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ORIGINAL ARTICLE

Water Sorption-Desorption-Resorption Effects on Mechanical Properties of Epoxy-Nanoclay Nanocomposites

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ABSTRACT – The present work aims to study the effect of water sorption–desorption–resorption conditions on the mechanical properties of epoxy-nanoclay nanocomposites (ENNCs). To prepare ENNCs specimens, nanoclay and epoxy are mixed together by a stirrer and a sonicator. The nanoclay-epoxy and hardener mixture are moulded into specimens that meet the dimensions prescribed by the ASTM standards. The specimens fabricated are subjected to three conditions viz., water sorption, desorption and resorption for a total of 140 days. Water sorption–desorption–resorption effects on the mechanical properties of pure epoxy and ENNCs are studied by tensile and flexural tests. Results showed that the nanoclay presence improved the mechanical properties and lowered the percentage of water uptake. Tensile and flexural strengths of epoxy and ENNCs are reduced under sorption conditions and recovered to more than 90% of their original strengths under desorption conditions. The lowest tensile and flexural strengths were displayed by specimens subjected to resorption in comparison to specimens subjected to the other two conditions. The flexural and tensile strengths of epoxy are more severely affected compared to ENNCs under water sorption–desorption–resorption conditions. Scanning electron microscopy images are employed to learn the causes of specimen failure under a tensile load.

INTRODUCTION

Epoxy resins are the most extensively used material in the marine, construction, electronics, aerospace, and automotive industries as adhesives, coatings, and composite matrix constituents owing to their outstanding mechanical, thermal, and corrosion resistance properties[1], [2]. In contrast, higher cross-linking density causes the epoxy resin to be brittle leading to lower impact strength, resistance to crack propagation, and fracture toughness. During the curing of epoxies, cross-linking occurs between the epoxy monomer and the reactive groups of the curing agent. The level of cross-linking determines the properties of the epoxy.

Epoxy resins are utilized in a variety of applications, where they are exposed to wet service conditions. Owing to their susceptibility to hydrolysis, swelling, crazing, plasticization, oxidation, and a decrease in the effective average cross-linked molecular weight, epoxies suffer irreversible harm when exposed to water for long periods [3]. As a result, the absorbed water molecules have a negative impact on the epoxy's physical properties which in turn would have a significant impact on their performance. Water absorption by the polymer causes permanent damage viz., microcavities, that further reduces the strength of the polymer. Numerous research efforts have been rendered to improve the properties of epoxy by incorporating various types of nanomaterials[4]–[7]. The development of nanoparticle reinforced composites is the most explored material in engineering fields. Researchers are discovering the use of various nanoparticles to reinforce epoxy that can improve its strength and stiffness.

In polymer nanocomposites, nanoclay is one of the most widely used and studied nanoparticles. Owing to its ease of usage, eco-friendly, and comprehensive chemistry, nanoclay has risen to prominence among nanoparticles. Nanoclay has a higher modulus, is inexpensive, has a lower density, and has a larger surface area. To be compatible with organic polymers, the nanoclay surface must be changed to organophilic prior to its use. Organic nanoclay modifiers such as ammonium or phosphonium ion are widely utilised. Ammonium salts are used to change commercially available nanoclays which are referred to as "organically modified nanoclays or organoclays". Nanoclay-reinforced polymer nanocomposites with the aforementioned properties have dramatically improved mechanical and wear characteristics[8]. Also, the addition of nanoclay to the polymer reduces the water uptake and the effect of water aging on the mechanical properties of the polymer[9], [10].

The present study investigates the effect of water sorption–desorption–resorption on the mechanical properties of the "epoxy-nanoclay nanocomposite" (ENNC). Also, the present study addresses the effect of varying weight percentages of nanoclay on water uptake, tensile and flexural strength of epoxy subjected to water aging. Also, fracture surfaces under tensile load are studied to learn the reasons for the failure of specimens. The effects of water sorption-desorption-resorption conditions on mechanical properties are not well documented in the literature on epoxy nanocomposites with varying weight percentages of nanoclay. This appears to be crucial in broadening the spectrum of applications for these

nanocomposites, particularly in the automotive, maritime, construction, and domestic sectors. The purpose of this research is to determine if the inclusion of nanoclay would contribute to the reduction of water degradation impact generated by water sorption and desorption of water-soaked specimens that would allow the properties of nanocomposites to be recovered. Also, the work aims to determine the effect of resorption on the desorption conditioned specimens.

METHODOLOGY

Materials

The present work uses L-12 epoxy resin and K-6 hardener with a mixing ratio of 10:1 (supplied by Atul Polymers). Lapox L-12 is an unmodified liquid epoxy resin of medium viscosity (9000-12000 mPa.s). K-6 hardener is a low viscosity room temperature curing liquid hardener. Lapox L-12 and Hardener K-6 can be mixed easily at room temperature, and the mixture gives a short pot life and rapid curing at ambient temperature.

Further, surface modified nanoclay consisting of 25–30 wt.% trimethyl stearyl ammonium obtained from Sigma Aldrich is used as the reinforcement. Nanoclay has a sheet-like structure (Figure 1) and a density of 0.2 to 0.5 g/cm^3. Each nanoclay sheet is only a few nanometers thick and has lateral dimensions of 200–600 nanometers. Nanoclay has a higher modulus than matrix materials in addition to exhibiting chemical resistance and flame retardant properties. Further, nanoclay has the potential to be used as a reinforcement for polymer resins due to its sheet shape and high aspect ratio.
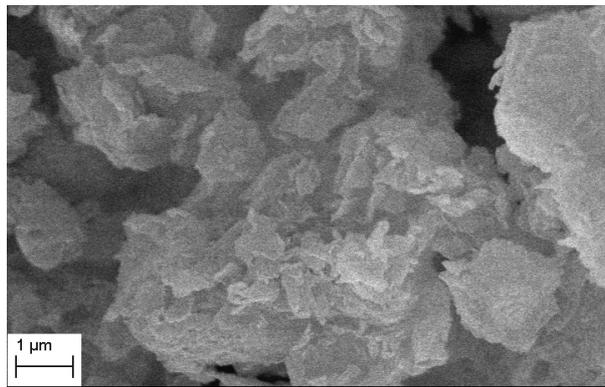

Figure 1. SEM image of nanoclay powder at 20.00K× magnification.

Specimen Preparation

Three sets of specimens were prepared by varying the nanoclay weight percentages viz., 0 (pure epoxy), 2, and 4 wt.%. Mechanical stirring for a period of 120 minutes is employed to mix nanoclay with epoxy. Sonication is employed for a period of 30 minutes post mechanical stirring in order to achieve effective mixing of nanoclay with epoxy. The nanoclay and epoxy mixture is kept in a vacuum chamber for 30 minutes to remove air bubbles. Furthermore, the K-6 hardener is exhaustively blended with the epoxy-nanoclay mixture with a spatula and poured into the moulds. Moulds for the preparation of nanocomposites are manufactured according to the prescribed dimensions of the ASTM standards D638 and D790.

Water Sorption-Desorption-Resorption Conditions

The prepared specimens are subjected to three conditions viz., water sorption–desorption–resorption for a total of 140 days. Water sorption–desorption–resorption experiments are performed as per ASTM D570-98 standard. Initially, a total of 15 dry/unaged specimens are placed in the container filled with water at room temperature (around 25 ℃) for 70 days. At the end of this period, five specimens were removed and subjected to tensile and flexural tests, and the remaining 10 specimens were dried in an oven at 50 ℃ for 35 days. At the end of this period, five out of 10 specimens were removed from the oven and subjected to mechanical testing. The remaining five specimens were further immersed in water at room temperature for a period of 35 days (resorption). Thus, at the end of 140 days, the last set of specimens were removed from the immersion container and subjected to mechanical testing.

The specimens were weighed weekly during the water sorption–desorption–resorption tests using a digital weighing apparatus (least count – 1 mg) to find the difference in weight and water uptake percentage. The water uptake percentage is calculated by using the following equation:

$$\text{Water uptake (\%)} = \frac{(Ws - Wd) \; x \; 100}{Wd} \tag{1}$$

where Ws is weight after sorption and Wd is weight of dry specimen.

Testing

Tensile tests are executed according to ASTM D638 on a universal testing machine. Throughout the test, the crosshead motion is maintained at a consistent speed of 5.0 mm/min. Five dumbbell-shaped specimens of each set and condition are subjected to testing. The ASTM D790 standard was used to conduct the three-point flexural tests. Each set and conditions require at least five specimens with dimensions of $140 \times 15 \times 3$ mm³. The flexural strength of epoxy-nanoclay nanocomposites is determined using a Zwick-Roell Z020, Loadcell 20 kN machine. A span length of 48 mm and a test speed of 1.28 mm/min are maintained during flexural strength testing.

Scanning Electron Microscope Analysis

Images of the morphology at the fractured surface of specimens subjected to tensile test are captured with the help of a scanning electron microscope (SEM) (ZEISS, Model: EVO18). Specimens are diced to the necessary dimensions in order to equip them in the specimen holder of the microscope. The specimen surface should be electrically conductive to produce effective imaging. To minimize electrostatic charge accumulation on the specimen surface, they must be electrically grounded in the course of electron irradiation. As a result, a very-thin conductive material, for example, silver, is deposited on the surface of the specimen using a low vacuum sputtering system. SEM images were utilized to investigate the reasons for the specimen failure under tensile loading. Images obtained from SEM images were also examined closely to further understand the water sorption, desorption, and resorption effects on nanocomposites.

RESULTS AND DISCUSSIONS

Water Sorption-Desorption-Resorption Characteristics

Figure 2 displays the water sorption–desorption–resorption curves of pure epoxy and ENNCs. In this figure, different stages are mentioned as sorption (70 days), desorption (35 days), and resorption (35 days). As the weight percentage of nanoclay increases, the total water sorption of ENNCs decreases. The usual water sorption behaviour of polymers is observed in all ENCCs. Water sorption could be caused due to the tendency of water molecules to penetrate the epoxy system. Owing to the inherent nature and natural tendency of the epoxy polymer to absorb water molecules, the presence of the same in epoxy is observed. Epoxy water molecules are associated with hydrophilic functional groups (amine or hydroxyl). The presence of nanoclay in the epoxy network cuts the mean free pathway of molecules of water (creating a "tortuous pathway" as shown in Figure 3) to traverse in the epoxy, leading to lesser water sorption[9], [11].
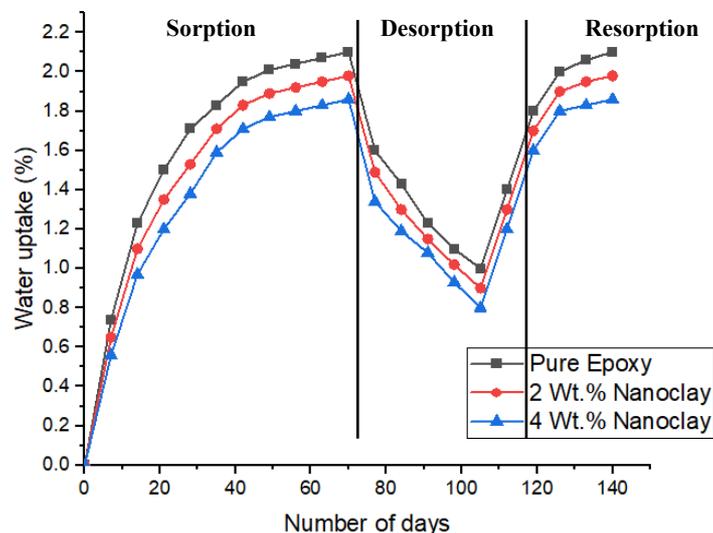

Figure 2. Water sorption–desorption–resorption curves.

Under the sorption stage, molecules of water strew through the epoxy network which plasticizes and swells the epoxy molecular network, diminishes the surface free energy, and enhances the free volume of the epoxy. Both desorption and resorption are quicker compared to sorption, as can be observed in Figure 2. Desorption is carried out at a higher temperature (50°C), partially reversing sorption effects. After desorption, the epoxy demonstrates a structural network with "frozen in" segmental configurations. The actuality that resorption occurs quicker than sorption indicates that material properties change following a sequence of sorption and desorption because the structural network of epoxy has previously been altered following a sequence of sorption and desorption. The resorption stage is distinct from the sorption stage. A sorption–desorption sequence can efficiently enhance the resin's preexistent free volume, resulting in a different and faster sorption process than the original[12], [13].
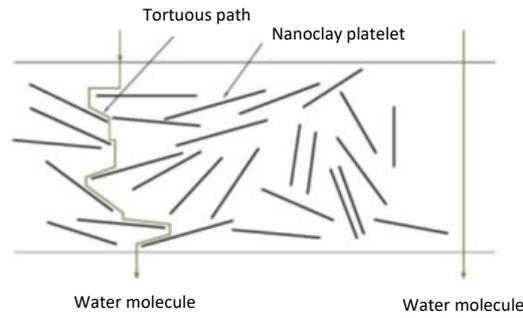
Figure 3. Movement of water molecules.

Effect of Water Sorption-Desorption-Resorption on Mechanical Properties

Tensile stress vs. strain curves

The conventional stress vs. strain curve under tensile load is depicted in Figure 4. All specimens fail immediately when the tensile stress approaches the absolute limit. However, the stress vs. strain curves displays significant non-linearity before reaching maximum stress. In comparison to pure epoxy in Figure 4 (a), the addition of nanoclay improves the stress value of ENNCs (as in Figures 4 (b) and (c)) before failure and decreases the strain to fail under tensile load. The strain value is lowered by the addition of nanoclay due to the enhanced stiffness of the ENNCs.

Under sorption conditions, stress vs. strain curves of pure epoxy, in Figure 4 (a), and ENNCs in Figure 4(b) and 4(c), indicate a decrease in initial slope, ultimate tensile stress, and increase in failure strain compared to dry condition specimens. In terms of tensile stress, ENNCs are less affected than pure epoxy due to the outstanding barrier properties of nanoclay.
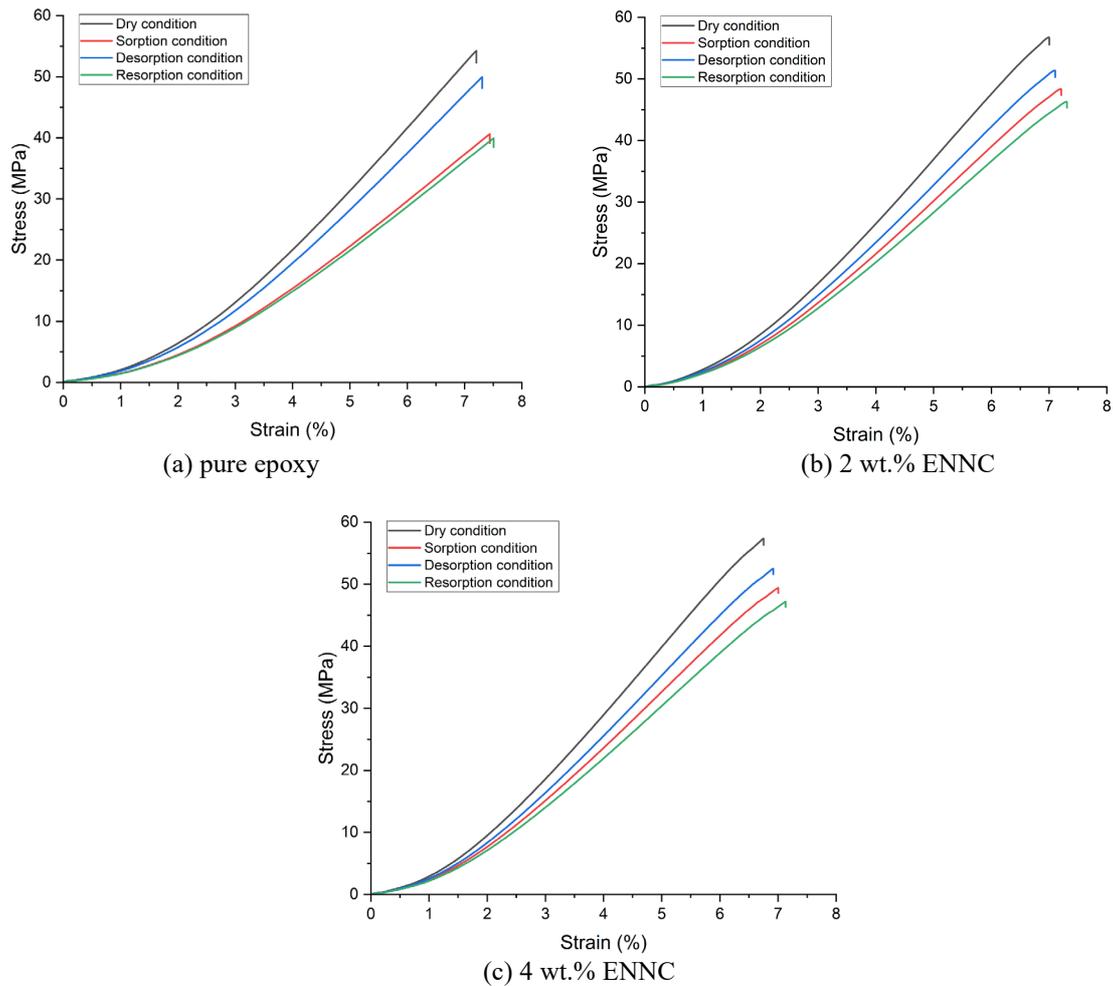

(a) pure epoxy

(b) 2 wt.% ENNC

(c) 4 wt.% ENNC

Figure 4. Tensile stress vs. strain curves.

Stress vs. strain curves of desorption conditioned pure epoxy (in Figure 4 (a)) and ENNCs (Figures 4 (b) and (c)) show a recovered maximum tensile stress compared to the sorption condition. The tensile stress of pure epoxy and ENNCs

are restored to more than 90% of its original value (dry condition specimens). Moreover, water resorption further reduced tensile stress and increased the tensile strain because reabsorbed water elevates the epoxy system's ductility.

Tensile Strength

Tensile strength of pure epoxy is improved by nanoclay addition, improving to 57.4 MPa and 56.7 MPa at 4 and 2 wt.% of nanoclay, respectively, from 54.2 MPa under dry/unaged condition, as shown in Figure 5. The inclusion of surface-modified nanoclay with trimethyl stearyl ammonium improves the cross-linking density of epoxy. Furthermore, during mixing and sonication, a certain number of styrene molecules may have been absorbed by nanoclay platelets, resulting in a change in cross-link density. In addition to the mixing processes and the size of the organic modifier, the compatibility between the organic modifier and the monomer influences the improvement in nanocomposite properties (higher toughness and tensile strength of the epoxy) [14], [15]. In ENNCs, nanoclay appears as an active stress transfer component causing epoxy to deform plastically, which eventually causes an enhancement in the tensile strength. The nanoclay inclusion stopped the crack dispersion owing to the massive amount of plastic deformation caused [16].
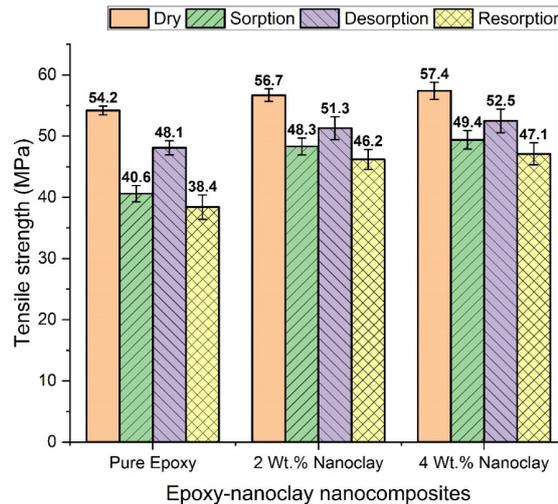

Figure 5. Effect of water sorption–desorption–resorption on tensile strength of ENNCs.

The tensile strength of epoxy and ENNCs is diminished by 25 and 14%, respectively, under sorption conditions because of its "hydrophilic nature" [17]. The presence of water in the epoxy network increases free volume due to the separation of hydrogen bonds among polymer chains, which raises the chain mobility and lessens the segmental motion when the load is applied to the nanocomposite. The observed lower tensile strength for water-absorbed specimens can be due to these physical changes. The effect of sorption is more severe in pure epoxy than in the ENNCs. It is also observed from Figure 1 that the addition of nanoclay in ENNCs has lessened the influence of sorption condition on tensile strength because of the exceptional barrier property of nanoclay. Nanoclay establishes the "tortuous pathway" (as in Figure 3) for water molecules to infiltrate in ENNCs, which delays the sorption condition's overall effect. In addition, the nanoclay's higher aspect ratio offers resistance to polymer chain agility in water-absorbing polymers, resulting in a lower tensile strength reduction as compared to pure epoxy [18].

As illustrated in Figure 5, desorption conditioned specimens show higher tensile strength than the sorption conditioned specimens. However, the tensile strength of desorption conditioned specimens is still lower compared to dry/unaged specimens. For desorption conditioned specimens, as the maximum of the water is taken out of the epoxy network and the plasticization effect is nominal, the tensile strength of sorption conditioned specimens is recuperated partially[17]. The tensile strength of pure epoxy and ENNCs is recovered to more than 90% of their original tensile strength. This tensile strength recovery can be endorsed to the reversible effects of the absorbed water, such as plasticization, while the unrecovered part of the tensile strength can be due to the irreversible damages imposed by water [19].

Moreover, water resorption caused a further reduction in tensile strength by 29 and 18% compared to dry specimens indicating the continued degrading effect of water in the re-wetting process. Resorption conditioned specimens displayed the lowest tensile strength in comparison to the specimens of all the other conditions. This result indicates that in a pre-plasticized epoxy network, moisture sorption and desorption lead to enhancement of the resin's preexisting free volume, resulting in increased plasticization [20].

SEM Analysis

Figure 6 to Figure 9 illustrate the morphology of fractured surfaces for pure epoxy and ENNC under dry and water sorption–desorption–resorption conditions. The fracture surfaces of pure epoxy and ENNC show significant variations. A completely smooth surface was observed with the dry/unaged epoxy is shown in Figure 6(a), thus signifying rapid crack propagation and low fracture toughness [21]. The fractured surface of ENNC appears to be rougher as in Figure 6 (b). The rough fractured surface of ENNC is most probably produced by the presence of nanoclay platelets onward of crack paths, stimulating several microcracks. A larger fracture surface and improved fracture toughness are a result of a circuitous route for crack propagation. The nanoclay platelets act as a barricade for the propagation of cracks [22].

Due to absorbed moisture, a complex linkage of micro-cracks on the surface of the fracture is found in sorption conditioned pure epoxy specimens (in Figure 7(a)), enhancing craze inception and dissemination in the epoxy, which endorses the plasticization effect of moisture [17], [21]. Since the crack propagates at such a fast rate that the crazes initiated near the crack front do not have adequate time to expand, stress is intense enough to trigger secondary local cracks at some stages of crack development, causing the rougher area next to the crack front to develop. Compared to the dry/unaged specimen, the sorption conditioned ENNC specimen (Figure 7(b)) reveals the presence of shear leaps and a less rough surface at the surface of fracture, indicating lower fracture toughness. Compared to ENNC, the sorption condition had a significant impact on the pure epoxy resin, as seen by SEM images. This could explain why epoxy exhibits a higher percentage reduction in tensile strength than ENNC. The addition of nanoclay to epoxy will improve the cross-linking density and make it difficult for water molecules to migrate[8]. In comparison to pure epoxy, nanoclay addition slows the effect of sorption conditions, resulting in a lower percentage reduction in tensile strength.
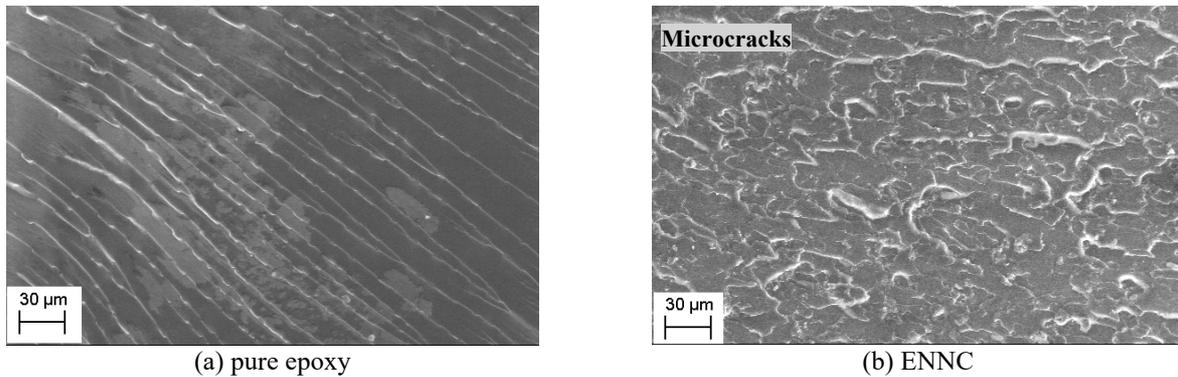

(a) pure epoxy   (b) ENNC

Figure 6. SEM images (750× magnification) at fracture surface of Dry/unaged specimens.

(a) pure epoxy   (b) ENNC
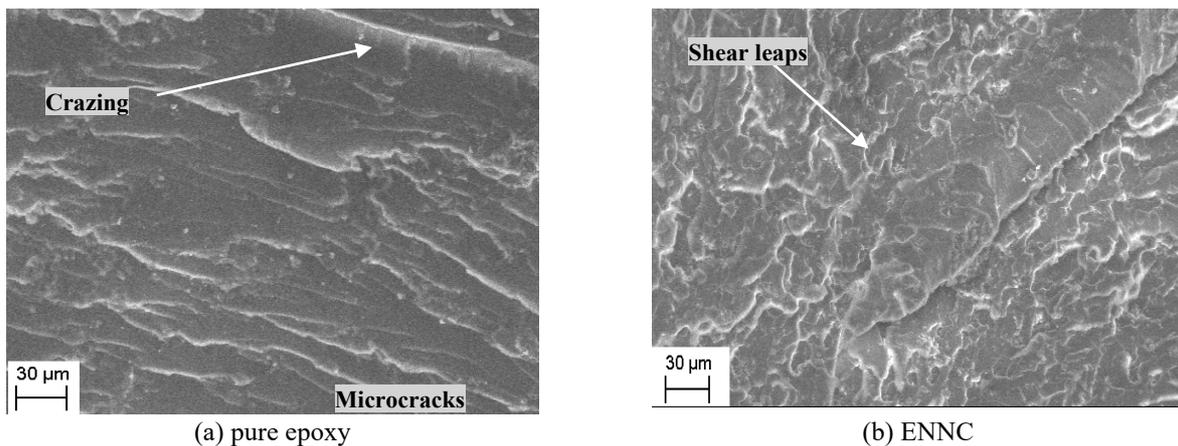
Figure 7. SEM images (750× magnification) at fracture surface of sorption conditioned specimens.

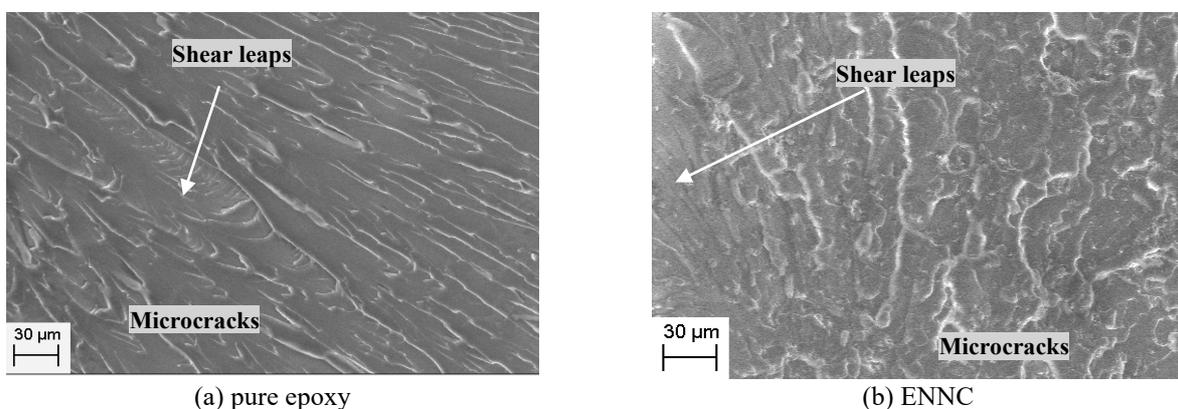(a) pure epoxy   (b) ENNC

Figure 8. SEM images (750× magnification) at fracture surface of desorption conditioned specimens.

For desorption conditioned pure epoxy and ENNC specimens in Figure 8, a network of microcrack and shear leaps on the fracture surface is found. The desorption process does not allow removing all water and reverses the effect of sorption. The development of these microcracks is due to the lower fracture toughness of desorption conditioned specimens compared to unaged specimens. This could be the reason for the incomplete recovery of tensile strength in these specimens in comparison to dry/unaged specimens.

Resorption conditioned pure epoxy, and ENNC specimens in Figure 9 display the bumpy fractured surface with additional shear leaps and microcracks. Resorption condition results in craze initiation and formation of water clusters in the epoxy, creating high plasticization zones, a reshuffle of molecular chain, and a change in cross-linking density. This is the reason for the display of the lowest tensile strength by resorption conditioned epoxy and ENNC specimens.
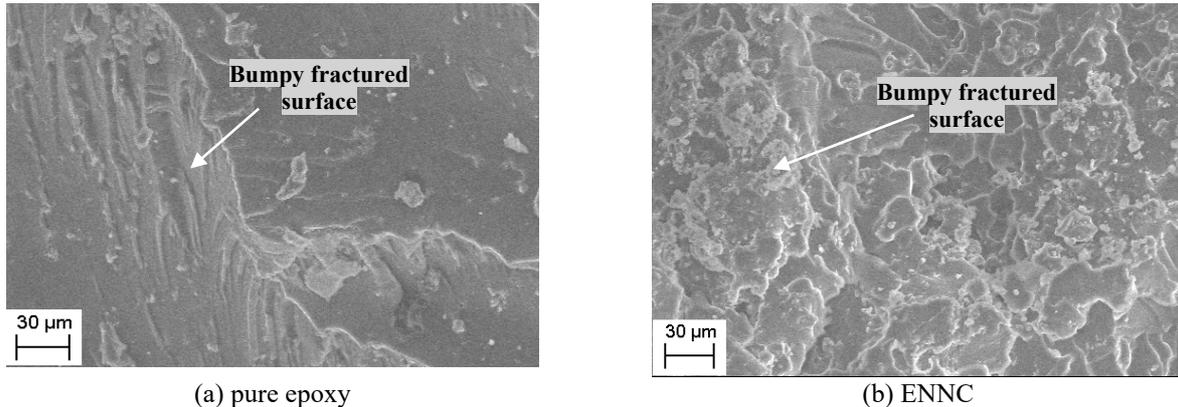

(a) pure epoxy   (b) ENNC

Figure 9. SEM images (750× magnification) at fracture surface of resorption conditioned specimens.

Flexural Strength

As shown in Figure 10, improvement in flexural strength of epoxy due to the addition of nanoclay by 4 and 9% at respective nanoclay weight percentages of 4 and 2 wt.% was observed in dry/unaged specimens. The enhanced interfacial bonding between nanoclay and epoxy is responsible for increased flexural strength. Nanoclay strengthens and stiffens the surrounding matrix [23]. The morphology of nanoclay layers or stacks, as shown in Figure 3, is particularly important in enhancing tensile strength while decreasing flexural strength at 4 wt.% nanoclay. In comparison to tensile properties, flexural properties are much greater matrix dependent. Assume the nanoclay layer is situated along the dumbbell axis; by slipping layers in between each other, the tensile strength can be increased. Flexural strength is reduced due to additional clay layers (at 4 wt. %) that are more parallel and situated perpendicular to the force inserted.
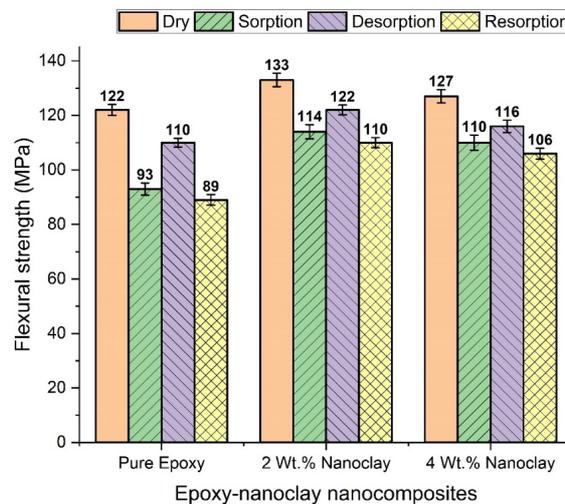

Figure 10. Effect of water sorption–desorption–resorption on flexural strength.

The flexural strength of pure epoxy and ENNC is decreased by 23 and 14%, respectively, under sorption conditions. A small amount of water might have a significant impact on the flexural strength of a composite because water molecules migrate from one group to another [24]. The flexural strength of epoxy and ENNC is partially recovered under desorption conditions. The percentage of reduction in flexural strength of epoxy and ENNC is declined to 10 and 8%, respectively. Resorption conditioned specimens displayed the lowest flexural strength of all the other conditions. The flexural strength of pure epoxy and ENNC is decreased by 27 and 18%, respectively, under resorption conditions.

The amount of flexural strength reduction of pure epoxy is more compared to ENNCs under water sorption–desorption–resorption conditions. The high aspect ratio of nanoclay prevents the passage of water molecules in epoxy by acting as a sheet-shaped barrier. Since the absorption of water molecules reduces the elastic properties of hydrophilic polymers, nanoclay is particularly important for reducing the negative influence of water [25].

CONCLUSION

In this work, a thorough investigation is conducted into the effects of water sorption–desorption–resorption conditions on the mechanical properties of epoxy-nanoclay nanocomposites. The effects of the water sorption–desorption–resorption

conditions on the mechanical properties of pure epoxy and ENNCs are studied by tensile and flexural tests followed by SEM analysis. It can be concluded that:

i. An increase in the weight percentage of nanoclay in epoxy resin led to a decrease in the total water sorption of ENNCs by 6 to 11%.

ii. Nanoclay addition enhanced the tensile (around 6%) and flexural strengths (around 9%) of epoxy and reduced the overall effect of absorbed water.

iii. The tensile strength of epoxy and ENNCs is diminished by 25 and 14%, and the flexural strength of pure epoxy and ENNC is decreased by 23 and 14% respectively, under sorption conditions.

iv. The tensile and flexural strengths of ENNCs are recovered to more than 90% of their original strengths under desorption conditions.

v. Resorption conditioned specimens displayed the least tensile and flexural strengths in comparison to specimens of all the other conditions.

vi. SEM analysis of the fracture surface revealed the reasons for specimen failure under tensile load.

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