

Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites

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Abstract

This study aimed to investigate the effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites as well as to study the influence of different types of nano-filler such as nano-clay platelets, halloysite nanotubes (HNTs) and nano-silicon carbide (n-SiC) particles on the water absorption behaviour of epoxy based nanocomposites. Results indicated that the addition of nano-fillers into epoxy matrix was found to decrease both water uptake and diffusivity compared to unfilled epoxy. Flexural strength and modulus of epoxy based nanocomposites were found to decrease due to the water absorption. However, the addition of nano-fillers enhanced the flexural strength and modulus of nanocomposites compared to wet unfilled epoxy. Surprisingly, fracture toughness and impact strength of all types of nanocomposites were found to increase after exposing to water. The presence of nano-fillers increased both fracture toughness and impact strength of nanocomposites compared to wet neat epoxy.

Keywords: Nano-clay platelet; Halloysite nanotube; nano-SiC; Epoxy resin; Water absorption. Mechanical properties

1 Introduction

Epoxy is characterized by unique properties such as relatively high strength and modulus, low shrinkage, and excellent chemical and heat resistance. It is an important matrix used for fibre-reinforced polymer. Due to its features, epoxy has been used in manufacturing applications such as adhesives, coatings, electronic and aerospace structures. Despite its use, cured epoxy systems indicated low impact strength, poor resistance to crack propagation and initiation and low fracture toughness [1]. A recent approach is advocated to try to enhance

polymer properties via incorporation of inorganic nanoparticles or fillers in the nanometre scale into the polymer matrices [2].

Nanoparticles embedded in polymer matrix have attracted increasing interest because of the unique mechanical, optical, electrical and magnetic properties compared to neat polymers [2,3]. Polymer nanocomposite materials possess two phases consisting of inorganic particles of nanometre scale in the range between 1 and 100 nm that are dispersed in a matrix of polymeric material [4]. Due to nanometre size of these particles, nanoparticles demonstrate remarkable properties because of their comparative large surface area per unit volume. Such properties are the results of the phase interactions that take place between the polymer matrix and the nanoparticles at the interfaces since many essential chemical and physical interactions are governed by surfaces [4,5]. The interest in polymer nanocomposites comes from the fact that the addition of nanosized fillers into a polymeric matrix would have a great effect on the properties of the matrix. In 1990, the Toyota research group carried out the first study on the polymer nanocomposites. These researchers synthesized polymer nanocomposites based on nylon-6/ montmorillonite clay via the in-situ polymerization method. When 5 wt% clay was added to Nylon-6 polymer, the tensile modulus increased by 68% and the flexural modulus by 224% [5,6]. This research was the fore-runner of the global trend researches in polymer/layered silicate nanocomposites and polymer nanocomposites in general [7].

Kaynak et al. [8] investigated the flexural strength and fracture toughness of nanoclay (Na- montmorillonite) based epoxy nanocomposites. Results showed an improvement in flexural strength and fracture toughness with maximum value at 0.5% nanoclay loading. Manfredi et al. [9] found that flexural strength, flexural modulus and impact strength were increased by 20%, 29% and 23%, respectively, for composites made with the addition of 5 wt% of nanoclay. Tang et al. [10] studied the mechanical properties of treated halloysite reinforced epoxy nanocomposites. It was reported that the fracture toughness of epoxy significantly increased by 78.3% due to the presence of 10 wt% of intercalated HNTs. Wetzel et al. [11] reported an increase in flexural strength (up to 15%), flexural modulus (up to 40%) and fracture toughness (up to 120%) for epoxy nanocomposites reinforced with aluminium oxide (Al_2O_3).

In our previous works [1, 12 and 13] we studied the mechanical and thermal properties of epoxy nanocomposites reinforced with organo-clay platelets (30B), halloysite nanotubes (HNTs) and nano-silicon carbide (n-SiC), respectively. Results showed that the addition of

only 1 wt% of intercalated nanoclay increased flexural strength (up to 45.6%), flexural modulus (up to 87.6 %), fracture toughness (up to 30%), and impact toughness (up to 50%) compared to neat epoxy. Likewise, the addition of 1 wt% HNT increased flexural strength (up to 20.8%), flexural modulus (up to 72.8%), fracture toughness (up to 56.5%), and impact toughness (up to 25.0%) over neat epoxy. Furthermore, the addition of 1 wt% n-SiC increased flexural strength (up to 21.5%), flexural modulus (up to 83.0%), fracture toughness (up to 89.4%), and impact toughness (up to 25.0%) compared to pure epoxy.

In this study, the effect of long term water absorption on the mechanical properties of epoxy based nanocomposites reinforced with organoclay, HNT and n-SiC has been studied. The influence of different types of nano-filler on the barrier properties of epoxy based nanocomposites has been examined in terms of the weight gain curve of water absorption. The effect of nano-filler addition on enhancing epoxy matrix mechanical properties in wet condition has been investigated in terms of flexural strength, flexural modulus, fracture toughness and impact strength. Transmitted electron microscopy (TEM), Fourier transforms infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) have been used to investigate the morphology, micro-structure and failure mechanism of epoxy based nanocomposites.

2 Materials and methods

2.1 Materials

Organoclay platelets (Cloisite 30B), halloysite nanotubes (HNTs) and nano-silicon carbide (n-SiC) particles were used in this study as reinforcements for the fabrication of epoxy-matrix nanocomposites. The organoclay platelets (Cloisite 30B) were provided by Southern Clay Products, a United States based company. The halloysite nanotubes (HNTs) (ultrafine grade) were provided by Imerys Tableware Asia Limited, New Zealand. The brightness of HNTs is about 98.9% as measured by a Minolta CR300 using D65 light source. The nano-silicon carbide (n-SiC) particles were supplied by Sigma-Aldrich Co. LLC, United State. Finally, general purpose low viscosity epoxy resin (FR-251) and epoxy hardener (Isophorone-diamine) were supplied by Fibreglass & Resin Sales Pty Ltd, WA, Perth, Australia. Table 1 represents the physical properties of Cloisite 30B and n-SiC particles and Table 2 shows the chemical composition and physical properties of HNT [12-14].

2.2 Sample fabrication

Nano-particles including nanolcay (30B), HNTs and n-SiC were first dried for 60 minutes at 70°C before they were mixed individually with epoxy resin. Nanocomposites were prepared by mixing the epoxy resin with three different weight percentages (1%, 3% and 5%) of each type of nanoparticles using high speed mechanical mixer for 10 minutes with a rotation speed of 1200 rpm. After that, a hardener was added to the mixture and then stirred slowly to minimize the formation of air bubbles within the sample. The final mixture was poured into silicon moulds and left for 24 hours at room temperature for curing. Pure epoxy sample was also made as a control.

2.3 Characterization

2.3.1 Transmission electron microscopy (TEM)

The transmission electron microscopy was performed on a Titan Cryotwin (FEI Company) equipped with a 4k x 4k CCD camera (Gatan) at an acceleration voltage of 300 kV. An ultramicrotome (Leica microsystem) was used to prepare cut ultra-thin sections (~80 nm) of samples before recovered on a copper grid.

2.3.2 Fourier Transform Infrared (FTIR) Spectra

The Fourier transform infrared spectroscopy (FTIR) was performed on Perkin Elmer Spectrum 100 FTIR spectrometer in the transmission mode at room temperature. FT-IR spectra were recorded in the range (600-4000 cm^{-1}) at a resolution of 2 cm^{-1} with 10 scans. Background spectra were taken in the empty chamber before measurements to eliminate the influence of water moisture and CO_2 in air.

2.3.3 Scanning electron microscopy (SEM)

A scanning electron microscopy imaging was obtained using Zeiss Evo 40XVP to investigate the microstructures and the fracture surfaces of composites. The samples were mounted on aluminium stubs using carbon tape. The samples were then coated with a thin layer of gold to prevent charging before the observation by SEM.

2.3.4 Differential scanning calorimetry (DSC)

DSC analysis was performed on a Perkin Elmer (DSC 6000) in dry nitrogen atmosphere with heating rate of 10 °C/min. In this study, DSC was only conducted for neat epoxy in both dry and wet conditions to investigate the effect of water absorption on the glass transition temperature (T_g).

2.4 Physical and mechanical properties

2.4.1 Water absorption

Specimens with dimensions 10 mm × 10 mm × 3.5 mm were cut from the fabricated composites and placed in water bath at room temperature for about 130 days. At regular intervals, each sample was first removed from water and dried with a tissue before weighting using electronic balance. The percentage of the water content (M_t) was determined using the following equation:

$$M_t(\%) = \left(\frac{W_t - W_o}{W_o} \right) \times 100 \quad (1)$$

where, W_t is the weight of the sample at time t and W_o is the initial weight of the sample.

Assuming that water absorption in the samples follows Fick's second law [15]. Thus, for one-dimensional diffusion during short immersion times the following formula can be used to calculate the diffusivity D_{eff} [15,16]:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{D_{eff} t}{\pi h^2} \right)^{1/2} \quad (2)$$

where, M_t is the water content at time t , M_∞ is the equilibrium water content, D_{eff} is the effective diffusion coefficient and h is the sample thickness. Therefore, the diffusivity D_{eff} can be determined from the initial slope of the water absorption versus the square root of time.

2.4.2 Mechanical properties

Five rectangular specimens of each composition with dimensions 60mm × 10mm × 6mm were cut from the fully cured samples for three-point tests and Charpy impact tests to evaluate the mechanical properties.

Flexural strength, flexural modulus and fracture toughness of the composites were determined using three-point bending test and performed on a LLOYD Material Testing Machines - Twin Column Bench Mounted (5-50 kN). A span of 40 mm was used during the test with a displacement rate of 1.0 mm/min. The flexural strength (σ_F) was evaluated using the following equation:

$$\sigma_F = \frac{3 P_m S}{2 W D^2} \quad (3)$$

where P_m is the maximum load at crack extension, S is the span of the sample, D is the specimen thickness and W is the specimen width. Values of the flexural modulus (E_F) were computed using the initial slope of the load–displacement curve, $\Delta P/\Delta X$, using the following formula:

$$E_F = \frac{S^3}{4 W D^3} \left(\frac{\Delta P}{\Delta X} \right) \quad (4)$$

Fracture toughness was evaluated using single edge notch bending (SENB) specimens. A notch was introduced at the central of the specimen bar using a diamond blade saw followed by introducing sharp pre-crack into the notch via tapping a sharp razor blade. The ratio of notch length to width (a/w) was about (0.4). Fracture toughness (K_{IC}) was calculated using the following equation according to [17].

$$K_{IC} = \frac{P_m S}{W D^{2/3}} f\left(\frac{a}{w}\right) \quad (5)$$

where a is the crack length, and $f(a/w)$ is the polynomial geometrical correction factor give as

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2} [1.99 - (a/W)(1 - a/W) \times (2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{2/3}} \quad (6)$$

Impact strength was measured using Zwick Charpy impact test with 1.0 J pendulum hammer. Un-notched impact strength in the units of kJ/m² was evaluated using the following formula:

$$\sigma_I = \frac{E}{A} \quad (7)$$

where E is the impact energy to break a sample with a ligament of area A .

3 Results and discussion

3.1 TEM observation

Figure 1 (a-c) shows the dispersion for 5wt% of nanoclay, HNT and n-SiC within the epoxy matrix, respectively. It can be seen that the dispersion of these fillers was quite homogenous with some particle agglomerations that found to increase as filler content increased due to the increase in matrix viscosity [1, 12 and 13]. Figure 1 (d-f) shows high magnification TEM images for nanoclay (Cloisite 30B), HNT and n-SiC in the epoxy matrix. It can be seen in Figure 1d that mixing the nanoclay platelet with epoxy resin resulted in intercalated structure with d-spacing ranges from 2.3 to 4.3 nm compared to 1.8 nm of nanoclay platelet. Separated single layers of clay platelet can be also observed. Figure 1e shows that HNT has hollow nanotubular structure with an average diameter of about 20–40 nm and length ranging from 500 nm to 1.6 μ m [12]. While Figure 1f indicates that n-SiC particles are spherical in shape with diameter ranging from 40 nm to \geq 100 nm [13]. More details including XRD and TEM analyses can be found in [1, 12 and 13].

3.2 Effect of nano-filler on the water absorption of epoxy based nanocomposites

The water absorption curve of nanoclay/epoxy nanocomposites, HNT/epoxy nanocomposites and n-SiC/epoxy nanocomposites are illustrated in Figure 2 (a-c), respectively. It can be seen that all nanocomposites exhibit typical water absorption behaviour of polymers that follow Fick's law [18,19]. In general, the presence of nano-fillers is found to decrease the water uptake of modified composites compared to neat epoxy. This phenomenon is due to the excellent barrier properties of these nano-fillers [18-20]. The

presence of high aspect ratio nano-fillers can create a tortuous pathway for water molecules to diffuse into the composites [20].

In the case of nanoclay reinforced epoxy nanocomposites, the maximum water uptake decreases gradually with increasing clay contents [19]. The maximum water absorption of nanoclay filled epoxy nanocomposites decreases by 14.1, 17.9 and 24.8% after the addition of 1, 3 and 5 wt% nanoclay, respectively, when compared to neat epoxy. Similarly, the presence of 1, 3 and 5 wt% HNT decreases the water absorption by 10.3, 18.8 and 20.1%, respectively. Interestingly, the nanocomposites filled with n-SiC show better barrier properties than other filled nanocomposites. The incorporation of 1, 3 and 5 wt% n-SiC decreases water uptake by 21.8, 28.6 and 33.3%, respectively, as compared to neat epoxy. For all nanocomposites, water uptake decreases with increasing filler content. This can be attributed to the increase in the tortuosity effect with increasing filler content [19,20]. Several studies showed that the maximum water absorption of polymer system decreased due the presence of nano-filler [16, 18-20]. Becker et al. [18] reported a reduction in maximum water uptake for different types of epoxy systems reinforced with layered silicate. Similarly, Zhao and Li [20] investigated the water absorption of Al₂O₃/epoxy nanocomposites. Results showed that the water uptake of epoxy decreased after the addition of Al₂O₃ nanoparticles.

Table 3 shows the maximum water uptake and the effective diffusion coefficient of neat epoxy and epoxy based nanocomposites filled with nanoclay, HNT and n-SiC. It can be seen that the diffusivity of nanocomposites generally decreases due to the addition of nano-fillers. Compared to neat epoxy, significant reduction in diffusivity (30.0, 31.7 and 36.3%) were achieved with only 5 wt% of nanoclay, HNT and n-SiC content, respectively. The reduction in the diffusivity may be attributed to the tortuosity of diffusion path created by the nano-filler addition [19]. Similar results were obtained by Kim et al. [15]. It was found that the addition of 5 wt% nanoclay (I30P and Cloisite 20A) decreased the diffusivity of epoxy by 36 and 39%, respectively.

3.3 FTIR analysis of epoxy based nanocomposites

The FTIR spectra of epoxy and epoxy based nanocomposites filled with nanoclay, HNT and n-SiC in dry condition is investigated.. Table 4 presents the main FTIR bands of epoxy and its nanocomposites. The FTIR spectra showed the broad band in the region 3317-3373

cm^{-1} corresponds to the stretching vibration of the hydroxyl groups (OH) of free and hydrogen bonded $-\text{OH}$ groups [21]. The peak at 1647 cm^{-1} is assigned to the (OH) bending vibration [21,22]. The absorption peaks at 2869 and 2921 cm^{-1} are attributed to C-H symmetric and asymmetric stretching vibration [23]. The absorption peaks at 1607 , 1582 and 1508 cm^{-1} are associated with characteristic adsorptions of the benzene ring of epoxy or C=C stretching of aromatic ring [24]. The absorption bands at 1362 and 1453 cm^{-1} can be attributed to CH_3 and CH_2 bending vibration, respectively [25]. The C-O stretching of epoxide ring vibration showed peaks at 1237 and 917 cm^{-1} [2]. The peak appeared at 826 cm^{-1} could be assigned to the 1,4-substitution of aromatic ring for epoxy resin [25]. There are number of peaks existed in the FTIR spectra due to the presence of nanoclay, HNT and n-SiC into epoxy system. For example, the peaks appeared at 3621 and 3695 cm^{-1} in the HNT/epoxy spectrum correspond to Al_2OH stretching of halloysite nanotube [26]. The absorption bands at 911 and 1031 cm^{-1} are attributed to $\text{Al}-\text{OH}$ vibrations and $\text{Si}-\text{O}$ stretching vibrations in the halloysite nanotube [23]. In the FTIR spectrum of n-SiC/epoxy nanocomposites, the peaks found at 911 and 1105 cm^{-1} may correspond to $\text{Si}-\text{C}$ bonds and $\text{Si}-\text{O}-\text{C}$ bonds between n-SiC and epoxy matrix, respectively [27]. The spectrum of nanoclay filled epoxy composite showed peak at 3631 cm^{-1} , which belongs to the (OH) stretching for $\text{Al}-\text{OH}$ and $\text{Si}-\text{OH}$ of nanoclay [24, 28]. Otherwise, it can be seen that the intensity of some peaks in the nanoclay/epoxy composites changed due to the presence of nanoclay.

Figure 3 (a-c) shows the principle peak of the hydroxyl group (OH) for dry and wet nanoclay/epoxy nanocomposites, HNT/epoxy nanocomposites and n-SiC/epoxy nanocomposites, respectively. This peak represents the water indirectly and directly bonded to the hydroxyl group and can be used as an indicator to water content in the materials [21]. It can be seen in Figure 3 (a-c) that after water absorption the peak of interest is found to increase compared to dry composites for all composites. Furthermore, the effect of nano-filler addition on the water absorption of epoxy system was investigated by studying the hydroxyl group (OH) peak at the range of 3317 to 3373 cm^{-1} . Figure 3 (d-f) shows the effect of nanoclay, HNT and n-SiC in reducing water uptake in epoxy based nanocomposites, respectively. In general, it can be observed that the peak of interest decreases as the filler content increases. This confirms that the addition of nano-filler decreases the amount of absorbed water. The reduction in water uptake is most pronounced for nanocomposites filled with n-SiC particles. This result is in agreement with the weight gain study of water absorption.

3.4 Effect of water absorption on the mechanical properties of epoxy based nanocomposites

The effect of water absorption on the mechanical properties of epoxy based nanocomposites was investigated after placing the specimens in water for 6 months period at room temperature and compared with the same nanocomposites in dry conditions. All mechanical tests were carried out at room temperature for wet samples. The data of the nanocomposites in dry condition have been demonstrated here only for the purpose of benchmarking. More details about the mechanical properties of epoxy based nanocomposites filled with nanoclay, HNT and n-SiC particles in dry condition can be found in [1, 12, 13], respectively.

3.4.1 Flexural strength and modulus

Table 5 summarizes the flexural strength and modulus of nano-filler reinforced epoxy nanocomposites in both dry and wet conditions. In general, it can be seen that water absorption has a negative influence on flexural strength and modulus of epoxy based nanocomposites. Flexural strength of unmodified epoxy and modified epoxy based nanocomposites decreases after subjecting to water compared to dry nanocomposites. This reduction in flexural strength can be attributed to the plasticization effect of water absorption in epoxy matrix. This can lead to reduction in the interfacial strength between the epoxy and reinforcing particles resulting in drop in flexural strength values [29]. For example, the flexural strength of water-absorbed epoxy decreases by 12.2% compared to epoxy in dry condition. In the case of nanoclay/epoxy nanocomposites, the flexural strengths of wet specimens filled with 1, 3 and 5 wt% nanoclay decrease by 38.3, 10.3 and 13.4%, respectively, compared to nanoclay filled epoxy in dry condition. Similarly, for HNT/epoxy nanocomposites, the flexural strengths of wet specimens modified with 1, 3 and 5 wt% HNT decrease by 21.1, 23.0 and 17.6%, respectively, compared to dry HNT filled epoxy. Furthermore, for n-SiC/epoxy nanocomposites, the flexural strengths of wet specimens filled with 1, 3 and 5 wt% n-SiC decrease by 15.9, 14.8 and 12.0%, respectively, in comparison to n-SiC filled epoxy. A number of studies have reported reduction in flexural strength of epoxy based nanocomposites due to water absorption. For instance, Abacha et al. [30] reported a decrease in flexural strength and modulus of clay/epoxy nanocomposites due to the water absorption. Buehler and Seferis [31] also reported a drop in flexural strength values of carbon fibre/epoxy and glass fibre/epoxy composites as a result of moisture absorption.

The effect of nano-fillers on enhancing the flexural strength of wet epoxy matrix was investigated and compared to neat epoxy in wet condition. Table 4 shows no significant change in flexural strength due to the presence of nanoclay. For example, the flexural strength increases by 2.2 and 3.0% after the addition of 1 and 5 wt% nanoclay, respectively. For HNT/epoxy nanocomposites, maximum flexural strength (about 8.5% over neat epoxy) is obtained at 1 wt% HNT loading. Similarly, the addition of 1 wt% n-SiC increases flexural strength by 16.3% over unmodified wet epoxy. The increase in flexural strength of water-treated nanocomposites after the addition of nano-fillers can be attributed to the enhancement in the interfacial bonding between the filler and the matrix, thus increasing the surface area of matrix/filler interaction. As a result, this leads to good stress transfer from the matrix to the nano-fillers, thus resulting in improved flexural strength. In a similar study, Hossain et al. [32] investigated the effect of nanoclay on the flexural strength of carbon fibre reinforced epoxy composites after immersing in sea water for 30, 60 and 180 days. Their results showed that flexural strength increased due to the presence of nanoclay.

The effect of water absorption on the flexural modulus of nano-filler reinforced epoxy nanocomposites is presented in Table 4. At a glance, it can be argued that flexural modulus was not significantly influenced by water absorption for most of the nanocomposites. However, the decrease in flexural modulus is more expressed for nanocomposites filled with nanoclay than other nanocomposites. The reduction in flexural modulus can be attributed to the plasticization effect of water absorption on the epoxy matrix [20]. DSC analysis was conducted on neat epoxy before and after water treatment to evaluate the effect of water absorption on T_g . Figure 4 showed that T_g significantly decreased from 53.1 to 47.5 due to the plasticization effect of absorbed water. Similar observation was obtained by Zhao and Li [20].

In the case of wet nanocomposites, it can be seen that the addition of nano-fillers increases the flexural modulus for all types of nanocomposites. The flexural modulus of epoxy modified with 1 wt% of nanoclay, HNT and n-SiC increases by 80.7, 89.5 and 98.2%, respectively, as compared to wet unmodified epoxy. The enhancement in flexural modulus can be due to the presence of rigid fillers that have higher modulus than epoxy matrix [13]. Any further increase in fillers loading shows slight decrease in the modulus values. The reduction in flexural modulus due to the water absorption was also observed in several studies. Hossain and co-workers [32] observed a reduction in flexural modulus of carbon fibre/epoxy composites filled with nanoclay after immersing in water for 180 days. However,

the addition of nanoclay increased flexural modulus of nanoclay filled composites in wet condition compared to unfilled composites. Buehler and Seferis [31] found that flexural modulus of carbon fibre/epoxy and glass fibre/epoxy composites decreased after water absorption.

3.4.2 Fracture toughness

Table 6 displays the fracture toughness of nano-filler/epoxy nanocomposites in both dry and wet conditions. Surprisingly, fracture toughness for all types of nanocomposites is observed to increase due to exposing to a moist environment. This can be explained by increasing the ductility of the composites due to the plasticization effect of absorbed water, which tends to increase in fracture toughness [31]. Similarly, Wang et al. [33] observed an increase in fracture toughness of neat epoxy and exfoliated clay/epoxy nanocomposites after subjecting to water for 30 days.

In details, fracture toughness of unmodified epoxy in wet condition increases by 48.9% compared to dry epoxy. In the case of nanoclay/epoxy nanocomposites, fracture toughness of wet composites modified with 1, 3 and 5 wt% nanoclay platelet increases by 29.3, 51.4 and 36.0%, respectively, compared to same nanocomposites in dry condition. Similarly, fracture toughness of wet HNT/epoxy nanocomposites filled with 1, 3 and 5 wt% HNT increases by 30.7, 57.4 and 11.1%, respectively, as compared to dry nanocomposites. Moreover, fracture toughness of n-SiC/epoxy nanocomposites reinforced with 1, 3 and 5 wt% n-SiC increases by 34.1, 67.2 and 76.4%, respectively, when compared to dry nanocomposites.

The effect of nano-filler addition on the fracture toughness of wet epoxy based nanocomposites was studied. All types of nanocomposites show similar fracture toughness trend. A maximum value achieved at 1 wt% filler loading, followed by a decrease in fracture toughness value with further increase in filler content. Fracture toughness of composites filled with 1 wt% of nanoclay, HNT and n-SiC increases by 10.6, 36.7 and 70.3%, respectively, compared to wet unfilled epoxy matrix. Nanocomposites reinforced with n-SiC particles show better fracture toughness than other nanocomposites. The enhancement in fracture toughness can be attributed to the increased resistance to crack propagation via number of possible toughness mechanisms such as crack pinning, crack deflection, particle-debonding, plastic void growth, plastic deformation and particle-pullout [13]. Similarly,

Buehler and Seferis [31] reported an increase in fracture toughness of carbon fibre/epoxy composites after placement in water medium for 1200 hours. Plasticization effect of water and increased fibre bridging were reported to be the reasons of the enhancement in fracture toughness.

3.4.3 Impact strength

The effect of water absorption on the impact strength of nano-filler reinforced epoxy nanocomposites is presented in Table 6. It can be seen that nanocomposites filled with either nanoclay or HNT show no clear trend of the influence of water on impact strength. For nanocomposites filled with n-SiC, a significant increase in impact strength can be observed due to water absorption. In the case of wet condition, the impact strength of epoxy matrix increases due to the presence of nano-fillers. The increase in impact strength is more pronounced for nanocomposites modified with n-SiC particles. For all types of nanocomposites, reinforcing with 1 wt% of nano-filler displays the highest value compared to other fillers content. Impact strength of nanocomposites reinforced with 1 wt% of nanoclay, HNT and n-SiC increases by 20.0, 4.9 and 46.1%, respectively, compared to wet unfilled epoxy matrix. The increase in impact strength is due to the increase in the flexibility of the epoxy chains as a result of the plasticization action of the absorbed water [35]. Low and co-worker [36] reported an increase in impact strength for recycled cellulose fibre reinforced epoxy composites due to the plasticization effect of sea water.

3.5 SEM observation

The SEM micrographs of fracture surfaces of the water treated epoxy and epoxy based nanocomposites are shown in Figure 5 and 6. Figure 5 (a-d) is low magnification images for unfilled epoxy and epoxy filled with nanoclay, HNT and n-SiC, respectively. All types of samples show different degree of surface roughness. The surface of neat epoxy displays lower roughness than nanocomposites as seen in Figure 5a. River markings can be clearly observed for neat epoxy with quite smooth fracture surface indicating very fast and straight crack propagation [13]. However, it is evident that the presence of nano-fillers increases the roughness of the fracture surfaces. An increase in fracture surface roughness is an indicator of crack deflection mechanism, which increases the absorbed energy of fracture by increasing

the crack length during deformation [13]. The formation of micro-voids are more pronounced in n-SiC nanocomposites. It was reported that the presence of micro-voids led to increase in fracture toughness [13]. This serves to explain why nanocomposites filled with n-SiC particles exhibited the highest fracture toughness among other nanocomposites.

Figure 6 (a-d) shows high magnification SEM images of epoxy nanocomposites filled with nanoclay, HNT and n-SiC. In general, several toughness mechanisms such as crack deflection, crack pinning, particle debonding, plastic void growth, plastic deformation and particle pullouts can be observed. Such toughness mechanisms can increase the energy dissipated by resisting crack propagation during deformation, which lead to an increase in fracture toughness values [12,13]. Close observation of Figures 5 and 6 indicates that crack deflection and plastic deformation due to the presence of clay clusters are the dominant toughening mechanisms for nanocomposites filled with nanoclay [10]. For nanocomposites filled with HNT, crack deflection and crack pinning and bowing are the main toughening mechanisms [37]. In the case of nanocomposites filled with n-SiC, Figures 5d and 6d show the existence of micro-voids, which reveals that the plastic deformation of the matrix around the voids and the crack deflection due to the presence of these voids are primary toughening mechanisms.

4 Conclusions

The effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites was studied. The influence of the nano-filler such as nanoclay platelet, HNT and n-SiC on enhancing the mechanical and barrier properties of epoxy based nanocomposites in wet condition was also investigated. Results indicated that the presence of nano-filler into epoxy matrix led to significant reduction in both water uptake and diffusion coefficients (D). This reduction was attributed to the tortuosity path created by the addition of the nano-fillers. Flexural strength and modulus of all types of nanocomposites decreased due to the plasticization effect of the water uptake compared to dry nanocomposites. However, fracture toughness and impact strength were found to increase as a result to water absorption. Water treatment increased the mobility of the epoxy chain, which led to increase the ductility of the epoxy matrix resulting in enhancing the toughness of the composites.

The addition of nanoclay, HNT and n-SiC particles improved the mechanical properties of the nanocomposites after exposing to water compared to neat epoxy in same condition. The reinforcement with 1 wt% nano-filler showed better mechanical properties than other filler

content. The enhancement in barrier and mechanical properties of nanocomposites were more pronounced for nanocomposites filled with n-SiC than those filled with nanoclay platelet and halloysite nanotubes.

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Figure captions

Figure 1. TEM images of epoxy-based nanocomposites filled with nanoclay (a and d), HNT (b and e), and n-SiC (c and f).

Figure 2. Water absorption curves of epoxy-based nanocomposites filled with nanoclay (a), HNT (b), and n-SiC (c).

Figure 3. FT-IR ($3000\text{-}3800\text{ cm}^{-1}$) of epoxy-based nanocomposites. (a) dry and wet nanoclay/epoxy, (b) dry and wet HNT/epoxy, (c) dry and wet n-SiC/epoxy, (d) wet nanoclay/epoxy series, (e) wet HNT/epoxy series, and (f) wet n-SiC/epoxy series.

Figure 4. The DSC curves of neat epoxy before and after water treatment.

Figure 5. SEM images showing the details fracture surfaces for (a) unfilled epoxy (b) epoxy/nanoclay 5wt%, (c) epoxy/HNT 5wt%, and (d) epoxy/n-SiC 5wt%. [White arrow indicates the direction of crack propagation]

Figure 6. SEM images showing the details of fracture surfaces e for epoxy-based nanocomposites filled with nanoclay (a and b), HNT (c), and n-SiC (d).

Tables

Table 1. Physical properties of (Cloisite 30B) and n-SiC particles.

Physical properties	Cloisite 30B	n-SiC
Colour	Off white	Light grey
Density(g/cm ³)	1.98	3.22
Surface area(m ² /g)	750	70-90
Particle size	2-13 μm	<100 nm
d-spacing (001)	1.85 nm	-----

Table 2. Chemical composition and physical properties of HNTs.

SiO ₂	50.4 wt%
Al ₂ O ₃	35.5 wt%
Fe ₂ O ₃	0.25 wt%
TiO ₂	0.05 wt%
Colour	Bright white
Surface area	20 m ² /gm
Particle size	0.2-6.0 μm
d-spacing (001)	0.74 nm

Table 3. Maximum water uptake and diffusion coefficient (D) of epoxy-based nanocomposites filled with nanoclay, HNT and n-SiC particles.

Sample	Maximum water uptake (%)	Diffusion coefficients (D) (10^{-7} mm ² /sec)
Epoxy	2.34	11.75
Epoxy/nanoclay (1%)	2.01	9.98
Epoxy/nanoclay (3%)	1.92	10.10
Epoxy/nanoclay (5%)	1.76	8.23
Epoxy/HNT (1%)	2.09	10.87
Epoxy/HNT (3%)	1.90	8.47
Epoxy/HNT (5%)	1.87	8.03
Epoxy/n-SiC (1%)	1.83	11.35
Epoxy/n-SiC (3%)	1.67	13.84
Epoxy/n-SiC (5%)	1.56	7.48

Table 4. FTIR bands of epoxy and its nanocomposites.

Band	Peak location (cm ⁻¹)
OH stretching	3359
OH bending	1647
C-H symmetric and asymmetric stretching	2869 and 2921
C=C stretching of aromatic ring	1508, 1582 and 1607
CH ₃ and CH ₂ bending	1362 and 1453
C-O stretching of epoxide ring	917 and 1237
1,4-substitution of aromatic ring for epoxy resin	826
Al ₂ OH stretching of halloysite nanotube	3621 and 3695
Si-C bonds and Si-O-C bonds	911 and 1105
OH stretching for Al-OH and Si-OH of nanoclay	3631

Table 5. Flexural strength and modulus of epoxy and its nanocomposites before and after water treatment.

Samples	Before placing in water		After placing in water	
	Flexural strength	Flexural modulus	Flexural strength	Flexural modulus
	(MPa)	(GPa)	(MPa)	(GPa)
Epoxy	58.5 ± 2.6	0.9 ± 0.1	51.4 ± 3.1	0.7 ± 0.2
+1% nanoclay	85.2 ± 2.5	1.6 ± 0.4	52.6 ± 4.3	1.3 ± 0.2
+3% nanoclay	58.7 ± 3.9	1.5 ± 0.1	52.7 ± 4.3	1.3 ± 0.2
+5% nanoclay	61.2 ± 3.5	1.4 ± 0.2	53.0 ± 3.9	1.3 ± 0.2
+1% HNT	70.7 ± 6.2	1.5 ± 0.2	55.8 ± 6.5	1.4 ± 0.2
+3% HNT	68.2 ± 8.1	1.3 ± 0.1	52.5 ± 4.9	1.3 ± 0.2
+5% HNT	64.5 ± 4.7	1.4 ± 0.1	53.1 ± 3.5	1.4 ± 0.2
+1% n-SiC	71.1 ± 3.2	1.6 ± 0.3	59.8 ± 4.3	1.4 ± 0.3
+3% n-SiC	66.3 ± 2.9	1.4 ± 0.2	56.5 ± 5.8	1.3 ± 0.3
+5% n-SiC	61.9 ± 3.2	1.4 ± 0.1	54.5 ± 3.4	1.4 ± 0.3

Table 6. Fracture toughness and impact strength of epoxy and its nanocomposites before and after water treatment.

Samples	Before placing in water		After placing in water	
	Fracture toughness	Impact strength	Fracture toughness	Impact strength
	MPa.m ^{1/2}	kJ/m ²	MPa.m ^{1/2}	kJ/m ²
Epoxy	0.9 ± 0.1	5.6 ± 0.7	1.3 ± 0.2	6.2 ± 1.4
+1% nanoclay	1.1 ± 0.1	6.1 ± 1.3	1.4 ± 0.3	7.4 ± 1.5
+3% nanoclay	0.9 ± 0.1	6.9 ± 1.4	1.4 ± 0.2	6.6 ± 1.5
+5% nanoclay	1.0 ± 0.2	7.8 ± 2.7	1.3 ± 0.3	7.3 ± 1.7
+1% HNT	1.3 ± 0.2	5.6 ± 1.1	1.7 ± 0.2	6.5 ± 1.8
+3% HNT	1.0 ± 0.1	6.4 ± 0.7	1.6 ± 0.5	6.3 ± 1.8
+5% HNT	1.2 ± 0.1	7.0 ± 0.9	1.3 ± 0.3	6.2 ± 1.5
+1% n-SiC	1.6 ± 0.3	7.5 ± 1.1	2.2 ± 0.3	9.1 ± 1.8
+3% n-SiC	1.2 ± 0.2	7.0 ± 0.8	2.1 ± 0.3	7.9 ± 2.2
+5% n-SiC	1.1 ± 0.1	7.6 ± 1.2	1.9 ± 0.3	8.2 ± 1.4