Organoclay Effect on Mechanical Properties of Glass/Epoxy Nanocomposites: Tensile, Flexure and Interlaminar Fracture Properties

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ABSTRACT

This research is aimed to perform a symmetric investigation regarding organoclay effect on mechanical behaviors of the glass/epoxy/organoclay nanocomposites. To demonstrate the organoclay effect, three different loadings, 2.5, 5 and 7.5 wt% of organoclay were dispersed in the epoxy resin using mechanical mixer followed by sonication. The corresponding glass/epoxy nanocomposites were prepared by impregnating the organoclay epoxy mixture into the dry glass fiber through a vacuum hand lay-up process. From the tensile tests, it was revealed that the longitudinal tensile strength decreases as the organoclay loading increases, on the other hand, the transverse tensile strength increases with the increases of the organoclay. Furthermore, SEM observation on the transverse failure specimens indicates that the enhancing mechanism is due to the improved interfacial bonding between the fibers and the surrounding matrix modified by organoclay. The similar tendency was also found in the transverse flexural strength of the composites. However, from the mode I fracture tests, it was revealed that with the increase of the organoclay, the corresponding fracture toughness of the composites declines appreciably.

INTRODUCTION

With the characteristics of superior mechanical behaviors and higher aspect ratio, the nano-materials are considered as a supreme reinforcement for improving matrix properties [1, 2]. Polymer reinforced with organoclay platelets are one particular class of nanocomposites and have attracted considerable attentions since Toyota researchers successfully enhanced the mechanical properties of nylon 6 a decade ago [3, 4]. The organoclay platelet is an ultra thin (1 nm) silicate film with lateral dimensions up to 1 μm. Through the ion exchange process, the sodium ions attracted on the surfaces of the platelets were replaced with organic cations which can not only improve the interfacial adhesion between the polymer and the platelet but also facilitate the exfoliation of the organoclay. After an appropriate fabrication process, such as melt compounding [5], in situ polymerization [6, 7] and solution method [8], the aggregated platelets can be exfoliated and dispersed uniformly in the polymer. Depending on the degree of exfoliation, three categories of nanocomposites, i.e., tactoid, intercalated and exfoliated, were produced [9]. Experimental observations show that the stiffness of nanocomposites will be enhanced appreciably if the platelets are well dispersed and exfoliated in the nanocomposites [5, 10].

Although the mechanical behaviors of nanocomposites can be increased by organoclay, as compared to the conventional fiber composites, the amount of enhancement is still limited. To be applicable for structural applications, the hybrid fiber/organoclay nanocomposites, combining the characteristics of the long fiber composites and the organoclay nanocomposites,

were then synthesized. Haque et al. [11] fabricated the glass/epoxy composites and glass/epoxy nanocomposites with low loading of organoclay. They pointed out that dispersion of 1 wt% organoclay could improve the interlaminar shear strength of glass/epoxy nanocomposites up to 44%. Similar positive tendency on the flexure properties of the laminates with organoclay were also observed by Kornmann et al [12]. Chowdhury et al [13] studied the flexural and thermo-mechanical properties of woven carbon carbon/nanoclay epoxy laminates pointing out that the maximum flexural strength and modulus as well as the highest Tg value appear at the samples with 2wt% nanoclay loading. Miyagawa et al [14] investigated the organoclay effect on flexural properties and the interlaminar shear strength (ILSS) of bio-based epoxy carbon fiber composites. It was found that the flexural strength and the modulus are not influenced substantially by the organoclay. In addition, little improvement on the ILSS was observed on the 5wt% organoclay samples. Vlasveld et al. [15] conducted single fiber fragmentation test to evaluate the fiber-matrix interfacial bonding properties of the glass fiber reinforced polymide-6 silicate nanocomposites. It was revealed that the interfacial bonding decreases with the inclusion of silicate into the matrix materials, which deviates from the early investigations provided by other researches [11-13]. This discrepancy could be due to the processing effect resulting in the changes of the microstructures of the nanocomposites. So far, the information related to the effect of organoclay on the mechanical responses of fiber/epoxy composites is still lacking.

In this study, a systematic investigation was carried out to understand the organoclay effect on the tensile, flexural and fracture behavior of glass fiber reinforced nanocomposites. Scanning Electron Microscopy (SEM) observations were conducted on the failure surfaces to determine the failure mechanism.

MATERIAL PREPARATION

To investigate the organoclay effect on tensile, flexural and fracture properties of glass/epoxy nanocomposites, the laminates with various organoclay loadings were prepared. Subsequently, based on different experimental purposes, the corresponding specimens were fabricated.

Preparation of Glass Fiber/Epoxy Nanocomposite

The glass fiber/epoxy nanocomposites were prepared by adding organoclay into epoxy resin and then, through vacuum assisted hand lay-up procedures, infusing the organoclay/epoxy compound into the glass fibers. The detail procedure was reported elsewhere [16, 17] and here are only briefly summarized. The organoclay/epoxy compound with organoclay loading, 2.5, 5 and 7.5 wt% respectively, were fabricated through the sonication followed by the mechanical blending. It is noted that from the X-ray diffraction (XRD) measurements and TEM observations, the present samples was regarded as intercalated nanocomposites [16, 17]. The epoxy/organoclay mixture was impregnated into the dry unidirectional glass fiber (E-LR0908-14 unidirectional E-glass fiber purchased from Vectorply Inc.) with the assistance of hand roller to ensure all fibers are wetted. After the wetted fiber perform was stacked together layer by layer, the fiber packing was sandwiched between two steel plates with porous Teflon fabric in between and sealed within a vacuum bag. The whole laminates were cured in a

hot press with suggested temperature profile under vacuum conditions. It is noted that the vacuum is essential for forming nanocomposites since it can facilitate the removal of the bubbles trapped within the laminates. For the comparison purpose, the fiber volume fractions for all samples with different organoclay loadings were remained the same.

Fabrication of Nanocomposite Specimens

There are several categories of specimens prepared for investigating the organoclay effect on the nanocomposite behaviors, such as the tensile, flexure and fracture properties. Unidirectional $[0]_5$ and $[90]_5$ laminates were prepared for evaluating the tensile strength and modulus of the nanocomposites in the longitudinal and transverse directions, respectively. In addition, the in-plane shear strength of the composites was determined from the tensile tests on off-axis $[10]_5$ and $[\pm 45]_s$ laminates. With regard to the flexure properties of the composites, three point bending tests were conducted on the $[0]_5$ and $[90]_5$ specimens. Mode I fracture toughness of the composites with various organoclay loadings were evaluated from Double Cantilever Beam (DCB) specimens.

MECHANICAL PROPERTY CHARACTERIZATION

Tensile Tests

To determine the tensile behavior, coupon specimens (200 mm long, 18 mm wide and 1.45 mm in thickness) obtained from five ply unidirectional nanocomposites were employed for tension tests. Because of the end tabs adhered on both ends of the specimens, the actual gage length is 100 mm. Tensile tests were conducted on the hydraulic MTS machine using stroke control mode at strain rate of 10^{-4}/s. During the tests, the strain histories were measured from the strain gauges adhered back to back on the central section of the specimens; while, at the same time, the corresponding loadings were obtained from the load cell mounted in the loading fixture. Both signals were recorded concurrently using a PC computer with Labview program.

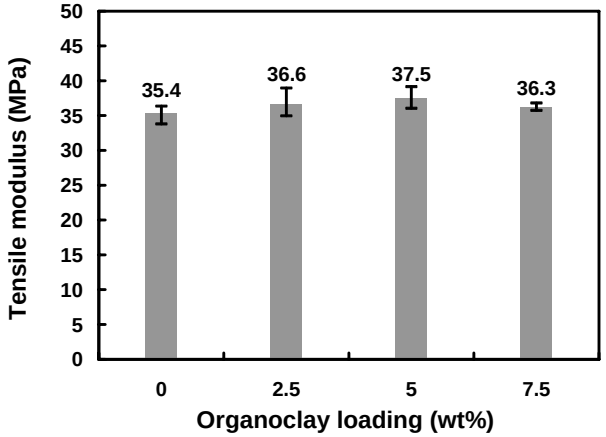


Figure 1. Longitudinal tensile modulus of glass fiber/epoxy nanocomposites with various organoclay loadings.

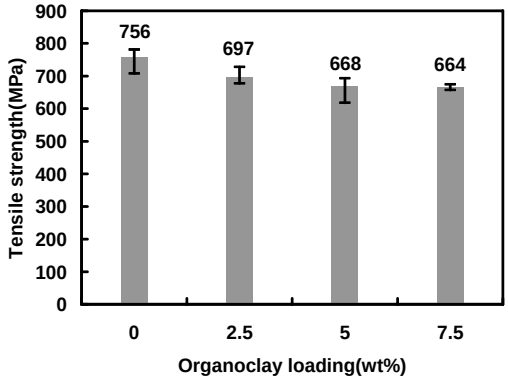


Figure 2. Longitudinal tensile strength of glass fiber/epoxy nanocomposites with various organoclay loadings.

$[0]_5$ tension

The tensile strength and the Young's modulus of the nanocomposites with different organoclay loading were evaluated from the peak values and the initial slope (0.1% strain) of the stress-strain curves of the $[0]_5$ specimens, respectively. Since it is fiber dominated properties, the stress-strain curve is linear and the sudden failure occurs as the ultimate strength is reached. Figures 1 and 2 illustrate Young's modulus and longitudinal tensile strength with respective to different organoclay loadings. At least five specimens were tested for each case. It is found that the Young's modulus is not affected significantly by the organoclay; however, the failure stresses are declining as the organoclay loading increases. In general, the tensile strength is fiber dominant property and should not be influenced by the matrix. It is noted that the fibers adopted for the study are stitched together by means of the woven threads which may cause the wavy fibers to occur in the nanocomposites. When the samples with the wavy fibers are tested in the fiber direction, the failure mechanism may not be dominated by the fiber breakages. Apparently, for the nanocomposites, the fiber brooming instead of breakages was found on the failure $[0]_5$ specimens. In addition, when the epoxy matrix is modified with the organoclay, the mechanical response become brittle and the fracture toughness decreases accordingly [16]. As a result, the effect of wavy fibers in conjunction with the brittle behaviors of the matrix should be responsible for the decreases of the tensile strength of nanocomposites.

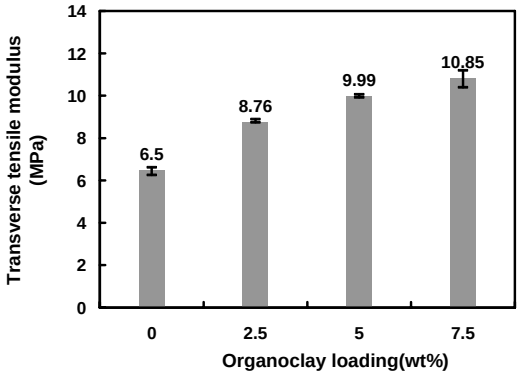


Figure 3. Transverse tensile modulus of glass fiber/epoxy nanocomposites with various organoclay loadings.

$[90]_5$ tension

Transverse tensile modulus and strength was measured from the tensile tests on $[90]_5$ specimens. In contrast to the tensile strength discussed previously, both transverse tensile modulus and strength exhibit increasing behaviors with the increment of organoclay loading as illustrated in Figures 3 and 4, respectively. To further understand the enhancing mechanism, the failure surfaces of the samples were examined using SEM. For the comparison purpose, the micrographics of the nanocomposites with 5 wt% organoclay as well as the one without any organoclay are shown in Figure 5. It is found that for the nanocomposites, the fibers are still surrounded and adhered with the matrix and consequently, the matrix cracking is the primary failure mechanism. On the other hand, for the conventional composites, the failure surfaces of the fibers are featureless and smooth, which provide an indication that the interfacial debonding is the main failure mechanism. From the SEM observations, it appears that the nanocomposites possess better interfacial bonding than the conventional one. As a result, the increasing behavior of the transverse tensile strength in the nanocomposites could be attributed to the improved interfacial strength modified by the organoclay. The organoclay effect on the interfacial bonding of glass fiber composites is currently under investigation using molecular mechanics analysis.

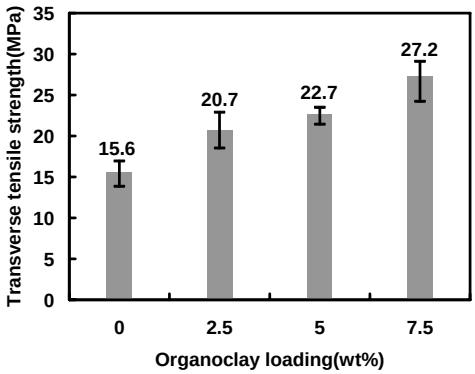
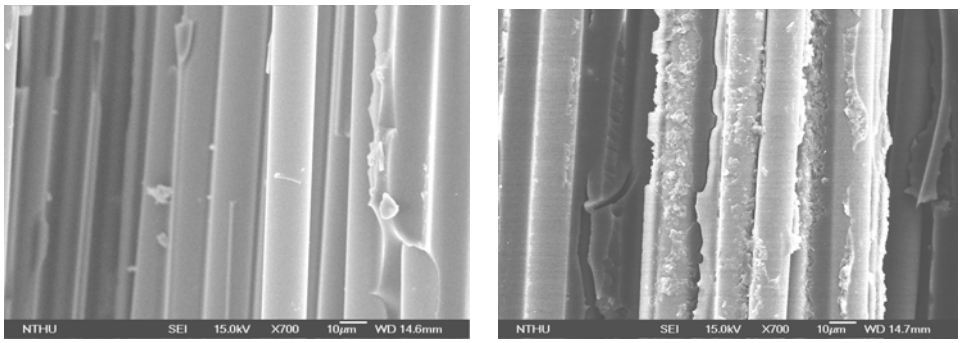


Figure 4. Transverse tensile strength of glass fiber/epoxy nanocomposites with various organoclay loadings.



(a) (b)

Figure 5. SEM micrographics of glass fiber/epoxy nanocomposites samples: (a) pure epoxy; (b) 5 wt% organoclay.

$[10]_5$ tension

In view of the forgoing, the interfacial adhesion between the glass fibers and the surrounding matrix could be improved by the organoclay. This implies that the in-plane shear strength of nanocomposites which is dominated by the interfacial properties could also be enhanced accordingly. To validate the organoclay effect, the in-plane shear strength of fiber composites were measured from off-axis 10^o specimens and the $[\pm 45]_s$ laminates as well [18]. The 10^o specimens will be introduced in this section and the $[\pm 45]_s$ laminates will be presented in the next section. It is noted that in the 10^o specimens, the tensile stress is always accompanied with the in-plane shear stress on the failure plane resulting in that the in-plane shear strength measured from 10^o specimens is relatively low as compared to that obtained from $[\pm 45]_s$. and considered as the lower bound solution. The in-plane shear strength obtained from the off-axis 10^o specimens are plotted in Figure 6 corresponding to different organoclay loadings. It is revealed that in-plane shear strength increase as the organoclay loading rises. SEM micrographics on the failure surfaces as shown in Figure 7 also indicate that the interfacial bounding in the nanocomposites is superior to that in the conventional composites. Thus, in addition to the transverse responses, the in-plane properties can be improved by the dispersion of the organoclay in the epoxy matrix.

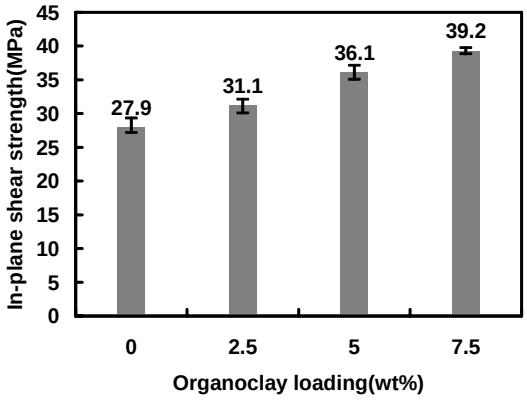
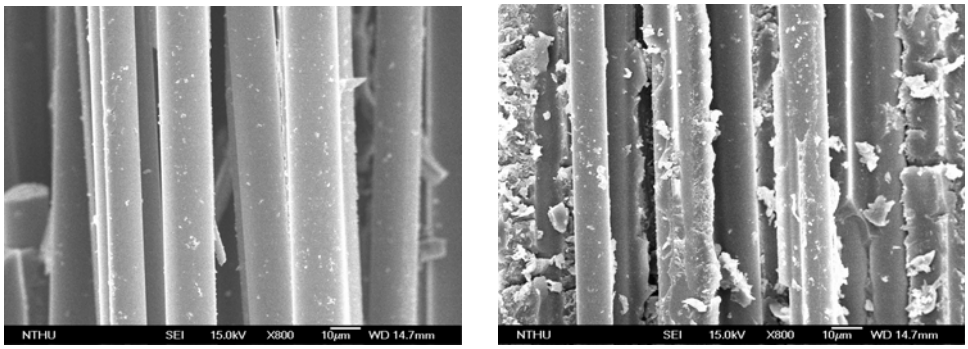


Figure 6. In-plane shear strength of glass fiber/epoxy nanocomposites obtained from 10^o off-axis specimens.



(a) (b)

Figure 7. SEM micrographics of 10^o off-axis glass fiber/epoxy nanocomposite specimens: (a) pure epoxy; (b) 5 wt% organoclay.

$[\pm 45]_s$ tension

The in-plane shear strength of the composites was also characterized from tensile tests on $[\pm 45]_s$ laminate. The experimental results are shown in Figure 8. As compared to the values obtained from the off-axis $[10]_5$ specimens, the in-plane shear strength measured from the $[\pm 45]_s$ laminate is relatively higher. This is because of the constraint effect caused by adjacent plies which often occurs in the angle-ply laminates, and thus, the associated measurement is regarded as the upper bound solution. Moreover, it is found that the in-plane shear strength obtained from $[\pm 45]_s$ laminate increases as the organoclay contents increase, which is consistent with that measured in $[10]_5$ specimens. It should be noted that in the failure mechanism of the $[\pm 45]_s$ laminate is matrix failure which can be verified by the failure specimens as shown in Figure 9.

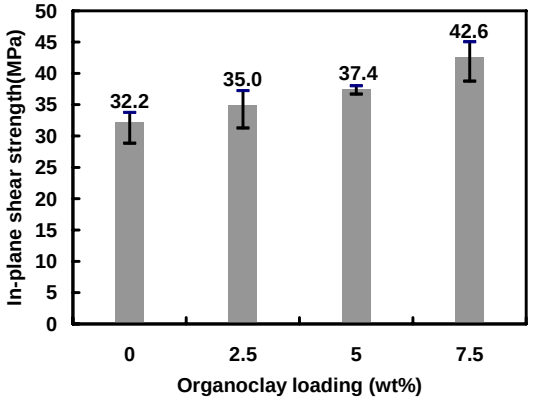


Figure 8. In-plane shear strength of glass fiber/epoxy nanocomposites obtained from $[\pm 45]_s$ laminates.

(a) (b)

Figure 9. Failure specimens of $[\pm 45]_s$ glass fiber/epoxy nanocomposites : (a) pure epoxy; (b) 5 wt% organoclay.

Three Point Bending Flexure Tests

The effect of organoclay on the flexural properties of the glass fiber reinforced composites was determined from the three point bending test in accordance with ASTM standard D790 [19]. During the tests, the crosshead is under stroke control and the corresponding speed is set to be 0.07mm min^{-1}. The flexural strength of the specimens is calculated from the following formulation

$$S = \frac{3PL}{2bd^2} \tag{1}$$

where P is the failure load, L is the support span, and b and d represent the width and thickness of the specimens, respectively.

$[0]_5$ flexure tests

Longitudinal flexural strengths of the nanocomposites as well as the conventional composites are shown in Figure 10. No significant improvement on the flexural strength was observed in the nanocomposites. This response is normal because the longitudinal flexural properties are dominated by the fiber properties.

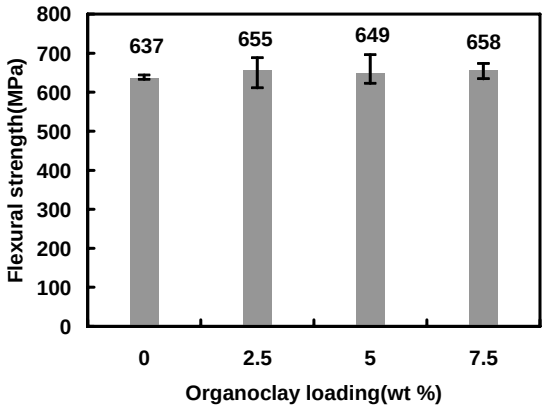


Figure 10. Longitudinal flexure strength of glass fiber/epoxy nanocomposites with various organoclay loadings.

$[90]_5$ flexure tests

For evaluating the transverse flexural strengths of the nanocomposites, the $[90]_5$ specimens were tested on the three point bending fixture. The experimental results are shown in Figure 11. It is appeared that as the organoclay increases, the transverse flexural strength is increasing accordingly. Since the transverse flexural behaviors are controlled by the matrix properties, based on the previous discussions, the failure strength should be enhanced when the organoclay is modified by organoclay.

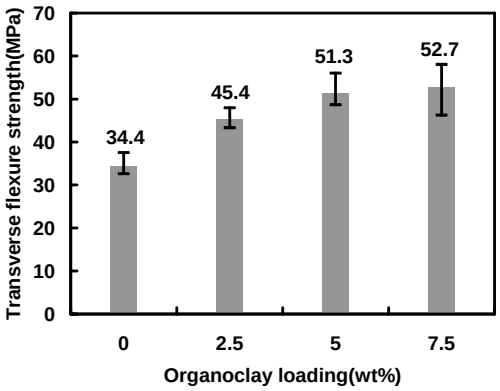


Figure 11. Transverse flexure strength of glass fiber/epoxy nanocomposites with various organoclay loadings.

Mode I Fracture Test

In addition to the tensile and flexural properties presented earlier, the effect of organoclay on the interlaminate fracture toughness of glass/epoxy nanocomposites was determined from double cantilever beam (DCB) specimens. The DCB specimens were 12-ply unidirectional laminates with a porous film inserted in the mid-plane during the lay-up process for creating the pre-crack. The dimension of specimen is 230mm long, 20mm wide and 3.3mm in thickness. Symmetric loadings applied in the opposite directions were transferred into the cracked end of the specimens through a pair of hinge bonded on the specimen surfaces resulting in the Mode I crack extension. During the tests, the crosshead speed is set to be 0.5 mm/min. All specimen preparations and experimental procedure were performed based on ASTM standard D5528-01 [20]. The fracture toughness was calculated using the modified beam theory [21]

$$G_{IC} = \frac{3P\delta}{2B(a+\Delta)} \tag{2}$$

where P is the load when crack begin to propagate and δ is the displacement associated with the load P, B is the width and a is the initial crack length of the specimen. In the conventional beam theory, the fracture toughness was calculated based on the assumption that the specimen is clamped at the delamination crack front. However, in reality, the DCB specimen is not a perfectly built-in cantilever but exhibits rotation and deformation around the crack tip. To compensate the deformation and ration effect, the beam theory was modified with a slightly longer crack length $a+\Delta$, where Δ can be evaluated experimentally from the plot of the cube root of compliance with respect to the crack length [21]. The interlaminar mode I fracture toughness of the nanocomposites calculated from the modified beam theory are plotted versus the organoclay loading in Figure 12. In contrast to the in-plane shear strength and transverse tensile strength, the interlaminar fracture toughness of the nanocomposites decreases as the organoclay loading increases. For the matrix modified with the organoclay, the corresponding mechanical properties become brittle such that the plastic zone around the crack tip is small and thus, the crack propagates easily. As a result, the presence of organoclay produces the negative effect on the interlaminar fracture toughness of the fiber composites.

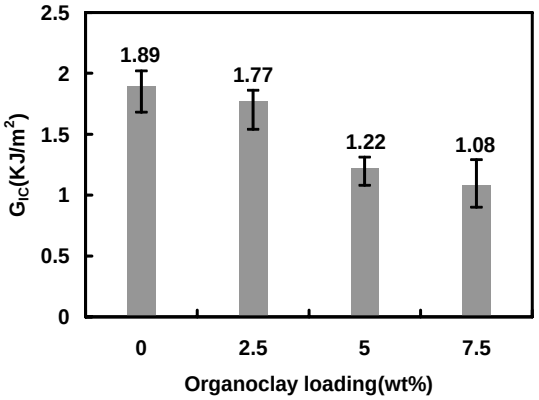


Figure 12. Interlaminar Mode I fracture toughness of glass fiber/epoxy nanocomposites with various organoclay loadings.

CONCLUSIONS

The tensile, flexural and fracture behaviors of the fiber nanocomposites with different organoclay loadings were investigated experimentally. From the tensile tests, it was found that the longitudinal tensile strength of the composites slightly decrease with the increase of organoclay loadings. However, the transverse tensile strength and modulus increases as the organoclay loading raises. The enhancing behaviors could be due to the improved interfacial bonding between the fibers and surrounding matrix modified by the organoclay. Moreover, from the tensile tests on $[10]_5$ and $[\pm 45]_s$ specimens as well as the transverse flexural tests, the organoclay also exhibit positive effect on the in-plane shear strength and the transverse flexural strength of the composites. Nevertheless, the Mode I fracture tests indicated that the interlaminar fracture toughness of the nanocomposites decreases with the inclusion of the organoclay. The declining phenomena could be attributed to the toughened matrix caused by the presence of the organoclay.

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