

An Investigation of Water Diffusion Behavior into Nanoorganoclay-Epoxy Composites

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ABSTRACT

Considered as new class of materials having excellent properties resulted from the incorporated nanoorganoclay by the epoxy matrix, the nanoclay-epoxy composites have been applied widely. However, the improved properties can degrade by presence of water in the epoxy matrix, leading to limitation of service life of the material. Diffusion of water having 40 and 60°C in the nanoclay-epoxy composite made by direct mixing process was investigated through immersion test. The strength of the materials was also measured by using the three point bending test. The results showed that the two-stage diffusion process occurred in which diffusivity and saturation was considerably influenced by temperature of water. Affect of the organoclay loading on the diffusion behavior was also observed. The mechanical test showed that retention of flexural strength of the materials was observed as long as the immersion time. Insignificant influence of the organoclay loading on this retention was found.

Keywords: *Diffusion, Nanoclay-Epoxy Composites, Flexural Strength.*

1. INTRODUCTION

Nanocomposites are found as a new class of materials with ultrafine phase dimensions ranging from 1 to 100 nm ([Komareni, 1992](#)). Much investigation has proven that these materials have new and improved properties in comparison to their micro- and macro-composite counterparts. Polymer nanocomposites, especially polymer-layered silicate nanocomposites, show an improvement to conventional filled polymers. The markedly improved properties such as modulus and strength ([Kojima, et al., 1993a](#)); permeability ([Yano, et al., 1993](#); [Kojima, et al., 1993b](#)); shrinkage ([Kelly et al., 1994](#); [Haque and Armeniades, 1986](#)); heat resistance and flammability ([Giannelis, 1996](#) and [Lee et al., 1997](#)) is attributed their nanometer-size dispersion.

Epoxy resins are considered as the best polymeric materials for many applications and widely used in industry as matrix materials of fiber-reinforced composites due to their superior characteristics such as good mechanical properties and good resistance to chemicals. Significant use of epoxy resins as the matrix material in fiber reinforced composites, for the application in the aerospace and automotive industry ([Kshirsagar et al., 2000](#) and [Becker et al., 2003](#)). However, such composites are highly susceptible to environmental conditions, primarily due to the degradation of epoxy matrix ([Kshirsagar et al., 2000](#) and [Kim et al., 2005](#)). Clay-epoxy nanocomposites is an

materials expecting to be not only overcome this degradation and also improve other properties.

The clay-epoxy nanocomposite materials can be produced by two common methods: the direct mixing and the solution mixing ([Jiankun et al., 2001](#); [Zerda and Lesser, 2001](#); [LeBaron et al., 1999](#) and [Kormmann et al., 2001](#)). These techniques produce intercalated or intercalated/exfoliated composites rather than fully exfoliated composites. One of the improved properties of these materials is the reduction of permeability of exposed environmental substances. The only exfoliation of the silicate layers in the epoxy matrix results in this property.

When exposed to aqueous environment, especially to water, the service life of the clay-epoxy composites depends upon the permeation/diffusion behavior of the environments into this material.

Degradation process, such as chemical degradation, reduction of mechanical properties etc., occur when the composite materials contacted to the environment. The environment penetration into a polymer composite is influenced by the composite's characteristics such as density and the order of pore, defects or contamination and the polymer-environment affinity ([Wong and Broutman, 1985](#); [Diamant et al., 1981](#); [Adamson, 1980](#); [Moy and Karasz, 1980](#)). In the studies of liquid molecular transport into a polymer membrane, diffusion has been classified as Case 1 (Fickian type), Case 2 (relaxation-

controlled) and non-Fickian (anomalous) (Thomas and Windle, 1980; Frisch, 1980; Peterlin, 1980; Hansen, 1980; Astaluta and Sarti, 1978). Penetrant molecules diffuse into the membrane until the concentration is equal over the whole of the membrane (saturation state). When Fickian

$$\frac{C_{(t,x)}}{C_{\infty}} = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \exp\left[-\frac{D(2m+1)^2 \pi^2 t}{l^2}\right] * \sin\left[\frac{(2m+1)\pi x}{h}\right] \quad (1)$$

in which C(t,x) and C∞ are the concentrations of the liquid inside the membrane at time t, position x and saturate state, D is diffusivity, which depends on the nature of liquid-polymer interactions and h is the thickness of the membrane. The diffusion coefficient has been calculated by (Crank, 1975):

$$\frac{M_t}{M_{\infty}} = \frac{4}{h} \sqrt{\frac{Dt}{\pi}} \quad (2)$$

where Mt and M∞ are the mass uptake at time t and saturation state, respectively. The diffusivity can be calculated from the initial slope of the curve generated from Equation (2).

In this paper, the influence of nanoclay loading on the diffusion behavior of the 40 and 60°C-de-ionized water into nanoclay-epoxy composite system was studied and discussed.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and Sample Preparation

Three components are need to form the clay-epoxy nanocomposites using for the investigation: the Bisphenol A Epoxy Epomik R140 made by Mitsui Chemical Co., Ltd used as the matrix component of the composites; the diamine having commercial name as Jeffamine D230 made by Huntsman Co. used as curing agent; and the organoclays received from Nanocor Inc. named as Nanomer I.28E.

The organoclay was swelled with the curing agent and mixed with a mechanical stirrer at 2500 rpm for 1.5 h at 60°C, followed by ultra-sonication for an additional 1 h. When the swelling process had been finished, the epoxy resin was added. It should notice that before the curing process started, degassing process under vacuum was applied. The curing was done in two stages: the first stage was carried out at 70°C for 6 h while the second was at 110°C for 6 h. The load of the clay varied from 0 to 6 phr

diffusion is assumed, the time-dependent relative concentration of the liquids into the polymer membrane can be expressed by the following equation (Vergnaud, 1991):

(parts per hundred resin). Table 1 shows code and formula of the prepared samples.

Table 1: Sample used for Investigation

CODE	ORGANOCLAY (phr)	CURING AGENT (phr)
CE0	0	29
CE2	2	29
CE4	4	29
CE6	6	29

The test pieces having dimension of 60 x 25 x 2 mm were cut out from the prepared sample sheets. The pieces were then dried up at 50°C for 72 hours to ensure that the remaining moisture/gas was removed before the immersion test was carried out.

2.2 Immersion Test

Immersion experiment was carried out by simply immersing the test pieces in de-ionized water. The test pieces were fixed in a polytetrafluoroethylene holder to avoid contact surface each other and immersed in separable flash bottles which filled with the water. Temperature of the water was constantly set at 40 and 60 °C. Figure 1 shows schematic of the immersion test apparatus.

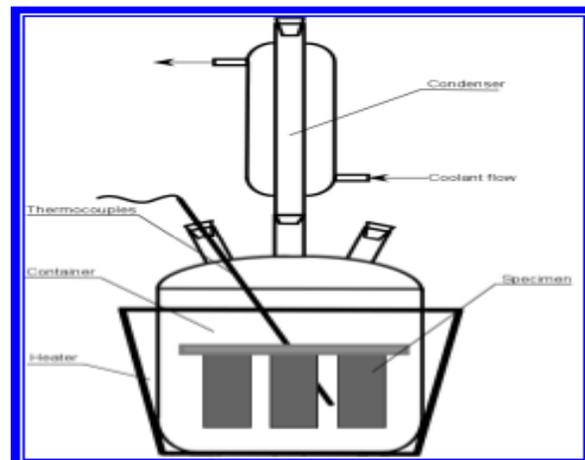


Fig.1. Schematic of the immersion test apparatus

At interval time, the specimens were taken out, wiped by filter paper to remove attached water on their surfaces and weighed by a balance with 0.1 mg accuracy. A change in mass was measured related to initial mass.

2.3 Bending Test

At interval time, the specimens were taken out, wiped by filter paper to remove attached water on their surfaces and then conducted to the three point bending test. Three test samples were taken for this test to obtain an average value. Bending test was done according to ASTM D790 with Shimadzu Autograph AGS-1KNJ machine.

3. RESULTS AND DISCUSSIONS

3.1 Diffusion Behavior of Water

The water uptake during immersion was measured by comparing the tested specimen's weight to its initial weight. The time dependent uptake amount is shown in Figures 2 and 3. It can be seen that the uptake increased

gradually with increasing time at first, then leveled off. This observation is attributed by diffusion of the water into the samples in which the leveling off is considered as saturation state of the diffusion and the tangent to square root of time axis related to diffusion rate. The diffusion rate and saturation value of water diffusion into the sample was influenced by the clay loading and water temperature. The higher clay loading was, the faster diffusion rate and the higher saturation value attained. This maybe explained by much more free volumes and spaces formed inside the composites samples comparing to those in the resin sample (CE0 sample). In general, added nanoclay in epoxy matrix may reduce the water uptake since it resulted in the reduction of the tortuosity path. However, the results show the contrary manner. It may be explained by un-fully exfoliated performance of the organoclay composition in the material structure and/or by an remaining hydrophilic characteristics of the clay even its form was changed in epoxy matrix. The similar results were also presented ([Becker et al., 2003](#); [Lan and Pinnavaia, 1994](#); [Massam and Pinnavaia, 1998](#)).

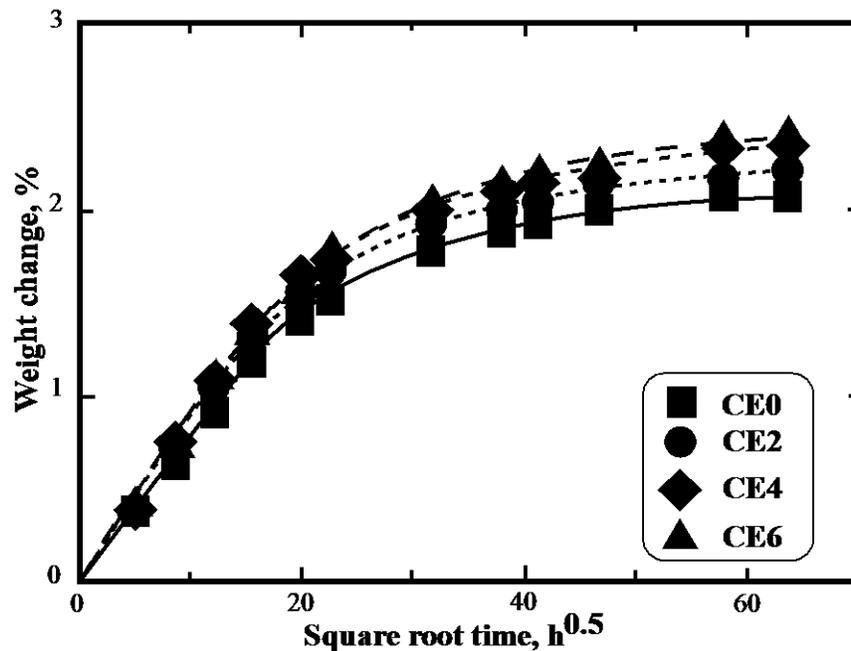


Fig.2. Weight change of samples exposed to deionised water at 40°C

Contrary to the affect of clay loading, temperature showed a significant effect to diffusion rate and saturation value (see Figure 4 for example). Diffusion rate and saturation value of the water diffusion increased with the increase of temperature. Figure 4 shows that the saturation increased about 30% for samples immersed in water at 60°C in comparison to saturation value of the same sample if they were immersed in water at 40°C. An interest finding is that different level of saturation value between CE0 and

CE2 at 60°C water expanded comparing to those at 40°C water. The similar tendency was also obtained for other clay loadings. By comparing tangent to x-axis in Figure 4, it shows that the higher diffusion rate obtained when samples immersed in water at 60°C. The significant affect of temperature to diffusion behavior of water into the composites may attribute to an increase of number of free volumes that resulted from relaxation of molecular chain of resin by heat.

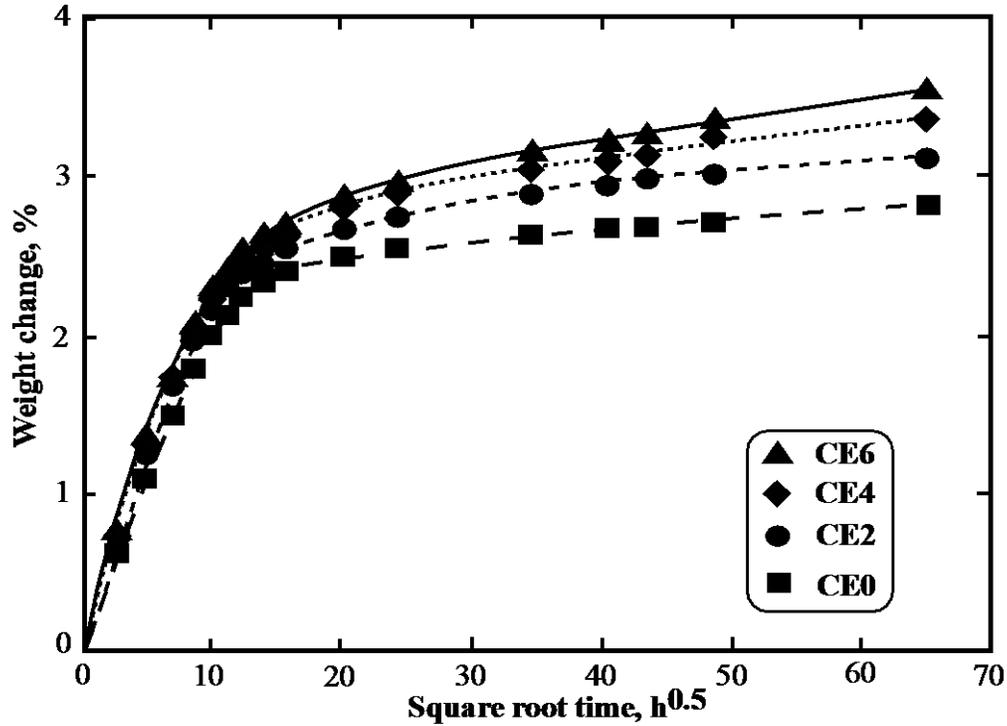


Fig.3. Weight change of sample during water exposure at 60°C

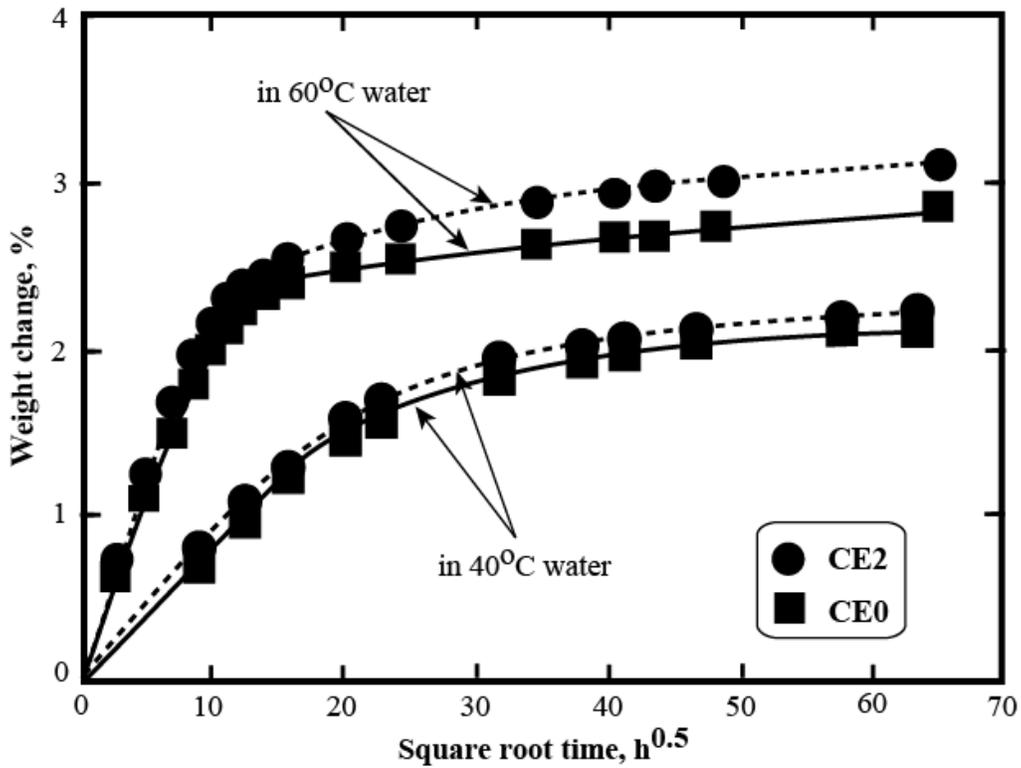


Fig.4. Weight change of sample during water exposure at 40 and 60 °C

Consideration of diffusion mode, it recognized that two stage diffusion was observed at the 40°C and 60°C water

for all samples. Detail is shown in Figure 5. Occurrence of the two stage maybe attributed to thermal relaxation

effects of polymer material.

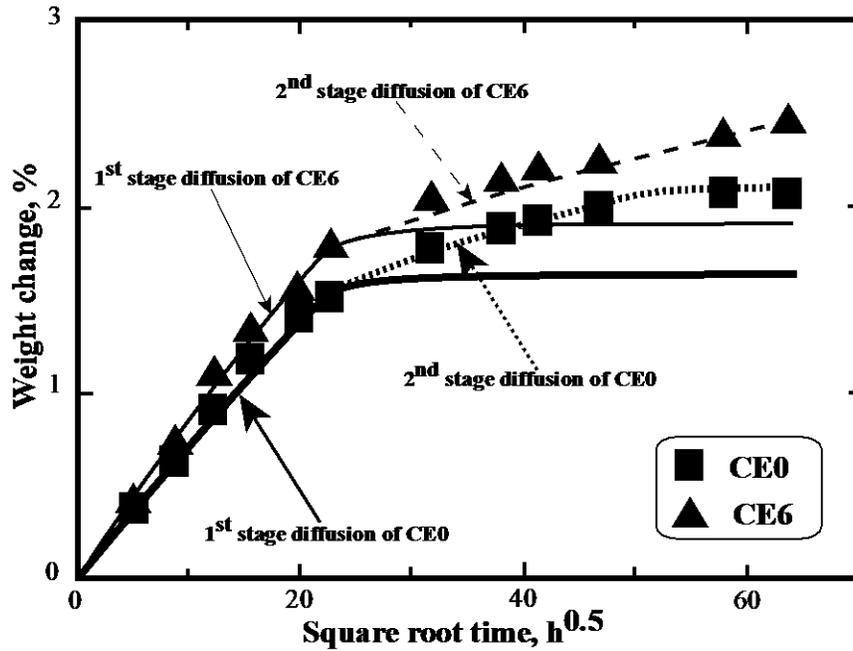


Fig.5. Diffusion model of 40°C-deionised water into samples

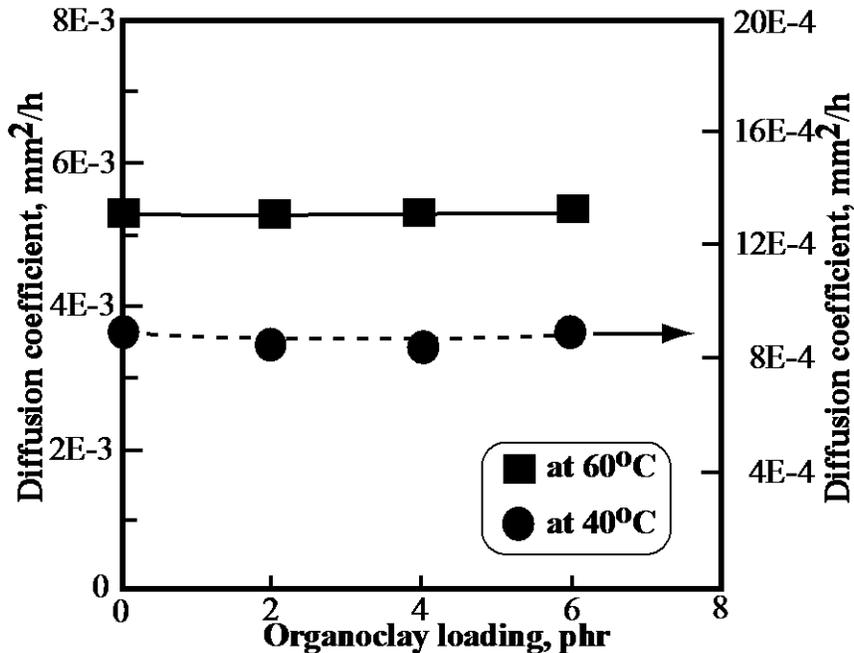


Fig.6. Diffusion coefficient of the 1st stage water diffusion into the nanoclay-epoxy composites samples

The diffusivities calculated by Equation 2 are shown in Figures 6 and 7. It can see that the diffusivity of water at 60°C into a sample is always about 6 times higher than those of the water at 40°C into that sample. This confirmed the importance of temperature to diffusion behavior of water into the test material. The diffusivity of

the 60°C water into the samples in the 2nd stage of diffusion is shown in Figure 7. In this stage, the diffusivity decreased with increasing the organoclay loading, then leveled off when the organoclay loading is higher than 4phr. It means that amount of organoclay loading can reduced rate of water diffusion into the

material. Combination to the diffusivity in the 1stage, an interest point is the organoclay composition seems only to play an importance in the 2nd stage of diffusion process.

The diffusivity of the 2nd stage is much smaller than those of the 2nd stage diffusion.

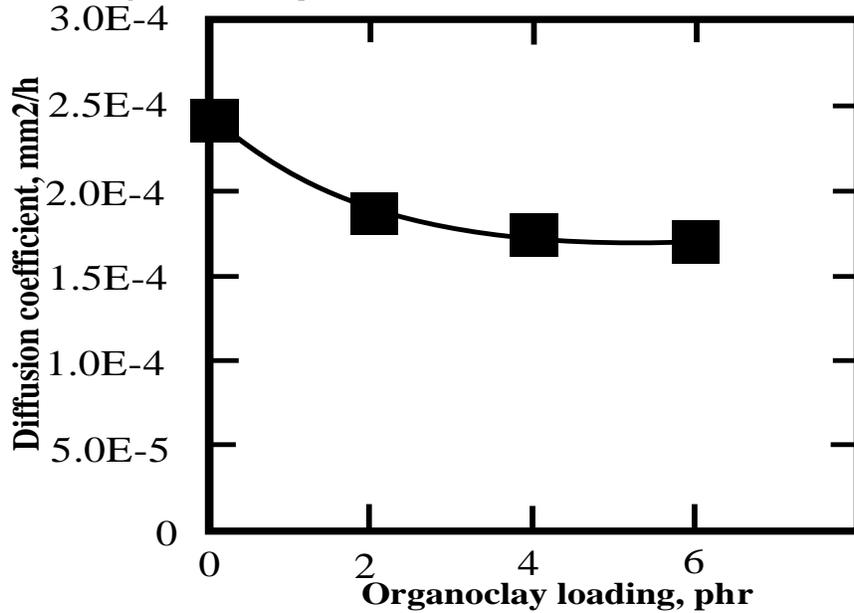


Fig.7. Diffusion coefficient of the 2nd stage water diffusion into the nanoclay-epoxy composites samples under 60°C condition

3.2 Mechanical Properties

The result of the three-point bending test under wet condition is shown in Figures 8 to 9. As seen in Figure 8, the initial flexural strength decreased with the increase of the nanoclay loading. It may result from agglomeration of the nanoclay in epoxy matrix. The adhesion strength and

interfacial stiffness of interface between the nanoclay particle and the epoxy matrix are the important factors which contribute flexural strength of the composites due to they are significant to stress transfer and elastic deformation from the epoxy matrix to the fillers. The result of flexural modulus showed in Figure 9 is accordance with the manner showed in Figure 8.

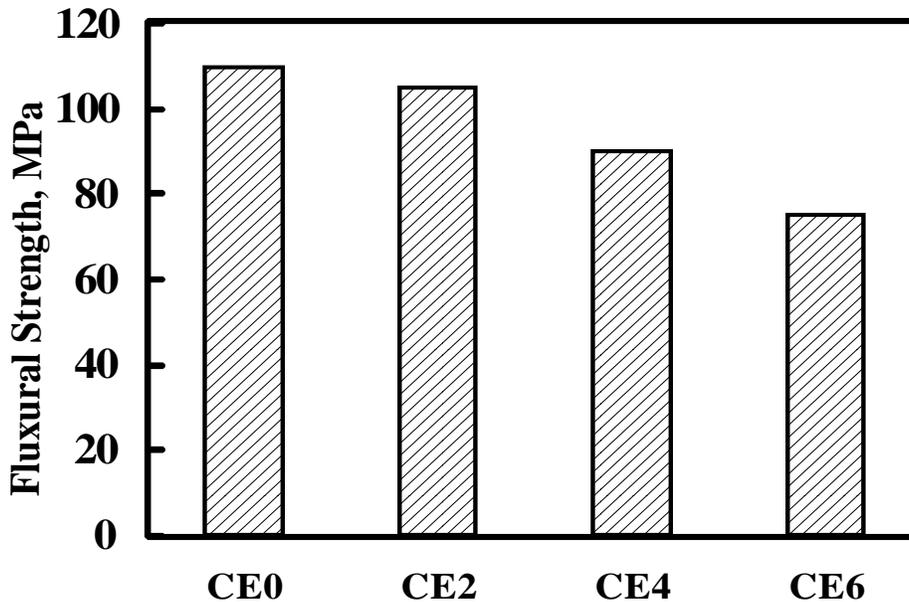


Fig.8. Flexural strength of samples

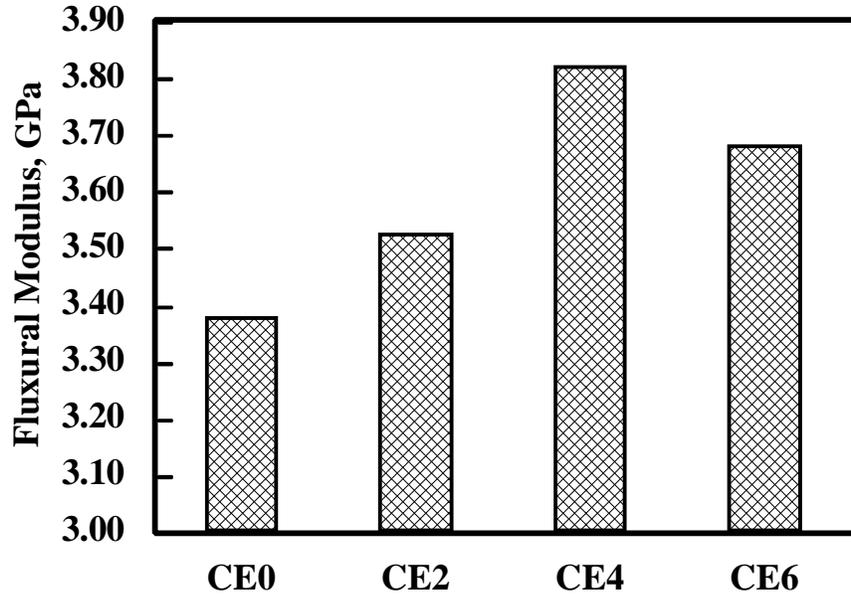


Fig.9. Flexural modulus of samples

Retention of properties as same as at initial, during service time, is an important criteria to evaluate application potential of any materials. In terms of mechanical properties, the flexural strength of the test pieces was measured during the immersion test and its result is shown in Figure 10. An evaluable information, as seen in this figure, is that there are not much change of the strength of nanoclay-epoxy composites samples while the

strength of the neat epoxy reduced about 20% after immersed 100 h, then maintaining as long as the immersion time. It can be explained by distortion produced around the amine salt resulted the decrease of the C-N bond of the epoxy matrix. When the organoclay is added, this distortion may be hindered, therefore, the strength is retention.

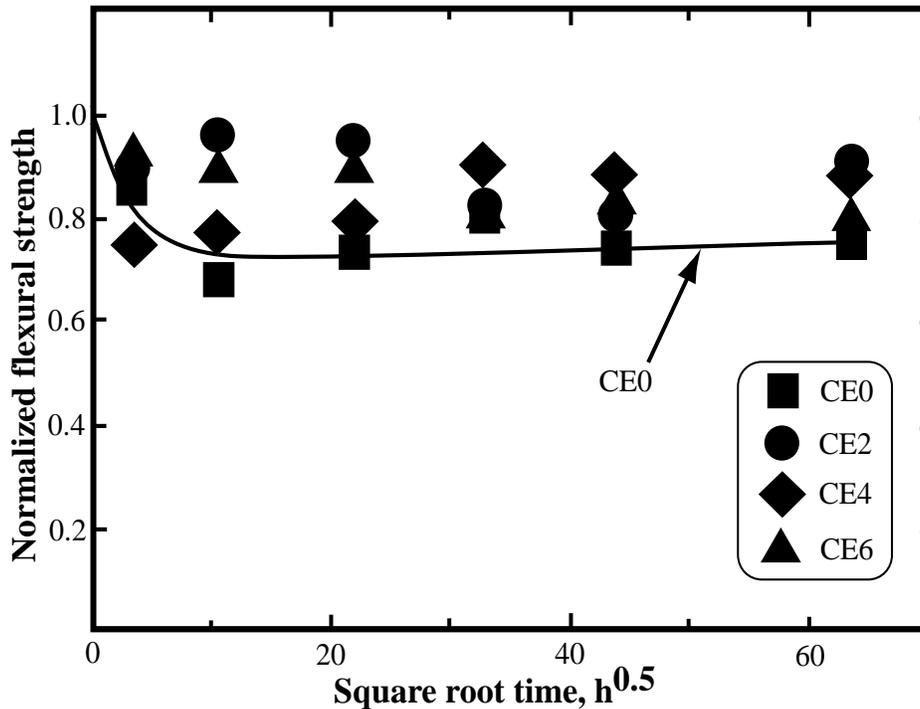


Fig. 10. Normalized flexural strength (wet condition) vs. immersion time in the 40°C de-ionized water.

4. CONCLUSION

Based on the obtained results and discussions, the followings are conclusion:

- Diffusion of the 40 and 60°C de-ionized water into the organoclay-epoxy composites obeyed the two-stage diffusion mode. The 2nd stage of this diffusion process observed much clear in case of the 60°C water. Addition of the nanoclay influenced the rate and saturation of the material as the more addition of the nanoclay was, the higher saturation occurred. Affect of temperature of the de-ionized water is similar as the influence of the nanoclay loading. The diffusivity in the second stage is always smaller than those of the first stage. The increase of organoclay loading seems to make the diffusivity of the 60°C water in 2nd stage decreased.
- Flexural strength of the samples decreased with increasing the organoclay loading for the composite samples. However, the retention of this property during immersion test is same as those at initial, which did not obtain for the neat resin sample.

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