

Diffusion Behavior of Water and Sulfuric Acid in Epoxy/Organoclay Nanocomposites

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ABSTRACT: The research on polymer-layered silicate nanocomposites is currently an expanding field of study because they often exhibit a wide range of improved properties over their unmodified starting polymers. Epoxy/organoclay nanocomposites have been prepared by intercalating epoxy into the organoclay montmorillonite. The intercalation and/or exfoliation of the clay within the nanocomposite were monitored using X-ray diffraction and transmission electron microscopy. Diffusion was studied through epoxy samples containing up to 10 phr of organically treated montmorillonite following the gravity method. The water and sulfuric acid diffusion within the epoxy-based nanocomposites were evaluated in terms of diffusivity, weight change and penetration depth of the sulfuric acid element S as function of immersion time and immersion temperature. An investigation of the resistance

of epoxy nanocomposite to a corrosive environment by immersion into sulfuric acid at elevated temperature was performed. The effect of the degree of exfoliation of the clay on moisture barrier effect and corrosion resistance is specifically studied. The data has been compared to those obtained from the neat epoxy resin to evaluate the diffusion properties of the nanocomposites. It was found that the diffusion of water and that of acid do not obey Fick's law, and that the higher the organoclay content the higher weight change was obtained. The presence of the organoclay enhanced the diffusivity and delayed the penetration of the sulfuric acid. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1021–1029, 2009

Key words: diffusion; epoxy; organoclay; nanocomposites; sulfuric acid

INTRODUCTION

Polymer nanocomposites are a new emerging class of composite materials derived from nanoparticles with at least one dimension in the nanometer range. The research on polymer-layered silicate nanocomposites is currently an expanding field of investigation, this is mainly due to the large potential to achieve property enhancement significantly greater than that attainable using conventional fillers or polymer blends.^{1–3}

A wide range of layered silicates are available, however; only few have found real applications.⁴ The most commonly used ones is montmorillonite (MMT) because it is mainly a cation-poor layered silicate, in which layers can be easily separated or delaminated.¹ Organic modification of MMT occurs by ion exchange of the sodium ions present on natural MMT with organic alkyl ammonium ions.^{1,4–5} The thermal stability of the organic moiety is of importance, as many composites are melt blended or cured at high temperature to yield the final product. Mainly, as the alkyl onium ion is thermally instable

at temperature of 200°C or less.^{6–8} When this decomposition occurs, the silicate layers become hydrophilic again and their ability to affect the properties positively are reduced.

Nanocomposites based on epoxy and organoclay have attracted considerable interest because epoxy is one of the most widely used and fastest growing class of thermosetting materials.^{9,10} However, the ability to process epoxy/organoclay into useful forms depends upon the ability to control the ingredients of the thermoset composition i.e., curing agent, catalyst, nanoparticles, etc.

Understanding and controlling the various factors that govern the making of exfoliated thermoset/layered silicate nanocomposite is rather complex, many researches have focused on and made contribution to the understanding of some of these issues.^{11–13}

Nanocomposites have the ability and the potential to reduce the permeability of polymer composites against ingress of corrosive substances and to enhance a variety of other mechanical properties.^{14,15}

The reduction in permeability that can be attained from the exfoliation of layered silicates into polymers depends on the permeating agent being investigated. The permeability reduction achieved depends also upon the specific aspect ratio of the clay being used.¹⁵ Few studies have been carried up

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to now on the effect of moisture on the barrier properties of layered silicates-based nanocomposites,^{15–17} but very limited ones have treated the corrosive environment on these materials.^{18–19}

Epoxy-based thermosetting polymer resins are widely used in the industry due to their superior characteristics such as high thermal resistance, good resistance to chemical and low shrinkage at elevated temperature.^{9,20–22} Despite their inherent advantages, such composites are highly susceptible to environmental liquid, primarily due to the degradation of epoxy matrix.

Hence, there are concerns regarding their overall long-term durability, especially as related to the capacity for sustained performance under harsh, corrosive environment.^{8,9,20,21}

The main goal of this article is to determine if specially modified clay could be incorporated and well dispersed with epoxy resin, and to investigate the improvement of the durability of the epoxy when in contact with water or with corrosive environments. Incorporating such clays into organic polymers has been shown to improve barrier properties mainly for gas permeation. This is believed to be a result of an exfoliated structure as the individual clay layers separate and become well dispersed within the polymer matrix generating a tortuous path for penetrant molecules.

EXPERIMENTS

Materials and sample preparation

The epoxy resin and the curing agent used in this study were a bisphenol, a type Epoxy Epomik R140 from Mitsui Chemical (Japan); Jeffamine D230, a diamine curing agent from Huntsman (USA). The montmorillonite-based organoclay used to prepare nanocomposites was Nanomer I.30E purchased from Nanocor (USA).

The following steps were involved in the preparation of Epoxy/organoclay¹⁸: First, epoxy resin was mixed with the desired amount of the organoclay (2–10 phr) at 80°C for 5 h; the mixture was then subjected to sonication for 30 min and then degassed under vacuum. After cooling to room temperature, the corresponding curing agent (32 phr) was added to the mixture stirred and degassed again before curing. The resin mixture was cured at 80°C for 5 h, followed by postcure at 120°C for 10 h. The cured plate were cut to specimens with the dimensions of 6 × 2.5 × 2 mm³.

Characterization

X-Ray diffraction (XRD) experiments were performed on a Philips Xpert MPD PW3050 X-ray

diffractometer with a CuK α as a radiation source ($\lambda = 1.54$), operated at 40 kV and 30 mA. Samples were scanned at diffraction angles (2θ 's) from 2 to 10 at a scan speed of 0.016°/s.

Transmission electron microscopy coupled to energy dispersive X-ray spectrometer (TEM/EDS) photographs were taken with a JEOL JEM 2010F using an acceleration voltage of 200 kV. A sample mechanical measurement was performed at ambient temperature.

A JEOL JSM-5310LV scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectrometer was used to investigate the penetration depth of sulfuric acid element S by analyzing the cross section of the immersed samples.

Sorption test of water and sulfuric acid

All samples were dried at 60°C for about 75 h and their initial weights and dimensions were measured before the test. Sorption test was performed by immersion of the samples, held by a teflon tube, in a beaker containing the specific investigated solution either deionized water or sulfuric acid (10 mass %). The beaker was sealed with a plastic film to avoid evaporation of the solution. It was immersed in a thermoregulated water bath oven. Immersion temperatures were set to 40, 60, and 80°C. An average of at least three specimens for each composition was used for one point data.

The specimens were periodically removed, wiped with filter paper to remove excess solution, and then were kept for 1 h at room temperature before they were weighed. Solution content was determined using the following equation:

$$M_t(\%) = (W_t - W_o)/W_o \times 100 \quad (1)$$

where M_t , W_t , and W_o are the solution content at a given time, weight of the sample at the time of the measurement, and initial weight, respectively.

RESULTS AND DISCUSSION

Nanocomposite morphology

Figure 1 shows the XRD pattern of the pristine organoclay and that of the cured epoxy/organoclay composites at different organoclay loading. The d -spacing was calculated using the Bragg's equation:

$$\lambda = 2d \sin\theta \quad (2)$$

The pristine organoclay has a single sharp peak at $2\theta = 3.9^\circ$, which corresponds to a d -spacing of 22.6 Å. However, in the case of the composite, it was difficult to find a prominent peak in all prepared samples. This result can be interpreted by the fact that epoxy resin diffused into the organoclay

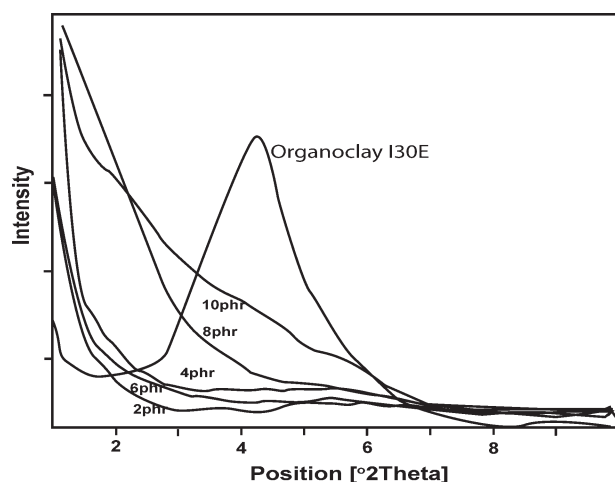


Figure 1 XRD patterns of epoxy/organoclay formulations.

galleries and formed intercalated or exfoliated nanocomposite. However, if the nanocomposites were disordered; peaks are not also observed in the XRD due to loss of the structural registry of the layers, the large d -spacing (>10 nm), or both.²³

The cured nanocomposites at high organoclay content 8 and 10 phr showed a broad shoulder around $2\theta = 3^\circ$. This is due to a possible agglomeration of the particles, as the organoclay content increases it becomes more difficult to mix mainly due to an increase in the viscosity.

These XRD patterns indicate that the clay particles have been either highly intercalated or exfoliated in epoxy to greater than 44 \AA ($2\theta = 2^\circ$, the wide angle XRD detection limit).

The change observed in the XRD can be explained by polymer entering the clay galleries pushing the platelets apart (i.e., intercalation). As more polymer

chains enter the galleries, two possible changes can occur. First, the platelets can loose their ordered, crystalline structure and become disordered with the platelets no longer parallel without pushing the platelets apart. The result is that the XRD peak broadens into the baseline (intercalated disordered). Secondly, the polymer that enters the galleries pushes the platelets far enough apart that the platelet separation exceeds the sensitivity of XRD (exfoliation).

Figure 2 shows the TEM micrographs of epoxy nanocomposite containing 2 phr organoclay as an illustration. TEM picture at low magnification showed that the clay particles are reasonably dispersed, uniformly distributed, and randomly oriented. At higher magnifications ($>100,000\times$), it was found that the clay particles existed in both as clusters or aggregates and as individual platelets in the form of dark lines. The presence of clay in the form of both aggregates and individual platelets suggests that the organoclay are not completely exfoliated within the epoxy matrix, improvement in the preparation process by adding high shear mixing device or longer time would help to have higher degree of exfoliation and also better dispersion of the organoclay.

The morphology of the investigated epoxy nanocomposite is revealed to be a combination of highly intercalated structure with minor exfoliated zone and stacked structure.

Mechanical properties

Mixing clay nanoparticles in an epoxy matrix is expected to improve mechanical properties. Nano-scale clay particles offer a larger surface contact area with the matrix polymer.

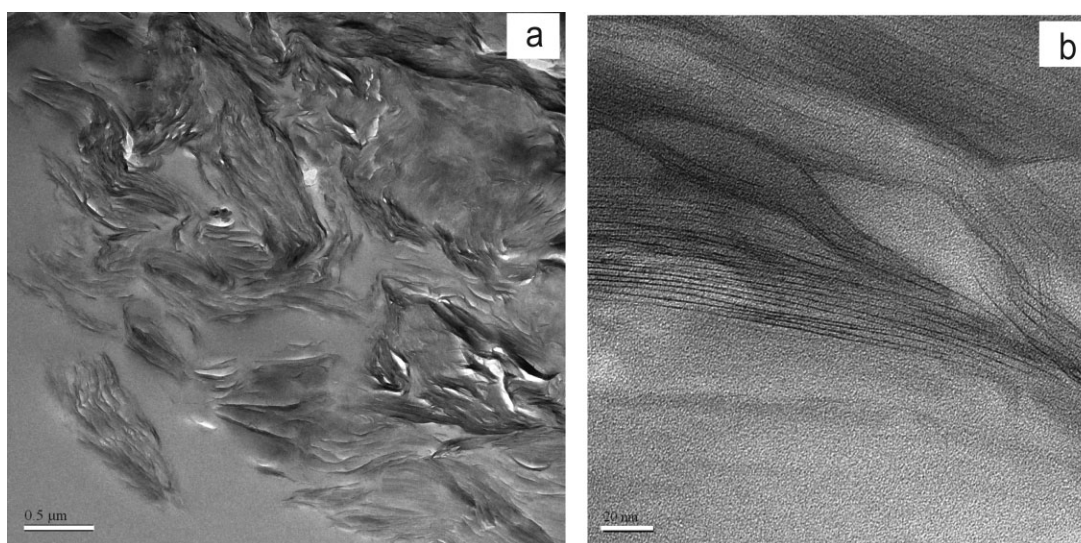


Figure 2 TEM micrograph of 2 phr epoxy/organoclay nanocomposite at: (a) low magnification, (b) high magnification.

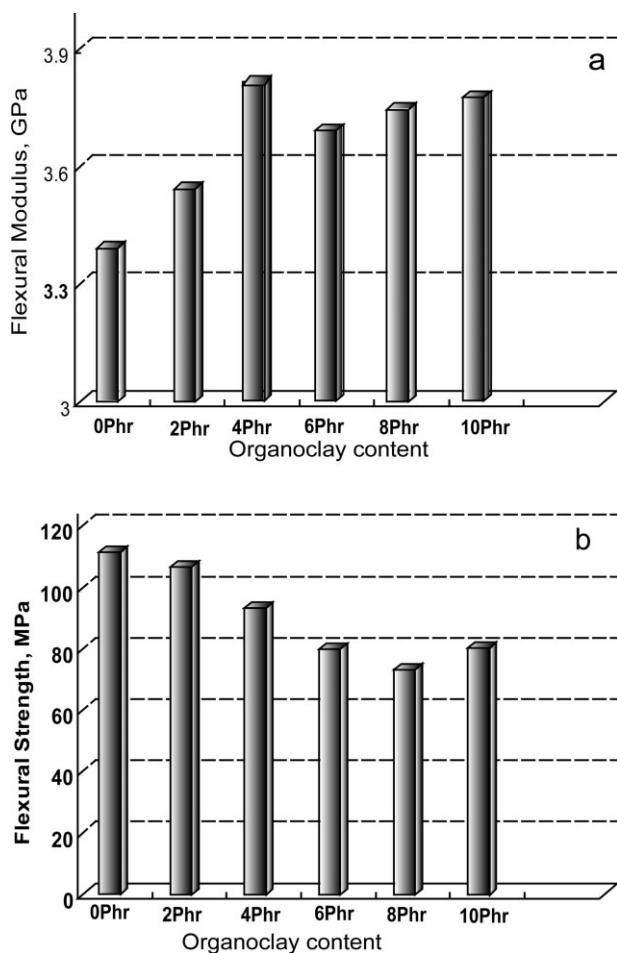


Figure 3 (a) Flexural modulus and (b) flexural strength as function of organoclay content.

Three point bending test was done according to ASTM D790 using a Shimadzu Autograph AGS-1KNJ machine.

Figure 3 shows the flexural modulus and flexural strength respectively, at different clay contents. As clay amount increases, the flexural modulus increases, in contrast the flexural strength decreases. An improvement of the elastic modulus is more evident at low concentration before it levels off at higher clay loading. This is similar to the decrease in the flexural strength before leveling off. This is attributed to the intercalation/exfoliation and good dispersion of the nanoscale clay particles that restricts the plastic elastic deformation of the polymer chains under loading as the good interfacial adhesion between the particles and epoxy matrix. At higher clay concentration, agglomeration may occur which may decrease the elasticity and also create crack propagation zone yielding a decrease in whole mechanical properties.

The SEMs micrographs of the fractured surface are shown in Figure 4. The neat epoxy represents a smooth flat surface [Fig. 4(a)] compared to that of

the nanocomposite. This indicates that the crack resistance of the unfilled materials is lower compared to the filled ones and leads to a brittle failure; however; the surface becomes rougher as the organoclay content increases. The roughness of the surface indicated that the crack propagation is more difficult in the case of the filled epoxy. This could increase the tortuous path and leads to higher strength.

Sorption test

Diffusion behavior of deionized water

Postcured samples were immersed in deionized water at different temperatures: 40, 60, and 80°C. The analysis aimed at finding the dependence of diffusivity on concentration difference and temperature. The sample thickness was about 2 ± 0.15 mm. Figure 5 shows the weight change as function of square root time of neat epoxy resin at 80°C that the diffusion of water may be considered as a Fickian diffusion. It is observed that initially the curves are linear with square root time and this suggests that in the respective initial time interval the absorption process is diffusion controlled. However, as the time passes, the specimens begin to fill with water, leading to a decrease in water absorption rate. As the equilibrium moisture content is approached, the rate becomes extremely low, so that actual equilibrium is not reached even after very long time.

A small tendency of the weight uptake increasing remains still after the observed equilibrium was reached around 100 h at 80°C, this behavior could be attributed to the physical ageing of the resin during the experiments. Even though, at 60 or 40°C it needs longer immersion time for such deviation to be observed.

Figure 6 illustrates the water uptake of epoxy organoclay nanocomposite at different organoclay concentration immersed in deionized water at 80, 60 and 40°C.

At 80°C [Fig. 6(a)] epoxy nanocomposite weight uptake continue to increase as function of immersion time, without reaching equilibrium even after 4000 h. It is noticed that the increase is more apparent in the case of higher organoclay concentration than in the case of low concentration where a tendency to level off is observed at longer time. The physical aspect of the transport process below glass transition (T_g) is postulated to occur on three stages, in which the absorbed water first occupies the free volume. In the second stage, swelling and finally water enters the densely crosslinked regions.

This deviation from the Fickian type may be explained by means of a Langmuir-type diffusion process in which the absorbed water can be divided into mobile and strongly bounded types.²⁴ Various

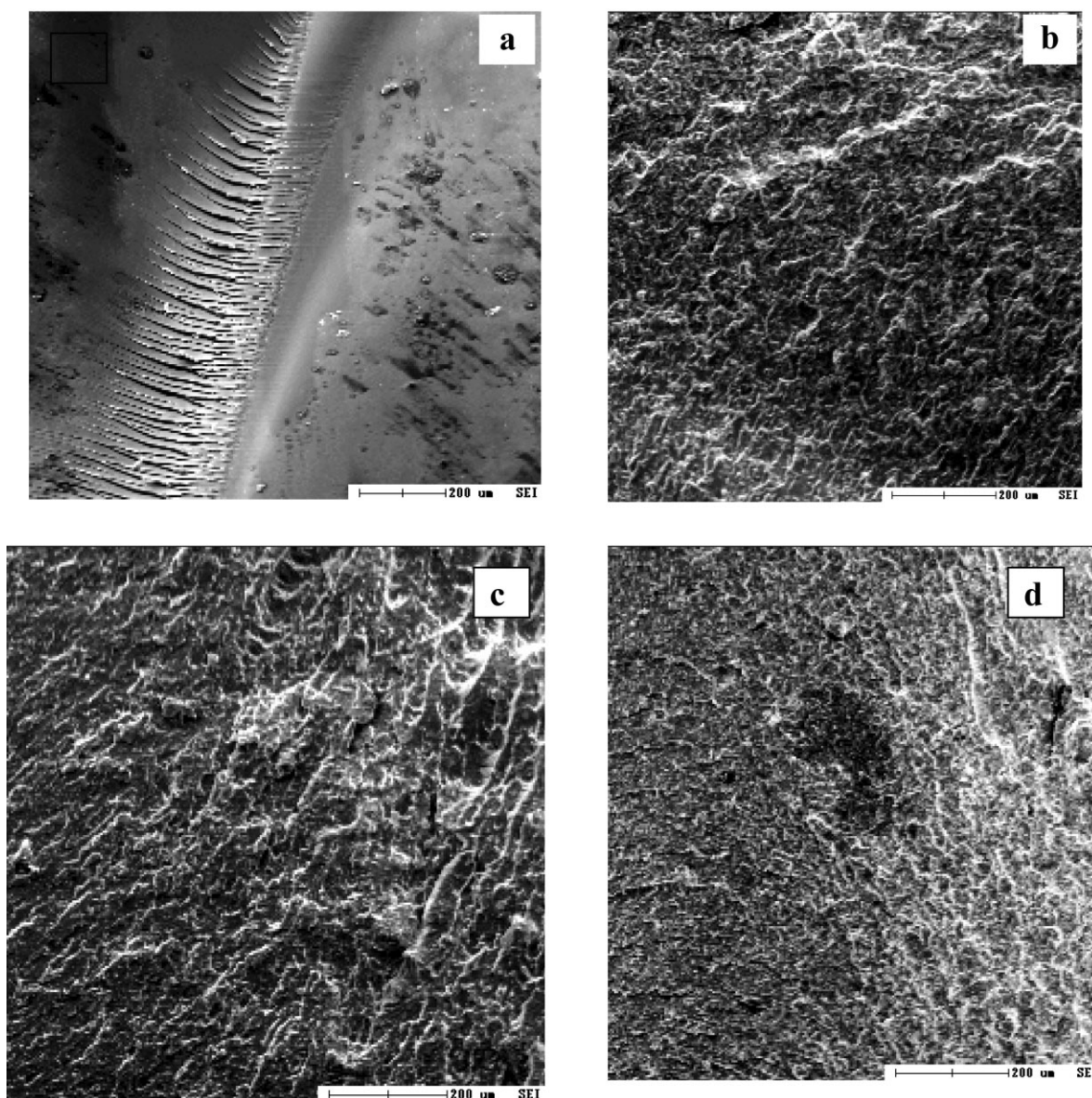


Figure 4 SEM micrographs of (a) neat epoxy, (b) 2 phr, (c) 4 phr, and (d) 8 phr organoclay.

propositions have been made concerning this dual sorption invoking, such as the existence of voids within the polymer, hydrogen bonding, heterogeneous morphology of the epoxy resin system, changes in free volume, degradation of epoxide material and the formation of clusters, crazes, and microcracks during hydration.²⁵

As discussed, the deviation from the Fickian behavior is more clearly observed for the case of epoxy nanocomposites at high loading concentration and becomes more pronounced as the clay content in the resin was increased. As the clay is hydrophilic, water molecules adsorbed onto the surface of clay platelets i.e., moisture is present in two forms inside the polymer: (1) free moisture and (2) bounded moisture. The bounded moisture certainly affects the results of transient experiments.

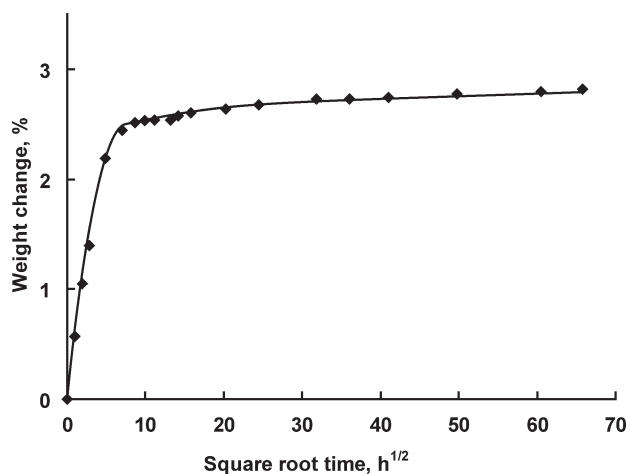


Figure 5 Weight changes of neat epoxy in deionized water at 80°C.

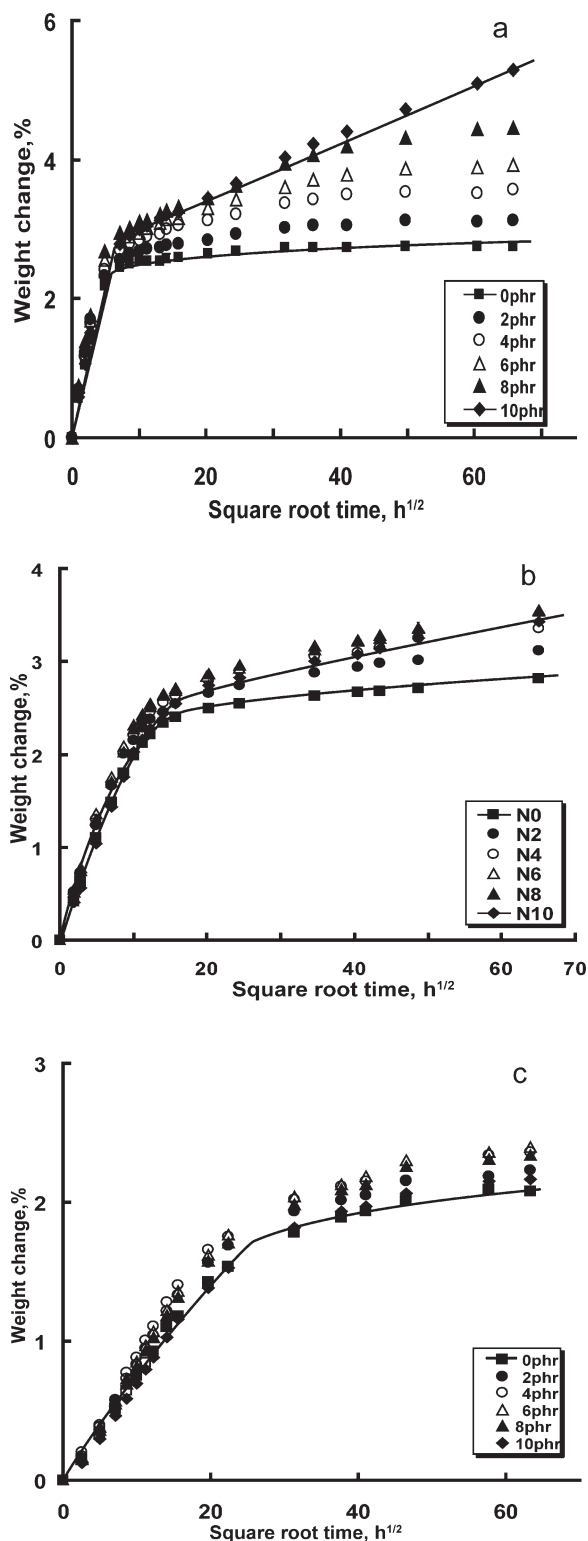


Figure 6 Weight change of epoxy organoclay nanocomposite in deionized water at (a) 80°C, (b) 60°C, and (c) 40°C.

Concerning the two-stage of water uptake observed, the first one began from the starting of the immersion up to around 100 h in the case of immersion at 80°C and may take longer time at lower

immersion temperature; in this stage the slopes of the weight change as function of square root immersion time of epoxy and that of epoxy organoclay are almost identical.²⁶ It is assumed that water first move through the neat epoxy matrix, which is described as free water, then it starts penetrating the clay galleries where the rate of diffusion within these galleries is lower than that within neat epoxy mainly due to the tortuous path created by the intercalation of the clay layers. This means that the clay platelets were preferentially absorbing water molecules and not allowing them to diffuse ahead. Water molecules kept on getting absorb until the clay platelet completely saturated with water. Once the platelet was saturated, the additional water molecules encountering the platelet followed the tortuous path to diffuse.

A similar behavior was observed at lower immersion temperature that are 60°C [Fig. 6(b)] and 40°C [Fig. 6(c)], however; at 40°C the process was not long enough to express clearly the same trend (even immersion time was longer than 4000 h). It is believed that longer immersion time will yield a similar trend that is binary mode of saturation will occur.

Diffusion behavior of sulfuric acid

Figure 7 shows the weight change of samples immersed in 10 mass% sulfuric acid solutions at different temperature. An important difference between the behavior of the diffusion in the neat epoxy and that in the epoxy/organoclay is observed. In the case of nanocomposite the increase in weight of immersed samples reached a maximum value before it start to decrease as immersion time increases. This observation is clearly observed at high temperature 80°C [Fig. 7(a)]; however; at 60°C [Fig. 7(b)] the increase in the weight change is not fully achieved. Similarly for the sorption test at 40°C [Fig. 7(c)] equilibrium was not also reached after an immersion time of more than 4000 h, the weight uptake is still in its first linear increase, therefore the data were not discussed in this article.

The increase in the weight uptake as function of immersion time is believed to be caused by various factors such as rearrangement of polymer chains following plasticization induced by a penetrant, a slow relaxation of polymer chains due to a more compact structure, and a release of indigenous components of polymer matrix after contact with the penetrant liquid. As the T_g of the resin is around 80°C i.e., the same as the test condition, thus one possible reason is the hydrolytic degradation.

Non-Fickian diffusion is generally considered to occur when the relaxation of the polymer influences the uptake behavior. Such responses are conventionally divided into two groups. One is known as Case

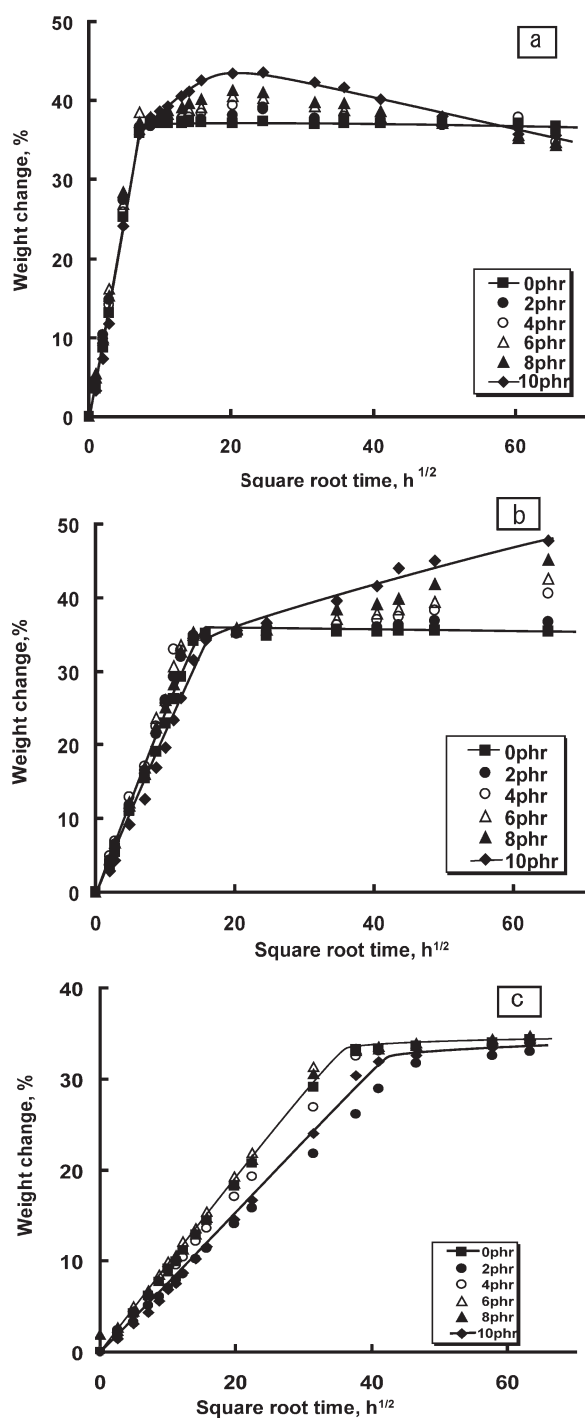


Figure 7 Weight change of epoxy organoclay nanocomposite in 10% mass sulfuric acid at (a) 80°C, (b) 60°C, and (c) 40°C.

II (Case I is being Fickian Diffusion) and generally occurs when the relaxation, rather than the diffusion rate, controls the uptake. In these cases, the uptake often increases linearly with time. The other group is termed anomalous uptake and generally occurs when diffusion and relaxation have comparable rates. A common moisture uptake profile within this group is dual stage uptake. This exhibits initial Fick-

ian diffusion uptake followed by reduced uptake rate, finally reaching a saturation level at extended exposure times.

The equilibrium mass uptake for neat epoxy is around 3% for immersion into water at 80°C and it is around 35% in the case of sulfuric acid which is almost 10 times higher in the case of acid solution as compared to the in immersion water, this can be explained simply by the fact that the molecular weight of the dissociated sulfuric acid molecule is approximately five times higher than that of the water molecule. An increase in concentration of sulfuric acid (decrease in pH) likely provides a larger number of dissociated sulfuric acid molecules within the diffusing solution to diffuse into the materials, resulting in an increase in the maximum weight uptake. Also, the higher mass uptake in acid solution than in water is due to the formation of tertiary amine salt amine group.²⁷ The increase in the weight change continue in this case till all the amines in the resin were converted to amine salt, therefore the weight gain reaches the equilibrium level.²⁸

Higher increase in the case of the nanocomposite materials is attributed to additional reactions of the sulfuric acid with the alkyl ammonium amines. Thus, higher organoclay content shows higher weight increase. However, the decrease in the weight change after the equilibrium is probably attributed to a possible dissociation of the formed amine salt from the clay itself and a possible desorption of this later outside the immersed samples. Hence, weight decrease reaches the level of the weight change of the neat epoxy. Further decrease may be expected at longer immersion time, mainly due to the additional formation of cracks and physical degradation. A physical observation of the samples along the immersion time revealed that the nanocomposite starts losing its transparency few hours after immersion. At extended immersion time (>500 h) small white spot appeared and at longer time visual crack were seen.

Acids diffuse quite easily into amine cured epoxy resin. The reaction between the resin and the penetrating acid cannot be excluded as already explained. The acid corrosivities are dependent rather on the chemical reaction running between the acidic group and that of the amine present in the epoxy as a curing agent. These chemical reactions run in parallel with a purely physical diffusion processes.

To confirm and measure the penetration of the sulfur (S) element, observation using SEM coupled with an energy dispersive X-ray spectrometer SEM/EDS was performed; analysis was carried on the cross section of the immersed samples. The penetration depth was calculated to be the distance from surface to level off the profile of the sulfuric element S as detected by EDS.

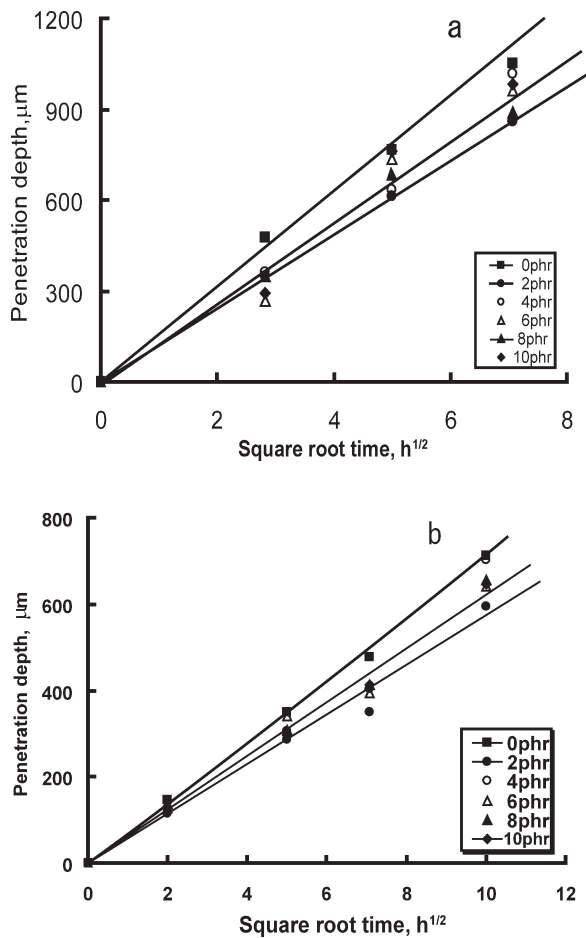


Figure 8 Penetration depth of sulfuric acid element S at (a) 80°C and (b) 60°C.

At short lap immersion time i.e., before saturation occurred an insignificant effect of the organoclay was noticed as pointed up by the penetration depth of the sulfuric acid element S measured by EDS shown in Figure 8. It reveals that nanocomposites have a lower penetration depth as compared to the neat resin for both systems investigated. Globally the penetration depth is lower at low organoclay content for the reason that at low clay content better dispersion and higher degree of exfoliation were achieved which may act as a barrier property for the diffusion of acid.

A deeper investigation of the diffusion of the sulfuric acid into the epoxy/organoclay nanocomposite was performed using a TEM/EDS analysis. It is shown in Figure 9 as an illustration of the immersed sample containing 2 phr organoclay in which two points were selected for the EDS analysis: First beside the organoclay and second inside the organoclay layers themselves. It was observed in point "1" [Fig. 9(b)] that Si element corresponding to the clay structure is present which means that even if most clay was stacked and remained intercalated some individual sheet or exfoliated layers may be present

within the bulk of the matrix and higher magnification is needed to check the presence of such single layer. Sulfuric acid element S is also detected corresponding to the diffusion of the sulfuric acid within the bulk of the matrix.

Similar to point "1" the second selected point "2" [Fig. 9(c)] i.e., within the clay layers shows a higher value of Si element, which is as expected due to a

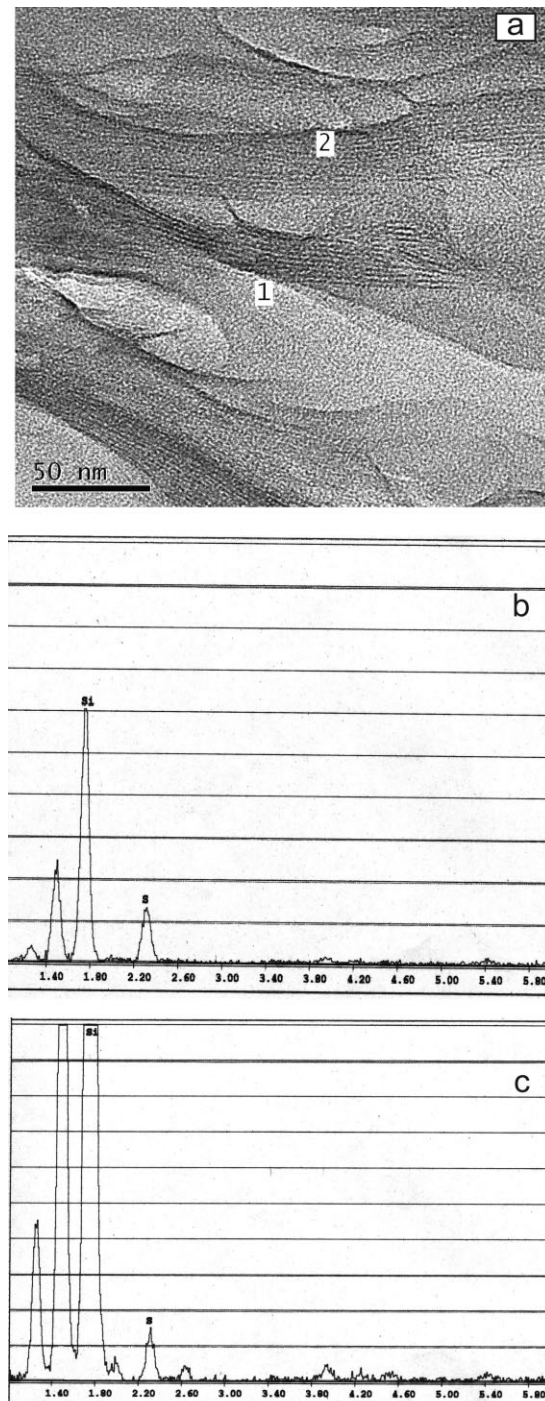


Figure 9 TEM/EDS Analysis of epoxy organoclay nanocomposite (2 phr) (a) TEM micrograph, (b) EDS patterns analysis for area1, and (c) EDS patterns analysis for area 2.

higher concentration of the organoclay, however, element S was also found which confirms that the sulfuric acid may also penetrate the clay layers and because it may not cross directly the layers and have to penetrate from the edge of the gap between the clay layers thus the tortuous path is confirmed. This behavior may explain the delay to reach the maximum weight change in the case of the epoxy organoclay nanocomposite where the penetration among the clay layers will take longer time as compared to the bulk matrix.

CONCLUSIONS

In this article, the water barrier characteristic and the resistance to corrosive environment influenced by solution absorption were studied for epoxy nanocomposites containing different amount of organoclay. A number of observations and conclusions can be drawn from the investigation:

- The materials prepared were found to have inhomogeneous degree of exfoliation with some agglomerates observed. Exfoliation of the clay depends mainly on the system used and also the processing conditions and curing process.
- Under the present processing conditions, the additions of nanoclay can significantly improve the barrier properties against corrosive acid.
- Diffusion behavior of water and acid do not obey Fick's law.
- The higher the organoclay content the higher the maximum weight change was obtained.
- At first, water diffuses within the neat resin; with constant diffusivity. Then water diffuses within the organoclay; with decreasing in diffusivity.
- Diffusion behavior of sulfuric acid showed an increase in the weight uptake as function of the organoclay content followed by salvation of the amine salt.
- Penetration depth and diffusivity were reduced for nanocomposites.

References

1. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Karauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
2. Wang, M. S.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 468.
3. Wang, Z.; Massam, J.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 2216.
4. Ke, Y. C.; Stroeve, P. *Polymer-Layered Silicate and Silicate Nanocomposite*; Elsevier: Netherlands, 2005.
5. Hackman, I.; Hollaway, L. *Compos A* 2006, 37, 1161.
6. Becker, O.; Varley, R. J.; Simon, G. P. *Eur Polym J* 2004, 40, 187.
7. Dean, D.; Walker, R.; Theodore, M.; Hampton, E.; Nyairo, E. *Polymer* 2005, 46, 3014.
8. Brown, J. M.; Curlis, D.; Vaia, R. A. *Chem Mater* 2000, 12, 3376.
9. Ganga Rao, H. V. S.; Craigo, C. *Struct Eng Int (IABSE)* 1999, 9, 286.
10. Kornmann, X.; Thomann, R.; Berglund, L. A.; Mulhaupt, R.; Finter, J. *Polym Eng Sci* 2002, 42, 1815.
11. Balabanovich, A. I.; Hornung, A.; Merz, D.; Seifert, H. *Polym Degrad Stab* 2004, 85, 713.
12. Zanetti, M.; Lomakin, L. S.; Camino, G. *Macromol Mater Eng* 2000, 1, 279.
13. Zilg, C.; Thomann, R.; Finter, J. *Macromol Mater Eng* 2000, 41, 280.
14. Frounchi, M.; Dadbin, S.; Salehpour, Z.; Noferesti, M. *J Membr Sci* 2006, 282, 1.
15. Shah, A. P.; Gupta, R. K. *Polym Eng Sci* 2002, 42, 9.
16. Kim, J. K.; Hu, C.; Woo, R. S. *Compos Sci Tech* 2005, 65, 805.
17. Rana, H. T.; Gupta, R. K.; GangaRao, H. V. S.; Sridhar, L. N. *AIChE J* 2005, 51, 12.
18. Abacha, N.; Skai, T.; Tsuda, K.; Kubouchi, M. *J Mater Sci Soc Jpn* 2006, 44, 163.
19. Abacha, N.; Kubouchi, M.; Tsuda, K.; Skai, T. *Express Polym Lett* 2007, 1, 364.
20. Kshirsaga, S.; Lopez-Anido, R. A.; Gupta, R. K. *ACI Mater J* 2000, 97, 703.
21. Becker, O.; Cheng, Y. B.; Varley, R. J.; Simon, G. P. *Macromolecules* 2003, 36, 1616.
22. Becker, O.; Cheng, Y. B.; Simon, G. P. *Polymer* 2002, 43, 4365.
23. Massam, J.; Pinnavaia, T. J. *Mater Res Soc Symp Proc* 1998, 520, 223.
24. Carter, H. G.; Kibler, K. G. *J Compos Mater* 1978, 12, 118.
25. Feng, J.; Berger, K. R.; Douglas, E. P. *J Mater Sci* 2004, 39, 3413.
26. Theocaris, P. S.; Kontou, E. A.; Papanicolaou, G. C. *Colloid Polym Sci* 1983, 261, 394.
27. Tsuda, K.; Kubouchi, M. *Corros Eng* 1995, 44, 141.
28. Ono, S.; Tsuda, K.; Kubouchi, M.; Nishiyama, T.; Hojo, H. *Int Conf Compos Mater* 1995, 4, 215.