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Influence of interface on epoxy/clay nanocomposites: 1. morphology structure

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Abstract

A current challenge for the material scientists nowadays is the design and invention of new material systems that have a low weight, low cost but possess high levels of mechanical performance, good design flexibility and processability. This challenge has arisen due to the modern trend of utilizing lightweight and high performance materials, which has the potential to contribute to the advanced future applications, such as in aerospace, automotives, biotechnology, electronics and many more. In this new world, polymer nanocomposites have developed to be one of the latest evolutionary steps in the polymer technology, besides showing a great deal to become the most versatile industrial advanced materials. In comparison with conventional composites, nanocomposites demonstrate significantly higher levels of mechanical performance with less content of particles. The particle interface has been known to play a critical role in conventional composites. Nevertheless, the understanding of the role of interface in morphology polymer nanocomposites remains in its infancy. Thus, this study aims to develop a series of epoxy polymer layered-clay nanocomposites with levels of interface strength by designing chemical reactions or physical entanglements between nanoparticles and matrix polymer. In order to achieve this goal, three types of modifier were adopted: ethanolamine (denoted *eth*), Jeffamine M2070 (*m27*) and Jeffamine XTJ502 (*xtj*). The interface strength was identified through the morphology observation such as X-ray diffraction and scanning electron microscopy of fracture surface, in which later are correlated with various mechanical properties of nanocomposites.

Keywords: Epoxy; interface; layered-clay; nanocomposites

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1. Introduction

Since 50 years ago, polymer composites have attracted a great attention, both in the industries and in the academia. Due to the current challenge of improving material system such as low weight and at the same time having highly mechanical properties and processability has provide new insight for polymer nanocomposites contribution to future applications. They represent a new class of composite materials, which serve as an alternative to overcome imperfections in the conventional composites, such as reduce fracture toughness, decrease glass transition temperature, increase moisture absorption and so on [1–3]. This has been proved by previous studies that a small addition of nanoparticles can enhance variety of properties without sacrifice the advantageous of matrix [4,5].

Generally, polymer nanocomposites refer to composites in which at least one phase filler contains nanometric size; polymers are the primary constituent, while fillers are reinforcing phase which provide the macroscopic strength. Polymer nanocomposites have been extended to various type of polymer system including thermoplastic [6,7] and thermosets [8,9] where eventually different levels of property enhancement are accomplished depending on the chosen polymer matrix and fillers. Among thermosets material, epoxies were widely used across industries because of its high chemical resistance against severe corrosive conditions, good thermal and mechanical properties and excellent adhesion to a wide range of materials. However, its behavior is inherently brittle and thus attracted more interest from researches to improve and obtain better understanding of brittle fracture of this polymer.

There are myriad attempt have been made over the past 15 years to improve the fracture toughness of epoxy resins by using inorganic particles. However, it has caused a loss on other desirable properties and advantageous of polymer matrix. Recently, polymer contains layered-structure particle such as layer silicate montmorillonite and graphene showed a potential of mechanical and toughness improvement because of easy functionality and cost-effective fabrication [10–12]. The high surface area and dispersion are thought to be mainly responsible for the enhanced mechanical properties and fracture toughness [13,14]. Despite of the preceding statement, the understanding of the role of interface in polymer nanocomposites remains in its infancy. No clear understanding and conclusion has yet been emerged regarding the influence of interface on the properties of polymer nanocomposites. Many critical questions are yet to be answered especially in relation to the interface of polymer nanocomposites, such as the development of interface between the nanoparticles and polymer matrix and could interface deliver better results in terms of morphology, properties of nanocomposites. All these issues are remained unanswered mainly due to the lack of reliable experimental data from a series of comparable nanocomposites of tailored interface strength.

Our intent is to investigate the effect of interface on the morphology structure, in particular involves the use of X-ray diffraction and scanning electron microscopy. This finding will build a correlation with the final properties of the epoxy/clay nanocomposites, which will be discussed in part 2.

2. Experimental

2.1. Materials

The matrix used was epoxy resin DGEBA with an EEW of 182–196 g/equiv. A hardener, namely polyoxyproppylene (J230) was used to mix with epoxy in an epoxy/hardener ratio of 100:33. Sodium clay with a cation exchange capacity (CEC) of 85 mequiv/100 g was modified by three types of surfactant agents, namely ethanolamine, Jeffamine® M-2070 and Jeffamine® XTJ-502.

2.2. Modification of clay surface

To modify clay surface, 10 g of sodium clay was dispersed in 2 kg of boiling deionized water for 10–15 min. Under such conditions the clay layers were readily expanded. A surfactant solution was prepared by diluting stoichiometric amount of *eth* or *m27* or *xtj* in deionized water, followed by adding 10 g of concentrated hydrochloric acid (37%). The surfactant solution was added slowly to the clay suspension, and stirred vigorously using a mechanical stirrer for 15–30 min at 90°C. The modified clay was later filtered off using a rotary vacuum evaporator followed by washing in acetone using a magnetic mixer, an ultrasonic bath and a centrifuge to remove excess surfactant. The characteristic of resulting modified clay was tabulated in Table 1 in ref. [15].

2.3. Preparation of nanocomposite

Epoxy was mixed with a desired amount of organoclay for 1 hr at 55°C using a mechanical mixer at 400 rpm in a round bottom flask with a condenser. This was followed by degassing in a vacuum oven at 120°C. A hardener J230 was added to the mixture and mixed for ~2 min at 50°C. The resultant mixture was highly degassed in a vacuum oven followed by pouring into a rubber mould and cured at 80°C for 3 hrs and at 120°C for 12 hrs.

2.4. Characterizations

X-ray diffraction (XRD) measurement was performed on Mini-Materials Analyzer diffractometer with tuned to Cu K radiation. The diffraction curves were collected at scanning rate of 1°/min and a step size of 0.02°. The fracture surface of the tested CT specimens was observed by a Philips 505 model scanning electron microscopy (SEM) at an accelerating voltage 10 kv. Prior to the test, the specimens were coated with a thin layer of gold.

3. Results and discussion

3.1. Formation of nanocomposites

As the clay is hydrophilic and not compatible with hydrophobic epoxy resin, it is essential to improve the miscibility and interface interaction between clay and matrix. In this study, the used surfactants consist of at least one amine-group, which was protonated by hydrochloric acid, so the amine group can graft onto the clay layer via cation exchange. The reaction between the clay surface and the surfactant amine group is illustrated in Fig. 1.
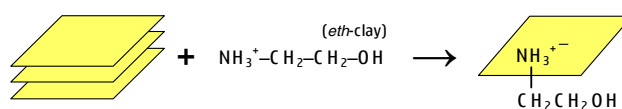

Fig. 1. Schematic of surfactant grafting onto clay surface via cation exchange.

Fig. 2 displays the X-ray diffraction of the epoxy nanocomposites. The diffraction intensity of surface-modified nanocomposites is weakened compare to raw clay. The diffraction angles are found move to lower values, due to more epoxy molecules migrating into the layer spacing with improved interface. As the clay loading increases from 0.46 to 1.87 vol%, the intensity becomes obvious which indicates the existence of layered structure. Overall, the epoxy/*eth*-clay composites indicate the lowest value of basal spacing increment due to the short chain of the *eth* molecules, while *xtj*-clay and *m27*-clay composites show almost similar basal spacing because of the similarity of molecular weight. Although initially it was expected that epoxy/*xtj*-clay will have exfoliated structure, but the results of XRD show quite an opposite. This could be caused by the bridging of nanolayers through bi-functional amines, which prevents layers expansion and causes re-aggregation of clay layers as illustrated in Fig. 3.

3.2. Fracture surface analysis

SEM was adopted in this study to capture the fracture surface in the zone of slow fracture (stress-whitened) of the fractured CT specimen at optimum clay fraction 1.16 vol%. The mirror-like fraction surface of neat epoxy is well-known; by contrast, the fracture surfaces of nanocomposites are highly rough. Figs. 4, 5 and 6 show microstructures on the fracture surface of epoxy nanocomposites derived from *eth*-clay, *m27*-clay and *xtj*-clay, respectively. The *eth*-clay produced the most extensive whitening zone, followed by *xtj*-clay and *m27*-clay (refer Figs. 4a, 5a and 6a).

In Fig. 4b, the fracture surface demonstrates that clay agglomerates are almost invisible, thus indicating that all nanolayers seem to disperse homogenously. Fig. 4c displays a low number of broken layers, whereas no crack is found. In contrast to Fig. 4b, some clusters with diameter of 4–5μm are visible in Fig. 5b. A magnified micrograph in Fig. 5c demonstrates that some clay layers are broken, where some cracks are found (as indicated by white

arrows); this implies the occurrence of a higher level of load transferring from matrix to nanolayers due to the improve interface strength, therefore predicting that a higher fracture toughness of *m27*-clay will be obtained compare to *eth*-clay.
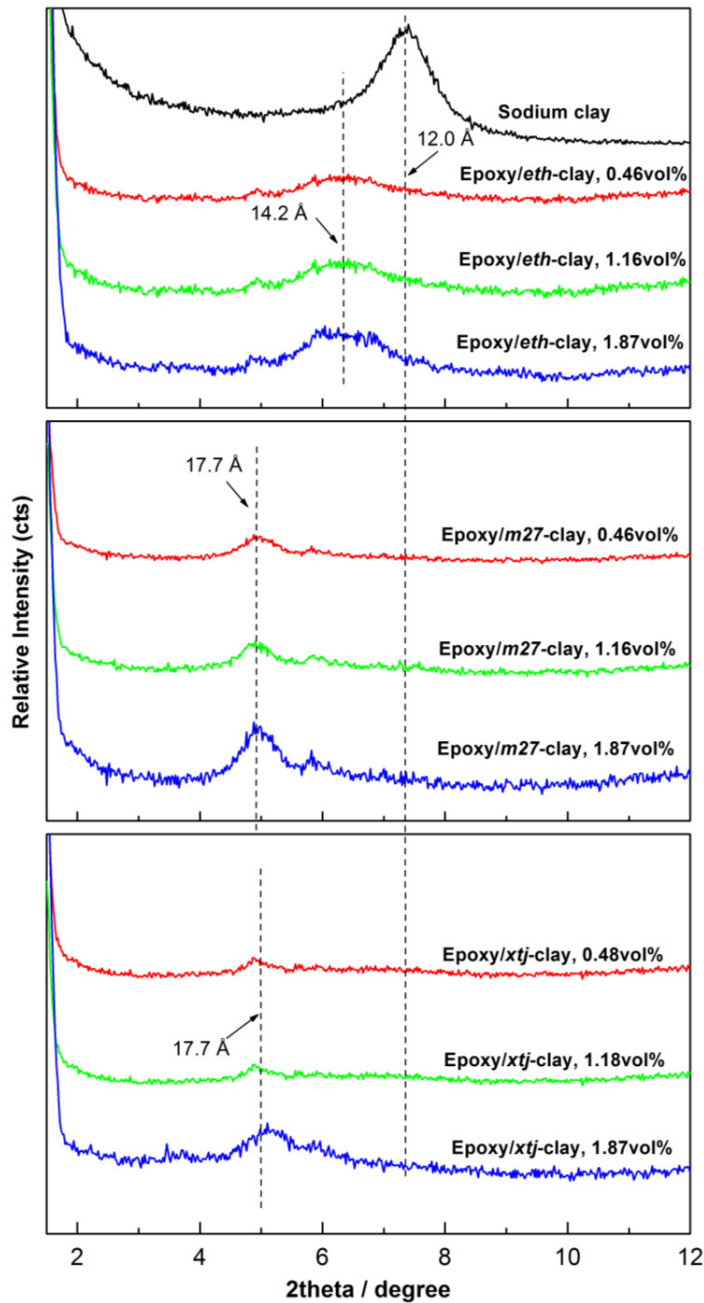

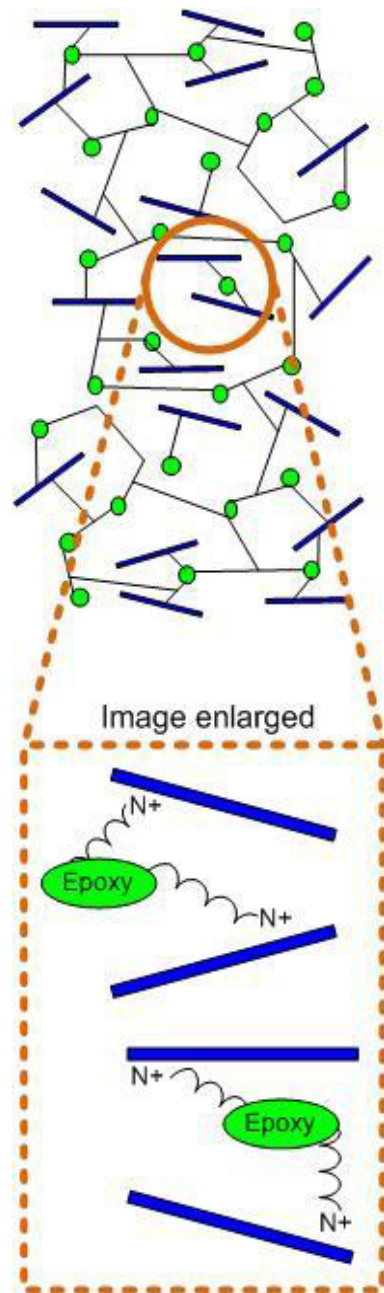Fig. 2. XRD spectra of sodium clay and epoxy nanocomposites.

Fig. 3. Schematic representation of bridging between clay layers.
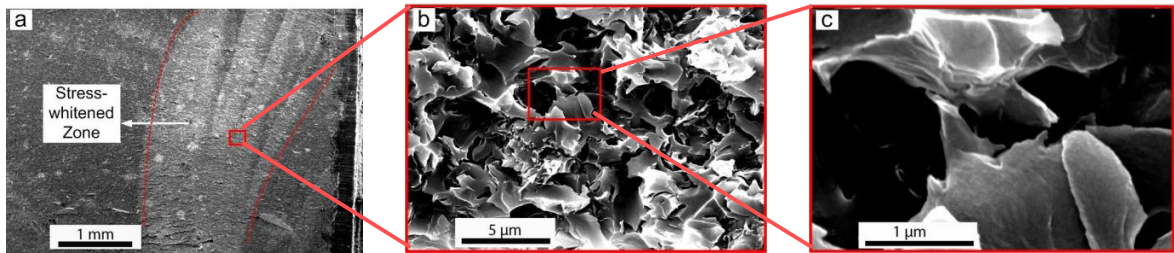
Fig. 4. SEM micrographs of CT fracture surface of 1.16 vol% epoxy/*eth*-clay nanocomposites.
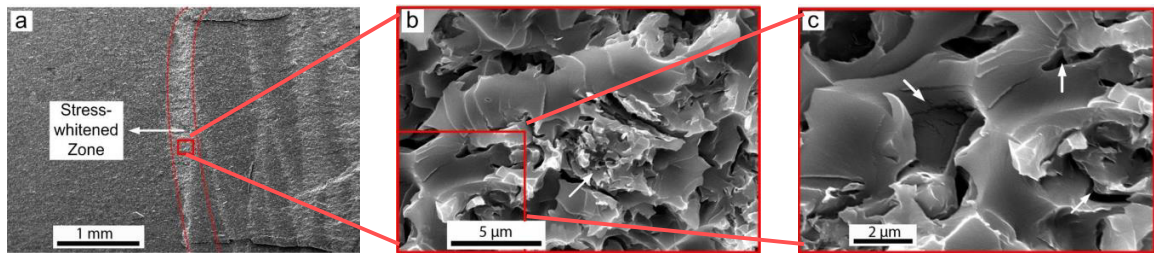

Fig. 5. SEM micrographs of CT fracture surface of 1.16 vol% epoxy/*m27*-clay nanocomposites.

Fig. 6b shows different sizes of clusters were formed in the epoxy/*xtj*-clay nanocomposites. Clusters of 3−5 μm in diameter are shown in Fig. 6b. In Fig. 6c, cracks, more broken layers and a higher degree of matrix deformation are found, and this means that stiffer, stronger nanolayers act as stress concentrators, thus promoting the formation of the microcracks during the loading and will increase the fracture toughness properties significantly.
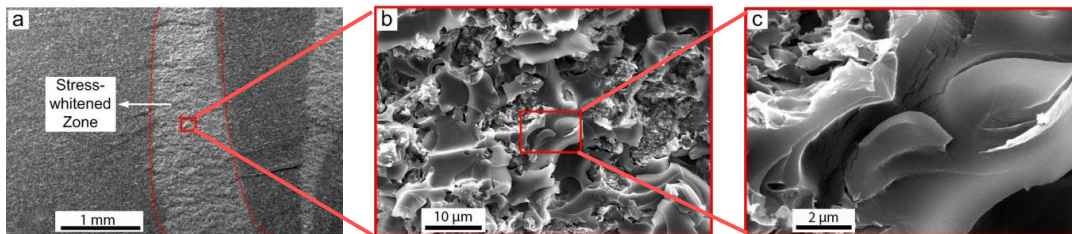

Fig. 6. SEM micrographs of CT fracture surface of 1.16 vol% epoxy/*xtj*-clay nanocomposites.

4. Conclusion

It was remarkable to see how the adopted systems had produce significant outcomes, which demonstrated the effects of different interface strength on the morphology structure of epoxy/clay nanocomposites. It was proved from the XRD and SEM that the chemical reaction of amino-groups of *xtj*-clay with epoxy created a better interface, thus will resulting in a significant mechanical properties enhancement.

Acknowledgements

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