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## Influence of interface on epoxy/clay nanocomposites: 2. mechanical and thermal dynamic properties

Izzuddin Zaman<sup>a,\*</sup>, Fethma M. Nor<sup>a</sup>, Bukhari Manshoor<sup>a</sup>, Amir Khalid<sup>a</sup>, Sherif Araby<sup>b</sup>

<sup>a</sup>Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat, Johor, Malaysia

<sup>b</sup>School of Engineering, University of South Australia, SA5095, Australia

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### Abstract

The particle interface has been known to play a critical role in conventional composites. Nevertheless, the understanding of the role of interface in mechanical and thermal properties of polymer nanocomposites remains in its infancy. Similar to the previous study, two different designs of interface modification—molecular entanglement and chemical reaction—were adopted by using three variants surfactants, i.e. ethanalamine (denoted *eth*), Jeffamine M2070 (*m27*) and Jeffamine XTJ502 (*xtj*). Epoxy nanocomposites were prepared via solution compounding with 0.46–1.87 vol% of the modified clay. To that end, the interface strength was measured by tensile test, fracture toughness and dynamic mechanical analysis. The results found that a consistent increase in  $T_g$ s with increases in clay fractions. With 1.16 vol% layer clays, the critical strain energy release rate  $G_{Ic}$  of neat epoxy improved from 188.6 to 405.3 kJ/m, 115% improvement and stiffness enhanced from 2.69 to 3.54 GPa, 31 % improvement. This result proved that the chemical reaction of amino-groups of *xtj*-clay with epoxy created a strong interface, thus resulting in a large enhancement of mechanical properties, fracture toughness and thermal dynamic properties.

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*Keywords:* Epoxy; interface; layered-clay; nanocomposites

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### 1. Introduction

It is a well-known fact that silicate layers (clays) have given tremendous impact on a variety of properties without sacrificing the advantages of polymer matrix, such as increase in modulus, strength, toughness, crack resistance and

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\* Corresponding author. Tel.: +607-453-8462; fax: +607-453-6080.

E-mail address: [izzuddin@uthm.edu.my](mailto:izzuddin@uthm.edu.my)

gas barrier ability, and decrease in flammability; these improvements are caused by the large specific area of nanolayers. In my perspective, the improvements can be further optimized if the clay layers are individually dispersed in the polymer with improved interface strength. That is why interface-modified, layered nanocomposites are always preferred as an alternative to overcome conventional composite imperfections in diverse applications.

Epoxy resins are one of the thermosetting polymers extensively used in industries. However, brittleness is the inherent problem for these highly crosslinked resins, and thus toughening attracted a great deal of interest. Clay features low cost, high strength (0.2 TPa in stiffness and 1 GPa in fracture strength) and large specific area [1,2], which act as a potential candidate in development of high-performance of epoxy. In general, there are two means in fabrication of polymer/clay nanocomposites: (i) intercalation—where the clay layers expand for polymer insertion and (ii) exfoliation—where the clay layers break-up to form single nanolayers in matrix. Early attempt by Lan et al. [3] made a breakthrough in clay exfoliation by using alkylammonium salts as surfactants. As a result, 10 Å-thick layers of clay were dispersed in the epoxy matrix. Since then, extensive studies have been conducted on exfoliation of epoxy/clay nanocomposites. A new route for disorderly exfoliated nanocomposites has been proposed by Ma et al. [4] using a diamine hardener to modify the clay, followed by grafting the modified clay with epoxy molecules. These fascinating studies have created much interest in the modification clay and its effect on the nanocomposites.

Although the exfoliated epoxy/clay nanocomposites are always preferred due to a markedly higher increment in mechanical performance compared to intercalated and conventional composites [5,6], the mechanisms of clay-epoxy interfaces are still not well understood and need much studies. The effect of interface on structure-property relation such as morphology, mechanical and dynamic properties remains rather vague. Brown et al. [7] reported the use of hydroxyl-substituted quaternary ammonium surfactants to form a strong interaction by hydrogen bonding with the epoxy, but unfortunately no fracture toughness measurement was made. A similar study by Wang et al. [8] showed the effect of interfacial interaction on properties of the epoxy clay nanocomposites by using a silane coupling agent and hexyltriphenylphosphonium bromide. None of these studies however, has provided sufficient information in relation to the effect of different interface strength on structure-property relationship of epoxy/clay nanocomposites.

Motivated by these matters, this project was carried out by developing a series of epoxy nanocomposites based on reinforcing clay with different levels of interface strength. The effect of interface on the morphology structure is presented in part 1 of the manuscript [9]; while the effects on mechanical properties, fracture toughness and thermal properties are discussed here. Through this work, an understanding of the interface effect on layered polymer nanocomposites is obtained.

## 2. Materials Preparation

The materials used for this study are epoxy DGEBA with EEW 182-196 g/equiv hardener Jeffamine J230, clay with a cation exchange capacity (CEC) of 85 mequiv/100 g, surfactant ethanolamine, Jeffamine M2070 and Jeffamine XTJ502. The modification of clay surface and preparation of nanocomposites were described in ref. [9]. Since the fraction used in preparing nanocomposite was weight fractions, eqn. 1 was applied to convert weight fractions (wt%) to volume fractions (vol%). Table 1 shows the relations between wt% and vol%.

$$V_f = \frac{\rho_m w_f}{\rho_f (1 - w_f) + \rho_m w_f} \quad (1)$$

where,  $\rho$  is the density,  $w$  is the weight fraction and subscripts  $m$  and  $f$  refer to matrix and filler, respectively.

Table 1. Conversion from weight to volume fraction.

Weight fraction (wt%)	Density of clay (g/cm <sup>3</sup> )	Density of epoxy (g/cm <sup>3</sup> )	Volume fraction (vol%)
1	2.4	1.1	0.46
2.5	2.4	1.1	1.16
4	2.4	1.1	1.87

### 3. Characterizations

The mechanical properties of nanocomposites were measured using the Instron 5567 tensile testing machine equipped with a 10 kN load cell and Bluehill data acquisition software. The tensile test was conducted according to ASTM D-638 at a crosshead speed of 0.5 mm/min and the extension was recorded by a 100 mm gauge length extensometer. The tensile properties of each sample were obtained from the average values of at least five specimens.

The critical stress intensity factor (known as fracture toughness,  $K_{Ic}$ ) and critical strain energy release rate (known as fracture energy,  $G_{Ic}$ ) were characterized by a compact tension (CT) sample by an Instron 5567 testing machine according to the ASTM D-5045. A notch of 15 mm was made by a band saw on one edge of the specimen. An instantly propagated sharp crack was then introduced by tapping a fresh razor blade to the samples. Again, the fracture toughness properties were obtained by averaging the values of five specimens for each sample.

Dynamic mechanical analysis (DMA) tests were performed on a Dynamic Mechanical Analyzer 2980 at 1 Hz. A DMA specimen is rectangular with a dimension of  $3.0 \times 6.0 \times 40.0$  mm. A single cantilever clamp with a supporting span of 20 mm was used to clamp the specimen.

### 4. Results and discussion

#### 4.1. Mechanical strength

Fig. 1 shows the Young's moduli and tensile strength of neat epoxy and its nanocomposites. Young's modulus markedly increases with filler fractions, while the tensile strength reduces. The significant improvement in stiffness is explained by restriction of polymer chain mobility through transferring stress because the much stiffer nanolayers share a portion of load by mainly shearing. The drop in tensile strength can be explained by the fact that the stiff matrix such as brittle epoxy would hardly improve the strength [10,11] in comparison to layered additive in elastomeric matrix [12]. The formation of layer stacking with increase of clay content (as supported by XRD results in Fig. 2 in ref. [9]) further decrease tensile strength of nanocomposites due to a phase separation introduces between the clay layers and epoxy.

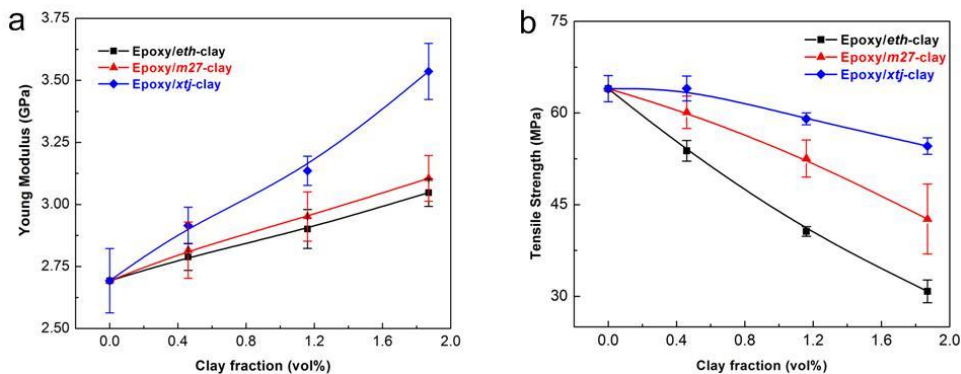


Fig. 1. (a) Young's modulus and (b) Tensile strength of epoxy/clay nanocomposites.

Of these nanocomposites, epoxy/*xtj*-clay shows the largest improvement in Young's modulus and lowest reduction in tensile strength. The 1.87 vol% of *xtj*-clay increase the modulus by 31% from 2.69 GPa to 3.54 GPa, while at the same weight concentration, the modulus of epoxy/*m27*-clay and epoxy/*eth*-clay only increase by 15% and 13%, respectively. This is because the long chain molecules of *xtj* with its high molecular-weight of 2000 g/mol not only enables physical entanglement with epoxy molecules, but provides a covalent bonding with the molecules [13]. By contrast, *eth*-clay and *m27*-clay are modified by *eth* of short-chained molecules and *m27* of long chain molecules, respectively, both of which have only one reactive site reacting with nanolayers but not with matrix.

## 4.2. Fracture Toughness

In Fig. 2, the nanocomposites demonstrate higher fracture toughness  $K_{Ic}$  and energy release rate  $G_{Ic}$  than neat epoxy. In all nanocomposites, the toughness enhances with increases in clay fractions until 1.16 vol%, and then reduces slightly. Thus, 1.16 vol% may present the optimum loading of clay in matrix, where nanolayers are well dispersed in matrix and have most chances to interact with epoxy matrix. At 0.46 vol%, nanolayers are must isolated in matrix, thereby providing a slight enhancement to the fracture toughness. By contrast, nanolayers create more clusters at 1.87 vol% (as proved by XRD in Fig. 2 and SEM in Figs. 4-6 in in ref. [9]), leading to less enhancements of fracture toughness.

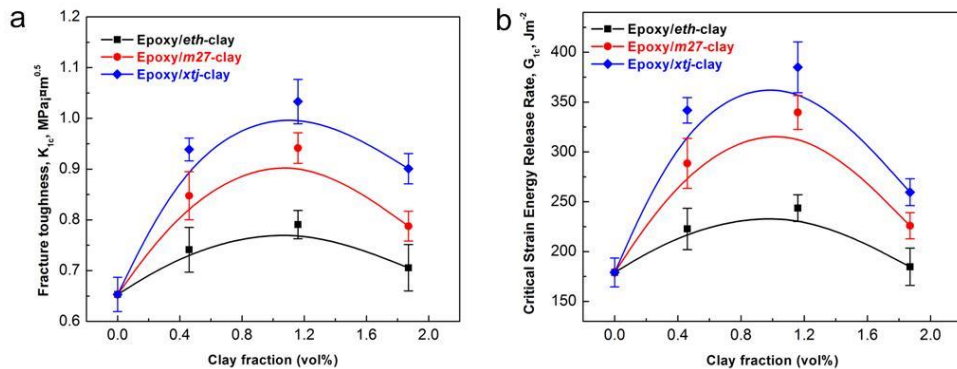


Fig. 2. Fracture toughness and energy release rate of epoxy nanocomposites.

## 4.3. Thermal dynamic analysis

Table 2 summarizes the dynamic mechanical properties of neat epoxy and its nanocomposites over a wide range of temperature from 50–120°C. The properties were measured in terms of the glass transition temperature ( $T_g$ )—which is taken at the maximum of  $\tan \delta$  curve, corresponding to the molecular chain relaxation.

Table 2. Glass transition temperatures of epoxy/clay nanocomposites.

	Clay content (vol%)	$T_g$ (°C)
Neat epoxy	0	93.7
eth-clay/epoxy	0.46	101.1
	1.16	92.8
	1.87	102.4
	1.87	102.4
m27-clay/epoxy	0.46	96.6
	1.16	96.3
	1.87	100.9
xtj-clay/epoxy	0.46	97.2
	1.16	99.6
	1.87	100.4

The observed increases in  $T_g$  agree with previous studies [11,14], thus proving that a large surface area of 1-nm thickness clay layer produced a significant effect on restricting the matrix chain movement through the  $T_g$  region. Albeit increments observed for most nanocomposites, there are relatively slight reductions observed for the

epoxy/*eth*-clay at 1.16 vol%. It is assumed that the reduction probably caused by variations of curing condition and excess surfactants left by modification [15], although great care was paid in fabrication. Of these nanocomposites, the epoxy *xtj*-clay produces a stable and consistent result of  $T_g$ s—which increased with the clay loading, although the highest  $T_g$  was achieved at 1.87 vol% epoxy/*eth*-clay.

This result indicates that: (1) the presence of the grafted long-chain molecules surfactants onto clay layers, such as *m27* and *xtj* does not compromise  $T_g$  at all, (2) the strong interaction exerted by *xtj*-clay with epoxy matrix resulting in the restriction of the molecular motion in the resin, therefore increased  $T_g$ s values gradually.

## 5. Conclusion

This paper introduced the epoxy/clay nanocomposites of three levels of interface strength, and discussed the effects of interface strength on the mechanical and thermal dynamic properties of nanocomposites. It was found that the molecular entanglement of the grafted long-chain molecules with matrix help the interaction of epoxy molecules and promote the nanolayer exfoliation, leading to highly improved mechanical properties; the highest interface strength was produced by combination of the molecular entanglement and the chemical bonding that bridges matrix with nanolayers, as where the highest improvement in modulus and fracture toughness were observed. The *xtj*-clay produced a stable, consistent increase in  $T_g$ s with increases in clay fractions. All nanocomposites demonstrated maximum toughness values at a clay loading of 1.16 vol%.

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