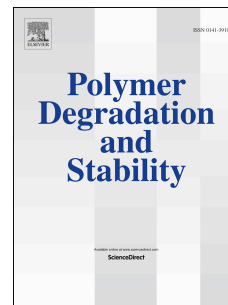# Accepted Manuscript

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Effects of the media and ageing condition on the tensile properties and fracture toughness of epoxy resin

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Abstract

This paper presents the water diffusion behaviour, tensile properties and fracture toughness of epoxy after it is aged in distilled and salt water in both steady and fluctuating conditions at a temperature of 50°C. In steady and fluctuating conditions, the equilibrium water uptake of epoxy aged in salt water is lower than that in distilled water, but the diffusion rate is unaffected. The effects of the media and ageing condition on the tensile properties and fracture toughness are insignificant. The absorbed water (0.6 - 1.8%) improves the epoxy fracture toughness up to three times, which is indicated by the complex fracture surfaces of aged epoxy.

1. Introduction

Epoxy resin has been widely used as a matrix for polymeric composite materials, adhesives, coatings and paint due to its good mechanical properties, low shrinkage, and good adhesion. However, in applications, epoxy resin absorbs water from the surrounding environment. It is well known that the absorbed water can degrade the physical and mechanical properties and

affect the performance of structures composed of epoxy resin, and this is of the utmost concern in the use of epoxy in engineering structures.

Water enters into epoxy through a diffusion process. Two important parameters that characterize the diffusion behaviour are the equilibrium water uptake and the diffusion rate. The diffusion parameters are affected by the relative humidity (RH) and temperature of the environment, the epoxy microstructure, and the thickness of the specimen. As reported in literature [1-3], the equilibrium water uptake generally increases as the relative humidity increases, for example, the equilibrium water uptake of epoxy EPON 828 exposed in 85%RH is higher (15-25%) than that in 75%RH [1]. In most cases, the temperature tends to cause an increase in the diffusion rate; however, its effect on the equilibrium water uptake depends on the type of epoxy [1,4-8]. For example, for epoxy EPON 828 [1] and particle-filled epoxy [6], both the diffusion rate and the equilibrium water uptake increase as the temperature increases. On the other hand, for other polymers, such as under-cured bismaleimide (BMI) and its composites, the diffusion rate increases as the temperature increases, but the equilibrium water uptake decreases [7,8]. The effect of microstructures on the diffusion rate and the equilibrium water uptake depends on the type of epoxy (i.e., the type of epoxy and hardener, the epoxy to hardener ratio, and the type of filler) [1,9-11]. For example, an increase in the dispersed polyetherimide (PEI) in the epoxy resin (5-15 parts per hundred resin) results in a decrease in the equilibrium water uptake but an increase in the diffusion rate [9]. On rubber-modified epoxy, increasing the rubber content increases both the equilibrium water uptake and the diffusion rate [10]. The specimen thickness seems to not affect the equilibrium water uptake and the diffusion rate, but it has more influence on the diffusion behaviour, either the Fickian or non-Fickian diffusion. The diffusion behaviour tends to follow the Fickian diffusion model as the specimen thickness increases [12,13].

Most studies revealed that water decreases the tensile strength, elastic modulus [14-19] and the glass transition temperature (T_g) of epoxy [5,20-22] due to the plasticization effect. An anomaly could occur, in particular, for prolonged ageing due to more complex interactions between water molecules and epoxy chain structures. Water molecules interact with epoxy chains to form multiple hydrogen bonds. This results in an increase in the T_g and the elastic modulus; however, their values were still relatively lower than those for un-aged epoxy [20,23]. Another important mechanical property of epoxy, which is also affected by water, is the fracture toughness. Epoxy is inherently brittle, and it has a low fracture toughness. In the neat form, the fracture toughness is in the range of $0.5 - 1.6$ MPa.m$^{1/2}$, depending on the epoxy and hardener type [24-28]. There is still controversy on the effect of water on the fracture toughness of epoxy. Quino et al. [23] reported that the fracture toughness of a mixture of cycloaliphatic epoxy resin and diglycidyl ether of bisphenol-A (DGEBA) cured with anhydride hardener decreased from 1.05 MPa.m$^{1/2}$ under dry conditions to approximately 0.85 MPa.m$^{1/2}$ with 0.8wt% of global water uptake. Salazar et al. [29] studied the effect of absorbed water on the fracture toughness of DGEBA cured with 4,4´-diaminodiphenylsulfone (DDS) and reported that after ageing in distilled water at a temperature of 60°C, the fracture toughness decreased from 1.12 MPa.m$^{1/2}$ under dry conditions to 0.9 MPa.m$^{1/2}$ at the saturation level. On the other hand, Buehler and Seferis [30] found that the mode I fracture toughness (G_{IC}) of glass fiber/epoxy and carbon fiber/epoxy composites aged in water at a temperature of 71°C for 1200 hours increased by approximately 21% compared to unaged specimens. Alamri and Low [31] reported that the fracture toughness of isophorone diamine-cured general-purpose low viscosity epoxy resin increased by 44% after it was aged in distilled water at a room temperature for 6 months relative to its fracture toughness under dry conditions. In addition, they observed that by adding 1% (by weight) of nanoclay, nanotubes,

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and nano-silicon carbide particles into the epoxy and ageing them in the same environment mentioned above, the fracture toughness increased by 27%, 31%, and 37%, respectively, compared to that under dry conditions. Wang et al. [32] also reported a slight increase in the fracture toughness of the aromatic diethyltoluenediamine (DETDA)-cured DGEBA after it was aged in distilled water at a temperature of 60°C for a month. As they used a different type of epoxy resin, there is not yet a conclusion on the effect of water on the fracture toughness, and the absorbed water can either increase or decrease depending on the chemical structure, degree of curing, and the epoxy reinforcement. Therefore, the development of epoxy, in both the neat and composite form, for future structural application exposed in harsh environments has attracted significant research attention.

A harsh environment is often a combination of corrosive media (i.e., salt water), high temperature and fluctuating conditions. The water diffusion behaviour and the level of the physical and mechanical degradation of the specimens aged in that environment may be different from that of specimens aged in both distilled water and stable conditions. Recent studies [33-35] have reported that the equilibrium water uptake in salt water was lower than that in distilled water, but there are still no clear trends for the diffusion rate. In most fluctuating conditions (absorption – desorption cycles), desorption processes were conducted at the same temperature as absorption processes [12,36], while studies on lower desorption temperature than absorption temperatures are rarely reported. Moreover, it is rarely found that water can be completely released from epoxy even if the same temperature is used for absorption and desorption. This paper investigates the effects of ageing media (distilled and salt water) and the ageing condition (steady and fluctuating) on the diffusion behaviour, the tensile properties and the fracture toughness of epoxy. In the following section, we present the material and the specimen preparation procedures, water uptake experiments, infrared

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analysis of the absorbed water and mechanical testing. The third section discusses the water uptake results, the analysis of the absorbed water in the epoxy, and the effect of water on the tensile properties and the fracture toughness, as well as the fractography results.

2. Materials and Methods

2.1 Materials

The epoxy resin is a diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight of 189±5 g/eq. The hardener is a cycloaliphatic amine (EPH 555), which mainly contains 3-aminomethyl-3,5,5-trimethylcyclohexylamine with an amine hydrogen equivalent weight of 86 g/eq and a viscosity of 0.5–1 Poise at a room temperature [37]. Both the epoxy resin and hardener are purchased from Justus Kimia Raya (Surabaya, Indonesia) and are under license from Germany. Distilled water was commercially purchased, while salt water was made by dissolving sodium chloride into distilled water. The sodium chloride content was 3.5% (by weight), which mimics the sodium chloride content in normal seawater.

2.2 Specimen preparations

Epoxy resin was mixed with the hardener with a mix ratio of 2:1 (by weight), according to the manufacturer's recommendation. The mixture was stirred well and then degassed in a vacuum chamber for approximately 20 minutes. This time was selected to prevent the epoxy from hardening before it was poured into a mould because the viscosity of the epoxy increased significantly after 30 minutes. Furthermore, most of the air bubbles had been released for the time selected. The mould was made of CNC machine-shaped silicon rubber, according to the specimen type; dog bone (DB) and single edge notch bending (SENB) specimens were used for the tensile and fracture toughness tests, respectively, as observed in Fig. 1. Those specimens are formed according to ASTM D638 [38] and ASTM D5045 [39], respectively.

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After degassing, the epoxy resin was poured into the mould and left at room temperature for 24 hours for curing. After curing, the specimen surfaces were carefully abraded using a 2000-grit emery paper to obtain smooth surfaces.

2.3 Water uptake

Water uptake studies were performed using the tensile and fracture toughness specimens. These were conducted to obtain the real water content in those specimens before mechanical testing. Furthermore, using a thin specimen that is usually used for water uptake studies may result in a different behaviour [12]. Hence, predicting the water content and the spatial water distribution for a larger specimen based upon the diffusion properties obtained from a thin specimen might be inaccurate.

The specimens were immersed in distilled water and salt water at a temperature of 50°C. There were two immersion conditions: a steady and a fluctuating condition. In the steady condition, the specimens were immersed continuously, while in the fluctuating condition, the specimens were alternating immersed for 24 hours and dried out for 24 hours. Drying was performed by taking out the specimens and leaving them in room temperature in an ambient environment. The lower drying temperature compared to the immersion temperature was used to obtain the accumulated residual water that increases continuously with time. Weighing was carried out periodically using a digital microbalance until a saturation level was reached. For the fluctuating condition, weighing was conducted at least three times for immersion and for drying. The water content was calculated using Eq. (1).

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

where M_t is the water content, and W_t and W_o are, respectively, the specimen weight at time t and the initial specimen weight.

The Fickian diffusion model was used for fitting the water uptake data, as given in Eq. (2) [40].

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-(2n+1)^2 \pi^2 Dt}{4l^2} \right) \tag{2}$$

where D is the diffusion rate, M_∞ is the equilibrium water uptake and l is a half of the specimen thickness. The initial part of Eq. (2) up to $M_t/M_\infty \approx 0.6$ is essentially linear and can be approximated as Eq. (3). The diffusion rate, D was calculated using Eq. (3) once the equilibrium water uptake was obtained.

$$D = \frac{\pi}{t} \left(\frac{l}{2} \right)^2 \left(\frac{M_t}{M_\infty} \right)^2 \tag{3}$$

2.4 Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

SEM-EDS was carried out to determine if salt ions entered into the epoxy. The test used a JEOL 6510 LA scanning electron microscope. The scanning was conducted at a voltage of 10 kV. The intensities of the X-rays emitted from the electron beam-bombarded specimen were measured by counting the pulse generated by X-rays photons in a detector at a counting rate of 2548 cps. Two locations were selected; the exposed surface and the inner part of fracture dog bone specimen were imaged after they were aged for 30 days.

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2.5 Fourier Transform Infra-Red spectroscopy (FTIR)

FTIR tests were performed using a Perkin Elmer Frontier FTIR spectrometer. Epoxy materials (dry and wet) from the dog bone specimens were ground to obtain powders. The weight of each ground specimen was approximately 2 gram. The difficulty arose in testing the wet epoxy, as grinding the wet epoxy may accelerate desorption of the absorbed water. It is possible that an amount of water was desorbed from the epoxy. Nevertheless, a very short time elapsed between the grinding and the testing to prevent desorption of the absorbed water. Furthermore, the test was conducted at room temperature, which is much lower than the absorption temperature; hence, it is likely that the desorbed water is lower.

2.6 Mechanical testing

For tensile and fracture toughness tests, four replications of specimens were prepared for every immersion time studied. For the SENB specimens, notches were carefully made by using a handsaw to obtain a notch length of approximately 9 mm. The notching was carried out very slowly to prevent residual thermal stress at the vicinity of the notch. A sharp crack was introduced in the middle of the notch using a fresh razor blade. Using this method, the length of the sharp crack produced was in the range of 0.2 – 0.3 mm. From this, the ratio of the total crack length (*a*) to the specimen width (*W*) was in the range of 0.45 – 0.55. Various types of sharp cracks have been studied, and there were no significant effects observed on the value of the fracture toughness [41]. Before testing, the specimens were immersed in distilled water and salt water at a temperature of 50°C for 0, 3, 7, 15 and 30 days; however, for the SENB specimens, the immersion time was refined to obtain a good correlation between the fracture toughness and water content. Prior to immersion, the specimens were weighed to obtain the initial weight. After the specimens were immersed and before they were tested, weighing was conducted to obtain the water content. After weighing, the specimens were

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tested immediately to prevent significant desorption. The tensile and fracture toughness tests were carried out using a Tensilon universal testing machine with a load cell capacity of 10 kN. The displacement rates of the tensile and the fracture tests were 5 mm/min and 10 mm/min, respectively. Those rates, respectively, are according to the ASTM D638 and ASTM D5045 standards.

Since the span length for the SENB test was 4 times the specimen width, the fracture toughness was calculated using Eqs. (4) and (5) [39].

$$K_Q = \left(\frac{P_Q}{BW^{1/2}} \right) f(x) \tag{4}$$

$$f(x) = 6x^{1/2} \frac{\left[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2) \right]}{(1+2x)(1-x)^{3/2}} \tag{5}$$

where K_Q is the trial K_{IC} value, P_Q is the maximum load, $x = a/W$, a is the crack length, W is the specimen width and B is the specimen thickness. To confirm the validity of $K_Q = K_{IC}$, the following criteria size must be satisfied:

$$B, a, (W-a) > 2.5 (K_Q/\sigma_y)^2 \tag{6}$$

where σ_y is the yield stress estimated from the tensile strength of the epoxy.
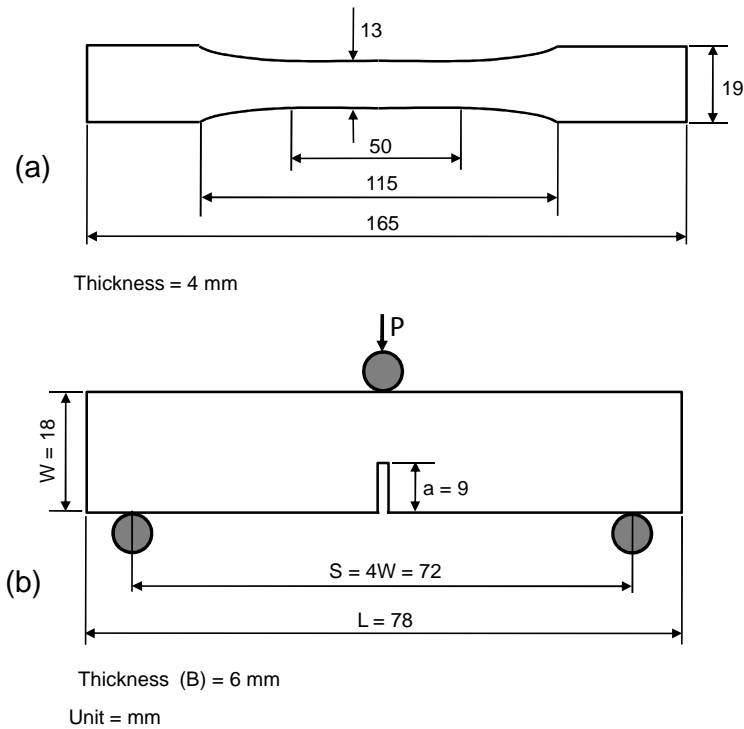
Fig. 1. (a) Dog bone specimen, (b) Single edge notch bend specimen (not to scale).

After testing, the fracture specimens (the tensile and SENB specimens) were cut (through the thickness), close to the fracture surface, into small pieces of approximately 1 mm in thickness. The fracture surfaces were then observed under an optical microscope. The source of light was put under the specimen (backlight). The light can be transmitted through the specimens, as the specimens are transparent.

3. Results and Discussion

3.1 Water uptake

Fig. 2(a) shows the water uptake versus the square root of time for different specimen thickness of epoxy under the steady condition for the dog bone and SENB specimens. In addition to absorption, desorption curves are also shown in the figure. Desorption was carried out at a certain water uptake, as observed in Fig. 2(a). Fickian fits are also indicated to determine whether the absorption follows the Fickian diffusion or not. The parameters for the

Fickian fits are shown in Table 1. It can be observed that the absorption behaviour is in agreement with the Fickian diffusion for all specimen types and ageing media. However, although the Fickian fit was not carried out for desorption, the behaviour of the desorption curve presumably does not follow Fickian diffusion. The deviation from the Fickian behaviour for desorption possibly occurs because the desorption was carried out below the absorption temperature. For most polymers, the desorption behaviour follows the Fickian diffusion when the desorption temperature is the same as the absorption temperature [12,36]; in addition, the desorption rate is faster than the absorption rate.
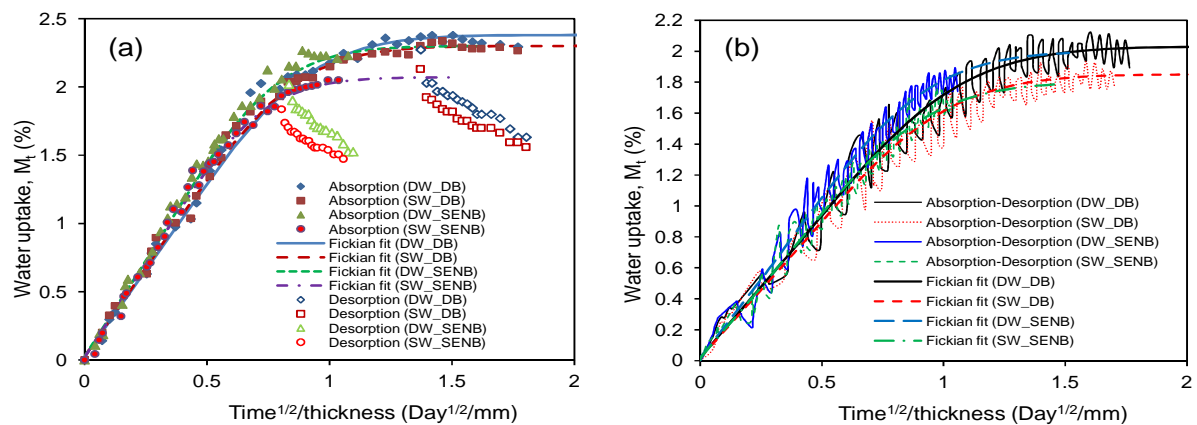

Fig. 2. Water uptake for epoxy resin in (a) a steady and (b) a fluctuating condition.

Comparing the water uptake in the dog bone and SENB specimens for the same ageing time, the water uptake in the dog bone specimens seems higher than that in the SENBs, as the dog bone specimen is thinner than the SENB. However, it is likely that the saturation levels of the dog bone and SENB specimens would be the same for longer ageing times. It is expected that the thicker specimen needs more time to saturate. Under a steady condition, the saturation levels for the dog bone specimens were reached in approximately 30 days, but those for the SENB specimens may be reached in longer than 50 days. Although the equilibrium water uptake for the dog bone specimen was reached earlier than in the SENB specimen, the

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diffusion rate is lower, as observed in Table 1. From a molecular dynamics study, Lin and

Chen [12] showed that a thicker specimen has more spaces for the conformation (relaxation)

of polymer molecules when water molecules were introduced into the polymer chain. Hence,

the diffusion rate, especially for the higher water content, tends to increase as the thickness

increases and is more likely to follow the Fickian diffusion.

Table 1. Water diffusion properties of epoxy resin in various conditions.

Condition	Dog bone specimen		SENB specimen	
	D (mm^2/day)	M_∞ (%)	D (mm^2/day)	M_∞ (%)
Steady				
• Distilled water	0.25	2.33	0.36	2.25
• Salt water	0.26	2.28	0.37	2.05
Fluctuating				
• Distilled water*	0.17	2.03	0.219	2.00
• Salt water*	0.19	1.85	0.220	1.80

*The equilibrium water uptake and the diffusion rate were taken as the average
between the upper and the lower water uptake level.

For the fluctuating condition, because the desorption temperature was lower than the

absorption temperature, the water uptake still increased, and there was also an equilibrium

water uptake. As shown in Table 1, the equilibrium water uptake and the diffusion rate were

taken at approximately the middle of the upper and the lower level of water uptake (average

values). The parameters obtained were then used to fit the experimental data using the Fickian

diffusion model. As observed in Fig. 2(b), a good agreement was found between the Fickian

diffusion model and the experimental data. Again, comparing the dog bone and SENB

specimens, the trends of the equilibrium water uptake and the diffusion rate are similar to

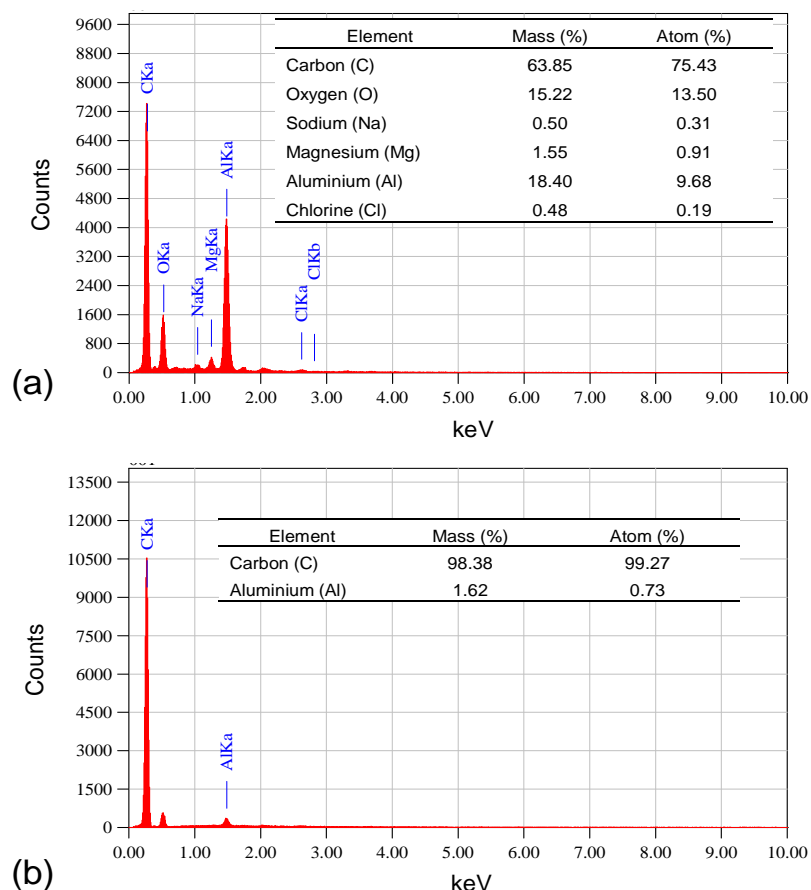those observed in the steady condition, but as expected, the values are lower.

Fig. 3. SEM-EDS results of the aged epoxy resin, (a) at the exposed surface and (b) at the inner of epoxy resin.

In salt water, compared to distilled water, the equilibrium water uptake is lower both in steady and fluctuating conditions, but the diffusion rate seems slightly higher (as shown in Table 1). However, based on the statistical analysis using analysis of variances (ANOVAs), at a 5% significance level, the effect of ageing media on the equilibrium water uptake is significant, whereas its effect on the diffusion rate is insignificant. This is consistent with the findings of other researchers [33,35]. Ions, such as Na^+ and Cl^-, are able to block the water diffusion, and hence, the equilibrium water uptake decreases. Reuvers et al. [33] compared the diffusion rate of water in a Nylon 66 fibre exposed to water, water vapour and some salt solutions such as NaCl, LiCl, KCl and KNO_3. These researchers concluded that the salt solution did not significantly affect the diffusion rate, as the water uptake in salt solution can be accurately

predicted using the diffusion rate obtained from pure water. From an elemental analysis carried out using SEM-EDS, as observed in Fig. 3, at the inner epoxy, the detected elements were mostly carbon (C) elements, but at the exposed surface, beside C, there were Na and Cl elements, which were the main components of salt solution, in addition to other elements, which were also detected, such as magnesium (Mg) and aluminium (Al). This indicates that the Na^+ and Cl^- ions seem to not enter into epoxy during ageing. According to Reuvers et al. [33], it was likely that the ions affected the water reactivity at the epoxy surface but did not affect the water mobility in the epoxy.

3.2 Fourier Transform Infrared (FTIR)

FTIR studies revealed the interaction between the absorbed water and the epoxy structure. Fig. 4 shows the FTIR spectra of the dry and aged epoxy both in distilled and salt water under the steady condition. The absorbed water interacts with the hydrophilic sites in the epoxy chains in the form of van der Waals and hydrogen bonds. The interactions change the absorption of the infrared radiation and affect the IR absorption spectrum, and hence, the transmittance of IR. Water molecules contain –OH, and the existence of –OH can be traced in the IR spectrum by analysing the peak intensities of the IR transmittance. Water is mostly detected at wavenumbers in the range of 3500 - 3700 cm^{-1} and 3200 - 3600 cm^{-1}. The former and the latter wavenumber ranges correspond to the stretching vibrations of free -OH and of bonded -OH, respectively [42]. Under dry conditions, in Fig. 4, a broad spectrum in the wavenumber range of 3100 – 3600 cm^{-1} is associated with the presence of alcohol, amine or carboxylic acid in the epoxy cured with cycloaliphatic amine. After 30 days of ageing in both distilled and salt water, the IR transmittance at the wavenumber of 3200 – 3600 cm^{-1} decreases slightly, while a higher decrease in the transmittance occurs after 60 days of ageing. These are due to the absorbed water. The decrease in the peak intensities obtained from

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ageing in distilled water and salt water is consistent with the trend observed for the amount of the absorbed water, which is discussed in the previous section. After 30 days of ageing, there are very sharp peaks at the wavenumber from 3500 - 3900 cm^{-1} with intensities below the dry spectrum; however, after 60 days, the spectra at that range have intensities above the dry spectrum. It is possibly that after 30 days of ageing, some absorbed water is present as free water, which is associated with the free –OH stretching vibrations, and then, at 60 days, the number of bound water molecules increases, which is associated with the bonded –OH stretching vibrations. This is supported by the greater decrease in the IR transmittance at 3200 - 3500 cm^{-1}. The peaks also shifted from approximately 3400 cm^{-1} to slightly above 3400 cm^{-1}.
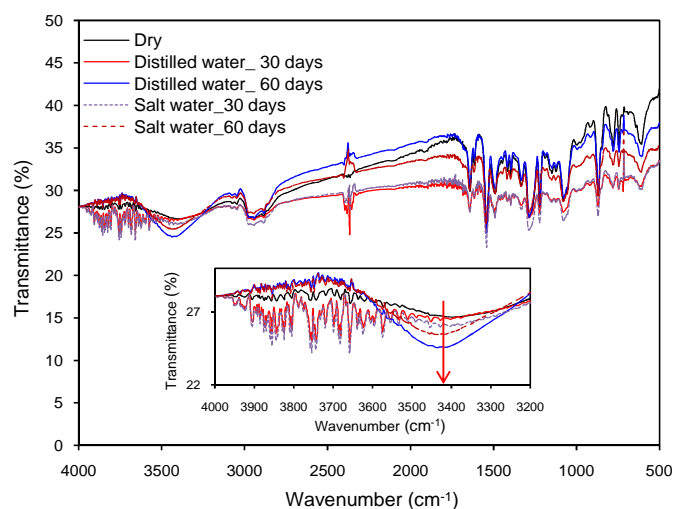

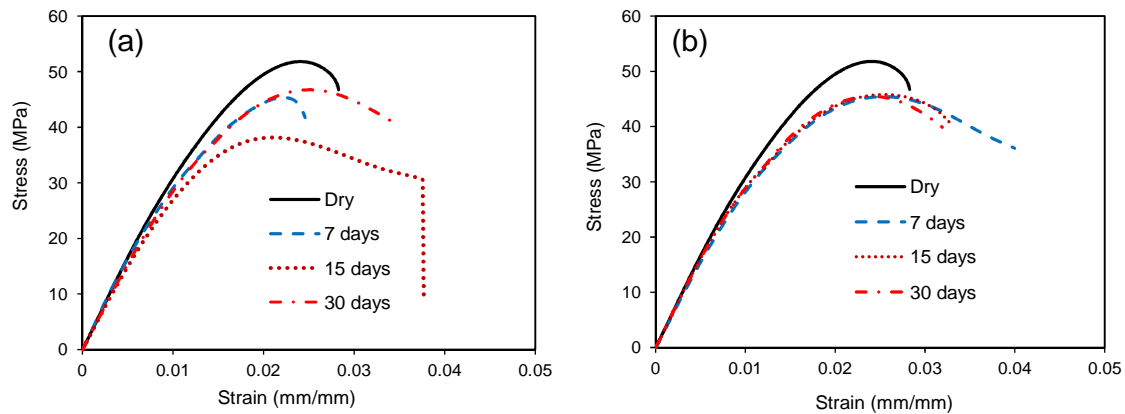**Fig. 4.** FTIR spectra of dry and aged epoxy resin.

Fig. 5. Typical stress-strain curves of dog bone specimens aged in (a) distilled water and (b) salt water.

3.3 Effect of water on the tensile properties of aged epoxy

Fig. 5 shows the typical stress-strain curves of epoxy before and after it is aged in distilled and salt water. The stress-strain curves shown in the figures were obtained only from ageing performed under the steady condition. The stress-strain curves clearly show softening after peak stress. It is also observed that the tensile stress and the elastic modulus tend to decrease while the strain at failure tends to increase with the immersion time. As observed in Fig. 6(a), in steady and fluctuating conditions, in both distilled and salt water, the tensile strength generally tends to decrease with the immersion time, and the absorbed water increases. However, after an immersion of 15 days, the decrease of the tensile strength tends to be recovered. Nevertheless, the tensile strength is still slightly lower than that in the dry condition. The decrease of the tensile strength after 15 days of immersion is approximately 15% and 9% for distilled and salt-water immersion, respectively, which correspond to a water content of approximately 2.18% and 2.15%. Compared to the 15 days immersion, the water content after 30 days of immersion is higher; however, the average tensile strength is slightly higher (7%) for distilled water and approximately the same for salt water. Generally, as reported in literature [14-19], the tensile properties decrease as the water content increases

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due to plasticization; however, an anomaly might occur, such as the recovery of the tensile properties with an increase in both the water content and ageing time [5,20,23]. This anomaly could be due to the competition between the plasticization effect and effect of additional cross-linking, where the positive effect of the additional cross-linking is more dominant than the negative effect of plasticization. This will be discussed further in the discussion on the elastic modulus. In the fluctuating condition, although literature showed that the absorption-desorption cycles seemed to have a more detrimental effect than the absorption cycle alone [12], in this study, this behaviour is presumably not followed. The decrease of the tensile strength in the fluctuating condition reaches a maximum of approximately 8%, which is slightly below the decrease observed in the steady condition.

Statistical analyses using ANOVA (at a 5% significance level) have been carried out to determine the significance of the media and ageing condition on the tensile properties. The results showed that the two media (distilled and salt water) and the ageing conditions (steady and fluctuating conditions) did not significantly affect the tensile strength. Thus, the tensile strength can be considered as a function of only the water content. If the overall data of the tensile strength are plotted against the water content, as described in Fig. 6(b), it is observed that the tensile strength degrades in an essentially linear manner with the water content until the saturation level is reached. This information is very useful for a numerical study that predicts the residual strength of adhesive joints, in case there is a cohesive failure in the adhesive.
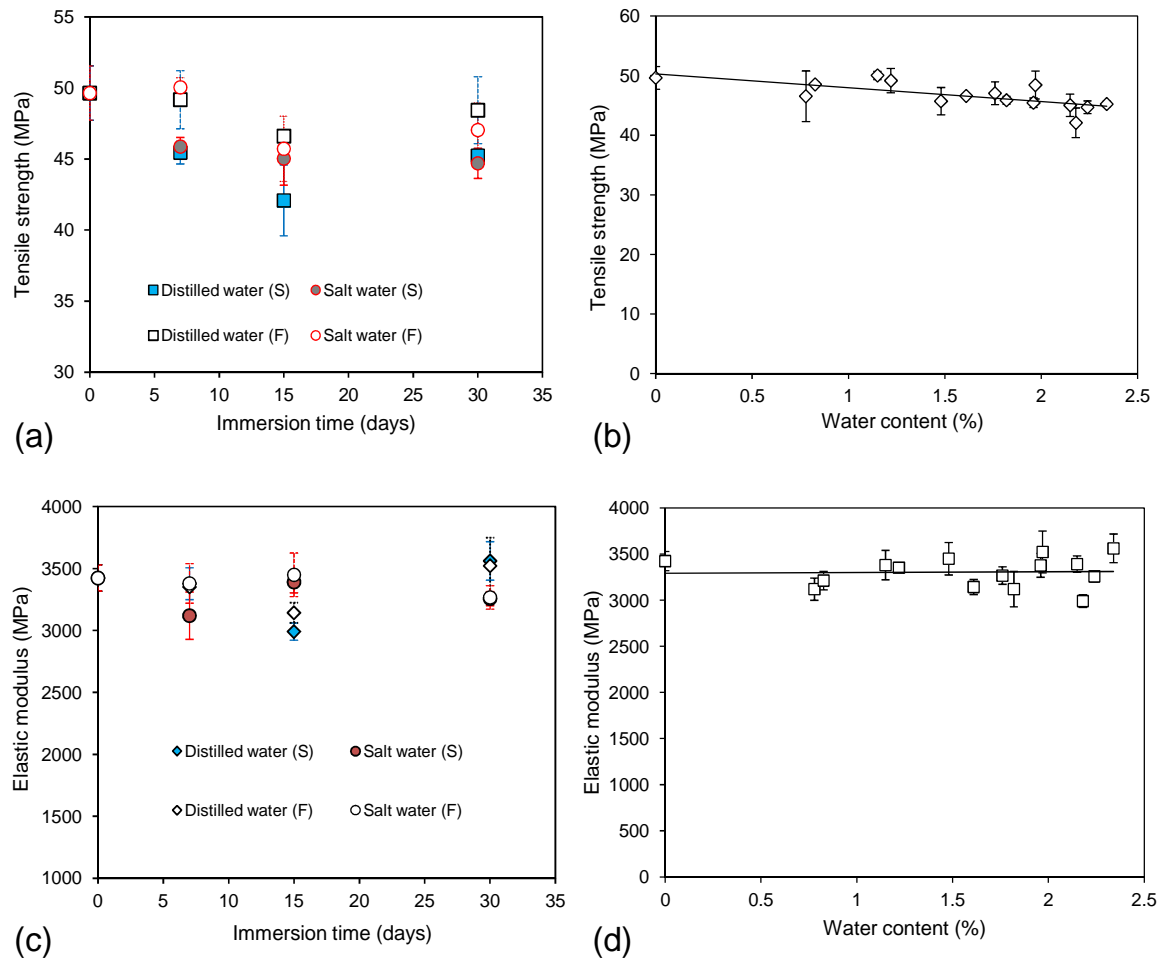
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Fig. 6. Tensile strength of the aged epoxy versus (a) the immersion time and (b) the water content, and the elastic modulus of the aged epoxy versus (c) the immersion time and (d) the water content.

The trend for the effect of the media and ageing condition on the tensile strength is also observed for the elastic modulus, particularly for the specimens immersed in distilled water; however, the decrease of the elastic modulus was lower than that of the tensile strength (Fig. 6(c)). After 15 days of immersion, the elastic modulus decreased by approximately 13% compared to that in the dry condition; however, after 30 days, it increased again to a value, which is even higher than that in the dry condition. Again, similar to the tensile strength, this peculiar behaviour may be caused by the competition between the plasticization effect and the effect of additional cross-linking. The additional cross-linking could be caused by the

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catalytic effect of water on the curing reaction of the epoxide-amine system and also the interaction between water molecules and polymer chains, which form multiple hydrogen bonds. The plasticization decreases the T_g and the tensile properties of epoxy [14-19]. On the other hand, the additional cross-link improves the T_g and the tensile properties. Referring to the works of Wu et al. [43] and Choi et al. [44], hydroxyls from water molecules can act as a catalyst to accelerate the curing reaction and increase the epoxide conversion or the degree of curing (which is indicated by T_g) for an almost fully cured epoxy (room temperature-cured epoxy). For example, the addition of 2wt% of water into epoxy EPON 828, which was cured at a temperature of 80°C, increased the rate of the curing reaction by approximately two times. Meanwhile, the increase of the T_g and the flexural storage modulus of the room temperature-cured EPON 828 were approximately 10% and 6%, respectively, relative to those of the neat epoxy (without water) [43]. In this study, the T_g and the flexural storage modulus (at a temperature of 30 °C) for neat epoxy are 58.6 ^{o}C and 2466 MPa. Another research group, Choi et al. [44], showed that the addition of water up to 3wt% accelerated the curing reaction of epoxy-poly(oxypropylene) diamine. For example, 3wt% of water was added into epoxy, and then the epoxy was cured at a temperature of 50°C for 650 min; the final epoxide conversion increased by approximately 12% compared to the neat epoxy. Furthermore, Choi et al. [45] evaluated the hygrothermal behaviours of the epoxy-amine system by measuring the T_g using differential scanning calorimetry (DSC). The samples were cured at room temperature for 28 days before they were immersed in deionised water at temperatures of 30, 40, 50 and 60°C. For the epoxy exposed at a temperature of 50°C for 28 days, the epoxide conversion and the T_g increased by approximately 24% and 22%, respectively, compared to the unexposed samples. The increase of T_g for the exposed samples was due to the additional cross-linking by the post-curing reaction in the presence of water molecules. In addition, for longer ageing times, water molecules tend to bond with polymer chains forming multiple

hydrogen bonds [5,20,46]. Referring to the literature, there is an indication that the decrease of the elastic modulus and the tensile strength after 15 days of ageing in our study due to the plasticization effect is more dominant than that due to the other two effects, while the increase after 15 days is attributed to the dominant effect of additional cross-linking as a result of both post-curing and multiple hydrogen bonds between water molecules and polymer chains.

Again, similar to the tensile strength, from the statistical point of view using ANOVA (at a 5% significance level), the media and ageing conditions did not have a significant effect on the elastic modulus, and hence the degradation of the elastic modulus (if any) was also considered as a function of only the water content (Fig. 6(d)). In fact, the effect of water on the degradation of the elastic modulus was lower than that of the tensile strength, or it tended to be negligible for longer ageing times.

Fig. 7 shows the transmission optical micrograph of the tensile fracture surface of the specimens in the dry condition and for various ageing times; however, only the specimens aged in the steady condition in distilled water are shown. It is observed that overall, the fracture surfaces of both the dry and aged specimens show brittle features, which are indicated by initiation (the mirror-like region), transition and final fracture regions [47,48]. The initiation region surrounds the origin of the crack and is associated with slow crack propagation. The fracture surface is relatively featureless, exhibiting a textured microflow [49]. The transition region is characterized by a steady increase in the surface roughness and the beginning of river lines. In the final fracture region, the crack grows rapidly, and the conical-shaped patterns develop. The parts of the figure symbolized by the numbers 1, 2 and 3, respectively, indicate the initiation, transition and the final fracture regions.
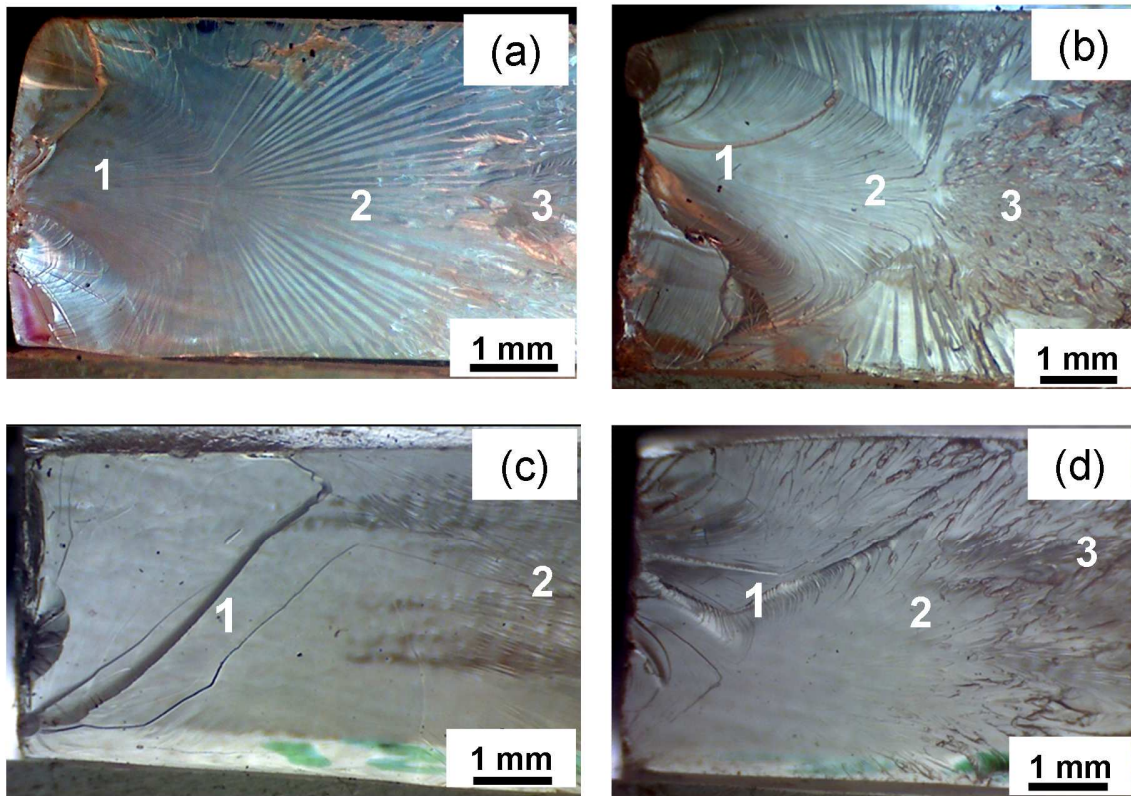
Fig. 7. The transmission optical micrographs of tensile fracture surfaces in (a) the dry condition and aged in distilled water for (b) 7 days, (c) 15 days, and (d) 30 days. Numbers 1, 2, and 3, respectively, indicate the initiation, the transition, and the final fracture regions.

For dry fracture surfaces (Fig. 7(a)), the initiation (mirror-like) region is not clearly observed around the crack initiation; however, it is more obvious when the immersion time (water content) increases, as observed in Fig. 7(b-d). The river lines are clearly observed in the transition region. The small mirror-like region in the dry fracture surfaces indicates that the material has a high tensile strength and brittleness [50]. The increase in the mirror-like region observed in the aged specimen is related to the reduced tensile strength due to the absorbed water. After 15 days of immersion, the damage zone seems dominated by the mirror-like region, which corresponds to the lowest tensile strength, as observed in Fig. 7(c). After 30

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days of immersion, the tensile strength increases again to the level of that after 7 days of immersion. Furthermore, the fracture surfaces areas of both also seem similar.

3.4 Effect of water on the fracture toughness of aged epoxy

Fig. 8 shows the typical load-displacement curves of the three-point bending test of SENB specimens aged in the steady condition, in both distilled and salt water. The displacement was measured at the position where the load was applied. For all specimens, the load-displacement curves increased linearly until the ultimate load where the specimen fractured. It is clearly observed that the load-displacement responses of the aged specimens significantly increased compared to that of the dry specimen for both ageing media, which indicates the improvement in the fracture toughness of the aged specimens compared to the dry specimen, as shown in Fig. 9(a). For the steady condition, in distilled water, the increase of the fracture toughness had been observed since 7 days of immersion, and then the fracture toughness tended to decrease after an immersion time of up to 30 days. In salt water, the fracture toughness increased after 15 days of immersion and then tended to decrease after 30 days of immersion. However, because the data scatter is high, the trend is likely to be the same as that in the distilled water.

For the fluctuating condition, in both ageing media, there is a similar trend for the fracture toughness with the immersion time; however, after 30 days of immersion, the fracture toughness of the specimen immersed in distilled water was lower than that in salt water. After 7 days, because the immersed specimens were removed and then left them in room temperature for a day before they were tested, the absorbed water had been desorbed. In the crack tip, where the fracture process (damage) zone occurred, water desorbed more quickly, and it was possible that the region had dried out; therefore, the fracture toughness was close to

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that of the dry specimen. It is likely that the desorption, particularly at the crack tip, is faster than that in salt water, as there are no obstacles from salt ions for water molecules to come out during desorption. This may result in a much lower fracture toughness of specimens aged in distilled water than in salt water, such as the result observed after 30 days of immersion.

Similar to the tensile properties, an ANOVA was carried out to determine the significant effect of the media and ageing condition on the fracture toughness. The same results were obtained, as the media and ageing condition did not significantly affect the fracture toughness; therefore, the fracture toughness can be considered as a function of only the water content, as described in Fig. 9(b). From the dry condition to a water content of approximately 0.6%, the fracture toughness increased almost linearly from 0.75 MPa.m$^{1/2}$ to 2.3 MPa.m$^{1/2}$, or it increased by approximately three times. For a water content from 0.6 to 1.8%, the fracture toughness was almost constant, but beyond a water content of 1.8%, it tended to decrease. For the specimens aged in distilled water (the steady condition), the increase of fracture toughness as the water content increases to 1.8% is due to the plasticization effect, while the slight decrease after could be due to the additional cross-linking, as discussed in the section on the tensile properties. According to Irwin's model [51], the decrease of yield stress increases the size of the plastic zone and therefore, the fracture toughness. For polymers, the yield stress is obtained at the ultimate stress of the stress-strain curves (the tensile strength) [52]. Referring to Fig. 5(a), the yield stress tended to decrease with the immersion time up to 15 days of immersion (i.e., from 49.6 MPa at dry condition to 42.1 MPa after 15 days of immersion), and it increased slightly to 45.2 MPa after 30 days of immersion. Kawaguchi and Pearson [53] indicated similar trends after exposing the silica-filled epoxy in water. The surface of the silica particles was treated using n-butyltrimethoxysilane. The specimens were aged in water at a temperature of 60°C for 1350 hours. They showed that the fracture toughness of the aged

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specimens increased (10%) relative to the unexposed specimens due to the decrease of the yield stress. The analysis of the fracture surfaces discussed in the next paragraph could further explain this trend.
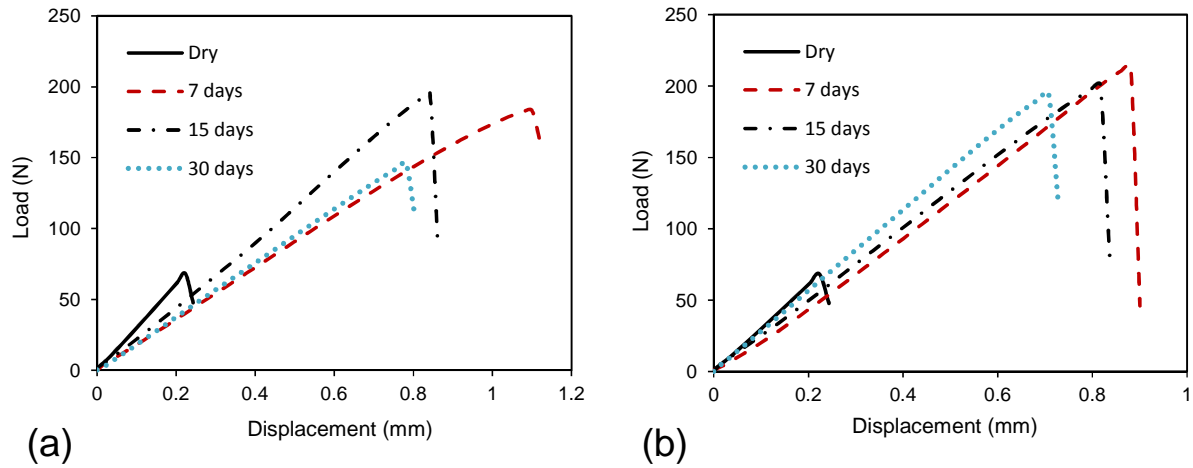

Fig. 8. (a) Load-displacement responses of the SENB specimens aged in (a) distilled water and (b) salt water.
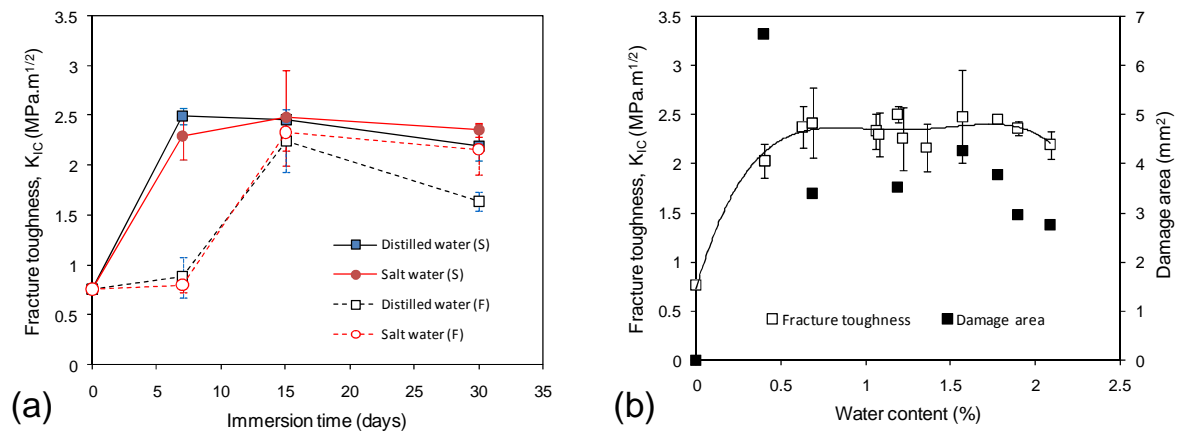

Fig. 9. Fracture toughness of aged epoxy resin versus (a) the immersion time and (b) the water content.

Fig. 10 shows the fracture surfaces of the SENB specimens in the dry condition and after they are aged in distilled water (the steady condition) for 1 day, 3 days, 7 days 15 days and 30 days. In the dry condition (Fig. 10(a)), the fracture surface is very smooth and featureless. This fracture surface indicates that the specimen absorbs low energy to propagate a crack, and hence, the fracture toughness is low. In the wet condition, the fracture surface is rough, and it has a more complex pattern. This complex fracture pattern needs high energy to propagate a crack, which results in a higher fracture toughness. There are three distinct regions in the SENB fracture surfaces, particularly in the fracture process (damage) zone, in the wet condition: the initiation (mirror-like region), transition and the final fracture regions. To determine the relationship between the damage zone and the fracture toughness, comparisons between the damage areas of the dry and aged specimens have been made (see Fig. 9(b)). The damage area was determined by multiplying the average length of the fracture process zone with the specimen width. The average length of the damage zone was calculated from measurements at six points across the width of the specimen. For the dry specimen, it is difficult to determine the damage area because the fracture surface was smooth, and the damage area was considered as zero. For a low water content, approximately 0.4% (for a 1 day immersion), the damage area was large, but it was dominated by large river lines (see Fig. 10(b)). The mirror-like region was small and relatively difficult to determine. This indicates that effect of water has not been able to fully result in the development of the fracture toughness, which is shown by an increase of the fracture toughness by 1.71% compared to that in the dry condition. As the water content increased, more water plasticised the epoxy, and the damage area tended to decrease. The mirror-like region was observed more easily, and the transition region tended to be finer and rougher. Although the damage area tended to decrease, the fracture surfaces became rougher, and as a result, the fracture toughness increased. This is clearly observed for immersion times between 3 days and 15 days (relating

to a water content between 0.6% and 1.8%), as observed in Fig. 10(c-e). At that water content range, the fracture surfaces and the damage area seem similar, and the fracture toughness is also similar (see Fig. 9(b). Beyond the water content of 1.8% (i.e., after 30 days of immersion, as observed in Fig. 10(f)), the fracture toughness tended to decrease. This is related to a further reduction of the damage area and an extension of the mirror-like region.
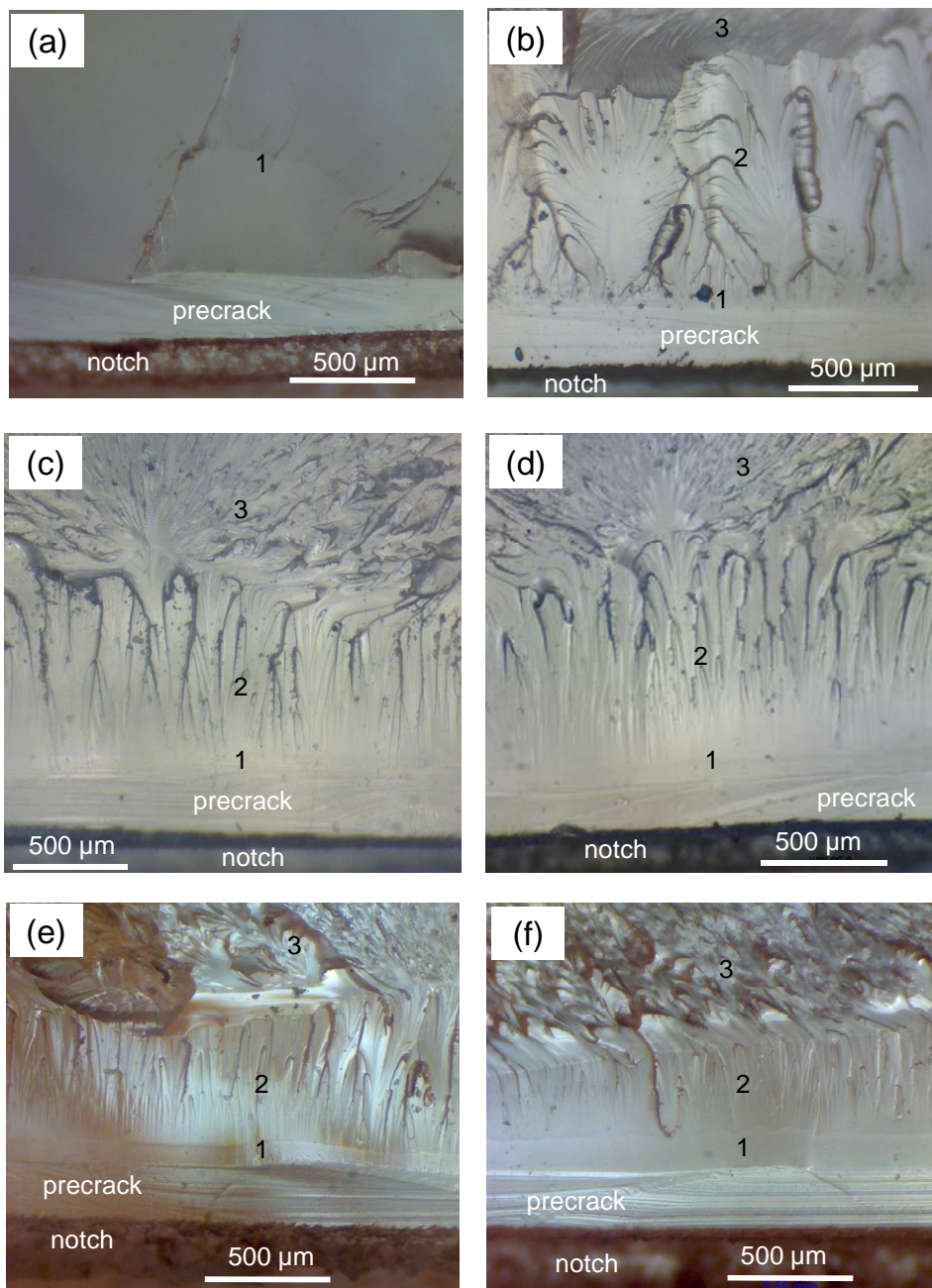
Fig. 10. The transmission optical micrographs of SENB fracture surfaces in (a) the dry condition, and after they were aged in distilled water for (b) 1 day, (c) 3 days, (d) 7 days, (e) 15 days, and (f) 30 days. Symbols 1, 2 and 3 indicate the initiation, transition and the final fracture regions, respectively.

4. Conclusions

An investigation of the water uptake of a cycloaliphatic amine-cured epoxy after it was aged in distilled and salt water in steady and fluctuating conditions has been undertaken. The effects of the absorbed water on the tensile properties and fracture toughness have also been discussed. The water diffusion behaviour follows a Fickian diffusion model in both the ageing media and in the fluctuating condition. In fluctuating conditions, the water uptake continues to increase until it reaches the saturation level, but the saturation level is below that observed under the steady condition. The equilibrium water uptake in distilled water is slightly higher than that in salt water, but the diffusion rate seems similar. The salt ions decrease the water reactivity at the surface, but they do not affect the mobility of water in the epoxy. FTIR analysis indicates a consistent trend between the water content obtained from the water uptake measurement and the FTIR spectrum in the wavenumber range from 3200-3600 cm^{-1}.

The media and ageing condition do not have a significant effect on the tensile properties and the fracture toughness; hence, the degradation of the tensile properties and fracture toughness is considered as a function of only the water content. The tensile strength tended to decrease as the water content increased, but the elastic modulus seemed to be unaffected by the water content. The fracture toughness increases approximately three times at a water content of 0.6 - 1.8% relative to the dry specimen, but then it tends to decrease when the water content

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increases beyond this level. This is related to the damage area that presumably decreases beyond a water content of 1.8%.

References

[1] Vanlandingham MR, Eduljee EF, Gillespie JR JW. Moisture diffusion in epoxy system. J Appl Polym Sci 1999;71:787-798.

[2] Loh WK, Crocombe AD, Wahab MMA, Ashcroft IA. Modelling anomalous moisture uptake, swelling and thermal characteristics of a rubber toughened epoxy adhesive. Int J Adhes Adhes 2005;25:1–12.

[3] Liljedahl CDM, Crocombe AD, Wahab MMA, Ashcroft IA. Modelling the environmental degradation of adhesively bonded aluminium and composite joints using a CZM approach. Int J Adhes Adhes 2007;27:505–518.

[4] Shen CH, Springer GS. Moisture absorption and desorption of composite Materials. J Compos Mater 1976;10(1):2-20.

[5] Perrin FX, Nguyen MH, Vernet JL. Water transport in epoxy–aliphatic amine networks – Influence of curing cycles. Eur Polym J 2009; 45:1524–1534.

[6] Chiang MYM, Garcia MF. Relation of swelling and T_g depression to the apparent free volume of a particle-filled, epoxy-based adhesive. J Appl Polym Sci 2003;87:1436-1444.

[7] Li Y, Miranda J, Sue HJ. Hygrothermal diffusion behaviour in bismaleimide resin. Polymer 2001;42:7791-7799.

[8] Bao LR, Yee AF. Effect of temperature on moisture absorption in bismaleimide resin and its carbon fiber composites. Polymer 2002;43:3987-3997.

[9] Li L, Liu M, Li S. Morphology effect on water sorption in a thermoplastic modified epoxy system. Polymer 2004;45:2837-2842.

[10] McEwan I, Pethrick RA, Shaw SJ. Water absorption in a rubber-modified epoxy resin; carboxy terminated butadiene acrylonitrile-amine cured epoxy resin system. Polymer 1999;40:4213-4222.

[11] Li L, Yu Y, Wu Q, Zhan G, Li S. Effect of chemical structure on the water sorption of amine-cured epoxy resins. Corros Sci 2009;51:3000–3006.

[12] Lin YC, Chen X. Moisture sorption-desorption-resorption characteristic and its effect on the mechanical behaviour of the epoxy system. Polymer 2005;45:11994-12003.

[13] Placette MD, Fan X, Zhao JH, Edwards D. Dual stage modeling of moisture absorption and desorption in epoxy mold compounds. Microelectron Reliab 2012;52:1401–1408.

[14] Butkus LM, Mathern PD, Johnson WS. Tensile properties and plane stress fracture toughness of thin film aerospace adhesives. J Adhesion 1998;66:251-273.

[15] Zanni-Deffargess MP, Shanahan MER. Diffusion of water into an epoxy adhesive: comparison between bulk behaviour and adhesive joints. Int J Adhes Adhes 1995;15:137-142.

[16] Ashcroft IA, Wahab MMA, Crocombe AD, Hughes DJ, Shaw SJ. The effect of environment on the fatigue of bonded composite joints. Part 1: testing and fractography. Compos Part A 2001;32:45-58.

[17] Liljedahl CDM, Crocombe AD, Wahab MMA, Ashcroft IA. Modelling the environmental degradation of the interface in adhesively bonded joints using cohesive zone approach. J Adhesion 2006;82:1061-1089.

29

[18] Shufeng L, Xiaoquan C, Qian Z, Jie Z, Jianwen B, Xin G. An investigation of hygrothermal effects on adhesive materials and double lap shear joints of CFRP composite laminates. Compos Part B 2016;92:431-440.

[19] Barbosa AQ, da Silva LFM, Öchsner A. Hygrothermal aging of an adhesive reinforced with microparticles of cork. J Adhes Sci Technol 2015; 29(16):1714–1732.

[20] Zhou J, Lucas JP. Hygrothermal effects of epoxy resin. Part II: variations of glass transition temperature. Polymer 1999;40:5513-5522.

[21] Ivanova KI, Pethrick RA, Affrossman S. Investigation of hydrothermal ageing of a filled rubber toughened epoxy resin using dynamic mechanical thermal analysis and dielectric spectroscopy. Polymer 2000;41:6787–6796.

[22] Suh DW, Ku MK, Nam JD, Kim BS, Yoon SC. Equilibrium water uptake of epoxy/carbon fiber Composites in hygrothermal environmental conditions. J Compos Mater 2001;35(3):264-278.

[23] Quino G, Yagoubi JE, Lubineau G. Characterizing the toughness of an epoxy resin after wet aging using compact tension specimens with non-uniform moisture content. Polym Degrad Stab 2014;109:319-326.

[24] Wetzel B, Rosso P, Haupert F, Friedrich K. Epoxy nanocomposites – fracture and toughening mechanisms. Eng Fract Mech 2006;73:2375–2398.

[25] Ayatollahi MR, Shadlou S, Shokrieh MM. Fracture toughness of epoxy/multi-walled carbon nanotube nano-composites under bending and shear loading conditions. Mater Design 2011;32:2115–2124.

[26] Zamanian M, Mortezaei M, Salehnia B, Jam JE. Fracture toughness of epoxy polymer modified with nanosilica particles: Particle size effect. Eng Fract Mech 2013;97:193–206.

[27] Kumar A, Li S, Roy S, King JA, Odegard GM. Fracture properties of nanographene reinforced EPON 862 thermoset polymer system. Compos Sci Technol 2015;114:87–93.

30

[28] Gomez-del Río T, Salazar A, Pearson RA, Rodríguez J. Fracture behaviour of epoxy nanocomposites modified with triblock copolymers and carbon nanotubes. Compos Part B 2016;87:343-349.

[29] Salazar A, Prolongo SG, Rodríguez J. The effect of hygrothermal conditions on the fracture toughness of epoxy/poly(styrene-co-allylalcohol) blends. Mater Lett 2010;64:167–169.

[30] Buehler FU, Seferis JC. Effect of reinforcement and solvent content on moisture absorption in epoxy composite materials. Compos Part A 2000;31:741–748.

[31] Alamri H, Low IM. Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites. Mater Design 2012;42:214–222.

[32] Wang L, Wang K, Chen L, He C, Wang L, Zhang Y, Hydrothermal effects on the thermomechanical properties of high performance epoxy/clay nanocomposites. Polym Eng Sci 2006;215-221. DOI 10.1002/pen.20453.

[33] Reuvers NJW, Huinink HP, Fischer HR, Adan OCG. The influence of ions on water transport in nylon 6 films. Polymer 2013;54:5419-5428.

[34] Deroiné M, Duigou AL, Corre YM, Gac PYL, Davies P, César G, Bruzaud S. Accelerated ageing of polylactide in aqueous environments: Comparative study between distilled water and seawater. Polym Degrad Stab 2014;108:319 – 329.

[35] Bal S, Saha S. Effect of sea and distilled water conditioning on the overall mechanical properties of carbon nanotube/epoxy composites. Int J Damage Mech 2015;0(0):1–13.

[36] Mubashar A, Ashcroft IA, Critchlow GW, Crocombe AD. Modelling cyclic moisture uptake in an epoxy adhesive. J Adhesion 2009;85:711-735.

[37] Suryanto H, Marsyahyo E, Irawan YS, Soenoko R, Aminudin. Improvement of interfacial shear strength of mendong fiber (*Fimbristylis globulosa*) reinforced epoxy

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composite using the AC electric fields. International Journal of Polymer Science 2015;2015:Article ID 542376. http://dx.doi.org/10.1155/2015/542376.

[38] ASTM D638-02a. Standard test method for tensile properties of plastics. Phennsylvania: ASTM International, 2003.

[39] ASTM D5045-99. Standard test methods for plane strain fracture toughness and strain energy release rate of plastic materials. Phennsylvania: ASTM International, 2007.

[40] Crank J. The mathematic of diffusion, 2nd ed. London: Oxford University Press, 1975.

[41] de Souza JM, Yoshimura HN, Peres FM, Schön CG. Effect of sample pre-cracking method and notch geometry in plane strain fracture toughness tests as applied to a PMMA resin. Polym Test 2012;31:834–840.

[42] González MG, Cabanelas JC, Baselga J. Applications of FTIR on epoxy resins – identification, monitoring the curing process, phase separation and water uptake. In: T. Theophile, editor. Infrared spectroscopy - materials science, engineering and technology, Rijeka: InTech Europe; 2012, p. 261-284.

[43] Wu L, Hoa SV, Ton-That MT. Effects of water on the curing and properties of epoxy adhesive used for bonding FRP composite sheet to concrete. J Appl Polym Sci 2004; 92:2261–2268.

[44] Choi S, Phantu A, Douglas EP. Effect of water addition on the cure kinetics of an epoxy-amine thermoset. J Polym Sci A1 2011;49:4650–4659.

[45] Choi S, Phantu A, Douglas EP. Evaluation of the complex hygrothermal behaviors of epoxy–amine systems. J Appl Polym Sci 2012;125:3778–3787.

[46] Wang H, Liu Y, Zhang J, Li T, Hu Z, Yu Y. Effect of curing conversion on the water sorption, corrosion resistance and thermo-mechanical properties of epoxy resin. RSC Adv. 2015;5:11358–11370.

[47] Chang TD, Brittain JO. Studies of epoxy resin systems: Part D: Fracture toughness of an epoxy resin: A study of the effect on crosslinking and sub-T_g aging. Polym Eng Sci 1982;22(18):1228-1236.

[48] Kinloch AJ, Young RJ. Fracture behaviour of polymers. London: Applied Science Publishers, 1983.

[49] Greenhalgh ES. Failure analysis and fractography of polymer composites. Cambridge: Woodhead Publishing Limited and CRC Press LLC, 2009.

[50] Sobrinho LL, Ferreira M, Bastian FL. The effects of water absorption on an ester vinyl resin system. Materials Research 2009;12(3):353-361.

[51] Irwin GR. Analysis of stresses and strains near the end of a crack traversing a plate. J Appl Mech 1957;24:361-364.

[52] Quan D, Ivankovic A. Effect of core-shell rubber (CSR) nano-particles on mechanical properties and fracture toughness of an epoxy polymer. Polymer 2015;66:16-28.

[53] Kawaguchi T, Pearson RA. The effect of particle–matrix adhesion on the mechanical behavior of glass filled epoxies. Part 2. A study on fracture toughness. Polymer 2003;44:4239–4247.