

Effect of surface-functionalization of Na⁺-montmorillonite nanoclay using 3-aminopropyltrimethoxy silane on the mechanical properties of E-glass chopped strand mat/epoxy composites

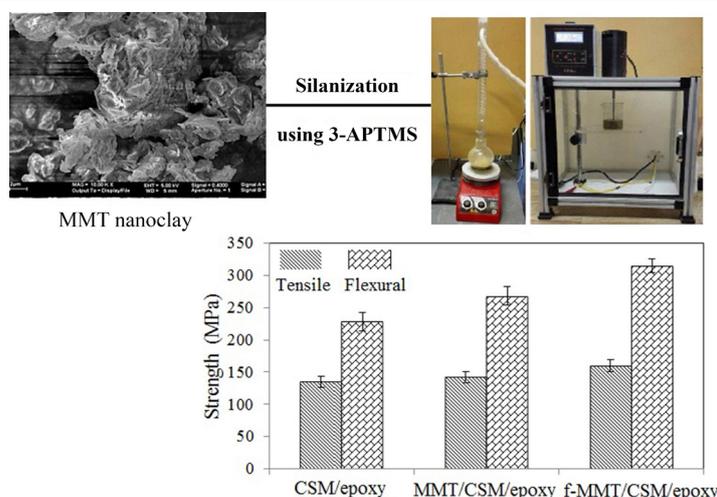
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HIGHLIGHTS

- Silane functionalization of MMT nanoclay was studied.
- Silanized MMT particles have a better strengthening effects than as-received ones.
- Improved interfacial adhesion between fibers and MMT-enhanced matrix was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, Na⁺-montmorillonite nanoclay (Na-MMT) was functionalized using 3-aminopropyltrimethoxysilane (3-APTMS) as a coupling agent. The covalent functionalization of MMT was confirmed by Fourier-transform infrared spectroscopy (FT-IR). In the specimen fabrication stage, 5 wt% of pristine MMT or silane-functionalized MMT (f-MMT) were incorporated into an epoxy system and the resultant mixture was applied on an E-glass chopped strand mat (CSM). A significant enhancement in the mechanical behavior (tensile and flexural properties) of CSM/epoxy composite was observed when enhanced with 5 wt% of f-MMT. The addition of 5 wt% of f-MMT enhanced the tensile strength, flexural strength, tensile modulus, and flexural modulus by 18%, 38%, 18%, and 28%, respectively. Compared to the MMT/CSM/epoxy composite, the f-MMT/CSM/epoxy specimen demonstrated 12%, 18%, 11%, and 16% increase, respectively, in the tensile strength, flexural strength, tensile modulus, and flexural modulus. The observed behavior is related to the enhanced interfacial interaction between f-MMT and the epoxy matrix due to the chemical functionalization of MMT.

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1. Introduction

Fiber-reinforced polymers (FRPs) have attracted considerable attention in automotive, aerospace, marine, and construction industries due to their unique characteristics such as high specific stiffness, high specific strength, high fatigue and corrosion resistance, and ease of fabrication [1,2]. Fibrous reinforcements can be added to the polymeric matrix in the form of continuous [3] or discontinuous [4]. One technique to maximize the applications of FRPs is reinforcing the matrix through the incorporation of nanoscale materials such as nanoclay [5,6], carbon nanotubes (CNTs) [7,8], graphene nanoplatelets (GNP) [9,10], carbon nanofibers (CNFs) [11,12], SiO₂ [13], Al₂O₃ [14], CaCO₃ [15], etc. This type of materials is called multiscale composites [16,17]. Among the various types of nanofillers, the high surface-to-volume ratio makes the nanoclay particles ideal reinforcing material in composites. A number of reports in the literature have shown the positive role of nanoclay on the mechanical properties of FRPs. For instance, Khosravi *et al.* [18] found that the addition of 5 wt% nanoclay resulted in 28%, 11% and 35% improvement in the flexural, tensile and compressive strengths of basalt fiber/epoxy composite. Rafiq *et al.* [19] reported a 23% increase in the peak load and 11% improvement in the stiffness of glass fiber reinforced epoxy (GFRE) composite under low-velocity impact with the addition of 1.5 wt% nanoclay in the matrix. Withers *et al.* [20] investigated the mechanical behavior of an epoxy glass-fiber composite filled with nanoclays, demonstrating a 7.9% greater fatigue strength than the pristine specimen. Khan *et al.* [21] studied the quasi-static and impact fracture behaviors of carbon fiber-epoxy matrix composites (CFRPs) with a nanoclay-filled epoxy matrix. They found that the addition of nanoclay improved the fracture resistance, flexural strength and modulus. Subramaniyan *et al.* [22] found that the compressive strength of unidirectional-glass polymeric composites substantially increased with the addition of the nanoclay.

Interfacial bonding and good dispersion of nanofillers should be considered to effectively enhance the various properties of polymers. If the nanoparticles are not dispersed uniformly within the matrix, the created agglomerates act as stress-concentration regions and as a result the cracks will propagate from these regions during mechanical loading [23,24]. A feasible technique

to overcome this problem is surface functionalization of nanoscale reinforcements. In this case, silane coupling agents are usually utilized for surface functionalization of nanofillers [25-28]. For instance, He *et al.* [25] reported that treated CaCO₃ nanoparticles in a carbon fiber/epoxy system have a better strengthening effect than untreated ones. Lee *et al.* [26] investigated the influence of CNT modification on the tensile behavior of CNT/basalt/epoxy composites and found that the tensile strength and Young's modulus of silanized CNT/basalt/epoxy composites were 34 and 60% higher, respectively, than that of untreated CNT/basalt/epoxy ones. Wang *et al.* [27] claimed that the modification of graphene with silane was favorable for their homogeneous dispersion in the polymeric matrix even at higher nanofiller contents. Park *et al.* [28] showed that the surface functionalization of MMT led to an increase of the specific component of the surface free energy of MMT.

To the best of our knowledge, no research on the mechanical properties of silane-modified MMT/CSM polymeric composites has been conducted. In the present study, the MMT nanoparticles were surface-functionalized with a 3-APTMS coupling agent and the influence of MMT functionalization on the tensile, flexural and wear properties of CSM/epoxy composite was investigated. The main aim of this work was to reinforce discussing how surface functionalization can affect the mechanical properties of fibrous composites.

2. Experimental

2.1. Materials

KER 828 epoxy resin produced from bisphenol A and epichlorohydrin was used as a matrix part. This resin possesses an epoxy group content of 5260-5420 mmol/kg, dynamic viscosity at 25 °C of 12-14 Pa.s, and a density of 1160 kg/m³. Both the epoxy resin and curing agent were supplied by the Kumho P&B Chemicals, Inc. in Korea. An E-glass chopped strand mat with a density of 450 g/m² was provided by China National Building Materials (CNBM) Co., Ltd. The Na⁺-MMT nanoclay was supplied by Sigma Aldrich Co, USA. The SEM image of as-received nanoclay particles are given in Figure 1a. 3-APTMS provided by Merck Chemical Co., Germany, was used as a coupling agent for surface functionalization of the nanoclay particles. The

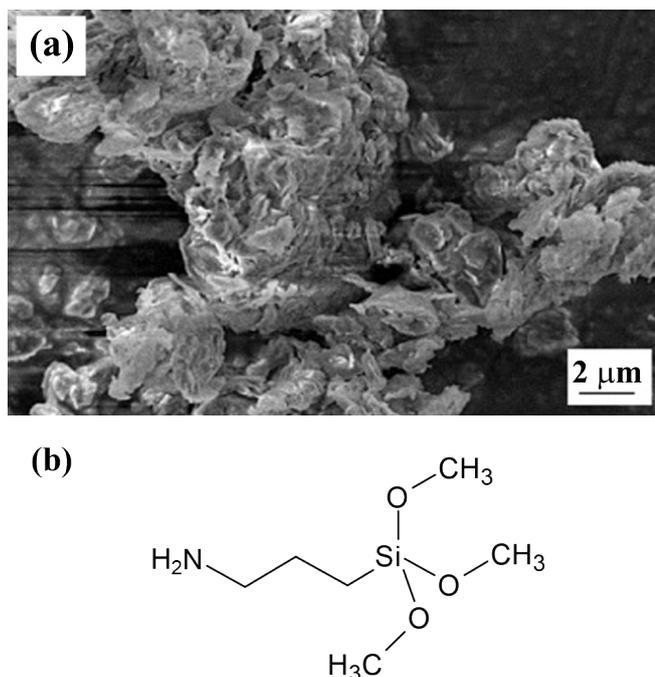


Fig. 1. (a) SEM image of as-received MMT nanoclay, and (b) the chemical structure of 3-APTMS.

structural formula of this compound is $C_6H_{17}NO_3Si$, as indicated in Figure 1b.

2.2. Silane functionalization of MMT nanoclay

Surface functionalization of nanoparticles was conducted to increase the interfacial interaction between the MMT and epoxy matrix. In the first step, 5 g of MMT particles were added to a 100 ml ethanol-water solution containing 5 vol% distilled water. In the next step, 3-APTMS with a weight ratio of 1:1 with respect to MMT was added. The resulting mixture was subjected to ultrasonic waves for 10 min and then refluxed at 80 °C for 7 h. pH of the solution was set in the range of 4-5 using HCl acid [17,18]. After this stage, to separate the particles the obtained mixture was centrifuged at a speed of 4000 rpm for 30 min. In the final step, obtained powders were washed three times with ethanol to remove the extra coupling agent on them and dried in oven for 12 h.

2.3. Specimen fabrication

To fabricate the multiscale composites, the epoxy/MMT mixture was first prepared. In all cases, the following procedure was conducted: first, 5 wt% MMT

(treated or non-treated) was added to the epoxy resin. The mixture was stirred by a high speed mechanical stirrer for 20 min at 2000 rpm. Then it was dispersed by a probe sonicator at 150 W (Ultrasonic homogenizer 400 W, 24 kHz, TOPSONICS Co., Iran) for 30 min. During the sonication process, a water-cooling system was utilized to keep the temperature of the mixture around 45 °C. Next, stoichiometry ratio of curing agent was added and the mixture was stirred manually for 3 min. Then it was quickly employed to fabricate the specimens. The multiscale composites were manufactured using the hand lay-up technique. The E-glass CSM was impregnated with the epoxy resin modified with nanofillers and then laid up layer by layer. For comparison purposes, a control specimen without MMT addition was also prepared. The total volume fraction of glass fibers was 48% in all specimens, respectively.

2.4. Mechanical testing

Tensile and flexural (3-point bending) tests were performed based on the requirements of ASTM: D3039-14 and ASTM D790-10, respectively. The dimensions of tensile and flexural specimens were 250×25×2.5 mm and 150×25×2.5 mm, respectively. An INSTRON test machine was used for testing the specimens. In the case of the 3-point bending test, the loading rate of the machine was chosen at 4.3 mm/min and span length was kept to 64 mm. In this condition, the span-to-thickness ratio was 32:1. The crosshead rate for the tensile test was 5 mm/min. All tests were carried out at room temperature and three specimens of each type were tested.

2.5. Characterization

In order to verify the surface functionalization of MMT nanoclay particles, the structure of as-received and functionalized powders was investigated using a PerkinElmer model FT-IR spectrometer with a resolution of 4 cm^{-1} .

Following the mechanical testing, the fracture surfaces of the composites were examined using a HITACHI S-4160 field-emission scanning electron microscopy (FESEM) with an accelerating voltage of 15 kV. Before examination, the fracture surfaces were sputter coated with a thin gold layer for conductivity.

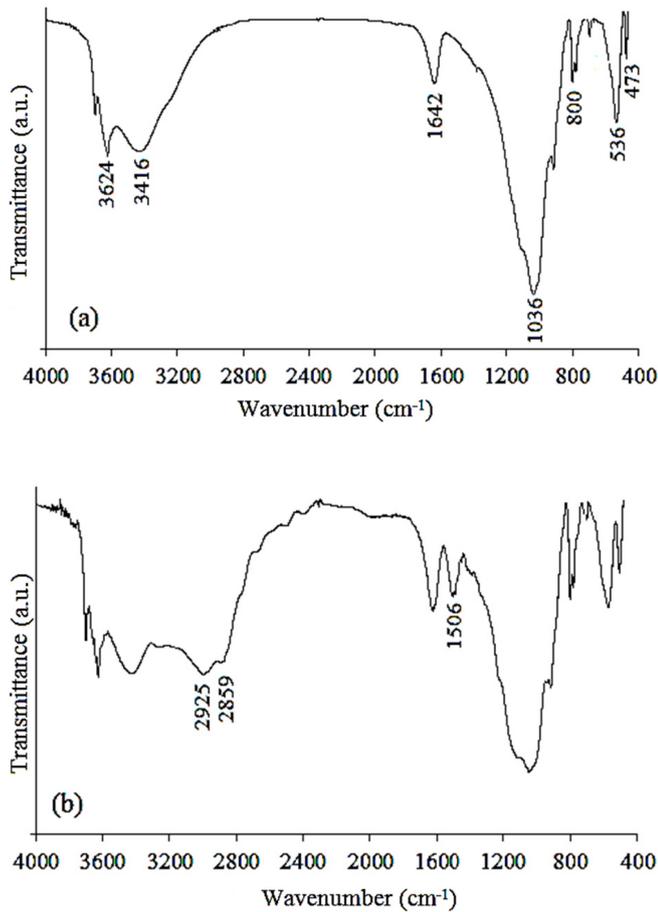


Fig. 2. FT-IR spectra of a) as-received MMT and b) f-MMT.

3. Results and discussion

Figure 2 depicts the FT-IR results of the as-received MMT and f-MMT. The FT-IR spectrum of MMT shows a broad peak at 3416 cm^{-1} , which corresponds to the stretching vibration of hydroxyl ($-\text{OH}$) groups [13,24]. The characteristic band at 1642 cm^{-1} is assigned to $\text{H}-\text{O}-\text{H}$ bending vibration, and the peak at 3624 cm^{-1} represents the stretching vibration of the OH groups bonded to the Al or Mg atoms [18]. The observed absorption band at 1036 cm^{-1} is attributed to the stretching vibration of the $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}$ bonds [29]. Although the absorption band positioned at 800 cm^{-1} is identified to be due to the symmetric stretching of the $\text{Si}-\text{O}-\text{Si}$, the bands at 536 and 473 cm^{-1} are characteristic of the bending vibration of $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}-\text{Al}$ [18]. Compared with as-received MMT, f-MMT exhibits two new characteristic absorption bands at 2925 and 2859 cm^{-1} , which are attributed to the stretching asymmetric and symmetric $-\text{CH}_2$ groups [18,24]. The band at 1506 cm^{-1} corresponds to the bending vibration of the $-\text{NH}_2$ group [15]. All these observations confirm that the surface of the MMT

has been successfully functionalized by a silane coupling agent.

Figures 3 and 4 present the experimental results of mechanical (tensile and flexural) strengths and moduli of the fabricated composites in this work. From the data presented, it can be found that the tensile and flexural strengths increase with MMT and f-MMT addition. The effect of the nanofiller addition on the flexural strength is more than that on the tensile strength. This is because flexural strength is a matrix-dominant property while tensile strength is fiber-dominant. By addition of 5 wt.% f-MMT, the tensile and flexural strengths increase about 18% and 38%, respectively. Such a finding may be due to the two main reasons: First, the fiber-matrix interfacial characteristics should be addressed. It has been well documented that the interfacial characteristics between the matrix and the reinforcement in fibrous composites play a significant role in determining their final performance [17,25]. When the matrix material is reinforced by MMT, the frictional slippage of the fiber-matrix interface against the applied load is restricted due to the presence of nanofillers. In fact, nanoclay acts as a mechanical interlocking between the E-glass fibers and matrix creating a high friction coefficient. This implies

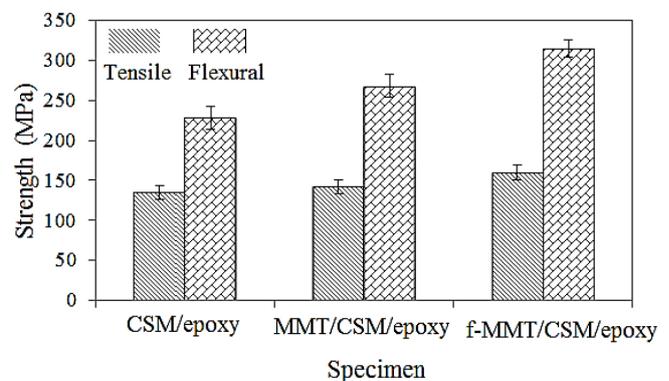


Fig. 3. Tensile and flexural strengths of specimens.

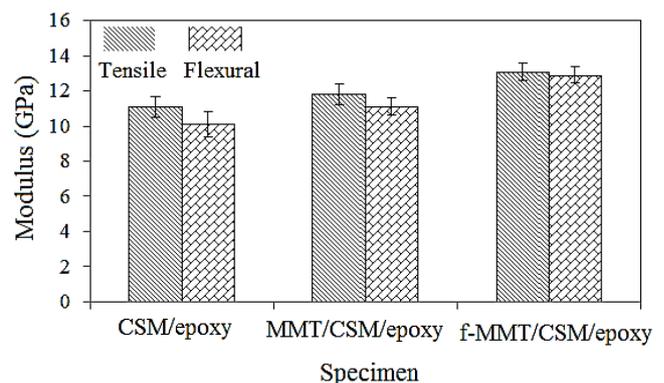


Fig. 4. Tensile and flexural moduli of specimens.

that in the case of a nanocomposite matrix, the applied load can be effectively transferred from the matrix to the fiber reinforcement. Therefore, the load bearing capacity of nanocomposite specimens is higher than the free-MMT one. The second reason is attributed to increasing the required stress level for fiber breakage and fiber microbuckling when the matrix is reinforced by MMT. In fibrous composites, fibers (especially fiber skin) and fiber-matrix interface are accounted as stress concentration regions. Introduction of MMT to the matrix can effectively reduce the stress concentration onto the fibers during loading.

The values of tensile and flexural moduli for the specimen containing 5 wt% of f-MMT are 13.1 GPa and 11.9 GPa, respectively, which shows an increase of 18% and 28%, respectively, as compared to the control specimen. The enhanced mechanical moduli observed for the 5 wt% f-MMT loaded specimen is expected because of the higher modulus of the MMT nanoclay particles compared with the epoxy matrix. Another reason for the observed trend is attributed to restricting the mobility of the polymer chains under loading due to the presence of functionalized MMT in the matrix.

Figures 3 and 4 also show the mechanical (tensile and flexural) properties of multiscale composites enhanced by 5 wt% unmodified and modified MMT. As can be seen in Figure 3, enhancements of 12% and 18% are observed for tensile and flexural strengths, respectively, through silane functionalization of MMT, and the tensile and flexural moduli are increased by 11% and 16%, respectively (Figure 4). This shows that the f-MMT particle has better strengthening effects than the as-received one. The observed results are attributed to the improvement in the interfacial bonding of f-MMT with the epoxy matrix. When the f-MMT particles are incorporated within the matrix, the amine groups of silane compounded onto their surfaces can easily react with the epoxide groups of epoxy matrix, forming covalent bonds.

The findings from FESEM observations support the quantitative results from the mechanical testing. Figure 5 shows the fracture surface of the CSM/epoxy, MMT/CSM/epoxy, and f-MMT/CSM specimens. On comparing Figures 5a, 5b and 5c, it can be seen that the interfacial bonding in the multiscale specimens containing MMT or f-MMT particles is superior to that in the control specimen. With regard to Figure 5a which is related to the control specimen, the surface

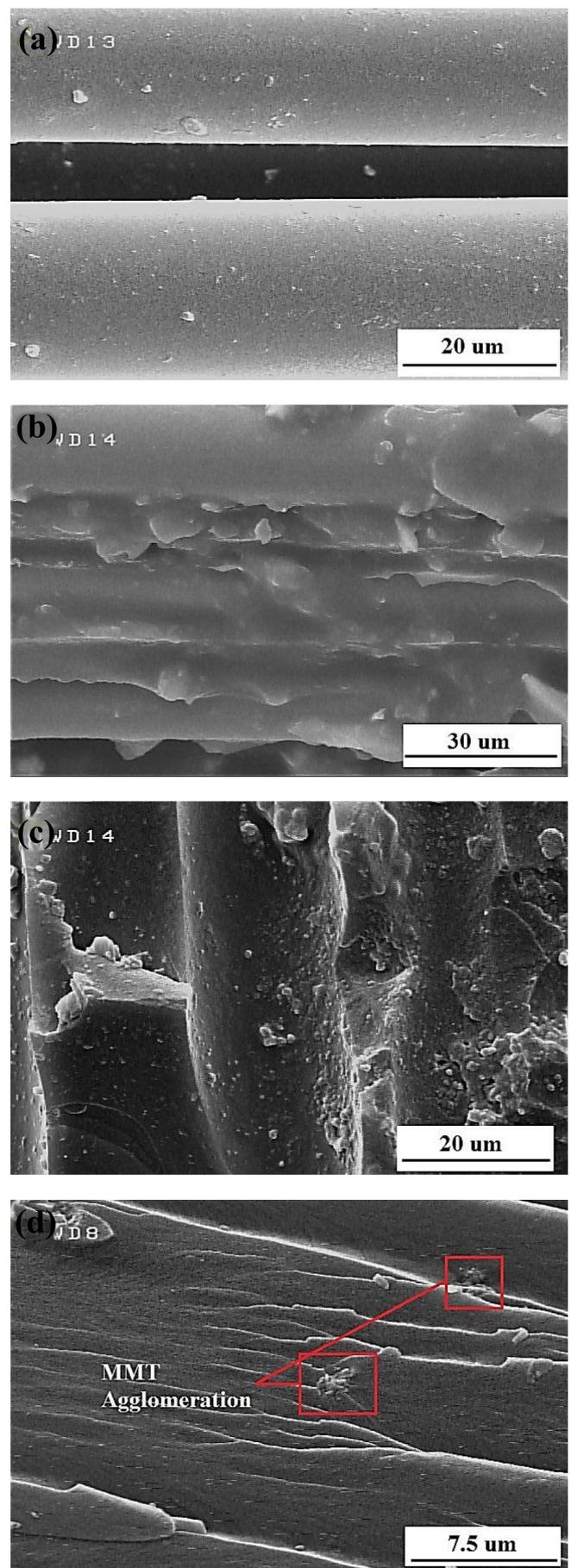


Fig. 5. Fracture surfaces of (a) CSM/epoxy, (b) f-MMT/CSM/epoxy, and (c),(d) MMT/CSM/epoxy composites.

morphology of the fibers is observed to be very clean and smooth. This indicates that the interfacial de-bonding is the main failure mechanism for this specimen [4,17]. On the contrary, as it can be clearly seen in Figures 5b and 5c, there is a good adhesion between the components for the multiscale specimens. Such findings indicate that matrix cracking is the primary failure mechanism for these specimens [4,17]. However, fracture surface of f-MMT/CSM/epoxy composite (Figure 5b) shows a better interfacial bonding between the fibers and the matrix than that of the f-MMT/CSM/epoxy due to silane-functionalization of MMT. Consequently, enhanced interfacial bonding fosters the stress transfer and facilitates the composite to endure higher loads without any plastically deforming. Figure 5d depicts the presence of MMT agglomerates in the case of the MMT/CSM/epoxy specimen, which creates some stress concentration regions and reduces the mechanical behaviors of the specimen.

4. Conclusion

In this work, multiscale E-glass chopped strand mat (CSM)/epoxy/MMT composites were fabricated and subjected to tensile and 3-point bending tests to investigate the effect of MMT silane functionalization on the mechanical properties of the specimens. The following conclusions can be drawn:

- MMT nanoclay particles were successfully functionalized by 3-APTMS coupling agent, and the FTIR analysis confirmed the successful grafting of 3-APTMS on the MMT surface.
- With the addition of 5 wt% f-MMT, compared to the neat CSM/epoxy composite, the tensile and flexural strengths of the specimen was increased by 18% and 38%, respectively.
- Compared to the control CSM/epoxy composite, the f-MMT/CSM/epoxy specimen demonstrated an 18% and 28% increase, respectively, in the tensile and flexural moduli.
- The silane-functionalized MMT nanoclay (f-MMT) showed better strengthening effects than the as-received one. In particular, the tensile strength, flexural strength, tensile modulus, and flexural modulus of f-MMT/CSM/epoxy composites were 12%, 18%, 11%, and 16% greater, respectively, than those of MMT/CSM/epoxy ones.
- The fracture surface examination of the specimens

showed improved interfacial adhesion between the E-glass fibers and MMT-enhanced matrix.

- Overall, this study demonstrates that f-MMT particles dispersed within the matrix can significantly enhance the tensile and flexural properties of the fibrous composite structures.

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