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Research Article

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Reinforcement of graphene nanoplatelets on water uptake and thermomechanical behaviour of epoxy adhesive subjected to water ageing conditions

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Abstract: Adhesive joints are frequently utilized due to their lightweight nature and minimal damage to the substrates. However, their application is constrained by a lack of reliable performance under moist conditions. This study assesses the impact of incorporating varying concentrations (0.25–0.75 wt%) of graphene nanoplatelets (GNPs) on moisture uptake, dynamic thermal properties, and tensile behaviour of engineered epoxy adhesives when subjected to water for periods of up to 8 weeks. The objective of this study is to ascertain the optimal concentration from the standpoint of degradation in the thermomechanical performance of the epoxy resulting from water ageing. The addition of GNP results in a 45% reduction in the diffusion coefficient of the 0.25 wt% GNP-modified epoxy relative to the unmodified epoxy. The reduced absorption of water by the GNP-reinforced adhesive results in diminished thermomechanical degradation, particularly during the initial immersion period (less than 14 days). The loss modulus exhibits an increase of up to 21% in comparison with the unmodified epoxy. The reduction in tensile strength of the modified epoxy is 53% less than that of the unmodified epoxy following 14 days of water ageing. Under the same water ageing conditions for 14 days, the epoxy modified with 0.25 wt% GNP exhibited a 75% increase in tensile strength compared to the unmodified epoxy. This work may facilitate the GNP application in epoxy adhesive joints, thereby enhancing their durability under high humidity conditions.

Keywords: nano-filler, moist conditions, water absorption

1 Introduction

The use of adhesive joints is widespread across a multitude of applications, predominantly due to their lightweight nature and uniform stress distribution, which confer them a distinctive advantage over alternative joining methods [1–3]. Of the various adhesive materials available, epoxy adhesives are the most widely used due to their outstanding structural properties and versatility in bonding a diverse range of substrates [4,5]. Nevertheless, due to their hygroscopic nature, epoxies contain polar groups that are highly attracted to water molecules, resulting in their properties being highly dependent on the extent of moisture in the environment [6]. The long-term thermal and mechanical performance of adhesives utilized in humid environments is frequently contingent upon the quantity of absorbed water and the resulting degradation in the thermomechanical properties of the epoxy adhesives [7–9]. The absorbed water causes adhesive hydrolysis, which has the potential to result in several effects, including the decomposition of polymer chains, an increase in free volume, and an overall increase in molecular mobility [10–12]. The permeation of moisture within the adhesive or the interface between the adhesive and adherend has the potential to significantly impact the durable lifespan of epoxy resin systems, resulting in an irreversible reduction in the mechanical performance of epoxy and bonded joints [8,9]. The ingress of water into the adhesive was found to reduce the stiffness and mechanical resistance of the adhesive by up to 27% [13,14]. The mode I and mode II fracture toughnesses of adhesives in demineralized water

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were observed to decrease by up to 50 and 35%, respectively [15–17]. Furthermore, the failure mode of adhesive joints shifted from cohesive failure to a combination of interfacial and cohesive failure under salt spray-aged conditions [18].

In addition to the strength and resistance to fracture of the adhesive, the thermodynamic performance of the adhesive, such as the glass transition temperature (T_g) and storage modulus, are also strongly influenced by the water ageing environment [19–21]. It is imperative that an adhesive be used at temperatures below its T_g in order to maintain its designed mechanical properties. A reduction in T_g is associated with a decline in the temperature threshold for the reliable use of the adhesive. It has been demonstrated that T_g of the polymer undergoes a reduction of between 8 and 30% after ageing in water [22,23]. This observation is attributable to the absorption of moisture, which increases the mobility of the polymer chain, thereby reducing the T_g [22].

The introduction of fillers into the adhesive matrix has been implemented to postpone the plasticization of the adhesive by filling the vacant space within the adhesive matrix, thereby reducing the mobility of the adhesive chain [24–27]. This approach has proven to be a powerful method for improving the durability of the adhesive [28,29]. However, the use of a significant quantity is necessary for microparticles to achieve the desired outcomes, which can result in viscosity enhancements in the epoxy and an increase in fabrication difficulty [29,30]. To overcome these limitations, nanofillers were incorporated into adhesives, including the nano-silicon carbide [31], carbon nanotubes (CNTs) [32], nano-clay [33], and GNP [34] to enhance the epoxy adhesive properties. The incorporation of carbon nanofillers into the epoxy adhesive impedes the intermolecular movements of the resin, thereby reducing the rate of water absorption [35]. The findings indicated that the incorporation of a fixed quantity of CNT (0.1 wt%) led to an elevated diffusion coefficient in the specimen, whereas the mixture of a fixed quantity of GNP (5 wt%) resulted in a diminished diffusion coefficient [7]. However, T_g and tensile-shear behaviour demonstrated an inverse relationship. The influence of altering the contents of carbon nanofillers on the properties of the adhesive under conditions of water ageing requires further investigation. In comparison to alternative nanofillers, the two-dimensional structure and high aspect ratio of GNPs may result in improved barrier properties against water ingress into adhesive materials. It is essential to evaluate the degradation of the thermomechanical performance of epoxy containing various contents in order to ascertain the efficacy of GNP in enhancing the durability under water ageing conditions.

In this study, the impact of varying the contents of GNP (0.25–0.75 wt%) on the water resistance performance of epoxy adhesives under different ageing conditions up to 56 days was investigated. The water uptake behaviour, tensile properties, storage, loss moduli, and T_g of the GNP-modified adhesive subjected to water immersion were evaluated under the specified ageing conditions. This was done to provide a thorough assessment of the effectiveness of GNP and to identify the optimal concentration from the perspective of degradation of the thermomechanical characteristics of the adhesive resulting from water absorption. This work may facilitate the GNP application in epoxy adhesive joints, thereby enhancing their durability under conditions of water ageing.

2 Experimental details

2.1 Materials

The epoxy adhesive used in this study was composed of two components, and the curing schedule was 96 h at room temperature (Kangda New Material Co. Ltd). GNPs were purchased from Kelude Company, and different concentrations (0.25, 0.5, 0.75 wt%) of GNPs were selected to modify the adhesive matrix [36]. The process entailed the incorporation of GNPs at a predetermined weight into acetone, followed by 6 h of ultrasonication. Subsequently, the GNP/acetone mixture was then mixed with the epoxide resin. To guarantee the complete evaporation of the acetone, the solutions were initially mixed at a temperature of 23°C. The subsequent step involved the elevation of the mixture's temperature to 100°C, and the entire mixing process was continued with a magnetic stirrer for approximately 3 h. Once the solutions had cooled to room temperature, the hardener was added in a weight ratio of 3:1.

2.2 Specimen fabrication

The bulk specimens were manufactured in accordance with the French Standard NF T 76–142 [37]. Rectangular sheets of an adhesive reinforced with varying contents of graphene nanoplatelets (GNPs) were produced using a curing process conducted between moulds and a frame composed of silicone rubber, as shown in Figure 1(a) [38]. The silicone ensures that the adhesive thickness is consistent with that of the silicone sheets and facilitates the peeling of excess adhesive when pressure (2 MPa) is

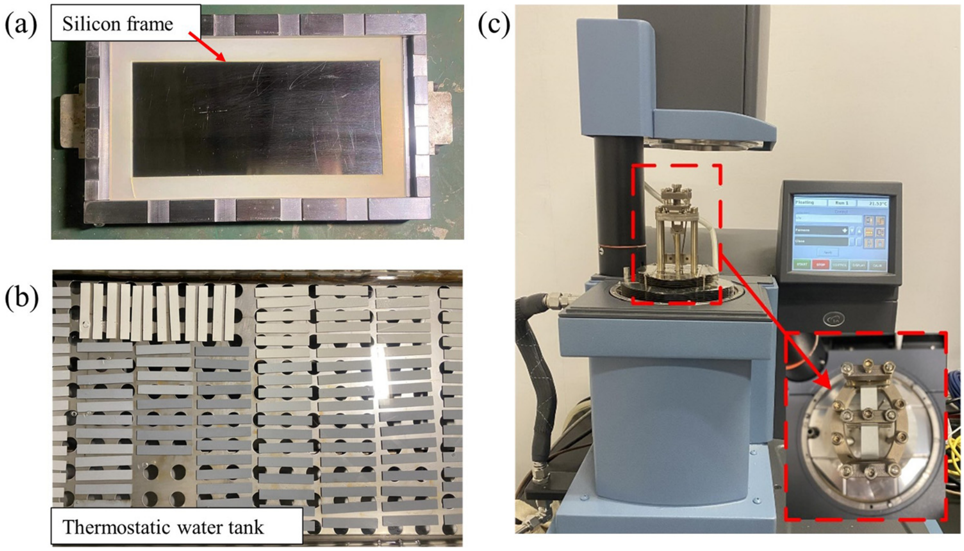

Figure 1: (a) Metal moulds for fabrication of rectangular sheets specimens. (b) Specimens water ageing conditions in thermostatic water tanks. (c) DMA test device for GNP-modified epoxy specimens.

applied to the lid of the mould. From these sheets, water absorption specimens, dynamic mechanical analysis (DMA) specimens, and tensile test specimens were machined. The specimen dimensions were 70 × 70 × 1 mm^3 and 60 × 10 × 2 mm^3 for water absorption specimens and DMA specimens, respectively. The tensile test specimens were produced according to the GB/T2567-2008 [38]. The specimens underwent an immersion process in distilled water at a constant temperature of 23°C in a thermostatic water tank, as shown in Figure 1(b).

2.3 Specimen test

2.3.1 Water uptake measurements

The water sorption capacity and the moisture diffusion coefficient are typically determined using straightforward gravimetric measurements [19]. Before the specimens underwent the water ageing process, they were kept in a desiccator until a stable weight was achieved. The initial mass of each specimen was recorded with an accuracy of 0.1 mg. Thereafter, the specimens underwent an immersion process in distilled water at a temperature of 23°C. Following immersion in water for the specified periods (6 h, 12 h, 24 h, 7 days, 14 days, 28 days, 56 days, and 90 days), the specimens were meticulously cleaned to prevent the adhesion of water droplets to the surface. Thereafter, the mass of the specimens was then measured. At least four specimens were aged per GNP content.

The mass uptake M_t (%) of epoxy adhesive specimens was quantified using the following equation:

$$M_t(\%) = \frac{w_t - w_0}{w_0} \times 100\%, \tag{1}$$

where w_t represents the mass of the adhesive sample aged in water at time t and w_0 is the initial mass of the specimen before the water ageing process.

The diffusion rate (D) being determined using equation (2) once equilibrium water uptake had been achieved [11,25]:

$$D = \left(\frac{M_t}{M_\infty}\right)^2 \times \frac{h^2}{t} \times \frac{\pi}{16}, \tag{2}$$

where D is the diffusion rate, M_∞ is the equilibrium water uptake amount, and h is the thickness of the specimen.

2.3.2 DMA test

The unmodified epoxy and GNP-modified samples were subjected to the same water ageing conditions for a period of 1, 2, 4, and 8 weeks. The storage modulus, loss factor, and the T_g of samples under both the unaged and water ageing conditions were determined by using a dynamic thermomechanical analyser (DMA Q800, TA, USA), as shown in Figure 1(c). The temperature range was set at 30°C and increased by 3°C/min, reaching a maximum of 150°C. During the test, specimens were tested at a dual cantilever clamp with a frequency of 1 Hz. To ensure the reliability of the results, at least three specimens were tested for each GNP content.

2.3.3 Tensile properties test

The tensile properties of the specimens were evaluated following the same ageing environment for a duration of 1, 2, 4, and 8 weeks, respectively. The ageing environment conditions were consistent throughout. A commercial testing instrument (Wance ETM 504C, Shenzhen, China) with a 5 KN load cell was used to ascertain the tensile behaviour of the specimens at a crosshead speed of 2 mm/min. The tensile strain of the specimens was measured using an extensometer and load and displacement were documented until the specimens failed. A minimum of four specimens were tested for each GNP content to ensure repeatability.

3 Results and discussion

3.1 Impact of GNP modification on water uptake behaviour of the adhesive

Figure 2 illustrates the water uptake of the epoxy specimens modified with varying concentrations of GNP, expressed as a function of the square root of water ageing time with respect to the actual specimen thickness. It can be observed that the actual tested water absorption and water absorption time do not exhibit a linear relationship, which is contrary to the predictions of Fick's law. One potential explanation is that Fick's law is built on the hypothesis that water diffuses solely into the adhesive, occupying the voids or free volumes therein and without engaging with the hydrophilic functional group present in the material. This is not expected to be the case in hygroscopic polymers, such as epoxies, which contain polar groups that exhibit a high degree of interaction with water molecules. Second, the weight of the experimental specimens is typically reported with an accuracy of four decimal places. The introduction of such precise data may potentially lead to errors due to the presence of irregularities in the measurement itself. Moreover, fluctuations in the testing environment, including temperature, humidity, and airflow velocity, could potentially lead to errors in the measurement data [25]. Additionally, other issues that may arise during the experiment, including the microscopically uneven surfaces of the specimens, the non-homogeneity in the samples, and the residual water adsorbed on the surface during measurement, may also result in a deviation from Ficken's law. The diffusion coefficient, denoted by *D*, is a quantitative measure of a water molecule's capacity to traverse the polymeric matrix. It can be utilized as a metric for assessing the adhesive's absorptive behaviour. The *D* of the neat epoxy was found to be greater than that of the GNP-modified adhesive. The greatest discrepancy was seen within the 0.25 wt% GNP-modified epoxy adhesive, which showed a 45% reduction in *D* relative to the unmodified adhesive specimens.

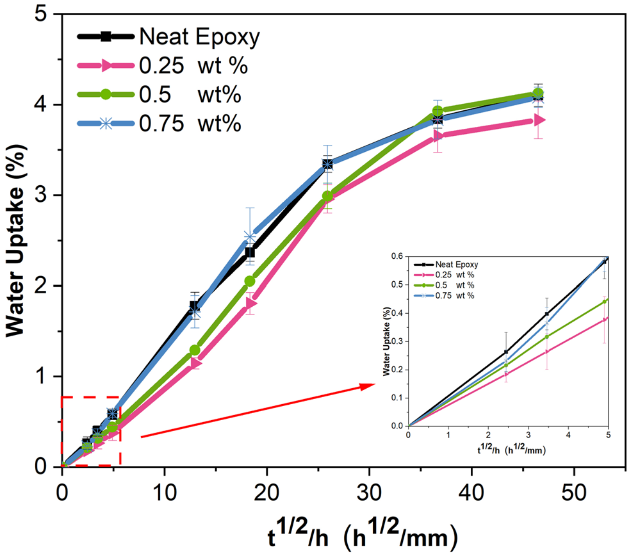

Figure 2: Water uptake of GNP-modified epoxy adhesives with varying concentrations under water immersion conditions.

In the initial ageing experiments, conducted prior to 28 days of ageing, the incorporation of GNP reinforcement resulted in a notable reduction in water absorption, particularly in the 0.25 and 0.5 wt% GNP-reinforced adhesives, which exhibited up to 36% decrease in water absorption relative to the neat epoxy at the same ageing time point (7 days). It can be attributed to the fact that the GNP acts as a diffusion barrier for water within the epoxide matrix, thereby limiting the permeability of water molecules. However, the water absorption of the 0.75 wt% GNP-modified adhesives equalled and surpassed the unmodified epoxy after 14 days of exposure. A hypothesis is that the high concentration of GNP, particularly in an agglomerated state, not only fills the voids but also causes the opening up of the polymer chains, thus effectively creating new channels for water to penetrate.

Upon prolonging the exposure to 56 and 90 days, respectively, the discrepancy in water absorption between the GNP-modified epoxy adhesive and the neat epoxy reduces gradually. Following a period of 90 days, the water absorption of the 0.25 wt% GNP-modified adhesive is less than that of the unmodified epoxy by a margin of 5–7%. In contrast, there is no large difference between the water absorption of the 0.5 and 0.75 wt% GNP-modified epoxy and unmodified epoxy. This is likely to be the swelling of adhesive's molecule chain, caused by the absorption of water molecules, resulting in a reduction in the barrier effect of the GNP in preventing the penetration of water into the epoxy over time. Furthermore, the swelling of the adhesive chain may result in the leaching of the nano-scale GNP. The morphology of the GNP, including the presence of agglomerations, can influence the interfacial area between the epoxy molecule and the GNP. The matrix/particle interface was subjected to an attack by the absorbed water, which resulted in bond failure at the interface and the formation of a pathway for increased water diffusion. This, in turn, affected the barrier properties of the GNP in the adhesive.

3.2 Impact of GNP modification on dynamic mechanical properties of an adhesive under water exposure conditions

The storage modulus of an epoxy adhesive reflects the ability of the elastic component to deform during the material deformation. An increase in the storage modulus is indicative of enhanced resistance to deformation in the material. The loss modulus is the energy dissipated by the material due to irreversible processes such as internal friction and structural damage. It reflects the viscous properties of the epoxy adhesive and is a measure of the energy loss of the material during dynamic processes. The loss factor is the ratio of the loss modulus to the storage modulus. The curves of the storage modulus (*E*′) and the loss factor (tan *δ*) of the adhesive specimens reinforced with different concentrations of GNP prior to the ageing conditions are shown in Figure 3. The T_g of the adhesives is determined by identifying the temperature at which the tan δ curve reaches its maximum value. The experimental results demonstrated that the loss modulus of GNP-modified adhesives were all superior to those of neat epoxy adhesives. This is likely to be due to the enhanced hindering effect of GNP on the adhesive molecular chain thermal movement. The energy dissipated during the thermal movement of the molecular chain is increased by the increase in internal friction and damping, which in turn causes the loss modulus to increase. An increase in the content of GNP results in an elevated loss modulus, indicative of enhanced internal energy dissipation. However, the incorporation of GNP did not result in an increase in the storage modulus or the T_g. This is likely due to the fact that the addition of GNP to the epoxy results in the formation of a relatively dense interfacial phase around the GNP. In the presence of GNP, the epoxy resin exhibits reduced molecular mobility, which impedes the diffusion of the curing agent molecules. This incomplete curing reaction results in a lower cross-linking density within the material, leading to a decline in T_g.

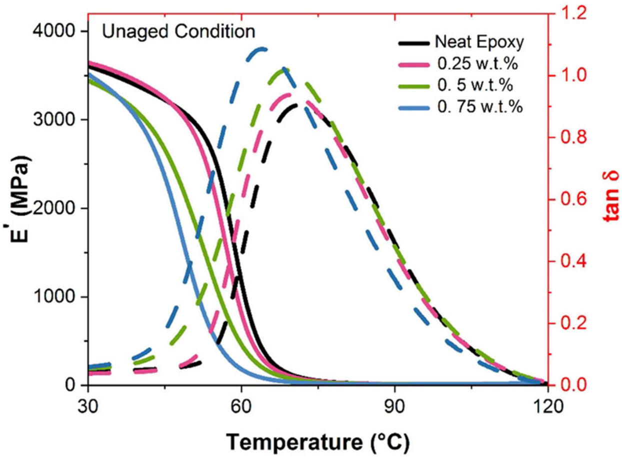

Figure 3: The storage modulus (solid lines) and tan *δ* (dashed lines) of the GNP-modified adhesive under unaged conditions.

Figure 4 depicts the storage moduli and tan *δ* curves for the GNP-reinforced adhesive and neat epoxy adhesive under conditions of water ageing. Following a 7 and 14 days water immersion ageing process, the loss modulus of the GNP-modified adhesive continues to exceed the neat adhesive. The loss modulus of the GNP-reinforced adhesive increases by up to 21% in comparison to the neat epoxy, which is a greater increase than that observed in unaged conditions. The adhesive exhibits water-absorbing capacity and exerts a lubricating effect on the adhesive's molecular chain, resulting in a reduction in the damping of the molecular thermal motion and a decline in the loss modulus under water ageing conditions. The loss modulus of the neat adhesive exhibits a notable decrease, reaching 53%, in comparison to the unaged conditions. Conversely, the presence of GNP mitigates the pronounced decline in loss modulus due to water ageing. After 7 and 14 days of water immersion, the storage modulus and T_g of the GNP-modified adhesive were observed to be superior to those of the neat adhesive, which displays a divergent trend from that observed under unaged conditions. The greatest increase in the storage modulus is 15%, while the highest increase in T_g is 5%. The introduction of GNP alleviates the decrease in T_g and storage modulus under the water ageing conditions, thereby improving the adhesive's resilience to degradation due to hydrolysis.

The extension of the water immersion ageing time to 28 and 56 days resulted in an improvement in the storage moduli, loss moduli, and T_g between the GNP-modified

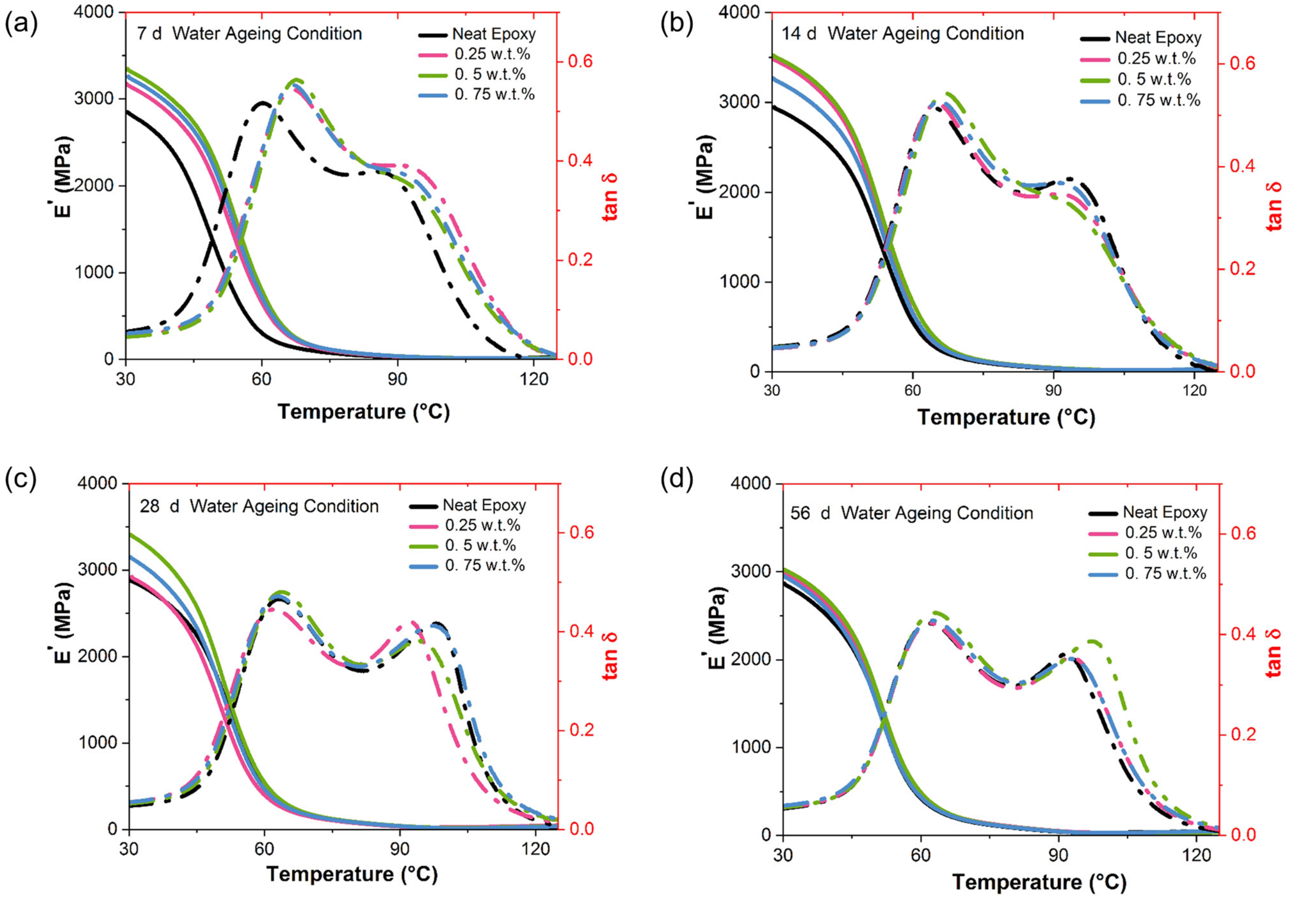

Figure 4: The storage modulus (solid lines) and tan δ (dashed lines) of the GNP-modified adhesive under water exposure for different periods: (a) 7 days, (b) 14 days, (c) 28 days, and (d) 56 days.

adhesive and neat adhesive. Nevertheless, the enhancement was not large when contrasted with the preliminary ageing interval (7 and 14 days). Following a 56-day period of water immersion ageing, the storage moduli, loss moduli, and T_g of the 0.5 wt% GNP-modified adhesives exhibited enhancements of 5, 9, and 2%, respectively, relative to the neat adhesive. It is hypothesized that following an extended exposure period, water molecules penetrate the molecular chains of the adhesive, which causes them to swell and expand. This results in the potential leaching out of the nanoscale GNP. This may result in a diminished efficacy of the GNP in mitigating the deterioration of the thermodynamic properties of the epoxy adhesive. This experimental phenomenon is consistent with the results of the previous water absorption experiment. In the later stages of the water absorption experiment, the disparity in water uptake between the GNP-modified adhesive and the unmodified epoxy also decreased. The results demonstrate that GNP exerts a favorable influence on the dynamic mechanical performance of the epoxy, particularly during the initial stages of water immersion ageing.

3.3 Impact of GNP modification on the tensile properties of the adhesive under water exposure

The representative tensile performance of the GNP-modified epoxy for unaged conditions and different water ageing times are shown in Figure 5. When unaged, Young's modulus and strength of the GNP-modified adhesives were enhanced in comparison to the neat adhesives, with a 15–18% improvement in Young's modulus and a 2–21% improvement in the tensile strength. It was observed that an increase in the GNP content resulted in a higher enhancement in tensile strength. This improvement was particularly evident in the 0.75 wt% GNP-modified epoxy, exhibiting a 21% increase in the tensile strength.

Following immersion ageing, a reduction in the tensile properties of both the unmodified epoxy and GNP-modified epoxy was observed. This decline was most pronounced at 14 days of immersion, with a 58% reduction in the tensile strength, a 78% reduction in Young's modulus, and a notable increase in elongation at failure in

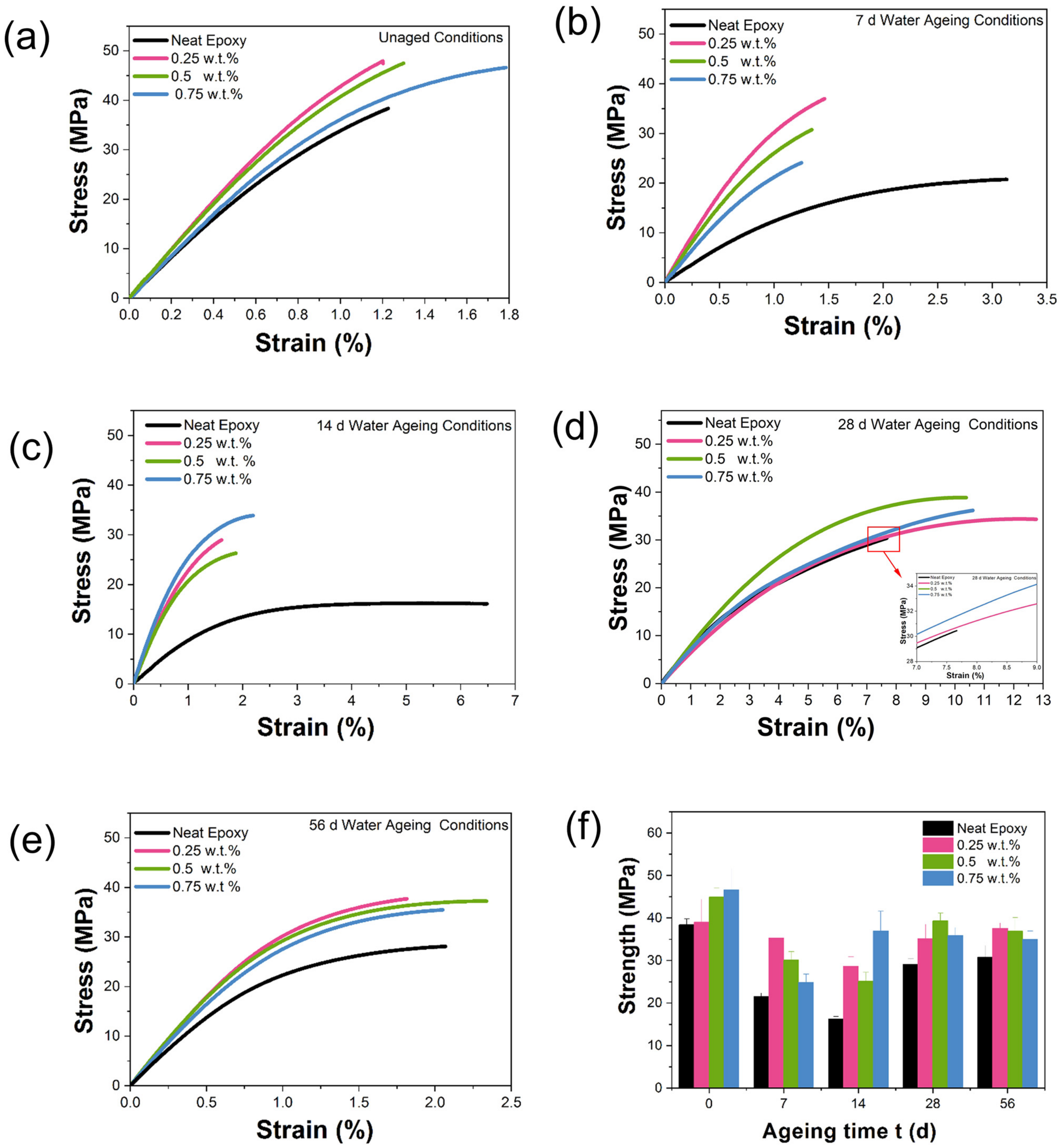

Figure 5: Representative tensile stress–strain curves of the GNP-modified adhesive for unaged conditions (a), aged for 7 days (b), 14 days (c), 28 days (d), and 56 days (e). Tensile strength variation of the GNP-modified adhesive for different ageing times (f).

comparison to the unaged conditions for neat epoxy. This phenomenon is attributed to hydrolysis-induced plasticization of the adhesive. As the duration of water exposure was increased to 28 and 56 days, a recovery in the tensile strength and Young's modulus of the unmodified epoxy adhesive was observed. This is thought to be due to the post-curing process. Following a 56-day immersion in water, the ultimate tensile strength of the neat epoxy displayed a reduction of 20% in contrast to the unaged adhesive.

Upon immersion in water for the ageing procedure, the tensile strength of the GNP-modified adhesive also exhibits a decline; however, the rate of this decline is markedly slower than that observed in the neat adhesive. In particular, for a low concentration of GNP, such as 0.25 wt%, after a period of 14 days, the decrease was found to be just 27%, which is significantly lower than the 58% decrease observed for the neat epoxy sample. The tensile strength was observed to increase by 75% in comparison to the neat sample. As the period of ageing is prolonged to 56 days, 0.25 wt% GNP-modified epoxy displays a reduction in tensile strength by only 4% in comparison with a 20% reduction observed in the unmodified adhesive. The degradation rate has been reduced by 80%. The tensile strength of the modified adhesive is 22% higher than that of the unmodified adhesive. It was observed that the 0.5 and 0.75 wt% GNP-modified adhesive resulted in an increase of 20 and 13%, respectively, under the immersion time of 56 days compared to the unmodified sample. As the GNP content increases, the observed increase in tensile strength under extended water ageing conditions tends to diminish.

The aim of this work is to enhance the scope for the use of adhesives and adhesive structures in humid ageing environments, and to improve their durability in such environments. Furthermore, in a longer immersion environment (such as 56 days), a lower concentration of GNP (such as 0.25 wt%) can enhance the mechanical performance of epoxy adhesives to a greater extent, as the cost improvement of incorporating GNP can also be minimized. The immersion environment employed in this study is more rigorous. In practical applications, for instance, in a high relative humidity environment, the enhancement in performance resulting from the use of GNP may be even more pronounced. It should also be noted that this study has some shortcomings, which could be addressed in future work. For example, the samples were placed in a water environment immediately following preparation, and no research was conducted to ascertain whether a different trend would be observed when the samples, which underwent natural ageing, were placed in a water immersion environment. Furthermore, the impact of other fillers on the enhancement of epoxy adhesives' performance in a humid ageing environment, in comparison to the GNP under investigation in this study, has not been examined. Subsequent research should address these issues. Further work could also characterize the morphology of the samples after immersion in water by electron microscopy.

4 Conclusions

In this study, the impact of varying GNP concentrations (0.25, 0.5, 0.75 wt%) on the moisture uptake, dynamic thermal properties, and tensile behaviour of epoxy adhesives subjected to water ageing was investigated.

The GNP at low concentrations (0.25 wt%) was found to act as a barrier for water diffusion within the epoxy adhesive, thereby limiting the permeation of water molecules. A reduction in water absorption by up to 36% was observed in GNP-reinforced adhesives relative to unmodified adhesive, with both materials exposed to the same ageing time point (7 days). The loss modulus of the GNP-modified adhesive increases by up to 21% compared with the neat epoxy adhesive when immersed in a shorter water ageing period (less than 14 days). In the same water ageing conditions for 14 days, the tensile strength of the 0.25 wt% GNP-modified adhesive exhibited an increase of 75% compared to the unmodified adhesive. The reinforced adhesive showed an increase in ultimate tensile strength, reaching up to 22% higher than the unmodified adhesive upon the water soak duration was extended to 56 days.

Overall, the optimal concentrations of the GNP were selected. The incorporation of 0.25 wt% GNP into adhesives results in a reduction in the amount of water absorbed, which in turn results in a less pronounced degradation of the thermomechanical and tensile behaviour of epoxy adhesive under water immersion conditions. In comparison to the unaged conditions or ageing for an extended period (28 and 56 days), the enhancement of GNP is most evident when the reinforced adhesives are immersed for a relatively short period (less than 14 days). The findings of this study may facilitate the use of GNP-modified epoxy adhesives under humid conditions, thereby enhancing their durability.

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