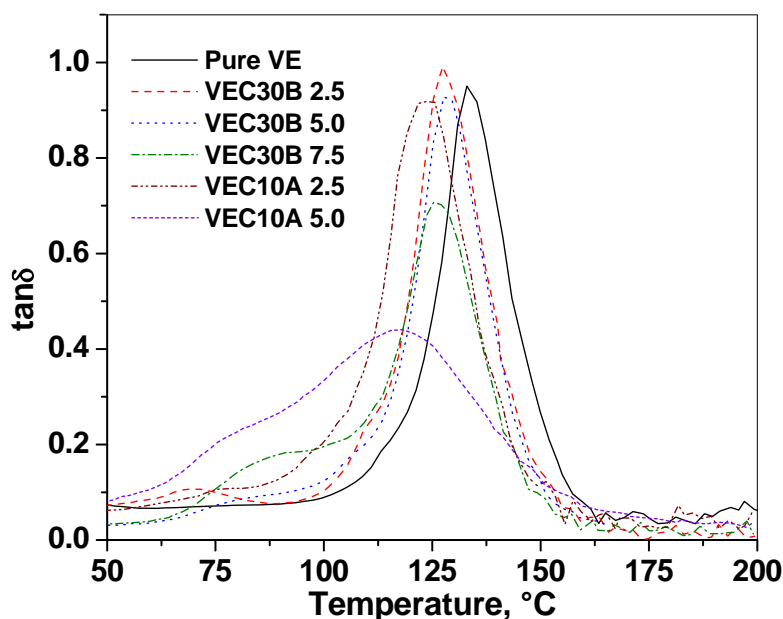


Fig. (3). $\tan\delta$ versus temperature plot of Cloisite30B and Cloisite10A vinyl ester nanocomposites.

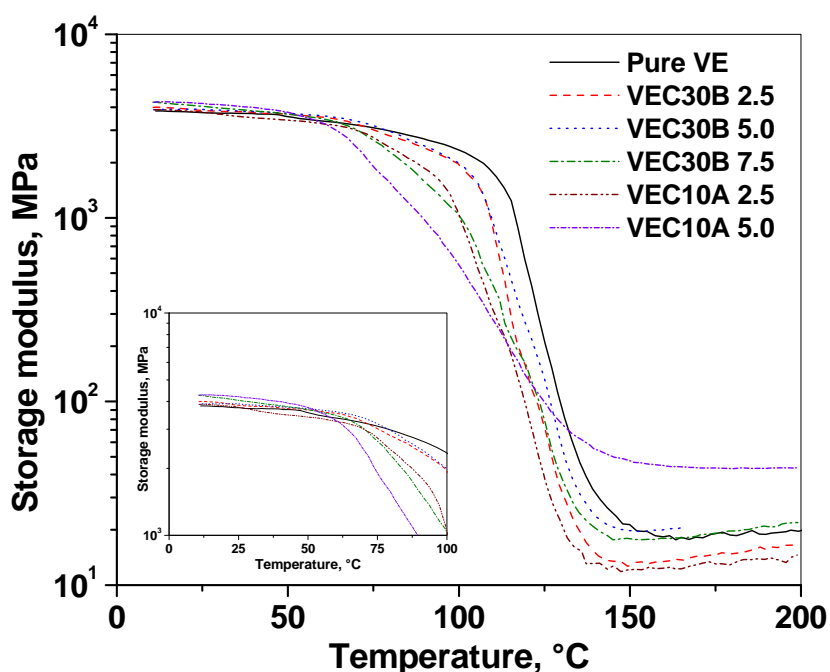


Fig. (4). Storage modulus versus temperature plot of Cloisite30B and Cloisite10A vinyl ester nanocomposites.

modulus, E' versus temperature plots is shown in Fig. (4). The storage modulus of the nanocomposites is higher than of the neat vinylester network at temperature below 50°C in accordance with the results of tensile tests at room temperature. This behaviour can be attributed to the extraordinary large aspect ratio of intercalated silicate layers which is frequently assumed to exceed 1000.

3.3. Mechanical Properties

The tensile test was conducted in order to obtain an idea of the effect of intercalation on the mechanical behaviour of nanocomposites with different clay loading. Fig. (5) depicts

the tensile strength of nanocomposites with various clay contents. The incorporation of clay into vinyl ester resin improved its tensile strength considerably. At 5 wt% of Cloisite30B and Cloisite10A, the nanocomposites have a tensile strength of 1.50 times and 1.44 times higher than unfilled vinyl ester respectively. The significant increase of tensile strength even with small clay content is from the nano scale dispersion of clay in the polymer matrix.

Figs. (6 & 7) shows the tensile modulus and flexural modulus vs. clay contents for both neat vinyl ester and vinyl ester/clay nanocomposites containing 2.5-7.5 wt% nanoclay particles. With the incorporation of clay into vinyl ester net-

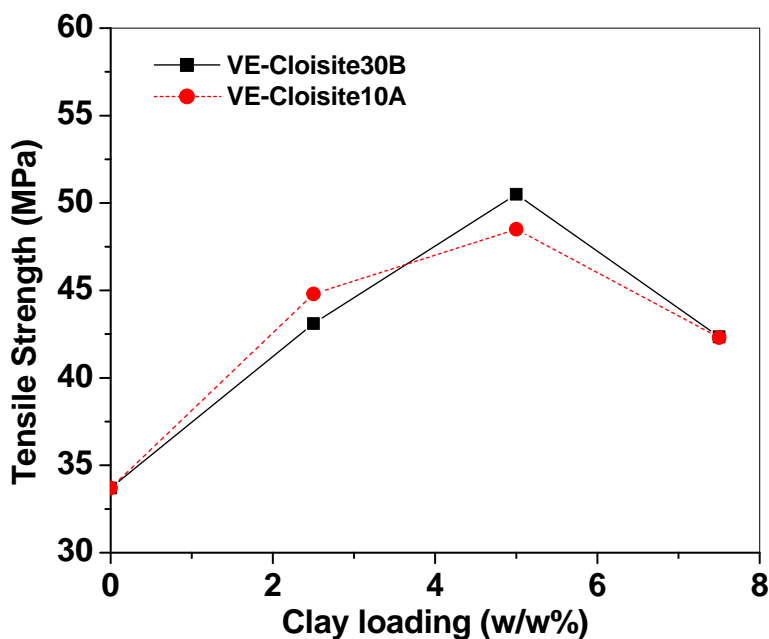


Fig. (5). Tensile strength of Cloisite30B and Cloisite10A vinyl ester nanocomposites with various clay content.

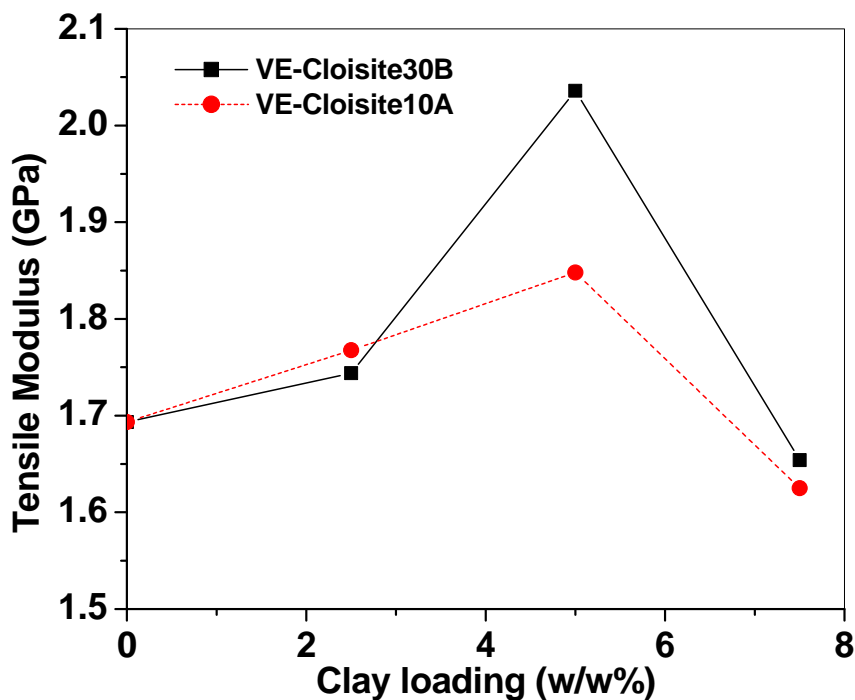


Fig. (6). Tensile Modulus of Cloisite30B and Cloisite10A vinyl ester nanocomposites with various clay content.

work modulus (both the elastic and flexural) increase considerably. It is clearly seen that the nanocomposites containing 5 wt% Cloisite30B nanoclay particles provide 1.2 times higher tensile modulus and 1.18 times higher flexural modulus than that of neat resin. Although the rate of improvement at the beginning is high, become optimum at certain concentration and then it decreases as the clay content becomes high.

The improvement in elastic modulus can be attributed to the exfoliation & good dispersion of nano-size clay particles

that restricts the mobility of polymer chains under loading as well as to the good adhesion between the particles & the vinyl ester matrix. However, the decreasing rate of elastic modulus with higher clay content can be attributed to the presence of unexfoliated aggregates that makes these composites much more brittle.

All the vinyl ester nanocomposites were evaluated with the respect of their impact studies as shown in the Fig. (8). The impact strength is highest in the vinyl ester nanocomposites containing 5 wt% Cloisite30B and Cloisite10A clay

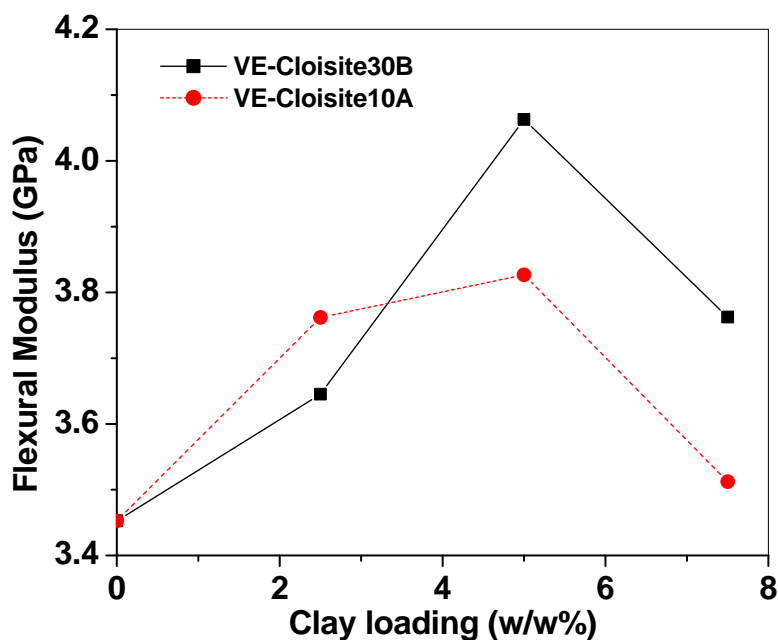


Fig. (7). Flexural modulus of Cloisite30B and Cloisite10A vinyl ester nanocomposites with various clay content.

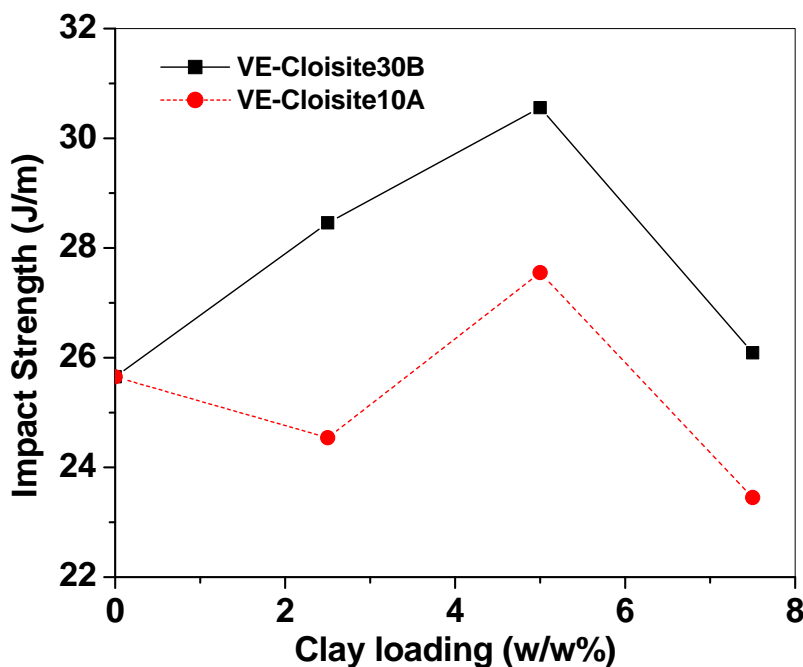


Fig. (8). Impact Strength of Cloisite30B and Cloisite10A vinyl ester nanocomposites with various clay content.

particle. The improvement of the impact resistance over the neat vinyl ester network is only due to the reinforcing effect caused by the dispersed clay particles. The dispersed clay imparts rigidity to the vinyl ester matrix and improves the impact strength. This indicates that incorporation of clay in vinyl ester network imparts both toughening and strengthening. However, beyond a certain concentration the matrix become brittle due to the presence of clay aggregates.

3.4. Water Absorption Study

The water absorption results of the vinylester and clay nanocomposites containing Cloisite30B and Cloisite10A

nanocomposites are given in Fig. (9). It shows that the water absorption of VE/Cloisite30B & VE/Cloisite10A nanocomposites is all slightly lower than that of pure VE. This phenomenon can be explained by the fact that the process of water absorption on VE/Cloisite30B & VE/Cloisite10A nanocomposites was controlled by two competing factors. The first one is the MMT itself is water rich, hence the water absorption ratio of the VE/Cloisite30B & VE/Cloisite10A nanocomposites will increased. The second factor is that, compared to pure VE, the organically modified MMT clay dispersed in the pure vinylester matrix at nanometer scale can increased the mean free path of water molecules to pass

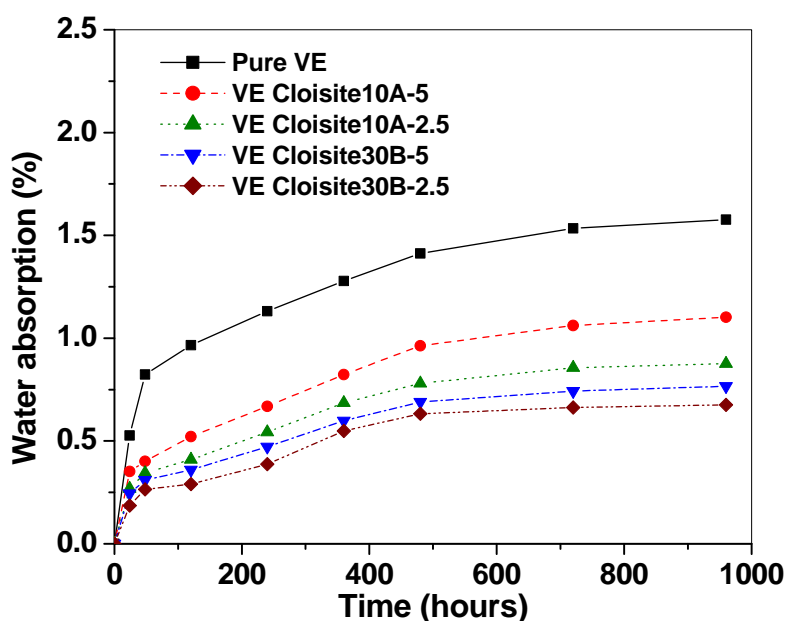


Fig. (9). Water absorption trend of vinyl ester nanocomposites with variation of clay.

through the network of VE/Cloisite30B & VE/Cloisite10A nanocomposites, and results in the decreases of the water absorption of the composites. Because of the lower water absorption for all Cloisite30B & Cloisite10A based vinyl ester nanocomposites than that of pure vinyl ester, it seems that the second factor would play the dominant role in the water absorption of VE/Cloisite30B & VE/Cloisite10A nanocomposites.

4. CONCLUSION

The XRD results prove that the nanoclay is highly intercalated and partially exfoliated for the samples containing 5 wt% of nanoclay. The tensile and flexural modulus values show a gradual increase with increase in percentage of nanoclay in both vinyl ester-Cloisite30B and vinyl ester-Cloisite10A systems as compared to that of the pure ones. Among the two different nanoclays employed, highest tensile, flexural modulus and impact strength are achieved for the samples containing Cloisite30B compared to that of the samples containing Cloisite10A. Also the thermal stability of the samples decreases with increasing clay percentage. From the swelling study it is inferred that, there is restricted water uptake for the samples with increasing nanoclay concentration in the matrix as compared to that of the pure one.

CONFLICT OF INTEREST

None declared.

ACKNOWLEDGEMENT

None declared.

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