Study of Mechanical Properties, Cure Kinetics and Rheology of Nanoclay/Vinyl Ester Resin Composites

Effat Jowdar[a], Fahime Alipor[b], Milad Jowdar[c], Mahdi Jowdar[d],
and Mehrnaz Darabiniya[d]

Abstract—In this work, the effect of quaternary ammonium salt containing nanoclay content (1-5 wt%) on phase morphology, rheology, cure kinetics and mechanical properties of the vinyl ester resin (VER) based nanocomposites was studied. The morphological characterization including d-spacing measurement, microscopy observation and phase-height image processing were performed on the prepared nanocomposites using small angel X-ray scattering (SAXS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). According to the results obtained from these techniques, it was concluded that an intercalated morphology existed for all the nanocomposites. The kinetic analyses of the isothermal curing followed by storage modulus obtained from the rheometry experiments is shown to be an affective rheological characteristic to investigate the cure behavior of VER/clay nanocomposites. In addition, the most important finding regarding the effect of nanoclay on the crosslinking behavior of VER systems lays on the chemisorption and physisorption of the reacting monomers and initiator molecules on the nanoclay platelets surface which is found to be responsible for the retardation of the cure reaction caused by organoclay. Eventually, the mechanical characterizations were performed through the tensile, flexural and impact analysis tests. In this case, a considerable improvement of the bulk mechanical responses such as tensile and flexural strengths and also the corresponding moduli were observed for the nanocomposites.

Keywords— Nanocomposite, Vinyl ester Resin, Rheology, Cure Kinetics, Morphology, Mechanical properties.

I. INTRODUCTION

POLYMER nanocomposites especially reinforced with layered silicates has recently found a great interest. This could be addressed to their potential in providing a noticeable improvement of physical, mechanical and chemical properties with even very low silicate content [1]. This superior level of enhancements is obtained because of the high surface-to-volume ratio which results into their high surface activity [2]. However, the main key to reach these improvements is the achievement of a high dispersion state, exfoliation and/or intercalation in nanoclay layers within the polymer matrix [3]. Nevertheless, the dispersion of nanoparticles within polymeric matrix because of high-energy hydrophilic surfaces of layered silicates is quite difficult [4]. Therefore, the nanoclay surface is usually modified with an organic surfactant in order to make the interlayer space sufficiently hydrophobic for increasing the polymer-clay interactions [5].

Even though, polymer/layered silicate nanocomposites have been widely studied [6-8], there is much less information available on the thermoset polymer based nanocomposites containing nanoclay. In the field of polymer resin nanocomposites, several studies have been devoted to the epoxy [9], polyester [10] and polyimide [11] nanocomposites containing nanoclay. Among these thermoset materials, vinyl ester resins (VERs) are widely used in marine and commercial applications due to their unique properties such as acceptable chemical resistance, thermal stability, mechanical strength, low weight and low cost [12-14].

Yebassa et al. investigated the effect of processing parameters on the chemically functionalized clay/VER nanocomposites [15]. They suggested that the addition of styrene as a comonomer and high-intensity ultrasonic mixing produces vinyl ester nanocomposites with the highest degree of clay exfoliation. Moreover, the correlation between morphology and mechanical properties of VER based nanocomposites containing nanoclay has been highlighted by Gefu and his colleagues [16]. They showed that partially or nearly fully exfoliated nanoclay morphology enhances the mechanical and thermal properties of nanocomposites compared to the pure VER. Furthermore, the viscoelastic properties of VER/clay nanocomposites have been intensively investigated by Drozdov and his coworkers [17]. They found that the response to the uniaxial tensile stress is strongly viscoelastic, whereas increasing the clay content results in a severe decrease of plastic strains observed in pure resin. In addition, Shah et al. [18] have reported that the equilibrium moisture content, the glass transition temperature (Tg) and the elastic modulus of VER/montmorillonite clay nanocomposites were higher than the neat resin.

Effat Jowdar[a] is Office of Standards and Industrial Research, Hormozgan Province Branch, Bandar abbas, Iran.

Fahime Aliporb[b] is with Science and Technology Park, Hormozgan Province Branch, Bandar abbas, Iran.

Milad Jowdar[c] is with Department of Electrical Engineering, slamic Azad University, Science & Research Branch, Bandar abbas, Iran

Mahdi Jowdar[d], and Mehrnaz Darabiniya[d] are with Islamic Azad University, Lengeh Branch, Hormozgan, Iran

* Corresponding author. Tel.: +989177635108.

E-mail address: e.jowdar@gmail.com (e.jowdar).

In spite of the fact that the chemical reactions involve the cure process which could largely affect the physical, mechanical and thermal behavior of the cured systems [19], investigations concerning the parameters which rule the mechanism and rates (kinetics) of VER/montmorillonite systems cure behavior are lacking in the open literature. To the best of our knowledge, the methods employed so far to follow the cure reaction of VER nanocomposites are only limited to differential scanning calorimetry (DSC) [13,20] and Fourier transform infrared spectroscopy (FTIR) [14]. However, DSC method only gives the overall cure kinetics by measuring the rate of produced heat and requires assumptions about the enthalpies of elementary reactions [21]. Moreover, FTIR cannot generally detect the increasing consumption of reactive groups at final curing stages [21]. Therefore, one could utilize rheological methods to investigate the curing process more successfully in order to overcome these impediments. The techniques not only are crucial for optimization of the processing cycle, but also can be applied to achieve a fundamental understanding the cross-linking between kinetics and the mechanical behavior of the system [22].

In addition, nano-structural morphological information is necessary for an in-depth understanding of the correlation between solid state structure after the curing process and other nanocomposites properties such as mechanical behavior. Generally, two characterization techniques are used in the investigation of polymer/clay nanocomposites morphology, namely X-ray diffraction (XRD) and transmission electron microscopy (TEM). Despite XRD is most useful technique for measurements of the nanoclay layers d-spacing, it cannot be the only method to adequately describe the nanoscale distribution of the layered silicate in nanocomposites. Therefore, XRD results should be combined with TEM analyses in order to give an obvious picture of actual dispersion of the nanoclay within the matrix [18]. On the other hand, atomic force microscopy (AFM) has recently become a more powerful technique for researchers to quantify a variety of surface topographies in nanometer scale. Therefore, XRD, TEM and AFM are the complimentary techniques for morphological characterization in this work.

The objectives of the present work include: evaluation the effect of nanoclay content on the cure kinetics of VER/clay nanocomposite using rheological measurement; and also the investigation of morphological structures by SAXS, TEM and AFM. In addition, tensile, flexural and impact experiments were performed to evaluate the effect of nanoclay addition on the mechanical properties of VER matrix.

II. Experimental

A. Materials

VER (DERAKANE 470-30) with 33% of styrene monomer was purchased from Dow Chemical Co. (USA). We used Cloisite 30B (C30B) which was a montmorillonite clay organically modified with a quaternary ammonium salt (MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium). Benzoyl Peroxide (BPO), as a thermal initiator was supplied from Fluka and used as received.

B. Sample preparation

At the beginning, nanoparticles were dried to remove the moisture absorbed by Montmorillonite. Vinyl ester resin was then mixed with 1, 3 and 5 wt% of C30B using a high shear rotor-stator homogenizer. The mixture obtained through this method was stable for several hours. Finally, BPO (1.5 wt%) was added to the mixtures and the compound was stirred for 15 min. The solutions containing 1, 3 and 5 wt% of organoclay were labeled as VER-1%OC, VER-3%OC and VER-5%OC, respectively and each of them was equipped with glass stoppers sealed with silicone grease stored at -10 °C in order to prevent the evaporation of styrene and to avoid any premature curing.

C. Characterization Methods

SAXS studies were preformed on a Hecus S3-Micro focus rotating anode generator with an accelerating voltage of 40 KV/30 mA. The data was collected on phosphor image plates at a sample-to-film distance of 40 cm.

Ultra-thin sections were prepared by using a Leica EM FCS cryoultra microtome equipped with a diamond knife. TEM images of VER/clay nanocomposites were obtained at 120 kV, under low-dose conditions, with a Philips 400T electron microscope.

AFM microscopy was performed using a Dualscope/ Rasterscope C26, DME with AC Probe and Aluminum coating Cantilever. All measurements were made at ambient temperature. Moreover, intermediate to hard tapping mode was employed to reveal good contrast in both height and phase images.

Rheological studies were conducted on a Rheoplus MCR300 rheometer (TA Instruments Inc., Delaware) using the parallel plate mode. The time sweep tests were carried out at different constant temperatures (80 °C, 90 °C, and 95 °C) and a constant shear frequency (1 Hz). In order to record the rheological characteristic functions in the linear viscoelastic range, a constant strain rate of 10% was applied for all the experiments.

Tensile tests were performed to compare the mechanical properties of pure VER and VER/clay nanocomposite samples with the use of a Universal Testing Machine, Model LR 10 K, according to the ASTM D638 at a cross head speed of 100 mm/min and a gripping length of 150 mm. Flexural test were performed on the same machine using the 3-point bending method according to ASTM D790-99. The specimen dimensions were 127 mm (L) x 12.7 mm (W) and had 3.2 mm thickness and a crosshead speed of 2 mm/min was applied for all the experiments. Impact tests on notched specimens were carried out using XCJ-500 Impact Tester (pendulum type) based on ASTMD256. All the results were reported as the average of five experiments for each testing method.

III. RESULTS AND DISCUSSION

A. *Morphological characterization*

D-spacing measurements (SAXS)

In order to evaluate the extent of intercalation/exfoliation of the organically modified montmorillonite particles within the VER matrix, SAXS measurements were performed whose results are given in Fig. 1. It is known that the position of peak provides information on the interlayer spaces between the silicate layers through the relationship between the basal plane separation, d, and the momentum transfer wave number or scattering vector, q:

$$q = 2\pi/d = (4\pi/\lambda)\sin\theta \qquad (1)$$

Where λ is the wavelength of the incident radiation (here $\lambda=1.514$) and θ is half the Bragg scattering angle [23]. Table 1 presents the characteristic q, 2θ and the corresponding basal spacing determined from Eq. (1) for pure clay nanoparticles and the prepared nanocomposites. As shown in Fig. 1, the Pure C30B depicts a strong basal reflection at q=0.34 Å-1 corresponding to a layer distance of 1.85 nm. Since, no scattering was detected for the sample containing 1 wt% nanoclay content. However, the existence of C30B particles in the nanocomposites with higher clay concentrations was confirmed by the additional scattering observed in their SAXS spectra. In this case, the corresponding diffraction peaks appeared at 0.25 and 0.27 Å-1 for the samples containing 3 and 5 wt% clay content which assign to interlayer spacing of 2.50 and 2.32 nm, respectively. Therefore, it can be understood from the peak position that an intercalated morphology is present in the two latter samples containing higher clay content. Moreover, the broadness of the peak appeared for the nanocomposites of 3 wt% nanoclay content, could also be an evidence of the local clay disorder which is known as partial exfoliated morphology. Nevertheless, according to Klug et al. [24], peak broadening can be developed by the defects, lattice strain and finite distribution of clay stack sizes. Hence, further investigations are required to verify the SAXS observations for deeper understanding of the results. Moreover, as given in Table 1, the interlayer spacing decreases as the clay content increases in the nanocomposites. This observation might be partly attributed to the fact that the low loadings of C30B in the nanocomposites allow relatively more VER chains to penetrate into the clay gallery. Moreover, the general distances between the neighboring clay clusters are much larger at low concentrations of the nanoclay. Consequently, as the gallery of the C30B expands, interaction between the nearby clusters should still be much smaller, and the expansion of the gallery can be continued more freely as reported previously [25].

B. *Microscopy observation (TEM)*

TEM characterization method was performed to interpret more precisely the morphological features discovered through SAXS studies. Fig. 2 shows the TEM images of VER nanocomposites containing 1, 3 and 5 wt% of C30B. According to Morgan et al. [26] the lack of peak obtained during X-ray analysis particularly in relatively small angels merely states that no peak was detected during spectroscopy while it does not prove whether the exfoliated clay platelets exist in the nanocomposite or not. Although, there are several numbers of exfoliated single nanoclay layers present inside the VER matrix in the sample containing 1 wt% nanoclay loading, it is hard to make a conclusion on the exfoliation of such a sample (Fig. 2(A)). Moreover, the TEM image for the nanocomposite containing 3 wt% nanoclay shows that although intercalated multilayer crystallites are observed, single exfoliated organoclay layers were also prevalent (Fig. 2(B)). Hence, one could suggest a mixed morphology of intercalated and partially exfoliated structures for such a sample. However, the TEM analyses revealed that the VER nanocomposite containing 5 wt% organoclay could only be designated as intercalated structure (Fig. 2(C)). Accordingly, it is inferred that the dispersion of the C30B platelets within the VER matrix is satisfactory and the TEM results corresponds well with the SAXS diffraction pattern information.

C. *Phase and height image processing (AFM)*

Employing AFM technique to identify high-resolution height images, a more comprehensive understanding of structure-function relationships could be achieved besides some advantages over TEM [27].

Representative AFM height and phase images of the nanocomposites containing 1, 3 and 5 wt% of C30B content with different magnifications are shown in Figs. 3, 4 and 5, respectively. Tapping mode AFM which was applied here; has the advantage of being non-destructive to the nanocomposite sheets surface compared to contact mode AFM. Furthermore, tapping mode AFM is sufficiently sensitive to small modulus differences between two phases and hence it could be utilized to investigate the surface of material in a nanometer scale. Although only a few small areas of each sample were analyzed, it is observed from AFM images (phase and height) that clay discreet phases (dark spots in Figs. 3 and 5, bright spot in Fig.4) are quite regularly distributed in the continuous VER phase without aggregation for all the nanoclay contents. This might be due to the presence of the quaternary ammonium salt on the C30B surface which enhanced the compatibility between the organoclay and the VER chains. Accordingly, this is along with SAXS and TEM studies; however, flipping of the phase contrast observed in nanocomposite with 3 wt% nanoclay may be addressed to the switching of AFM tip and sample interactions from the attraction to repulsion or vice-versa [29].

Upon close examination of the VER/clay nanocomposites AFM phase image analysis, one can determine the clay domains sizes on average are 1.21, 2.54 and 3.71 nm for nanocomposites with 1, 3 and 5 wt% clay content, respectively. These results point to the increment of average size of nanoparticles with increasing the clay weight content. As expected, dispersion process is less efficient at high amount of clay concentration. In addition, the variations in surface topography could be determined quantitatively by Sa and Sq parameters which represent mean and root mean square surface roughness, respectively. Before the roughness measurement begins, the height images were flattened using first-order flattening. This eliminates image artifacts which might lead to a vertical offset between the scan lines.

Numerical values of Sa and Sq parameters and their differences are given in Table 1. The most interesting point concerning the Sa data was the increment of the mean roughness value of the VER/clay nanocomposites upon increasing the clay content. This may be interpreted in terms of a poor dispersion of the nanoparticles in the nanocomposites with high clay concentration which is well consistent with the SAXS and TEM results. Furthermore, the value of (Sa-Sq) for nanocomposite with 5 wt% clay loading is higher than the ones filled with 1 and 3 wt% clay content as expected. This could confirm the presence of a larger undulation in the effective surface height of VER based nanocomposites containing high amount of clay loadings [30]

IV. RHEOLOGICAL CHARACTERIZATION

A. Isothermal cure behavior

One of the major objectives of the present work is to study the effect of nanoclay on the cure behavior of the VER based nanocomposites. Therefore, rheological characterization as a highly sensitive technique to the state of curing was performed to elucidate the role of nanoclay on curing mechanism.

Fig. 6 illustrates the isothermal time dependent storage modulus of the VER/clay nanocomposites and that of neat VER at various curing temperatures. As depicted, G′ remains constant before the onset of curing; once the cross-linking process begins, a remarkable increase in G′ at all the experiment temperatures occurs. The characteristic parameters such as G′$_\infty$ (the values of the storage modulus of the maximally cross-linked polymer), the onset of curing (the time at which G′ increases) and the whole curing time were determined from the curves as listed in Table 2. It can be clearly understood that for the samples with the same organoclay loadings, the onset of curing and curing time decreases with increasing the temperature. This might be attributed to the availability of more thermal energy for the curing reaction at higher curing temperatures. However, it could be understood that the organoclay nanoparticles are acting as inhibitors regarding to the cure reaction times. It might be because of the fact that the organoclay can capture the reacting monomers and chemically absorb them to their surface. Thereby, the curing reaction is hampered or even inhibited. Also, another mechanism of retardation may be due to the physically sorption of the reactants on the surface of clay galleries which affects the stoichiometry and results into some sterical hindrance respect to the forming network [31]. These phenomena which are referred to as "chemisorption" and "physisorption" could also cause the retardation in decomposition of the BPO used as initiator and hence result into the delay in onset of curing process [32]. Moreover, the reaction between the nanoclay and VER chains leads to more restricted motion of the chains which further decelerates the cure reaction [33]. Similar results were also obtained by Zhou et al. [34] on DGEBA/nanoSiC Systems. Nevertheless, the value of G′$_\infty$ seems to be decreased by the increase of curing

temperature. The increase in the curing temperature favors the molecular mobility which in turn causes the rheometer detectors to show lower storage modulus. Moreover, it is worth mentioning here that G′$_\infty$ of the neat VER systems increases with the addition of C30B. This can be assigned to the presence of well dispersed silicate layers in the VER matrix which decreases the polymer chain mobility.

B. Isothermal cure kinetics

All the cure kinetic studies begin with a basic equation of reactant rate, dθ/dt, which is related to the concentration of reactant, θ, through a temperature-dependent constant rate of reaction, K(T). In this case, a phenomenological model as a relatively simple rate of equation represents the main features of the cure kinetics ignoring how the reactive species take part in the reaction [35]. Although, a variety of phenomenological models have been proposed so far by different authors [35-37], all theories could be generally expressed as:

$$d\theta/dt = K(T)f(\theta) \qquad (2)$$

where θ is the degree of curing used to indicate the extent of resin crosslinking and can be obtained from the time dependent storage modulus (G′) using the following equation:

$$\theta = (G'(t) - G'_0)/(G'_\infty - G'_0) \qquad (3)$$

where G′(t) is the value of the storage modulus at time t.

There are two primary mechanisms describing the cure kinetics of the most thermoset resins including nth-order and autocatalytic theories [36]. The nth-order model assumes that the reaction rate is proportional to the concentration of unreacted material (1-θ), as shown in Eq. (4), where n is the order of reaction [37]:

$$d\theta/dt = K(1-\theta)^n \qquad (4)$$

Nevertheless, the nth-order model does not describe the progress of the entire reaction, because several simultaneous reactions occur during the crosslinking process [35]. For an isothermal reaction, nth-order mechanism predicts the maximum of reaction rate at t = 0, which is not the case for autocatalytic cure processes. In the latter case the final products of the curing process can subsequently catalyze the reaction between resin and hardener. On the other hand, in an autocatalytic model, the rate of conversion is proportional to both the concentration of unreacted and reacted material [37]:

$$d\theta/dt = K(1-\theta)^n \theta^m \qquad (5)$$

where m is also the reaction order. In both autocatalytic and nth-order models, K represents the temperature-dependent constant rate of reaction obeying the well-known Arrhenius equation [35] as:

$$K = A\exp(\frac{-E}{RT}) \qquad (6)$$

where A is a frequency factor corresponding to the frequency of the molecular collisions and E, R and T are the activation energy, the gas constant and the absolute temperature, respectively.

Commonly, isothermal curing of thermoset material may be the result of more than one type of chemical reaction. In this situation, one reaction may be nth-order or the other autocatalytic reactions [37]. This combination of reactions can

be represented by a generalized expression given by Kamal and Sourour:

$$d\theta/dt = A_1 \exp\left(\frac{-E_1}{RT}\right)(1-\theta)^n + A_2 \exp\left(\frac{-E_2}{RT}\right)(1-\theta)^n \theta^m \quad (7)$$

The first term in this model corresponds to an nth-order reaction and the second one attributes to an autocatalytic reaction during the curing process of the material. This equation has been widely used in the literature to represent the curing of thermosetting resins [22, 38-39].

Fig. 7 shows the representative plots of conversion, θ, against curing time for the entire samples at different curing temperatures. Fig. 8 also shows the plots of $d\theta/dt$ versus θ for the neat VER and VER based nanocomposites containing 1, 3 and 5 wt% clay content at three different curing temperatures. Apparently, the reaction rate increases with conversion up to a practically constant value; however, followed by the increment of molecular weight with the time, chain mobility is hindered at higher time and the crosslinking reaction stops consequently. As shown in Fig. 8, at given clay content, the cure rate ($d\theta/dt$) increased upon rising the curing temperature. Additionally, the maximum curing rate, $(d\theta/dt)_{max}$, is shifted to the higher conversions by the decrease of isothermal curing temperature. This shifting could be ascribed to the higher viscosity of the compounds at lower temperatures which hinders the formation of crosslinks between the polymer chains.

One can evaluate the kinetic parameters (m, n, K_1, K_2) by fitting the experimental data of Fig. 8 to Eq. (7) using the nonlinear regression method for further understanding the cure kinetics of VER based nanocomposites in the presence of C30B. Accordingly, the kinetic parameters were determined as listed in Table 2. All the values were rounded to two decimal places according to error bands associated with 95% confidence bounds. As expected, the kinetic analysis shows a direct proportionality between both nth-order and autocatalytic constant rate of reaction and the curing temperature. However, for the systems containing organoclay, K_2 values were higher than K_1 which proves that the autocatalytic mechanism was predominant over the other one. The large K_2 value could be justified by different reasons including the fact that the reaction mixture is very viscous. Indeed, due to the high viscosity, upon completing the initial uncatalyzed reaction, the reactants cannot move away but they would rather to be sequestered together. Consequently, they are ready for subsequent catalyzed reactions to occur [40]. Nevertheless, at higher clay content, the lower constant rate was obtained for the system. A closer view to the determined kinetic parameters shows that both m and n were not found to be temperature dependent which is expected theoretically. Moreover, contour graphs of C30B percentage (Fig. 9) show the variation of kinetic parameters (m and n) at the analyzed temperatures. It is interesting to notice that there is not any systematic variation of m and n exponents either with the weight percent of nanoclay.

In addition, the value of activation energies (E_1 and E_2) can be determined from the slope of the linear relationship between ln (K_1) and ln (K_2) versus $1/T$ (plots not shown here). Accordingly, the nth-order activation energies were found 79,

81, 84 and 87 KJ/mol for neat and 1, 3 and 5% nanocomposites, respectively. Also, the autocatalytic activation energy of the neat resin is 59 KJ/mol whereas the value is 41, 42 and 44 KJ/mol for the VER nanocomposite containing 1, 3 and 5 wt% organoclay. It seems that the activation energy increases with the increment of organoclay weight percentage which is clearly the indicative of higher activation energy necessary for a three dimensional network development.

It is well known that relaxation process plays a significant role in polymer physics [41]. According to Hsich et al [42] any chemical relaxation can be described based on the concept of nonequilibrium thermodynamics in which the variation of physical and mechanical properties during the chemical reaction can be interpreted and predicted from the thermodynamic parameters like relaxation time. Accordingly, if the cure reaction is considered as multiple chemical reactions, then the variations of mechanical properties of curing systems like storage modulus, G′, can be expressed by a distribution relaxation function during cure process:

$$G'(t) = G'_0 + (G'_\infty - G'_0)\left\{1 - \exp\left(\frac{t - t_0}{\tau}\right)^\beta\right\} \quad (8)$$

and

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right) \quad (9)$$

Where τ is the relaxation time of the system reaction and β is the constant describing the width of the relaxation spectrum. Also, τ_0 is a time constant which is usually neglected in the measurements [42].

Actually, more than one distribution function should be applied in Hsich model to cover both nth-order and autocatalytic mechanism of the cure reactions. Nevertheless, it is more favorable to reduce the number of model parameters for more convenience [43]. Therefore, only one distribution function, as shown in Eq. (8) was used in this model. The parameters τ and β were obtained from the curve-fitting of rheological data on this model as listed in Table 2 for the entire samples at studied temperatures. The results indicate that all β values are larger than 1. Therefore, one could conclude that the cure reaction of the VER/clay nanocomposites behave as a high-order chemical reaction [42]. Moreover, the increase in the C30B loading decreases the value of β thus the relaxation spectrum starts broadening. This observation is in agreement with the conclusions reported in the previous literature as well [42-43]. Furthermore, a careful speculation of determined relaxation spectrum leads to assume that both the curing temperature and the clay content dictate a reduction effect on τ parameter. The increment of the former factor results into the availability of more thermal energy which facilitates segmental motions as well as diffusional chain motions leading to shorter relaxation times. Also, the reduction effect of the latter factor can be correlated to the plasticizing effect of long-chain organic moiety in the clay which is more pronounced for larger amount of clay contents. A semi-logarithmic plot of τ against $1/T$ was calculated (result not shown here), to estimate the apparent activation energy of the curing reaction. Activation energies were found in this

case to be 44.32, 64.7, 71.35 and 83.47 KJ/mol for neat VER and its nanocomposites with 1, 3 and 5 wt% C30B, respectively. The comparison of activation energies of VER systems with and without organoclay calculated from Kamal-Sourour model with those of Hsich distribution relaxation function shows almost similar trend in both models.

V. MECHANICAL CHARACTERIZATION

Finally, the mechanical characterizations were performed to ascertain the resultant nanocomposites suitability in final practical applications. The measured tensile strength and modulus for the entire samples are listed in Table 3 as a function of clay content. The results clearly indicate a significant improvement in the tensile modulus of the nanocomposites compared to those of the neat resin. Indeed, clay has a much higher modulus than the polymeric matrix and thus the modulus enhancement by the inclusion of the C30B could be easily understood based on the rule of mixtures [44]. Moreover, according to the direct dependence between the Young modulus and the dispersion level of clay platelets, the increase in tensile modulus addresses to the existence of highly dispersed organoclay in the matrix which is consistent with the SAXS, TEM and AFM analyses. Indeed, this fact is more pronounced for the sample containing 1 wt% C30B which has already been discussed to have highly dispersed morphology. Also, the tensile strength of every VER/clay nanocomposite in our experiments is higher than that of neat VER and a maximum value of 45.04 MPa (increment of 20%) is obtained for the VER nanocomposite with C30B content of 3 wt%.

Eventually, the flexural and impact properties of the samples were evaluated and the results are listed in Table 3. It is obvious that increasing the clay loading to 5 wt% shows improvements of about 60 and 50% in flexural strength and modulus, respectively. Of course, the network formed by clay platelets and VER chains is responsible for the significant improvement on the flexural properties. As given in Table 3, although an improvement in the impact strength of the nanocomposites with the addition of clay (up to 3 wt%) is obtained, but the standard deviations of the measurements are uncommonly large. Therefore, it is hard to reach any conclusions about the effectiveness of organoclay on the impact strength of VER systems. The aforementioned results are similar to those reported by other researchers [18,45]. .

VI. CONCLUSION

This study set out to investigate the morphology, rheology, cure behavior and mechanical properties of VER based nanocomposites containing various C30B loadings. The presence of the well dispersed clay with an interlayer spacing of 2.3-2.5 nm in the VER matrix was approved by SAXS studies for the entire samples. Moreover, additional confirmations in support of the SAXS results were obtained by TEM and AFM analyses. The influence of the clay loading and curing temperature on the crosslinking reaction of the prepared nanocomposites was also investigated under

isothermal condition. The results showed that the addition of the C30B to VER systems slowed down the curing reaction. However the curing time decreases upon the rising of curing temperature. Also, the modified Kamal-sourour model was found to adequately replicate the kinetic data over the entire cure life. Furthermore, a kinetic model proposed by Hsich et al. was used to determine a characteristic relaxation time for the nanocomposites at different curing temperature which implied that organoclay not only reduces the systems relaxation time but also broadens the relaxation spectrum of the cure reactions. Finally, the mechanical properties of VER/organoclay nanocomposites in terms of tensile, flexural and impact strengths and corresponding moduli were evaluated as a function of clay loading. The results pointed to a significant improvement of tensile and flexural properties comparing to the neat matrix. Although, the impact tests results superficially indicated that clay addition increased the impact strength. However, due to the unusual large standard deviation of measurements, one can assume that the addition of clay does not adversely affect the impact strength of the VER.

REFERENCES

[1] H. Mirzazadeh, A. A. Katbab. Polymers for Advanced Technologies. 2006, 17, 975-980.
[2] M. E. Romero-Guzman, A. Romo-Uribe, E. Ovalle-Garcia, R. Olayo, C. A. Cruz-Ramos. Polymers for Advanced Technologies. 2008, 19, 1168-1176.
[3] X. P. Wang, A. Huang, D. Jia, Y. Li. European Polymer Journal. 2008, 44, 2784-2789.
[4] E. S. Kim, J. H. Shim, S. H. Jung, J. H. Joo, J. S. Yoon, S.H. Lee. Polymer International. 2010, 59, 479-485.
[5] D. Wang, C. A. Wilkie. Polymer Degradation and Stability. 2003, 82, 309-315.
[6] J. Zhang, D. D. Jiang, D. Wang, C. A. Wilkie. Polymers for Advanced Technologies. 2005, 16, 800-806.
[7] M. Bartholmai, B. Schartel. Polymers for Advanced Technologies. 2004, 15, 355-364.
[8] L. A. Utracki, M. Sepehr, E. Boccaleri. Polymers for Advanced Technologies. 2007, 18, 1-37.
[9] B. Schartel, U. Knoll, A. Hartwig, D. Putz. Polymers for Advanced Technologies. 2006, 281-293.
[10] E. Pollet, C. Delcourt, M. Alexandre, P. Dubois. European Polymer Journal. 2006, 42, 1330-1341.
[11] Z. Liang, J. Yin, J. Wu, Z. Qiu, F. He. European Polymer Journal. 2004, 40, 307-314.
[12] S. Dua, R. L. Mccullough, G. R. Palmese. Polymer composites. 1999, 20, 379-391.
[13] M. A. Stone, B. K. Fink, T. A. Bogetti, J. W. Gillespie. Polymer Engineering and Science. 2000, 40, 2489-2497.
[14] M. Frigione, E. Calo, A. Maffezzoli, C. Carfagna, G. Malucelli. Macromolecular Chemistry and Physics. 2004, 205, 2175-2184.
[15] D. Yebassa, S. Balakrishnan, E. Feresenbet, D. Raghavan, P. R. Start, S. D. Hudson. Journal of Polymer Science: Part A: Polymer Chemistry. 2004, 42, 1310-1321.
[16] J. Gefu, L. Guoqiang. Materials Science and Engineering A. 2008, 498, 327–334.
[17] A. D. Drozdov, J. C. Christiansen, R. K. Gupta, A. P. Shah. Journal of Polymer Science: Part B: Polymer Physics. 2003, 41, 476-492.
[18] A. P. Shah, R. K. Gufta. H. V. S. Gangarao, C. E. Powell. Polymer Engineering and Science. 2002, 42,1852-1863.
[19] R. Thomas, S. Durix, Ch. Sinturel, T. Omonov, S. Goossens, G. Groeninckx, P. Moldenaers, S. Thomas. Polymer 2007, 48,1695-1710.
[20] J. H. Lee, J. W. Lee. Polymer Engineering and Science. 1994, 34, 742-749.

[21] B. G. Min, Z. H. Stachurski, J. H. Hodgkin. Polymer. 1993, 34, 4488-4495.

[22] M. R. Kalaee, M. H. N. Famili, H. Mahdavi. Polymer-Plastics Technology and Engineering. 2009, 48, 627-632.

[23] T. B. Tollea, D. P. Anderson. Composites Science and Technology 2002, 62, 1033-1041.

[24] H. P. Klug, L. E. Alexander. X-Ray Diffraction Procedures. New York, John Wiley Inc, 1974, 261.

[25] Ch. Chen, D. Curliss. Journal of Applied Polymer Science. 2003, 90, 2276-2287.

[26] A. B. Morgan, J. W. Gilman. Journal of Applied Polymer Science. 2003, 87, 1329-1338.

[27] D. Wang, S. Fujinami, K. Nakajima, Sh. Inukai, H. Ueki, A. Magario, T. Noguchi, M. Endo, T. Nishi. Polymer. 2010, 51, 2455-2459.

[28] D. Choi, M. Abdul Kader, B. H. Cho, Y. Huh, Ch. Nah. Journal of Applied Polymer Science. 2005, 98, 1688-1696.

[29] D. Raghavan, M. Van Landingham, X. Gu, T. Nguyen. Langmuir 2000, 16, 9448-9459.

[30] J. K. Mishra, I. Kim, C. S. Ha. Macromolecular Rapid Communications. 2003, 24, 671-675.

[31] M. Lu, M. Shim, S. Kim. Polymer Engineering and Science. 1999, 39, 274-285.

[32] M. Harsch, J. Z. Karger-Kocsis, M. Holst. European Polymer Journal 2007, 43, 1168-1178.

[33] D. Aussawasathien, E. Sancaktar. Macromolecular Symposia. 2008, 264, 26-33.

[34] T. Zhou, M. Gu, Y. Jin, J. Wang. Journal of Polymer Science: Part A: Polymer Chemistry. 2006, 44, 371-379.

[35] A. Yousefi, P. G. Lafleur, R. Gauvin. Polymer Composites. 1997, 18, 157-168.

[36] A. D. Rogers, P. Lee-Sullivan. Polymer Engineering and Science. 2003, 43, 14-25.

[37] T. A. Bullions, J. E. Mcgrath, A. C. Loos. Polymer Engineering and Science 2002, 42, 1058-1069.

[38] E. G. Karayannidou, D. S. Achilias, I. D. Sideridou. European Polymer Journal. 2006, 42, 3311-3323.

[39] A. Omrani, L. C. Simon, A. A. Rostami, M. Ghaemy. European Polymer Journal. 2008, 44, 769-779.

[40] M. Fischer, D. T. Chieu. Analytical Chemistry. 1999, 71, 953-959.

[41] V. I. Vettegren, S. V. Bronnikov, S. Y. Frenkel. Polymer Science U.S.S.R. 1984, 26, 1046-1054.

[42] H. S. Y. Hsich. Journal of Applied Polymer Science. 1982, 27, 3265-3277.

[43] D. Chen, P. He. Composites Science and Technology. 2004, 64, 2501-2507.

[44] Y. P. Wu, Q. X. Jia, D. S. Yu, L. Q. Zhang. Polymer Testing. 2004, 23, 903-909.

[45] E. Fekete, S. Z. Molnar, G. M. Kim, G. H. Michler, B. Pukanszky. Journal of Macromolecular Science, Part B. 1999, 38, 885-899.

TABLE I

CHARACTERISTIC SCATTERING VECTOR, BRAGG ANGLE AND CORRESPONDING LATERAL SPACING OF PURE C30B AND VER BASED NANOCOMPOSITES FILLED WITH 1, 3 AND 5 WT% CLAY LOADING TOGETHER WITH THE VALUE OF MEAN AND ROOT MEAN SQUARE SURFACE ROUGHNESS AND THEIR DIFFERENCES AS A FUNCTION OF CLAY LOADING.

sample	q (Å^{-1})	2θ (deg)	d (nm)	S_a (nm)	S_q (nm)	$S_a - S_q$
C30B	0.34	4.80	1.85	-	-	-
VER-1%OC	No peak	No peak	No peak	20.3	25.5	5.2
VER-3%OC	0.25	3.51	2.50	40.8	47.3	6.5
VER-5%OC	0.27	3.79	2.32	48.4	55.8	7.4

TABLE II
VALUES OF G´∞, ONSET OF CURE, CURE TIME, K1, K2, M, N, T AND B FOR THE ENTIRE SAMPLES AT THE ANALYZED TEMPERATURES

Sample	Curing Temperature (°C)	G'_∞ (MPa)	Onset of cure (s)	Curing time (s)	K_1 $\times10^{-4}$ (s^{-1})	K_2 $\times10^{-2}$ (s^{-1})	m	n	τ (s)	β
Neat	80	14600	425	255	8.67	2.71	0.80	0.81	87.32	2.71
	90	11500	345	165	15.49	3.29	0.76	0.89	56.31	2.96
	95	9300	195	150	27.41	6.81	0.84	0.95	41.08	3.34
VER-1%OC	80	18200	580	270	7.77	2.56	0.97	0.78	61.25	2.51
	90	14700	375	180	13.21	3.27	0.87	0.83	48.76	2.80
	95	13500	200	155	25.73	4.74	0.72	0.93	34.25	3.10
VER-3%OC	80	21300	625	275	7.23	2.47	1.40	1.10	47.86	2.64
	90	20100	420	190	12.02	3.86	0.72	0.95	34.59	2.68
	95	19400	265	165	20.19	4.37	1.01	0.81	31.37	3.11
VER-5%OC	80	23300	680	330	5.21	2.20	0.95	1.03	36.68	2.48
	90	22000	440	205	9.69	3.24	0.83	0.98	28.56	2.61
	95	19900	335	175	18.45	4.11	1.11	1.15	19.00	3.03

TABLE III
FLEXURAL AND IMPACT PROPERTIES OF VER NANOCOMPOSITES AS A FUNCTION OF CLAY LOADING.

sample	Tensile modulus (GPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)	Impact strength (J/m)
Neat	3.6±0.17%	37.53±2.10%	83.12±0.17%	3.80±0.32%	38.31±19.85%
VER-1%OC	3.8±0.24%	39.95±1.18%	110.91±0.05%	4.45±0.87%	76.93±27.71%
VER-3%OC	4.1±0.12%	45.04±2.13%	127.24±0.09%	4.60±0.78%	55.85±23.43%
VER-5%OC	4.6±0.11%	44.4±1.21%	133.15±0.19%	5.70±0.64%	38.12±34.95%