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# Moisture Absorption and Diffusivity of Epoxy Filled Layered-Structure Nanocomposite

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### ABSTRACT

This paper studies moisture absorption and diffusivity of epoxy reinforced layered structure nanocomposites and its effect on fracture toughness. Two different types of layered fillers employed in the study were clay and graphene platelets, in which both surface layers were unmodified and modified by surfactant. The nanocomposites were characterized by swelling analysis and fracture toughness measurement. The outcomes showed that the moisture absorption and diffusivity decreased with the addition of layered fillers. It was found that the modified graphene platelets and clay outperformed the unmodified layers and neat epoxy in terms of reduction of moisture absorption and diffusivity. The modified graphene platelets reduced the moisture uptake and diffusivity about 30% and 33%, respectively compare to neat epoxy, thus indicates its outstanding performance in barrier applications. However, once the nanocomposites were swelling in the water for 5 days, it is noticed that the fracture toughness of nanocomposites were reduced significantly about 35% in average. Nevertheless, the modified graphene platelets still display the better performance compare to the other samples although there was reduction of fracture toughness.

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## INTRODUCTION

There has been growing interest in the study of barrier properties of polymer recently. This because water atmosphere, moisture absorption and solvent attack have been regarded as unintentionally destructive tool for weakens the structures of polymer material in the long-term exposure by causing plasticization, chain rupture and chemical degradation to the polymer [8,7,17]. For infrastructures based on polymer that intended to have service life more than 30 years, these kind of 'effects' hinder the polymer application especially those subjected to moisture or solvent environment. Thus, promote the development of polymer composites—a combination of two or more materials has the potential to provide value-added properties absent in the neat polymers [1,11,2].

On the other hand, nanofillers reinforced polymer composites have attracted tremendous attention because of their unique properties which do not exist in the parent constituent and their outperforming to conventional composite counterparts. This has been proved in our recent research conducted in the field of epoxy nanocomposites [12,19,20]. Previously, it has been reported that nanofiller addition improved the barrier properties of polymer and reduced water absorption [14,3,16]. This is caused by the permeating molecules have to travel around impermeable fillers and increases the path tortuosity, therefore reduces the rates of permeability [15].

Though fluid permeability (water and solvent) is recognized to be the utmost important parameter to avoid loss in composites properties, lacking of knowledge and experimental work specifically with regards to epoxy reinforced filler composites in this field stimulate research to be carried out even until today. In the work of [9] they used commercially available nanoclay embedded into epoxy and they found that there was significant reduction in the diffusivity and the maximum water uptake of the epoxy resin with the addition of the nanoclay. However, there is no further investigation on the after effect on mechanical properties and fracture toughness of composites. A similar work was carried out by [4,6] in studying moisture absorption and found that the barrier properties of polymer composites increase with the inclusion of nanoclays.

The main purposes of this paper are to investigate the swelling and absorption properties of epoxy composites based on layered structure fillers as well as utilizing them to see the effect towards the mechanical

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properties of composites. The swelling testing was carried out in water. This is because water is not only can soften the polymer but also increased the diffusion rates because of its small molecular size. Two types of nanolayers were used as epoxy reinforcement, including clay and graphene platelets (GnP) and their surface modification which contribute to better interface and dispersion in matrix were experimented in terms of diffusivity and permeability of fluid into polymer.

#### Materials:

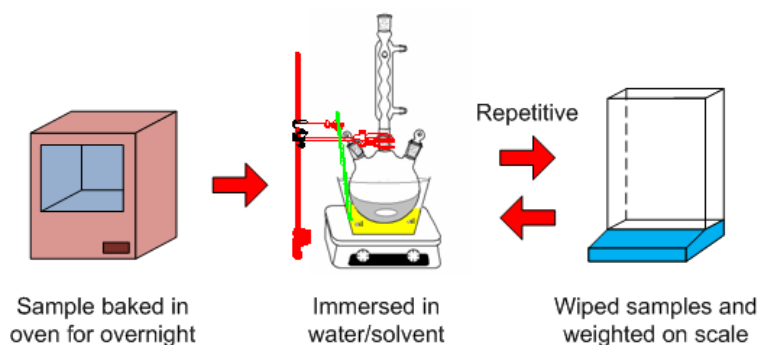
Table 1 shows the list of material investigated in the experiments. The matrix used was an Epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Araldite-F) with an epoxide equivalent weight of 182-196 g/equiv. It was supplied by Ciba-Geigy, Australia. The hardener used was polyoxypropylene (Jeffamine® J230) and it was supplied by Huntsman. Sodium montmorillonite was purchased by Southern Clay Products along with a cation exchange capacity (CEC) of 85 mequiv/100 g. The commercially available acid-treated graphite (GIC, Ashbury 3494) was supplied by Ashbury Carbons, Ashbury, NJ. The surfactants Jeffamine® XTJ502 and Jeffamine® D2000 were both provided by Huntsman. Details on surface modification of clay and GnP can be referred from studied of [19,20,21], respectively.

**Table 1:** Material used in the testing.

Materials	Abbreviation
Neat epoxy	Epoxy
Epoxy/unmodified clay composite with 2.5 wt%	Epoxy/u-clay
Epoxy/unmodified GnP composite with 2.5 wt%	Epoxy/u-GnP
Epoxy/clay modified by XTJ502 nanocomposite with 2.5 wt%	Epoxy/m-clay
Epoxy/GnP modified by J2000 nanocomposite with 2.5 wt%	Epoxy/m--GnP

#### Swelling Testing:

The swelling test was performed using water according to ASTM D570-98. In prior to immersion, the samples of approximate dimensions  $40 \times 40 \times 1.5 \text{ mm}^3$  were baked in oven for overnight at  $80^\circ\text{C}$ . The water uptake was then determined by immersing the samples in round bottom flask connected with condenser and then placing in oil bath at constant temperature of  $70^\circ\text{C}$  for water for 18 days. At certain intervals, the samples were removed from the round bottom flask, wiped all the surfaces with tissue paper followed by weighing. After that the samples were placed again in the round bottom. This measurement process was repeated until an extended period of time when there was no further increase in water uptake. Figure 1 illustrated the schematic for the swelling testing process.



**Fig. 1:** Schematic procedure of immersion testing.

#### Fracture toughness Test:

The preparation of compact tension (CT) fracture toughness requires great care to produce an instantly propagated crack [13]. The main difficulty was in producing the instantly propagated crack due to restrictions on cross sectional area. The CT samples were approximately  $30 \times 5 \text{ mm}^2$  of wide and thick in accordance with ASTM D-5045. Using a sharp razor blade, an instantly propagated crack was produced on each CT sample. The cracked CT samples were tested using the Instron 5567 system with a 2 kN load cell at a strain rate of 0.5 mm/min. The fracture toughness properties are expressed by a stress intensity factor,  $K_{1C}$  and critical strain energy release rate,  $G_{1C}$ , and the test is performed on the samples before and after swelling.

#### Theoretical Equations of Swelling Properties:

The moisture mass gain,  $M_t$  is calculated as follows:

$$M_t = W_t - W_o \quad (1)$$

where  $W_o$  is weight of sample before swelling and  $W_t$  is weight of sample at time  $t$ .

The percentage weight gain,  $\%M_t$  is also known as swelling value,  $S_v$  is calculated based on Equation (2).

$$\%M_t = \frac{W_\infty - W_o}{W_o} \times 100 \quad (2)$$

where  $W_\infty$  is weight of sample at infinite time.

The solubility,  $S$  at the given temperature and humidity is calculated by using Equation (3):

$$S = \frac{M_\infty}{vol} \quad (3)$$

where  $M_\infty$  is saturated moisture mass at temperature  $T$  (unit in  $mg$ ), and  $vol$  is sample volume (unit in  $mm^3$ )

The moisture diffusivity,  $D$  can be calculated as follows:

$$D = \frac{0.04919\Delta x^2}{t_{0.5}} \quad (4)$$

where  $\Delta x$  is a sample's thickness and  $t_{0.5}$  is the time at which the sorbed mass of moisture is equal to one-half the saturated mass, i.e.,  $M_t/M_\infty = 0.5$ . Using the moisture mass gain curve, the moisture diffusivity also can be calculated using Equation (5).

$$\frac{M_t}{M_\infty} = \frac{4\sqrt{D}}{\sqrt{\pi}} \left[ \frac{\sqrt{t}}{\Delta x^2} \right] \quad (5)$$

where  $D$  can be determined from the slope of plot  $\frac{M_t}{M_\infty}$  against  $\frac{\sqrt{t}}{\Delta x}$ .

## RESULTS AND DISCUSSIONS

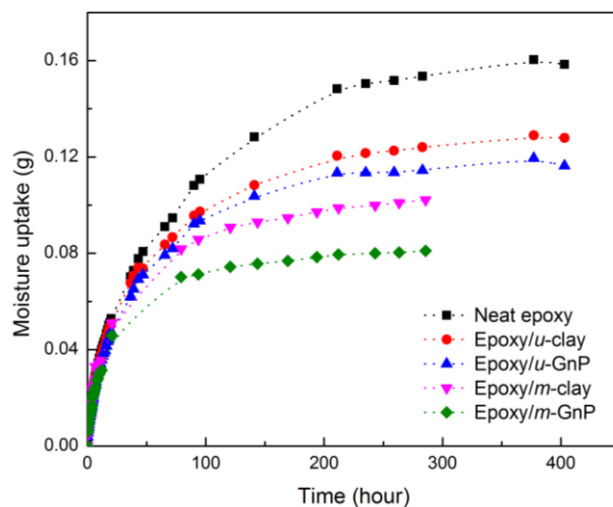
Table 2 tabulates the results of swelling test measurement for samples soaked over a period of 12–18 days in deionised water at 70°C. Obviously there is a significant decrease in water uptake or moisture mass gain as a result of nanolayer structured fillers addition. The moisture absorption of all nanocomposites was found stabilized after approximately 12 days (200 h). However, the modified layered shows better in reduction of water uptake in comparison to unmodified. A similar trend was observed for diffusivity. It is seen that the addition of nanolayer fillers has a very dominant effect on moisture diffusivity that reduces to almost one fourth of neat epoxy value.

**Table 2:** Moisture mass, solubility and diffusivity of tested materials

Materials	$M_{sat}$ (g)	Solubility (mg/cm <sup>3</sup> )	Diffusivity ( $\times 10^{-3}$ mm <sup>2</sup> /s)
Neat epoxy	0.11464	32.06289	8.33
Epoxy/u-clay	0.15400	39.23265	6.75
Epoxy/u-GnP	0.12373	40.59995	6.20
Epoxy/m-clay	0.10350	40.22685	5.85
Epoxy/m-GnP	0.08080	36.64065	5.59

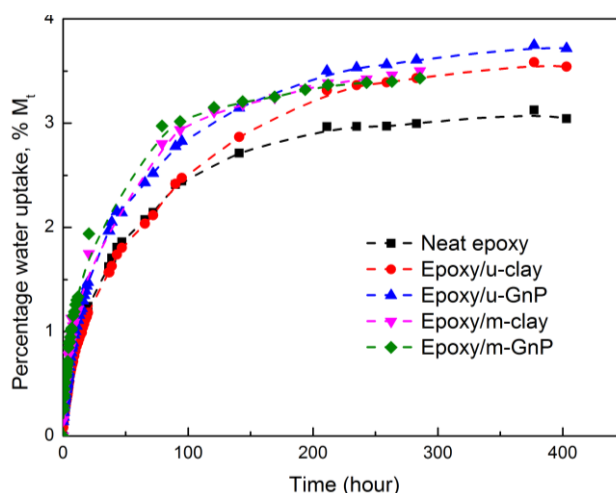
Figure 2 clearly shows the pattern of moisture absorption for all tested samples, thus proves that the addition of nanolayer fillers enhanced the moisture diffusion barrier properties of epoxy composites. It is important to note that for modified layered nanocomposites, the water ingress seems to have reached equilibrium saturation point after 10 days compared to unmodified layer composites and neat epoxy which continues to increase steadily. Therefore, it was observed that this effect to be dependent on modification of layered fillers. This result agreed with [10] who discovered that not only polymer adsorbs water, but also the interfaces introduced by the addition of layered fillers. This was further verified by [5] who suggested that there

are three mechanisms that contribute to water penetration at the interface in polymer adhesive structures: (i) bulk diffusion, (ii) wicking along the interface, and (iii) capillary action associated with micro-cracking.



**Fig. 2:** Moisture mass gain of water as a function of time

Figure 3 shows the percentage of water uptake values for all samples. As opposed to the decrease in diffusivity with clay addition, the equilibrium percentage water uptake content of the nanocomposite sample was found to increase with addition of layered structure fillers. The reason for the higher percentage of water uptake value for layered fillers reinforced nanocomposites is due to the natural tendency of clay and graphene platelets to adsorb water and higher exposed surface area of platelets. In this case, the hydrophilic of clay has better capability to adsorb water than graphene platelets, even though the clay's surface was modified by surfactant, the clay remained hydrophilic.



**Fig. 3:** Percentage of water uptake as a function of time.

Table 3 shows the fracture toughness,  $K_{Ic}$  and critical energy release rate,  $G_{Ic}$  of neat epoxy (0 wt%) and epoxy layered nanocomposites. From the table, it can be seen that fracture toughness of epoxy improved significantly with the addition of the 2.5 wt% of nano-layered fillers, such as clay and graphene platelets. The result indicates that epoxy/m-clay shows higher fracture toughness the  $K_{Ic}$  of neat epoxy increases by 103% from  $0.653\text{MPa}\cdot\text{m}^{0.5}$  to  $1.326\text{MPa}\cdot\text{m}^{0.5}$ . At the same fraction, m-clay improves the  $K_{Ic}$  by only 40% to  $0.90\text{MPa}\cdot\text{m}^{0.5}$  although both modified layered fillers had outperformed the unmodified. A similar improvement was found for  $G_{Ic}$ . Graphene platelets provides greater toughening because the covalent bonds between the carbon atoms of graphene sheets are much stronger.

The fracture toughness was also performed on the samples after swelling which have been soaked into water for 5 days. Obviously from Table 3, the fracture toughness of all the samples after swelling decreases significantly with average of 35% reduction compare to before swelling. These reduction In comparison to all

types of samples after swelling, modified graphene platelets reinforced epoxy composites shows higher values in term of  $K_{Ic}$  and  $G_{Ic}$ , followed by unmodified graphene platelet, modified clay, unmodified clay and neat epoxy.

**Table 3:** Fracture toughness properties of nanocomposites.

Materials	$K_{Ic}$ (MPa·m <sup>1/2</sup> )		$G_{Ic}$ (J/m <sup>2</sup> )	
	Before swelling	After swelling	Before swelling	After swelling
Neat epoxy	0.66 ± 0.03	0.30 ± 0.05	140.7 ± 14.0	27.9 ± 9.9
Epoxy/u-clay	0.79 ± 0.03	0.47 ± 0.08	243.9 ± 13.4	60.9 ± 21.1
Epoxy/u-GnP	1.12 ± 0.04	1.02 ± 0.04	378.9 ± 49.0	280.2 ± 43.7
Epoxy/m-clay	1.03 ± 0.04	0.52 ± 0.11	384.7 ± 25.5	119.4 ± 23.0
Epoxy/m-GnP	1.55 ± 0.05	1.23 ± 0.09	694.9 ± 47.8	577.8 ± 82.4

#### Conclusion:

Moisture behavior of epoxy composites is mainly dominated by the diffusion of water through epoxy resin. However, it is well known that the amount of filler and its shape can influence the moisture diffusivity. In this study, a moisture absorption analysis of layered structure nanofillers such as clay and graphene platelet was determined including the effect of filler's surface modification. The results indicated that the modified layered shows better in reduction of water uptake and diffusivity compare to unmodified layered fillers and neat epoxy, thus improved the barrier properties of polymer. Nevertheless, it was found that after swelling in the water for few days, the fracture toughness properties of composites decrease significantly, although the modified layered fillers nanocomposites still show the better outcomes compare to unmodified and neat polymer.

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