

Enhanced mechanical properties of unidirectional basalt fiber/epoxy composites using silane-modified Na⁺-montmorillonite nanoclay

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Abstract

This study explores the effects of 3-glycidoxypopyltrimethoxysilane (3-GPTS) modified Na-montmorillonite (Na-Mt) nanoclay addition on mechanical response of unidirectional basalt fiber (UD-BF)/epoxy composite laminates under tensile, flexural and compressive loadings. Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and simultaneous thermal analysis (STA) data confirmed the reaction mechanism between the silane compound and Mt. It was demonstrated that addition of 5 wt.% 3-GPTS/Mt resulted in 28%, 11%, and 35% increase in flexural, tensile, and compressive strengths. Scanning electron microscopy (SEM) clarified the improvement in the adhesion between the basalt fibers and matrix in the case of Mt-enhanced epoxy specimen. Also, a theoretical route based on an Euler-Bernoulli beam-based approach was employed to estimate the compressive properties of the composites. The results demonstrated good agreement between theoretical and experimental approaches. Totally, the results of the study show that matrix modification is an effective strategy to improve the mechanical behavior of fibrous composites.

Keywords: Multiscale composites, Basalt fiber, Nanoclay, Salinization, Mechanical response, Microstructure.

1. Introduction

Over the last century, fiber reinforced polymers (FRPs) have been widely used in structural components due to their specific characteristics such as high specific strength and specific stiffness, high fatigue and corrosion resistance, easy to fabricate, and favorable price. FRPs structures undergo various loading conditions in service [1,2].

Natural fibers are increasingly being recognized as a favorable substitute for synthetic fibers. They may be obtained from plant (cotton, flax and hemp, although sisal, jute, kenaf, bamboo and coconut), animal and mineral sources. Natural fibers are nontoxic and more easily recyclable when compared with other classes of fibers [3-5]. Basalt fiber (BF), which is made from the basalt rock, is considered as a mineral fiber. BF possess outstanding properties such as good modulus, excellent stability, good chemical resistance, high mechanical strength and high temperature resistance, and easy to produce [6,7]. A scan through the literature reveals that there are many studies focusing on the different characteristics of the continuous or chopped BF polymeric composites [8-12]. Also, two comprehensive review papers on BF-reinforced composites have been recently presented in 2015 [13,14].

Using nanoclay particles as filler within the polymeric matrix has attracted considerable attention due to the improved mechanical, thermal and physical properties of the resultant material. In recent years, intensive research efforts have been devoted to the study of the response of nanoclay-reinforced polymers to the various loads (tensile, compression, bending and impact) [15-19]. It is believed that the effect of nanoclay particles on the mechanical properties of the polymers is considerable. The improvements are due to the high surface-to-volume ratio of the nanoclay particles [20].

An acceptable dispersion of nanoclay and also good adhesion at the nanoclay/polymer matrix interface are essential to improve the mechanical performance of resultant nanocomposite. For this purpose, modification of the nanoclay (especially with organo-silane compounds) was one of the most important research works in the last years and some papers in this field can be found in literature [21-25]. Appropriate dispersion of the nanoclay minimizes the stress concentration regions, leading to improvement in the uniformity of stress distribution within the matrix. Silane grafting has proved to be a highly efficient strategy to modify the nanoclay surfaces [22,23]. In a clay/polymer system, organo-silane compound creates a bridge between two constituents by a covalent bond. This can lead to great enhancement of the mechanical properties of the resultant composite.

Recently, great efforts have been made to develop polymeric composites with a mixture of micro-scale fibers and a nano-scale filler. Such materials are termed multiscale composites [26]. There are two general methods for fabrication of multiscale composites, nanoparticle-dispersion within the matrix [27] or nanoparticle-grafting onto the fibrous reinforcement [28]. It has been well documented that a multiscale composite possesses enhanced mechanical properties compared to a FRP one [29-35]. Eslami-Farsani et al. [29] investigated the effects of thermal conditions on the tensile properties of BF-reinforced polypropylene (PP)-clay nanocomposites. They reported that the reinforcing efficiency of the nanoclay and BF for the tensile responses of PP composites is higher at low temperatures compared to room and high temperatures. Subramaniyan et al. [30] studied the compressive strength of unidirectional-glass polymeric composites containing nanoclay and reported that the addition of the nanoclay resulted a substantial increase in longitudinal compressive strength of the composites. Iqbal et al. [31] assessed impact damage resistance of carbon fiber-reinforced epoxy with nanoclay-filled matrix, and 3 wt.% clay addition was shown to be an optimal

content for the highest damage resistance. In Ref. [32], mechanical response of carbon fiber reinforced epoxy/clay nanocomposites was assessed. It showed that the interlaminar fracture toughness of the composites was enhanced by 85% through the addition of 4 phr nanoclay. Indeed, 2 phr of nanoclay can enhance the flexural strength by 38%. Withers et al. [33] investigated mechanical properties of an epoxy glass-fiber composite reinforced with surface organo-modified nanoclay. The results showed 11.7% improvement in the ultimate tensile strength, 10.6% improvement in tensile modulus and 10.5% improvement in tensile ductility at 60 °C in the presence of nanoclay minerals. Dorigato et al. [34] evaluated the thermo-mechanical characterization of epoxy/clay nanocomposites as matrices for carbon/nanoclay/epoxy laminates. The mechanical behavior, both under quasi-static and impact conditions, was positively affected by resin nanomodification. Gabr et al. [35] investigated the effect of organoclay on the mechanical and thermal properties of woven carbon fiber/compatibilized polypropylene composites. The results of this work demonstrated that at 3 wt.% of organoclay, initiation and propagation interlaminar fracture toughness in mode I was enhanced by 64% and 67%, respectively.

Although there are a good number of published surveys on the mechanical properties of multiscale polymeric composites, to our knowledge no systematic work has been reported on the mechanical behavior of UD-BF/epoxy composites containing organoclay minerals. The focus of the study is on the effects of the Mt nanoclay modified by 3-GPTS at various contents with respect to the matrix (1-7 wt.% at a step of 2 wt.%) on the mechanical response of UD-BF/epoxy composites. Tensile, flexural and quasi-static compressive characteristics of the specimens were evaluated. The features of the fractured surfaces were also characterized using field-emission scanning electron microscopy (FESEM) observations.

2. Experiments

2.1. Materials

Commercially available ML-506 epoxy resin and HA-11 amine hardener were purchased from Mokarrar Engineering Materials Company, Iran. The resin- hardener ratio was 100:15 by weight, as recommended by the manufacturer. The fibrous reinforcement was basalt roving fibers (trade name: BCF13-150-KV12) which were supplied by Kamenny Vek, Russia. Sodium Montmorillonite (Na⁺-Mt) nanoclay particles were provided by Sigma-Aldrich Co., USA. Fig. 1 shows SEM image of nanoclay particles. 3-GPTS produced by Merck Chemical Co., Germany was used as a silane coupling agent for modification of the nanoparticles. This compound possesses epoxide groups and it is one of the most commonly used organic silane compounds in synthesis of various materials [36]. The molecular formula of the 3-GPTS is C₉H₂₀O₅Si and its molecular weight is 236.4 g/mol.

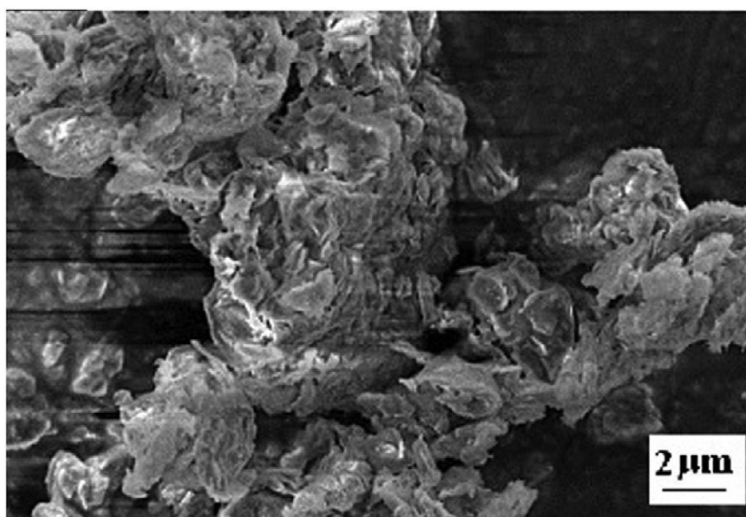


Fig. 1. SEM image of as-received Na-Mt.

2.2. Silanization of Na⁺-Mt

In order to increase the chemical affinity of Mt nanoclay to epoxy matrix, surface modification of nanoparticles is necessary. The silane-modified Mt nanoclays were prepared using a method based on the following sequence: 5 g of the Na⁺-Mt particles was added into 100 mL of the solution of distilled water in ethanol (5 to 95 ratio) and then 3-GPTS coupling agent was added to the system in a weight ratio of 1:1 with respect to the Mt. The mixture was sonicated for 10 min and then refluxed for 8 h. The pH of the system was adjusted to be ~4.5 using HCl acid (37%) [37,38]. The modified Mt powder was centrifuged, washed three times with ethanol and dried at 80 °C for 12 h.

2.3. Characterization techniques for Mt nanoclays

The chemical interactions between the Na-Mt and 3-GPTMS were evaluated using a JASCO FT-IR spectrometer (FT-IR 460 plus). Vibration bands were reported as wavenumber (cm⁻¹). The FT-IR spectra were recorded in the 400-4000 cm⁻¹ range with a resolution of 4 cm⁻¹. The specimens for the FT-IR analysis were prepared by using KBr pellets.

The STA analysis (TGA+DTA -- model: STA504) was carried out using a nitrogen atmosphere, with a flow rate of 50 mL.min⁻¹, in the temperature range of 25-800 °C at a heating rate of 10 °C.min⁻¹. The percentage of grafted silane (PGS) can be expressed by Eq. 1 as follows [39]:

$$PGS(\%) = \frac{100 \times W_{200-600}}{100 - W_{200-600}} \quad (1)$$

where, $W_{200-600}$ is the weight loss in the temperature range of 200-600°C and M corresponds to the molecular weight of the silane coupling agent. Here, the PGS is considered as the percentage of organic 3-GPTS moieties with respect to the total mass of nanoclay. The structure of the Na-Mt and modified nanoclays and their nanocomposites were characterized

by XRD measurements using a Cu K α radiation source operated at a voltage of 30 kV and a current of 20 mA.

2.4. Fabrication of composite laminates

To fabricate the multiscale composites, the epoxy/Mt mixture were first prepared. To this end, required amounts of nanoclay were firstly dried in an oven at 80 °C for 12 h. To lower the viscosity of the epoxy resin, and thus to obtain a good dispersion of modified Mt within the matrix, the epoxy resin was diluted by acetone in a ratio of 100:15 [40]. Initial mixing of nanoclay and epoxy was conducted at a shear rate of 2000 rpm for 20 min using an overhead mechanical stirrer (SDS-11D, Fintek Co., Korea). After that, in order to break the residual aggregates and to obtain a good dispersion of nanoclay particles, the mixture was subjected to sonication using a probe of 14-mm tip diameter, at 120 W and 30% duty cycle (Ultrasonic Homogenizer 400 W, 24 kHz, FAPAN Co., Ltd., Iran) for 90 min, while holding the mixture temperature at 45 °C using a water cooling system. The resultant mixture was then degassed at 80 °C for 30 min under vacuum. After dispersion of modified Mt within the ML-506 epoxy, the resultant mixture was manually mixed with HA-11 hardener at a hardener-epoxy ratio of 15:100. The multiscale and pristine UD-BF/epoxy laminated composites were fabricated using a combination of hand lay-up and vacuum bagging techniques. More details about the employed method can be found in our previous work [41]. In the present study, various amounts of modified nanoclay (1-7 wt.% at a step of 2 wt.%) were chosen. Also, with the purpose of comparison, a pristine UD-BF/epoxy composite (free from the nanoclay) was also fabricated with the same method reported for nanocomposite fabrication. The prepared laminates were cured at room temperature for 7 days (recommended by manufacturer). The BF volume fraction for all of the specimens was the same and found to be around 50%.

2.5. Mechanical tests

2.5.1. Tensile and flexural tests

Tensile and flexural tests were conducted according to ISO 527 and 178, respectively. A universal testing machine, Santam STM-150 (Tehran, Iran) was used to run the tests. All tests were carried out at room temperature and five specimens of each type were tested. Cross-head speed was set to 5 and 4.3 mm/min for tensile and flexural tests, respectively. An extensometer of 50 mm gage length was used to determine the strain in tensile tests.

2.5.2. Quasi-static compression test

The compressive properties of the specimens were experimentally measured as per the ISO 604 specifications. The compression test was carried out under a crosshead speed of 2 mm/min. The E_c was also determined from a theoretical approach developed by Mujika et al. [42]. With this theory, the E_c can be given through a combination of Eqs. 2-4, as follows:

$$\frac{E_f}{E_t} = \frac{4}{(1 + \sqrt{\lambda})^2} \quad (2)$$

$$E_c = \frac{1}{\lambda} E_t \quad (3)$$

$$\sigma_{\max(c)} = \sigma_{\max(f)} \cdot \frac{1 + \sqrt{\lambda}}{2\sqrt{\lambda}} \quad (4)$$

2.5. Microstructural observations

Following the mechanical testing, the fracture surfaces of the composites were examined using a HITACHI S-4160 field-emission scanning electron microscopy (FESEM) by using an accelerating voltage of 15 kV. All specimens were gold-coated in a vacuum chamber prior to inspection, to improve conductivity.

3. Results and discussions

3.1. Characterization results of the surface modified Na⁺-Mt

Fig. 2 shows the FT-IR spectra of the Na-Mt, 3-GPTS and Na-Mt/3-GPTS. The FT-IR spectrum of the Na-Mt indicates a broad peak at 3444 cm⁻¹ which is due to the stretching vibration of hydroxyl (-OH) groups, while the peak at 1649 cm⁻¹ represents the H-O-H bending vibration [43]. The incidence of 3636 cm⁻¹ band is attributed to the stretching vibration of the OH groups bonded to the Al atoms [44]. Absorption at 1058 cm⁻¹ is due to the stretching vibration of the Si-O-Si and Si-O [43]. Also, the absorption peaks at 526 cm⁻¹ and 471 cm⁻¹ are attributed to the bending vibration of the Si-O-Si and Si-O-Al groups [45]. The band appearing at 802 cm⁻¹ is due to the symmetric stretching of the Si-O-Si. The FT-IR spectrum of the Na-Mt/3-GPTS shows additional peaks introduced by the 3-GPTS, at 2926 cm⁻¹ and 2869 cm⁻¹ (related to the CH₃ asymmetric stretching and CH₂ stretching), as well as a weak peak at 1254 cm⁻¹ (corresponding to the epoxide ring vibration) which are absent in the FT-IR spectrum of the pristine Na-Mt, confirming the successful 3-GPTS grafting to the Na-Mt.

To understand how a chemical reaction between the 3-GPTS and nanoclay can take place, a schematic representation of possible reactions of silane compound in ethanol-water solution such as hydrolysis and condensation is shown in Fig. 3. In the following, the hydroxyl (OH) silane groups will react with the hydroxyl groups onto the Mt surface, forming a covalent link between them. Therefore, with the introduction of 3-GPTS/Mt into the epoxy matrix, the epoxide groups of 3-GPTS and epoxy matrix can react in the presence of amino hardener, as indicated in Fig. 4.

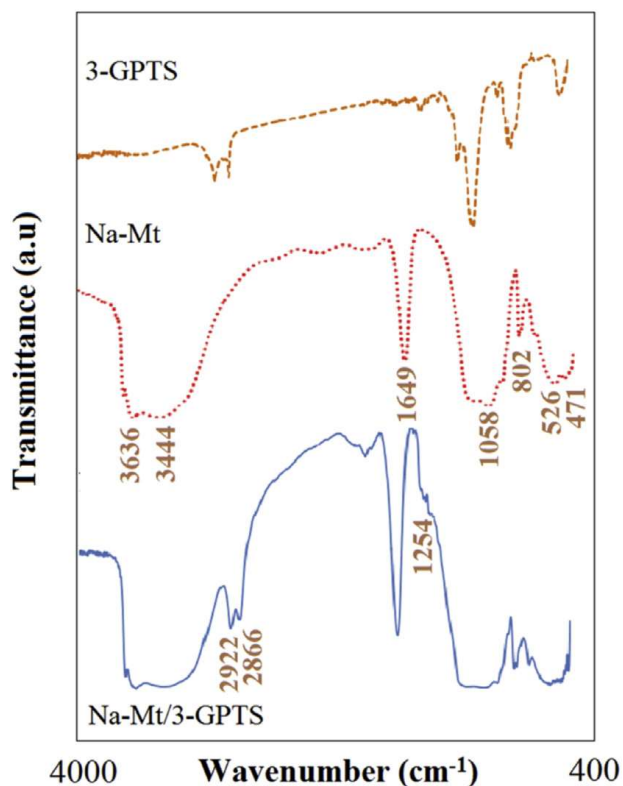


Fig. 2. FT-IR spectra of the Na-Mt, 3-GPTS and Na-Mt/3-GPTS.

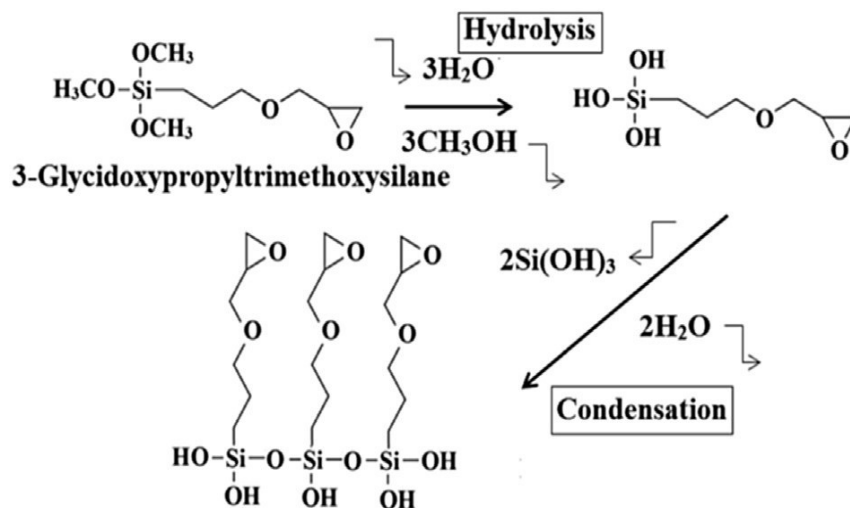


Fig. 3. The hydrolysis and condensation reactions of 3-GPTS in acidic ethanol-water solution.

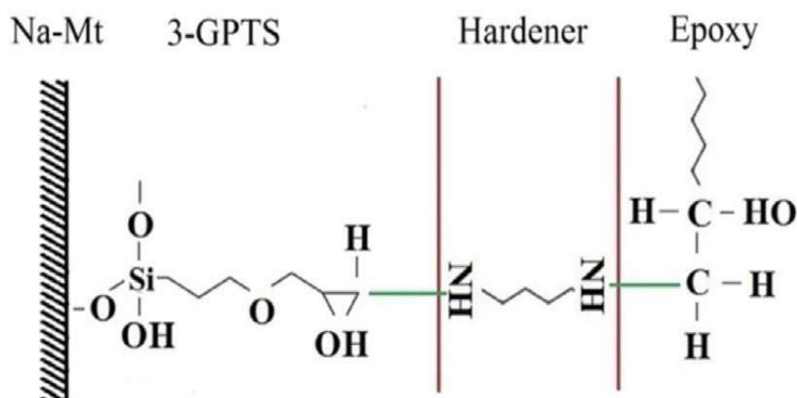


Fig. 4. The reaction between 3-GPTS/Mt and epoxy matrix in the presence of hardener.

STA thermal analysis was conducted on the Mt and 3-GPTS/Mt powders to verify that the surface modification of Mt has successfully occurred. The results are given in Fig. 5. With reference to the TGA graph (Fig. 5a) and employing Eq. 1, the value of PGS was obtained 8.1% (with respect to the total weight of modified Mt). Three stages of weight loss can be found in the thermal behavior of Mt nanoparticles. The weight lost in the range of 200-600 °C is due to the water removal from the interlayer zone. The peak at 652 °C which is observed on the DTA graph of Mt, corresponds to the dehydroxylation of the Mt. This peak is diminished in the case of 3-GPTS/Na-Mt, indicating the consumption of OH groups in the silylation reactions. For the 3-GPTS/Na-Mt, two new peaks are observed in the range of 200 to 600 °C due to the decomposition of 3-GPTS compound covalently bonded to the Mt [46]. Totally; the STA results verify the presence of 3-GPTS coupling agent on the Mt surface.

Fig. 6 depicts the XRD patterns of Na-Mt and modified Na-Mt. The XRD pattern of Na-Mt shows a diffraction maximum at $2\theta=5.83$, which corresponds to basal spacing d_{001} of 15.2 Å (calculated from Bragg's law of $n\lambda=2d\sin\theta$). On the contrary, the diffraction peak angle for 3-GPTS/Na-Mt is obtained at $2\theta=3.81$ Å, which corresponds to d-spacing value of 23.2 Å. This implies that the introduction of 3-GPTS on the surface of Na-Mt caused a shift of the

diffraction peak towards lower angle, manifesting larger interlayer d-spacing. An increase of 52% in d-spacing of Mt is observed through its surface modification by 3-GPTS.

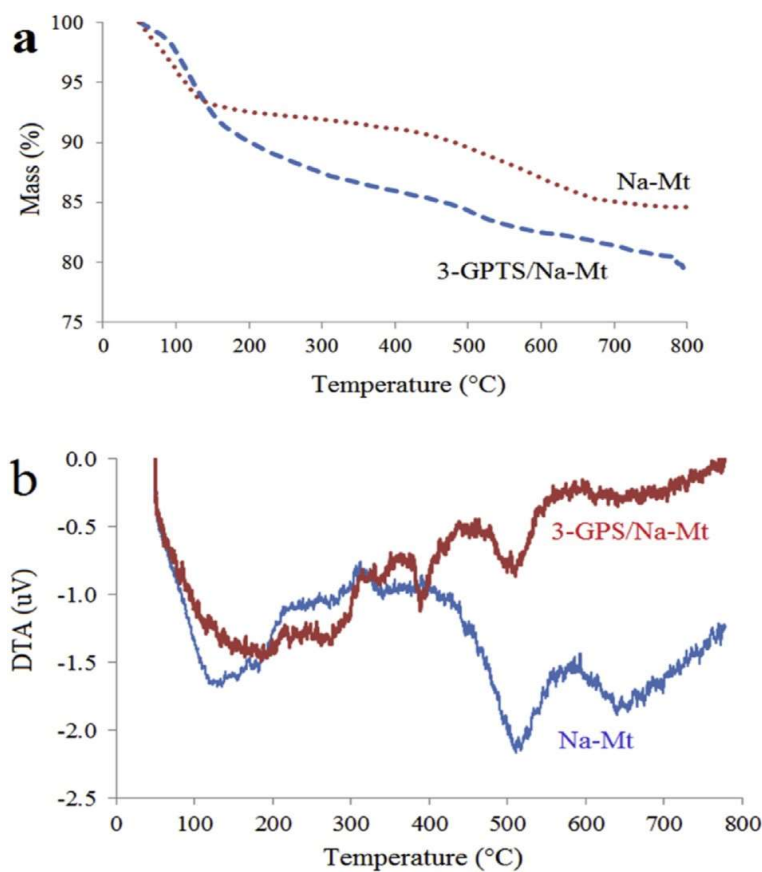


Fig. 5. a) TGA and b) DTA curves of Na-Mt and Na-Mt/3-GPTS.

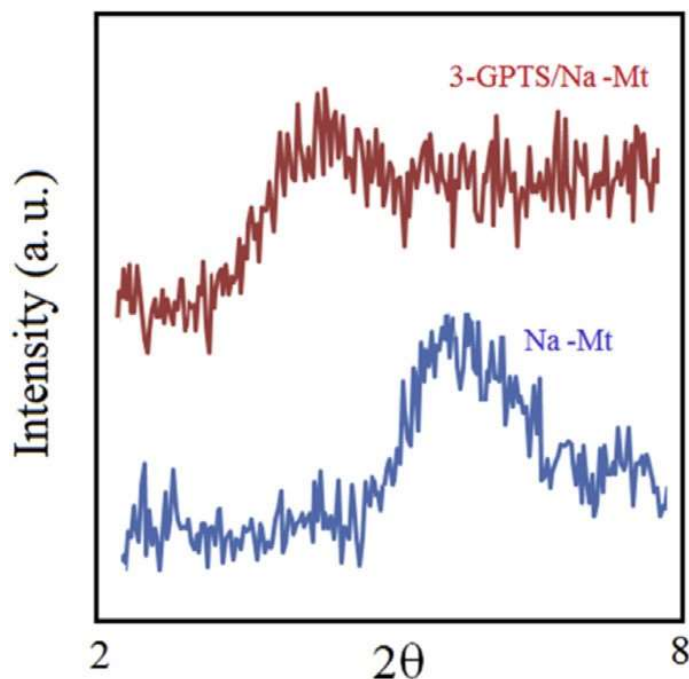


Fig. 6. XRD pattern of Na-Mt and Na-Mt/3-GPTS.

3.2. Mechanical properties of the composites

Fig. 7 represents the results of mechanical (tensile, flexural and compressive) moduli of nanoclay/UD-BF/epoxy composites at different nanoclay loadings. Based on the results, there is an increasing trend in the mechanical moduli with increasing nanoclay loading. The maximum mechanical moduli are related to the nanocomposite containing 5 wt.% of nanoclay minerals, when the tensile, flexural and compressive moduli are enhanced by 23%, 28%, and 34%, respectively, as compared to the neat composite without clay addition. These improvements can be explained by an enhancement of mechanical characteristics of the matrix as well as an improved interfacial strength between the BF and matrix modified by the 3-GTPS functionalized nanoclay. The surface modification of nanoclay particles with 3-GTPS can enhance their interfacial interactions with the epoxy matrix. This can lead to

restricting the mobility of polymer chains under loading, resulting in improved mechanical moduli. To confirm the dispersion quality of nanoclay in the epoxy, XRD analysis was conducted. Table 1 summarizes the values of interlayer d-spacing for various amounts of nanoclay particles in the matrix. It is observed that the d-spacing of nanoclay in the matrix is decreased by increasing the nanoclay loading, enhancing the interaction of nanoclay with the matrix.

The compressive modulus of nanoclay/UD-BF/epoxy composites having various nanoclay contents was estimated analytically using Eqs. 1 & 2. The results are also depicted in Fig. 7. Comparing the results shown in this figure verifies the existence of very good agreement between the values of compressive moduli obtained from the theoretical and experimental routes. There are 4.2%, 5.0%, 4.5%, and 3.2% difference between the theoretical and experimental values for the specimens containing 0, 1, 3, and 5 wt.% of nanoclay particles, respectively.

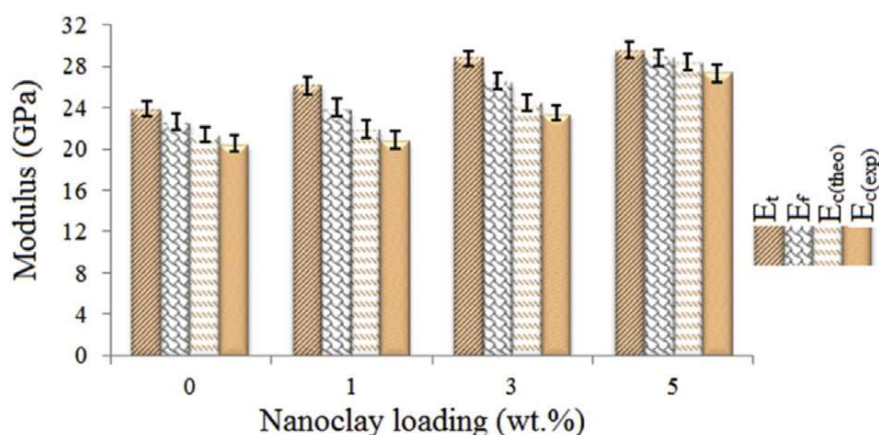


Fig. 7. Tensile, flexural and compressive moduli of nanoclay/UD-BF/epoxy composites at different nanoclay loadings.

Table 1- Interlayer d-spacing of modified Mt in the epoxy matrix

Nanoclay (wt.%)	d-spacing (Å)
1	62.2
3	44.5
5	35.2

The values of tensile and flexural strengths of nanoclay/UD-BF/epoxy composites for various weight percent additions of nanoclay particles are presented in Fig. 8. As shown in Fig. 8, the strength (tensile or flexural) of composites follows an enhancing trend by increasing the nanoclay loading. The neat UD-BF/epoxy composite shows a tensile strength of 745.2 MPa in comparison to which the value for 5 wt.% nanoclay loading (817.2) shows a 9.7% increase. Indeed, the value of flexural strength for 5 wt.% nanoclay-loaded specimen is 976.3 MPa, which indicates 35% increase when compared to the flexural strength of neat UD-BF/epoxy composite at 723.4 MPa. It seems that the observed improvements in the flexural and tensile strengths of nanoclay/UD-BF/epoxy composite as compared to the neat UD-BF/epoxy one are due to two reasons: First, when the matrix material is reinforced by the 3-GPTS modified clay nanoparticles, the frictional slippage of the fiber-matrix interface against applied load is restricted due to the presence of nanoclay particles. This implies that, in the case of nanocomposite matrix, the applied load can be effectively transferred from the matrix to the BF. The second reason is attributed to increasing the stress level required for fiber failure when the matrix is reinforced by nanoclay particles. In fibrous composites, fibers (especially fiber skin) and fiber-matrix interface are accounted as stress concentration regions. Introduction of 3-GPTS modified nanoclays to the matrix can effectively decline the stress concentration onto the fibers. This indicates the development of strong interfacial bonding between the epoxy and the nanoclay particles. When 3-GPTS/nanoclay is added into the epoxy resin, epoxide groups of 3-GPTS and epoxy matrix can react in the presence of

amine hardener, enhancing the interfacial interaction between them. The results also clearly indicate that the nanoclay incorporation into the epoxy matrix exerts more influence on flexural strength rather than on tensile strength. This can be explained by this fact that the tensile strength of a fibrous composite is a fiber-dominant property, while the flexural strength is a matrix-dominant property [47].

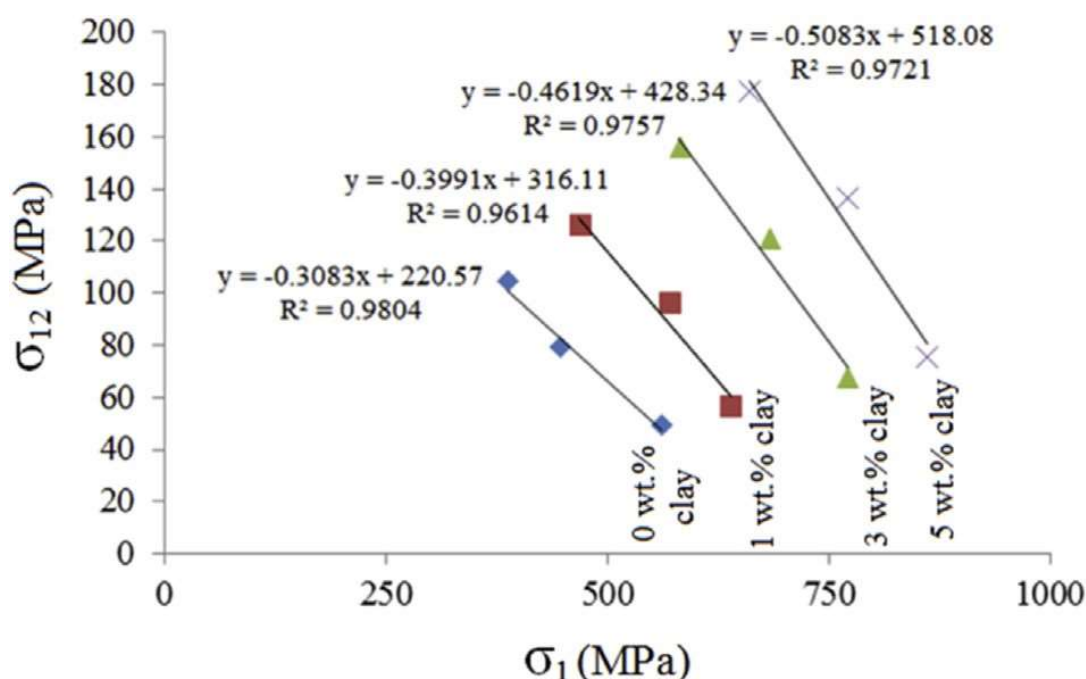


Fig. 8. Tensile and flexural strengths of nanoclay/UD-BF/epoxy composites at different nanoclay loadings.

In order to measuring the longitudinal compressive strengths of the specimens, their off-axis compressive strengths at the angles (θ) of 5°, 10° and 15° were obtained. The results are given in Fig. 9. As indicated in this graph, the compressive strength of nanoclay/UD-BF/epoxy composites increases by decreasing the off-axis angle or enhancing the weight percent of nanoclay particles in the matrix. In the next step, the longitudinal compressive strengths of the composites with different nanoclay loadings were measured. For this purpose,

the off-axis strengths (σ_x) were converted to the normal (σ_1) and shear (σ_{12}) stresses according to the following equations [41]:

$$\sigma_1 = \sigma_x \cos^2 \theta \quad (5)$$

$$\sigma_{12} = -\sigma_x \cos \theta \sin \theta \quad (6)$$

The correlation between σ_1 and σ_{12} is given in Fig. 10. The best estimation of the relationship between the σ_1 and σ_{12} for various nanoclay contents was drawn as straight lines. The value of σ_1 at $\sigma_{12}=0$ for each regression line is an indicative for the longitudinal compressive strength (σ_x) of the related composite. The obtained results are illustrated in Fig. 11.

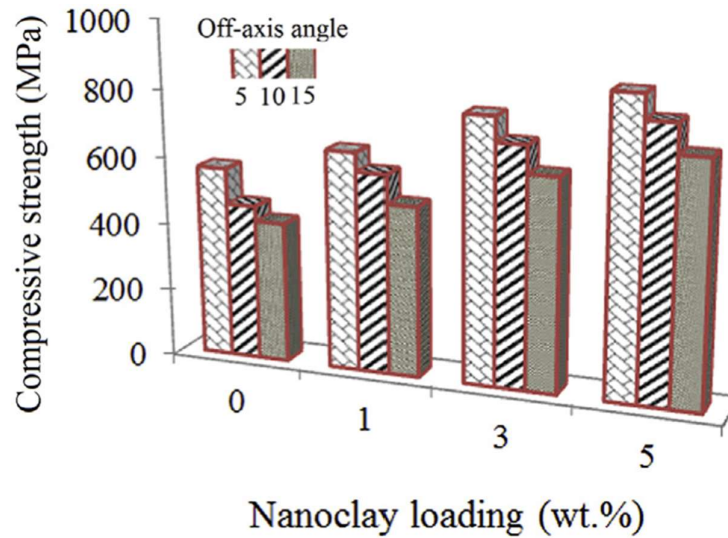


Fig. 9. Off-axis compressive strengths of nanoclay/UD-BF/epoxy composites at different nanoclay loadings.

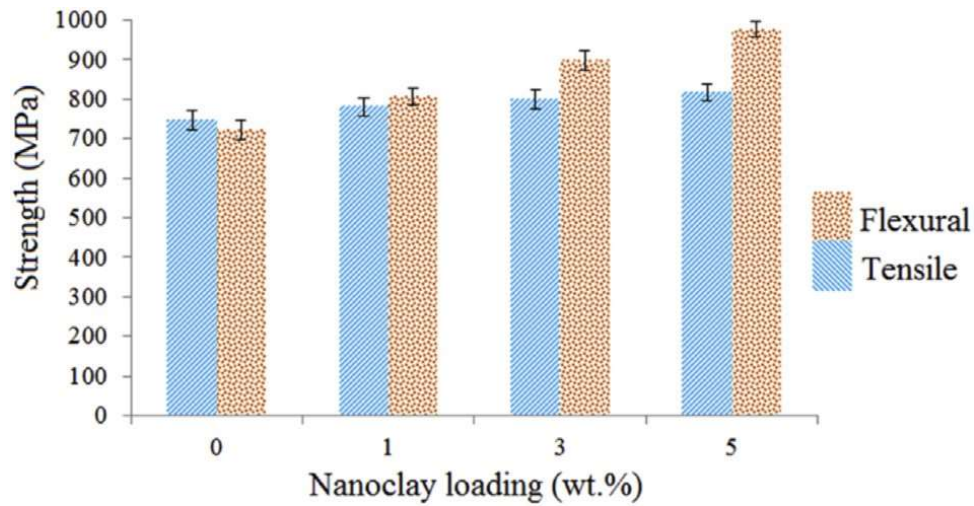


Fig. 10. The relationship between normal compressive and shear stresses for the nanoclay/UD-BF/epoxy composites at different nanoclay loadings.

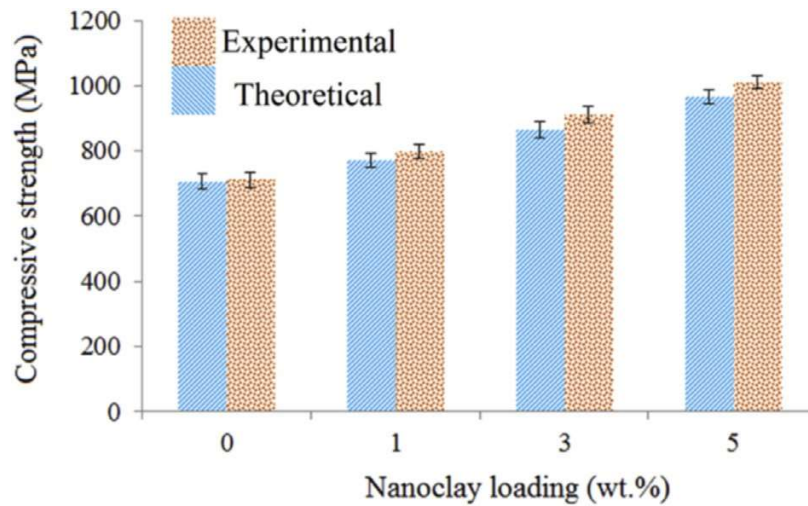


Fig. 11. Experimental and theoretical compressive strengths of nanoclay/UD-BF/epoxy composites at different nanoclay loadings.

The value of compressive strength for the 5 wt.% nanoclay-loaded composite is 1019 MPa, which shows an increase of 43 % when compared to the compressive strength of the neat composite (i. e. 715 MPa). Fiber micro-buckling and shear failure are identified as the dominant compressive failure mechanisms in UD-fibrous composites [48]. Initial model

proposed by Rosen [49] suggested that the compressive failure of a UD-fibrous composite is due to the fiber micro-buckling involving linear elastic matrix deformation. Based on this model, the compressive strength with a high fiber loading depends on the matrix shear modulus. This is due to this fact that enhanced matrix modulus increases the lateral support of the fibers, declining their tendency to micro-buckling. The results of experimental work shows, however, that there exists a large difference between the experimental data and those obtained from a Rosen model due to introducing ideal assumptions in this model. According to Cho et al. approach [50], the longitudinal compressive strength of a UD-fibrous composite is a function of in-plan shear properties of the matrix. Here, the substantial improvement in the longitudinal compressive strength of the BF/epoxy specimen with nanoclay addition is correlated to the increased in-plan shear properties of matrix provided by nanoparticle incorporation. The improvement can also explained by a decrease in the stress concentration onto the BF when the matrix is reinforced by 3-GPTS/nanoclays, producing an increase in the required stress for fiber micro-buckling. The results of theoretical approach (Mujika model) also confirmed the positive effect of nanoclay addition on the longitudinal compressive strength of BF/epoxy composites. Very good agreement between the theoretical predictions and experimental results was found, as indicated in Fig. 11.

3.3. Fracture surface observations

Fig. 12 shows SEM micrographs taken from the fracture surface of the BF/epoxy composite with and without nanoclay addition. Different microstructural features are observable on the fracture surfaces of these specimens. The micrograph for unfilled BF/epoxy composite (Fig. 12a) demonstrates BF with a clean and smooth surface, indicating fiber-matrix deboning [29]. Apparently, the matrix is detached from the BF due to the weak

interfacial adhesion. With reference to the Fig. 12b which is related to the fracture surface of the 5 wt.% nanoclay-reinforced BF/epoxy composite, it is observed that the BFs are covered by the matrix resin, indicative of increasing fiber-matrix interfacial bonding strength. For this specimen, matrix cracking is the primary fracture mechanism [29]. On the contrary, Fig. 13 illustrates the SEM images from the fracture surface of the matrix resin for the neat and clay-reinforced epoxy. For the SEM image of neat epoxy as shown in Fig. 13a, the cleavage surface is smooth and thin cracks are hardly observable. This is a typical characteristic of brittle failure. The SEM image from the fracture surface of the specimen with a nanocomposite matrix, however, shows irregular cleavage resulting from the presence of nanoclay with a 2-dimensional surface area in the matrix. This phenomenon is due to the crack deflection mechanism and can be explained as: when a crack is propagated in the matrix and encountered a nanoclay particle, crack deflection occurs, resulting in an increase in the stress intensity factor at the crack tip. For this reason, it can be concluded that the energy absorption capability of a clay/epoxy composite is higher than that of the neat epoxy.

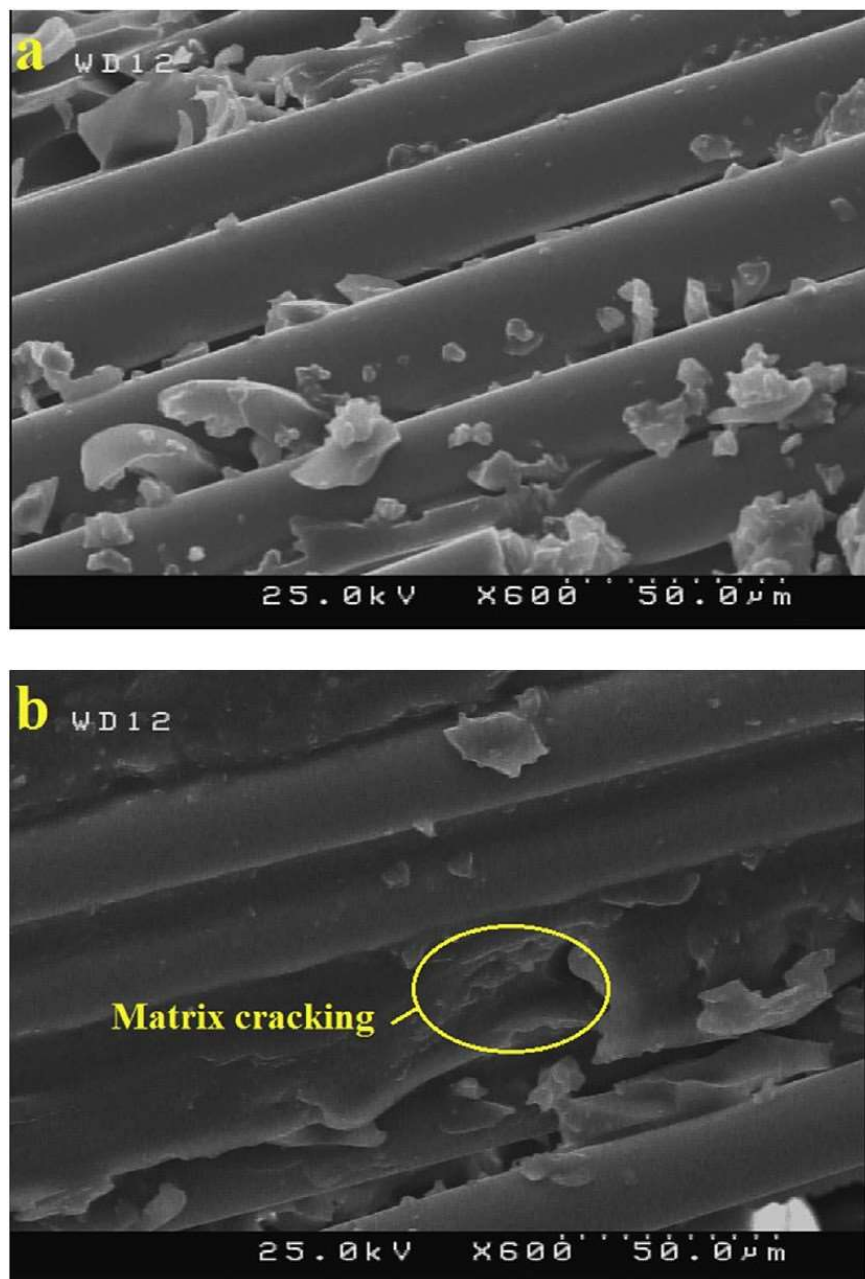


Fig. 12. Fracture surface of the BF/epoxy composite a) neat b) containing 5 wt.% nanoclay in the matrix.

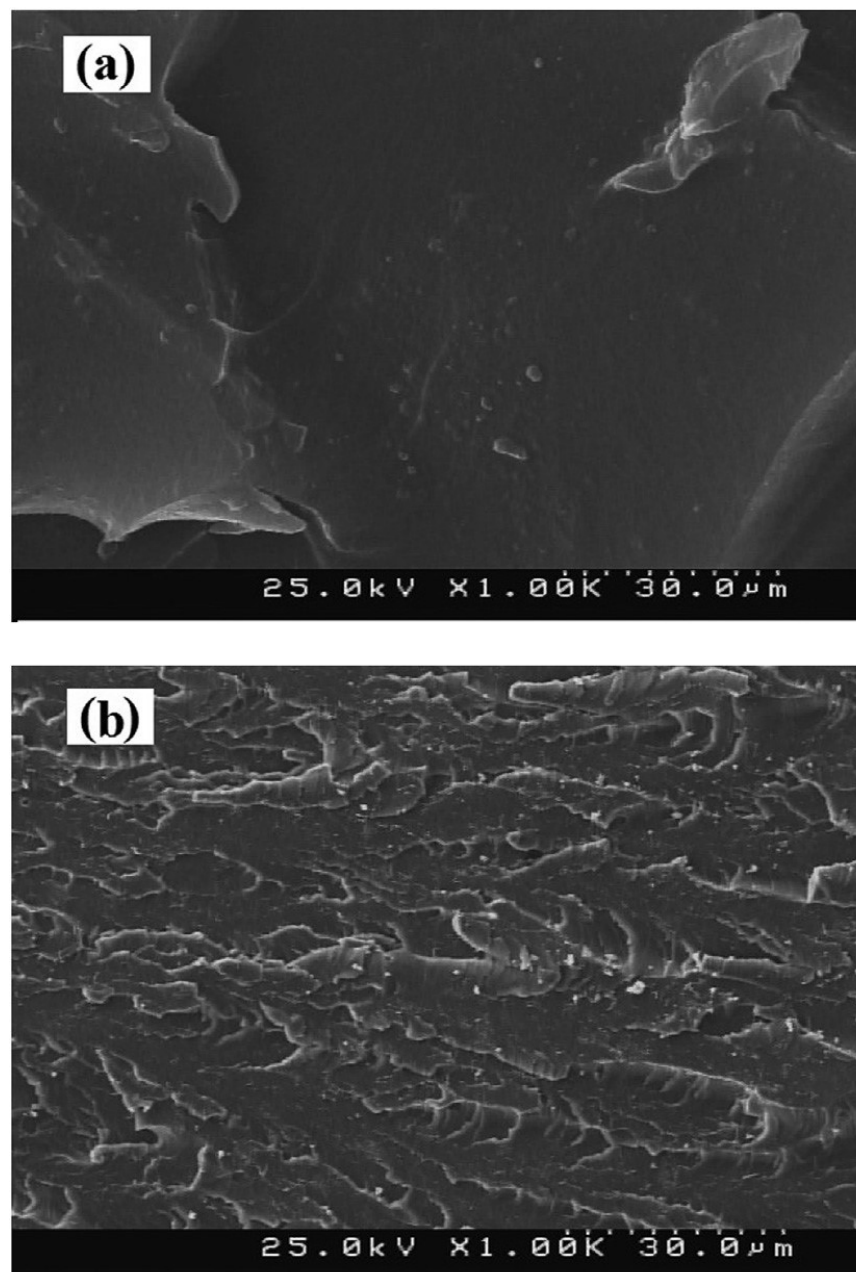


Fig.13. SEM micrograph of matrix fracture surface for a) neat epoxy and b) epoxy/5 wt.% nanoclay.

4. Conclusions

A comprehensive investigation (theoretical and experimental) into the effects of adding various amounts of 3-GPTS modified Na-Mt nanoclay (0, 1, 3 & 5 wt.% with respect to the

matrix) on mechanical (tensile, flexural and quasi-compression) behavior of multistate clay/UD-BF/epoxy composites was conducted. The conclusions drawn from the results can be summarized as follows:

- 1) Na-Mt nanoclays were successfully surface-modified using 3-GPTS. The FT-IR, XRD and STA analyses confirmed the presence of 3-GPTS in the structure of Na-Mt nanoparticles after the modification stage.
- 2) The flexural and tensile properties (modulus and strength) of the BF/epoxy composite were enhanced through the addition of 3-GPTS nanoclay. The maximum improvements were corroborated to the specimens containing 5 wt.% nanoclay, with 11%, 28%, 23% and 28% increase for tensile strength, flexural strength, tensile modulus and flexural modulus, respectively.
- 3) The longitudinal compressive strengths of the specimens were obtained using the off-axis strengths. An increase of 43% in the compressive strength of the UD-BF/epoxy composite was observed by the addition of 5 wt.% nanoclay in the matrix. In this case, the compressive modulus was increased up to 34%.
- 4) The compressive modulus and strength of the specimens were also obtained theoretically using a Euler-Bernoulli beam-based approach. Very good agreement between the theoretical and experimental results was observed.
- 5) The FESEM observations of the fracture surfaces of the specimens clearly indicated that the enhancements in the mechanical properties of the multiscale composites as compared to the neat ones were due to the improvement in the interfacial adhesion between the BF and clay-epoxy matrix.
- 6) Matrix reinforcing with surface-modified Mt nanoclay was found to significantly enhance the mechanical responses of basalt reinforced epoxy composites.

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