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Mechanism of reinforcement in a nanoclay/polymer composite

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ABSTRACT

Using organomodified montmorillonite (MMT) (commonly called "Nanoclay") to reinforce polymer-based composites have raised much attention to academic and industrial sectors due to the addition of small amount of nanoclay could substantially enhance the mechanical properties of pristine polymers. However, most of the works done previously have neglected to comprehensively study the basic reinforcing mechanism of the composites, particular the interaction between nanoclay and surrounding matrix even though high tensile strength and modulus were obtained. In this paper, uniformly-dispersed nanoclay/epoxy composite samples, based on our tailor-made experiment setup were fabricated. A tensile property test was conducted to examine the mechanical properties of the samples with different nanoclay content. It was found that the Young's modulus and tensile strength of a composite with 5 wt.% of nanoclay increased up to 34% and 25% respectively, as compared with a pristine sample. Images obtained from scanning electron microscopy (SEM) and results extracted from transmission electron microscope (TEM) proved that interlocking and bridging effects did exist in the composites. Nanoclay clusters with the diameter of 10 nm could enhance the mechanical interlocking inside the composites and thus, breaking up the crack propagation. The formation of boundaries between the nanoclay clusters and epoxy can refine the matrix grains and further improve the flexural strength of the composites.

1. Introduction

Using organomodified montmorillonite (MMT) (commonly called "Nanoclay") to reinforce polymer-based composites have raised much attention to academic and industrial sectors due to the addition of small amount of nanoclay could substantially enhance the mechanical properties of pristine polymers. However, most of them have neglected to comprehensively study the basic reinforcing mechanism of the composites, particular the interaction between nanoclay and surrounding matrix even though high tensile strength and modulus were obtained. However, without carefully studying any single step in the production process of the composites, some key parameters that may affect their homogeneity due to the existence of surface tension between stirring materials (like stirrers) and mixture of nanoclay and resin, may be ignored [1,2]. Agglomeration of nanoclay, formation of nanoclay clusters and uncured resin may be resulted if large amount of nanoclay are added into the resin. Changing of resin viscosity and controlling of sonication time may also be the keys to produce desirable composites with moderate strength and ductility. Extra energy imposed into the mixture under sonication may also cause early curing of the resin, which results in brittling resultant composites.

Many attempts have been reported recently on studying the mechanical, morphological and thermal properties of nanoclay/polymer composites by using mechanical stirring and sonication processes [3,4]. However, most of them can only produce evidences extracted from localized regions of samples and it is hard to achieve homogeneity of the samples as in global scale. These methods are;

(i) Mechanical stirring (at 400 rpm) during the stage of mixing nanoclay/polymer at the temperature of 80 °C for 2 h followed by sonication. Continuously, degassed at 120 °C followed by pre-curing at 170 °C for 5 h and post-curing at 200 °C for 2 h;
(ii) Mixing process was performed in an oil bath at the temperature 50 °C and 70 °C followed by sonication for 8–12 h. Hardener is then added afterward;
(iii) Magnetic stirring (with a magnetic bar) followed by high shear mixer and sonication during the stage of mixing nanoclay/resin at room temperature. Continuously stirring after hardener is added and then followed by vacuum curing at the temperature of 75 °C for 3 h;

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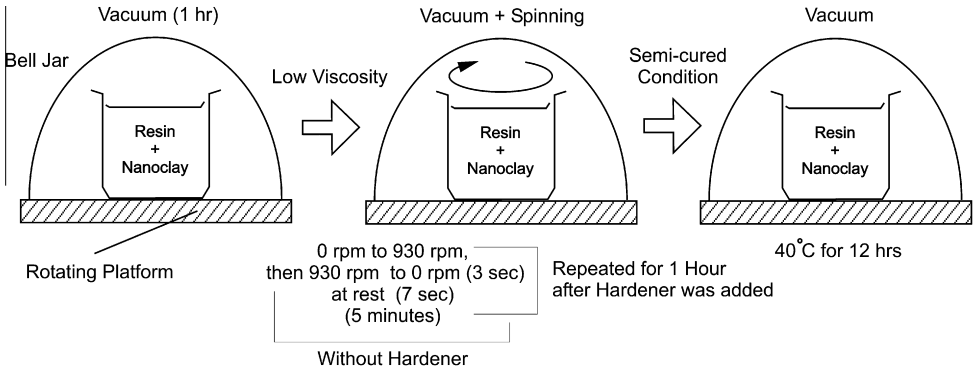

Fig. 1. Principal of experiment set-up.

(iv) Similar to (i), but the mixing process was controlled at the temperature of 180 °C and 60 rpm to lower down the viscosity [4] and
(v) Similar to (i), but the stirring was at 1500 rpm for an hour and no degassed by pre-curing and post-curing.

Due to the fact that non-uniformly dispersed nanoclay and/or agglomeration of the nanoclay existed inside the composites, large discrepancies of the results were obtained from different tests. Nano-indentation has been appreciated as an excellent tool to exam local properties of nanoclay/polymer composites, however, due to an uneven distribution of nanoclay inside the composites, indented marks being measured after indentation may not provide repeatable readings, which is highly depending on the condition and material properties underneath the indentations. Some works were focused on modeling of nanoclay/polymer composites analytically and computationally, both molecular dynamics (MD) simulations and finite element analysis (FEA). Their results cannot be used directly to explain the physical properties of the composites due to ideal assumptions were used [5,6]. MD can only be used to understand the local bonding properties between the nanoclay (in planar structure scale) and surround matrix molecules. The results cannot be used to further estimate the global properties of the composites. Therefore, a new method should be proposed to produce uniformly-dispersed nanoclay/polymer composites and systematically analyze their mechanical properties at both macro and micro scale levels. The influences due to certain manufacturing parameters such as processing and curing temperatures, stirring type and time, and the curing method should be studied in detail.

This paper is a continuous work of our previous study [7]. A set-up based on the spinning of the mixture of nanoclay and epoxy subject to a controllable curing temperature and pressure environment was used to produce uniformly-dispersed nanoclay/epoxy composite samples with different nanoclay content (see Fig. 1). A tensile property test was then conducted and followed by the investigation on their fracture behavior by using scanning electron microscope (SEM) and transmission electron microscope (TEM).

2. Materials and sample fabrication

Araldite GY251 epoxy resin and hardener HY956 in the ratio of 5:1 were used to produce nanoclay/epoxy composites. Organo-modified nanoclay particles (SiO_2, DK4 series from the Zhejiang FengHong Clay Chemical Co., Ltd. Chain) were then added into the mixture of epoxy resin and hardener to form nanoclay/epoxy composites. All composites with the nanoclay content of 1 wt.%, 3 wt.%, 4 wt.% 5 wt.% and 7 wt.% and four identical samples for each type of composites were made.

In this newly experiment setup, it is comprised of two parts, which are an extracting part and a stirring part. For the extracting part, a pressure pump is connected to a bell jar (Fig. 2a) with a pressure valve and a pressure gauge for controlling and measuring the pressure supply, respectively. The bell jar contains a rotating platform (Fig. 2b), in which the spinning speed can be adjusted by changing the supply voltage. The mixture of nanoclay/epoxy is placed on the platform and spinning at a pre-determined angular speed, ω [6].

In the experiment setup, the variable supply voltage is used to provide accelerating and decelerating effects. Centrifugal acceleration and deceleration of the mixture can be calculated by $G_a = \omega^{2r}$ [7]. Creating the acceleration from zero to maximum velocity on the rotating platform is to ensure that all nanoclay is well mixed together and uniformly-distributed in the through-the-height direction of samples. The effects at acceleration, deceleration and rest conditions will create the movement of the nanoclay to produce uniformly-dispersed samples. The centrifugal acceleration G for nanoclay can be calculated by $G = 9.81 \times 5.5893 \times 10^{-7}(r)^2(D)$, where r is rpm of motor and D is diameter of the container. During the spinning process, the viscosity of the resin increases with time, which ultimately restricts the motion of the nanoclay inside the semi-cured resin. This process can greatly minimize the possibility of sedimentary effect.

However, air bubbles trapped inside nanoclay platelets and between the nanoclay and surrounding matrix may also be another critical factor that may weaken the strength of the composites. During the centrifuging process accompanied with the vacuum environment, all these bubbles will be taken away from the samples. The samples will be remained under vacuum and at spinning condition for 2 h after adding the hardener.

During the process of fabricating the composites, the nanoclay was added into the resin in predetermined weight content. The nanoclay/epoxy resin was placed on a rotating platform and put into a bell jar under vacuum for 55 min to extract gas bubbles. Angular acceleration and deceleration motions were applied through the rotation of the platform from 0 to 930 rpm for 2 s and then returned back to 0 rpm for 1 s. The mixture was then rest for another 7 s. In order to ensure that the nanoclay inside the mixture was uniformly-dispersed, repeated motions by following the previous steps were applied for 5 min. The hardener was then added to the mixture. Spinning of a new mixture was then applied again by using aforementioned procedure for 1 h under vacuum condition till the viscosity increased to avoid any movement of the nanoclay inside the resin. All samples were then removed from the jar. The tensile property test was then conducted after the

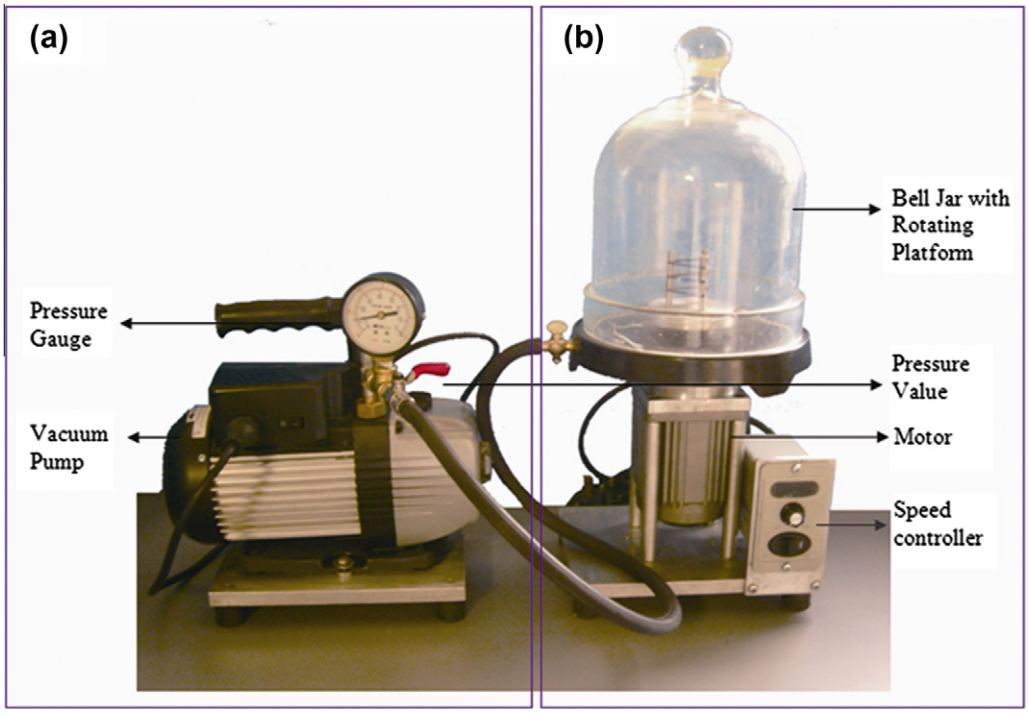

Fig. 2. Experiment set-up.

samples storing inside the chamber for 12 h with the temperature at 40 °C.

3. Experimental results and discussions

3.1. Scanning electron microscope (SEM)

To investigate the homogeneity of the samples with different weight content of nanoclay, the fractographic observation through the use of SEM (Leica Stereo scan 440) was conducted. The SEM was acquired by examining the dispersion condition of nanoclay inside the epoxy matrix.

The samples with 3 wt.% and 4 wt.% of nanoclay are shown in Figs. 3 and 4 respectively, the size of nanoclay clusters were similar with each other. Those particles, indicated by circles, are nanoclay clusters as indicated by EDX. All nano-sized nanoclay clusters (~<200 nm) were found uniformly dispersed. It proves that the fabrication of uniformly-dispersed samples could only be achieved under the following two procedures: (1) Spinning at a condition when the viscosity of resin is low and then (2) mixing the samples when the viscosity of resin start to increase so as the movement of nanoclay is restricted.

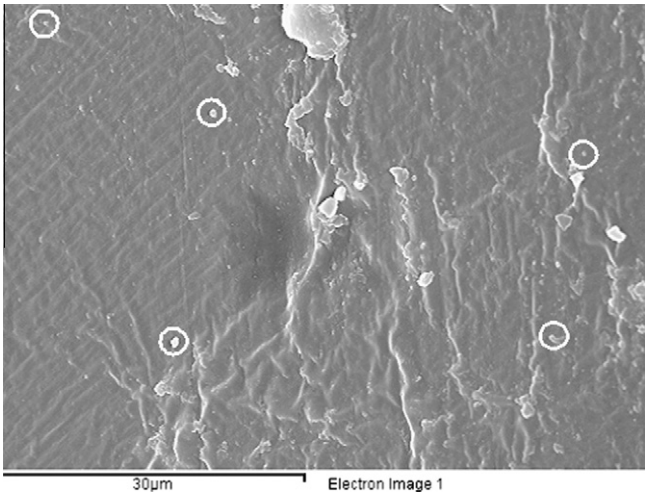

Fig. 3. SEM photograph of the sample 1 (3 wt.% of Manoclay).

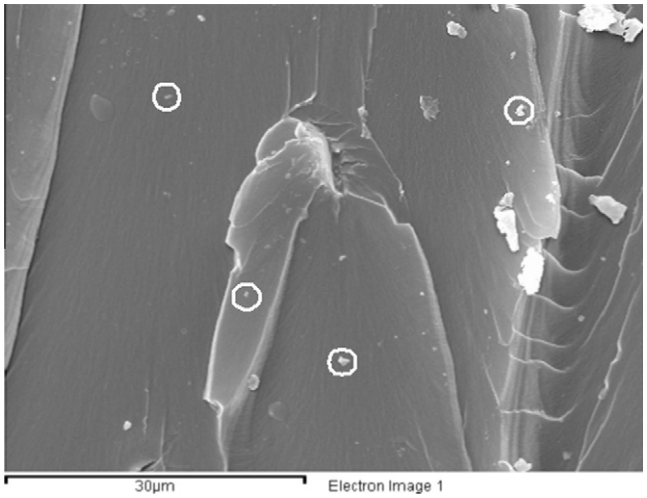

Fig. 4. SEM photograph of the sample 2 (4 wt.% of Manoclay).

During the pouring process of semi-cured nanoclay/epoxy mixture into a dog-bone shape mould for self curing and forming, the viscosity of the composite, at that status, should be high enough to restrict the movement of nanoclay. All samples should be developed in a vacuum environment in order to prevent the formation of air void and moisture.

3.2. Transmission electron microscope (TEM)

TEM can provide direct visualization of the fracture structure morphology. A pristine epoxy and an epoxy with 4 wt.% nanoclay samples are shown in Figs. 5 and 6 respectively, the pattern of

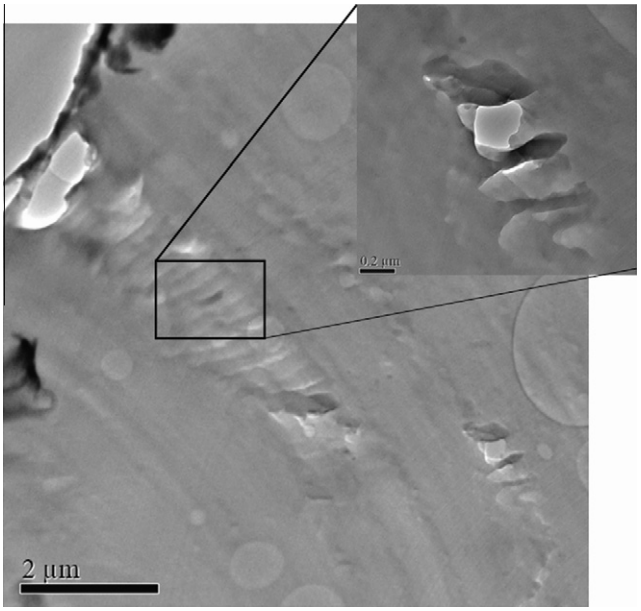

Fig. 5. TEM photograph of the sample 3 (pristine epoxy).

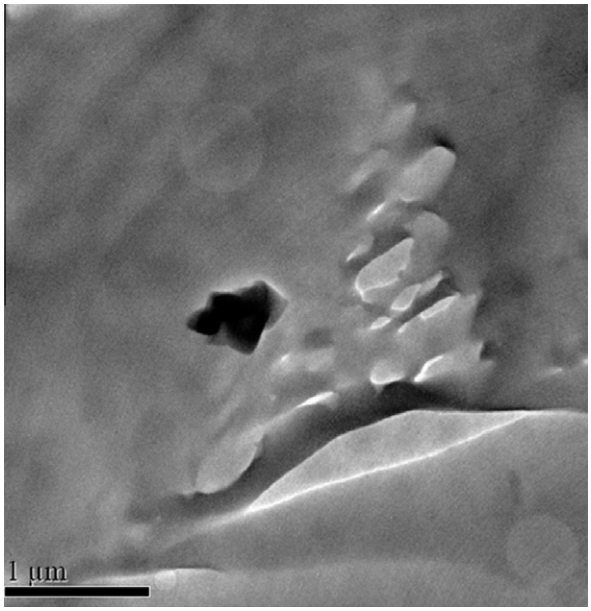

Fig. 6. TEM photograph of the sample 2 (4 wt.% of Manoclay).

the cracks along the loading direction of the samples is easily observed. The mode I crack opening was created inside the pristine and 4 wt.% of nanoclay samples. By comparing with these two samples, the pristine sample had more voids that subsequently may form crack easily once it is subject to a tensile load.

For the nanoclay sample, due to the interlocking effect, the addition of the nanoclay can alter the crack formation mechanism. Meanwhile, a bridging effect due to the good bonding between a nanoclay cluster and surrounding matrix could resist the crack, located near the cluster, opening in the sample. The nanoclay clusters can interlock the polymer chains and eventually form strong barriers to stop crack propagation. High residual stress due to the existence of nanoclay clusters inside the micrometer sized polymer matrix grains, would be created at the surface of the nanoclay clusters and polymer matrix interface. According to the Hall–Petch equation, the formation of the boundaries between the nanoclay clusters and polymer matrix can fine the matrix grains and further improve the flexural strength of nanocomposites. At the same time, this effect causes the nanoclay clusters work as dislocations. Therefore, it results in increasing the fracture energy of the nanocomposites and thus to improve its fracture toughness.

3.2.1. Mechanical properties

As shown in Fig. 7 and Table 1, the increase of Young's Modulus of nanoclay/epoxy samples is dependent on the amount of nanoclay being added. The stiffness of the samples with 3 wt.%, 4 wt.% and 5 wt.% of nanoclay increased by 24%, 31% and 34% respectively.

Table 2 shows that all the nanoclay/epoxy samples achieved higher ultimate tensile strength as compared with the pristine sample. The increase of the strength of the samples with 3 wt.%,

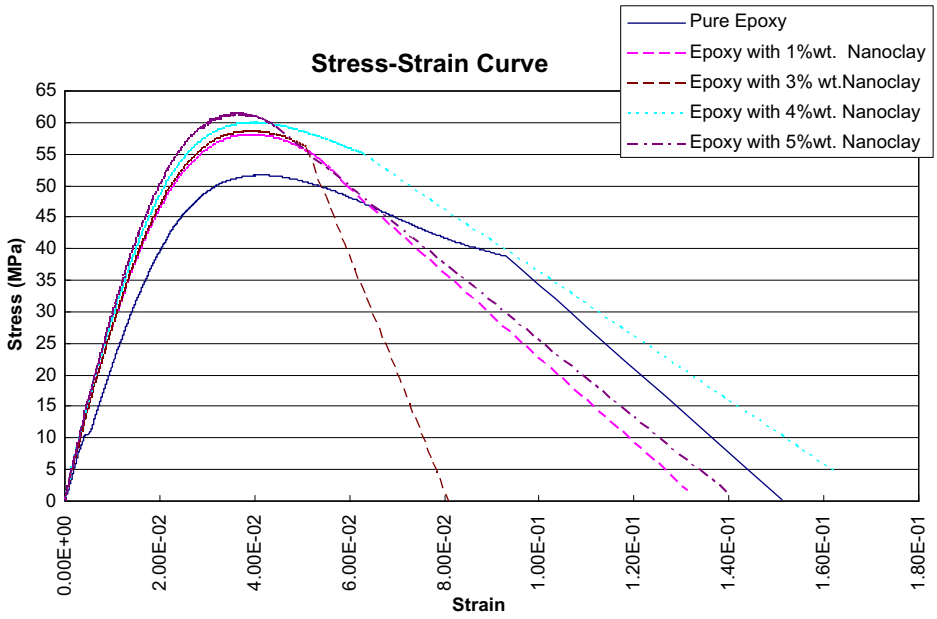

Fig. 7. Stress–Strain curve extracted from tensile test of nanocomposites with different percentage of nanoclay particles.

Table 1
Measured Young's modulus of the samples.

Sample	Young modulus (MPa)	Percentage improvement (%)
Pristine epoxy	2120.30	0
1 wt.% of nanoclay inside epoxy	2474.06	16.68
3 wt.% of nanoclay inside epoxy	2625.09	23.81
4 wt.% of nanoclay inside epoxy	2771.74	30.72
5 wt.% of nanoclay inside epoxy	2841.28	34.00
7 wt.% of nanoclay inside epoxy	3334.00	57.24
9 wt.% of nanoclay inside epoxy	2431.98	14.70

Table 2
Measured ultimate strength of all samples.

Sample	Mean of ultimate strength (MPa)	Percentage improvement (%)
Pristine epoxy	52.4	0
1 wt.% of nanoclay inside epoxy	58.02	10.72
3 wt.% of nanoclay inside epoxy	58.49	11.23
4 wt.% of nanoclay inside epoxy	60.72	15.88
5 wt.% of nanoclay inside epoxy	65.22	24.47
7 wt.% of nanoclay inside epoxy	54.43	3.87
9 wt.% of nanoclay inside epoxy	32.82	−43.43

4 wt.% and 5 wt.% of nanoclay are 12%, 16% and 25% respectively. The results are consistent with our previous studies and the nanoclay provided a mechanical interlocking effect, like micro-pins inside the matrix environment.

4. Conclusion

This paper introduces the use of our newly-proposed experimental set-up to produce homogenous nanoclay/epoxy composites. As in realty, a pure exfoliated nanoclay structure cannot be easily formed by using traditional plastic injection moulding process, our investigation was mainly focused on the nanoclay cluster effect to pristine epoxy. During our test, it was found that the Young modulus and tensile strength of the composites increased with increasing the nanoclay content. The optimal amount of nanoclay should not exceed 5 wt.%. The increases of Young's modulus and tensile strength of a composite sample with 5 wt.% were 28% and 25%, respectively. Further increasing the content of nanoclay would result in decreasing the mechanical properties of resultant composites.

The fracture surface of the sample after the test was then investigated morphologically using SEM and TEM. It was found that the samples with 3 wt.% and 4 wt.% of nanoclay formed nanoclay clusters with uniform size and dispersion. TEM also retrieved that the addition of nanoclay can bridge up the voids to avoid the formation of crack due to the interlocking effect. Nanoclay clusters with the diameter of 10 nm enhanced the mechanical interlocking inside the composites and thus, breaking up the crack propagation. The formation of boundaries between the nanoclay clusters and epoxy can fine the matrix grains and further improve the flexural strength of the composites.

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