

Hygrothermal Ageing of an Epoxy Adhesive Used in FRP Strengthening of Concrete

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ABSTRACT: The efficiency of strengthening of deteriorating concrete through the external bonding of prefabricated fiber reinforced composite strips to the concrete substrate depends on the durability of the adhesive. In this application, adhesives can be exposed to water and salt water, as well as alkali solution resulting from the permeation of water through concrete. This paper presents the results of a durability program designed to study the effects of ageing and environment on the durability of a typical adhesive used in external bonding, through characterization of moisture uptake and cure and investigation by dynamic thermal mechanical analysis, thermogravimetric analysis, differential scanning calorimetry, and tensile testing. It is seen that the adhesive shows two-stage diffusion with primary dete-

rioration taking place in the first phase. Exposure to moisture is seen to cause plasticization and decreases in performance characteristics. The decrease in glass transition temperature due to hygrothermal ageing is such that the level is very close to the Federal Aviation Authority (FAA) recommended value of the wet glass transition temperature being at least 30°F higher than the maximum operation temperature. Overall, the effect of salt solution exposure is seen to have the least effect, whereas exposure to concrete based alkali solution has the greatest deteriorative effect. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2607–2617, 2008

Key words: adhesives; epoxy; durability; ageing; water; salt water; alkali

INTRODUCTION

Fiber reinforced polymer (FRP) composites are being used increasingly in the form of externally bonded reinforcement to aid in the rehabilitation of deteriorating and under-strength structural concrete components. Although the structural effectiveness is based on the fibrous reinforcement in the composite, the efficacy of the technique depends on the bond between the FRP material and the concrete substrate. Among the more common techniques for the application of FRP to the substrate is the adhesive bonding of prefabricated strips to the concrete using a thixotropic ambient temperature-curing adhesive. The use of the prefabricated FRP strip ensures both higher performance characteristic of the composite (through its being processed using techniques such as pultrusion or pulforming, which result in higher aligned fiber volume fractions and elevated temperature cure of the composite) and significantly greater uniformity in the product itself. However, the adhesive is still applied manually in the field and cured under ambient conditions, which often result in incomplete or retarded pro-

gression of cure. This causes a relatively low glass transition temperature, which affects the overall performance and durability of the adhesive and increases the sensitivity of the bond to environmental factors.¹

The presence of hydrophilic groups in epoxy adhesives, caused by hydroxyl groups, which can also react with water molecules to form weak hydrogen bonds, is known to cause degradation due to moisture uptake.^{2,3} In addition, sorbed moisture can result in plasticization, hydrolysis, and irreversible deterioration of the network, resulting in significant degradation of the adhesive itself. Given the expectations of long service-life and the criticality of the rehabilitation scheme to the integrity of the concrete component and structural system, it is crucial that a thorough understanding be developed of the response and the mechanisms of degradation of adhesives used under various environmental exposure conditions.

This article investigates the response of a commonly used two-part adhesive under a variety of aqueous environments with a focus on the development of an understanding of both the potential mechanisms of deterioration and the overall response over a 36-month period of exposure. It is anticipated that the results will provide the basis for the development of predictive models at both the materials and structural levels.

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MATERIALS AND TEST METHODS

The adhesive is a two-component thixotropic mortar based on a solvent free epoxy resin with component A being an aromatic hydrocarbon and component B being an aliphatic amine. (The specific system is sold commercially as Sikadur 30. Designation is provided to enable identification, and is not intended to imply recommendation, endorsement, or implication that the material identified is necessarily the best available.) Both components contain solids in the form of calcium carbonate and silica quartz and are mixed in a 3 : 1 ratio by volume. The system is representative of the high solids content adhesives used for bonding prefabricated carbon/epoxy strips to concrete substrates and is in fact the same system used in Ref. 1. The system has a gel time of about 70 min at 23°C. Adhesive plates of 5-mm thickness were cast on acrylic sheets with dams to provide edges under ambient conditions and were allowed to cure without application of pressure. All specimens were pre-conditioned for 30 days at 23°C and 30% relative humidity (RH) to ensure a uniform baseline, prior to testing and exposure. For purposes of exposure testing appropriate specimens were immersed in deionized water at 23°C, 37.8°C, and 60°C (the three temperatures are used to enable investigation of hygrothermal ageing through accelerated testing), in a 5% NaCl solution at 23°C in an alkaline solution from concrete at 23°C following procedures detailed in Ref. 4 and were also stored under controlled conditions of 23°C and 30% RH for comparison. Tests were conducted over a period of 24 months, with moisture uptake tests being continued for a longer period of 36 months.

Moisture uptake and desorption

Specimens of size $25.4 \times 25.4 \times 5$ mm were used for assessment of moisture uptake using gravimetric means. At periodic intervals, specimens were removed from the exposure environments, dried superficially using paper tissue, weighed, and then returned to solution. For each environmental condition, a minimum of 10 specimens were used to allow for a good statistical representation.

Moisture specimens aged through environmental conditioning for a period of 36 months were carefully cut using a microtome to thicknesses of 0.5 mm, and the central regions were used for characterization of desorption response. Once prepared, the specimens were surface dried, weighed, and then reconditioned in an oven at 60°C until a stable condition of weight was achieved. A minimum of three specimens were used for each time period and condition. The 60°C temperature was selected since water absorption by resins at lower temperature is

desorbed only with difficulty at the same temperature due to the formation of strong interaction of functional groups with water, necessitating a higher temperature for desorption.⁵ It is noted that a similar temperature was used earlier by Zhao and Lucas⁶ for a range of epoxies.

Thermogravimetric analysis (TGA)

To assess the deterioration of primary chemical constituents with temperature and to gain a better understanding of absorbed and inherent moisture content in the material, thermogravimetric analysis was performed using a Mettler Toledo TGA/SDTA 851^e. The initial weight of each TGA specimen was around 10 mg. Dry nitrogen gas was introduced into the test furnace at a flow rate of 10 mL/min. Two different scans were conducted on samples. For the study of moisture samples were heated at 1°C/min from 25 to 250°C, whereas a rate of 10°C/min was used for the temperature scans from 25 to 750°C.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) characterization was conducted to assess both extent and progression of cure. Samples having a mass of 10–20 mg were put in aluminum pans and heated in an inert nitrogen gas environment at rates of 2, 5, 10, and 20°C/min from 25 to 250°C. The flow rate of nitrogen gas was controlled at 10 mL/min.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was conducted to investigate the effects of environmental exposure on the viscoelastic response of the adhesives and to characterize the effects of deterioration through changes in the loss tangent. Specimens of $35 \times 9 \times 5$ mm size were tested in a DMTA at a frequency of 1 Hz and a preload strain of 0.025% with a heating rate of 5°C/min between 30°C and 150°C in a three-point bending mode. Three specimens were used for the characterization of effects at each time period and exposure condition. The peak of the loss tangent curve was used as an indicator of the glass transition temperature (T_g).

Mechanical characterization

The effects of exposure on tensile characteristics were assessed through the use of dog-bone shaped specimens following ASTM D638 at a loading rate of 2 mm/min. A minimum of five replicates were used for each time period and exposure condition.

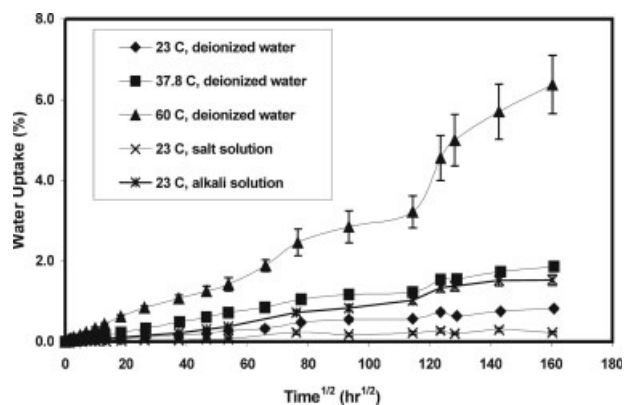


Figure 1 Water uptake curves.

RESULTS AND DISCUSSION

Moisture uptake

The diffusion of water into an adhesive is intrinsically related to the polymer structure of the adhesive, water-polymer interaction, and the degradation processes resulting thereof. Adhesives can show both Fickian and non-Fickian moisture absorption characteristics with the former occurring when the diffusion rate dominates uptake response, whereas the latter is seen when relaxation characteristics dominate. In some polymers, the response is modeled better by a two-stage diffusion model with the first and second stages being diffusion- and relaxation-controlled, respectively.⁷ The two-stage diffusion model takes consideration of the polymer structural relaxation induced by absorbed water and has been used with some success in explaining non-Fickian moisture response in polymers and polymeric composites.^{8,9}

Water uptake in the adhesive appears to follow the two-stage diffusion model, wherein moisture uptake, M_t , at time, t , can be approximated following⁸ as

$$M_t = M_\infty \left(1 + k\sqrt{t} \right) \left\{ 1 - \exp \left[-7.3 \left(\frac{Dt}{h^2} \right)^{0.75} \right] \right\} \quad (1)$$

where M_∞ and D are the equilibrium moisture uptake level and diffusion coefficient associated with

stage 1 diffusion; k is a time-dependent coefficient representing the rate of polymer relaxation due to water uptake; and h is the specimen thickness. It is emphasized that these parameters are different from those associated with conventional Fickian diffusion since the equilibrium level considered herein is just that associated with stage 1 equilibrium rather than with final equilibrium. It should also be noted, in this vein, that although a 36-month period of study was used, the time may not have been sufficient for attainment of final equilibrium in all cases. Diffusion parameters were obtained through the best fitting of the water uptake curves in Figure 1 with Eq. (1), and characteristics such as the maximum water uptake associated with the time period of study (M_{\max}), the equilibrium water uptake in stage 1 (M_∞), the diffusivities D in stage 1, and the polymer relaxation related parameter k in stage 2 are listed in Table I for the different immersion conditions studied. It can be seen that both the equilibrium water uptake in stage 1, M_∞ , and the stage 1 diffusion coefficient, D , increase with increase in temperature of immersion in deionized water although the values of the stage 1 equilibrium moisture contents are close to each other. The dependence of M_∞ on the immersion temperature can be linked to the polarity of the polymer itself.¹⁰ The activation energy for stage 1 (Fickian type diffusion), E_d , which provides an indication of the energy barrier that must be overcome for moisture diffusion, can be determined to be 57.47 kJ/mol, using the Arrhenius relation

$$D = D_0 e^{\left(\frac{E_d}{RT} \right)} \quad (2)$$

where D_0 is a constant, R is the universal gas constant (8.31 J/mol K), and T is the temperature expressed in degrees Kelvin.

Stage 2 water uptake is assumed to be relaxation dominated and can be described by the parameter k , which is related to the molecular relaxation due to water absorption.⁹ As can be seen in Table I, k increases, as expected, with the immersion temperature due to the acceleration of molecular relaxation. The variation of k with the immersion temperature follows the classical Arrhenius equation, and the activation energy can be determined as 72.43 kJ/mol

TABLE I
Parameters from Two-Stage Diffusion Analysis of Absorption Data

Immersion conditions	M_{\max} (%)	M_∞ (%) in stage 1	D (mm ² /s) in stage 1	k (1/s ^{0.5}) in stage 2
23°C Deionized water	0.83	0.76	3.41×10^{-8}	2.00×10^{-5}
37.8°C Deionized water	1.86	0.78	1.12×10^{-7}	1.40×10^{-4}
60°C Deionized water	6.38	0.86	4.59×10^{-7}	5.50×10^{-4}
23°C Salt solution	0.29	0.20	6.15×10^{-8}	4.00×10^{-5}
23°C Alkali solution	1.53	0.67	4.40×10^{-8}	1.70×10^{-4}

by plotting $\ln(k)$ versus $(1/T)$. It must be remembered that although stage 2 is dominated by polymer relaxation, diffusion is still taking place. By isolating the second stage and assuming a Fickian diffusion response, the activation energy of diffusion can be determined to be 13.68 kJ/mol, by applying Eq. (2) to the apparent diffusivities for stage 2. The much smaller value of activation energy than that of the stage 1 indicates the difference in the mechanism of water uptake in stage 2 from that of stage 1.

Since materials used in civil infrastructure can be exposed to saline (from sea water or marine conditions) and alkaline (from the permeation of water through concrete) solutions, it is of interest to assess the effects of these solutions on moisture uptake as well. It is noted that although samples immersed in 23°C salt solution have higher diffusivity than those immersed in 23°C deionized water and alkali solutions, and the overall level of uptake is lower (35% and 19% of the maximum levels recorded for the deionized water and alkali solution at 23°C, respectively). The higher diffusivity associated with lower water uptake in salt solution was also reported by Kahraman et al.,¹¹ who attributed the lower level of water uptake in the salt solution to a reverse osmosis mechanism. The higher values of water uptake in the alkali solution are due to a higher level of deterioration caused by the alkali salts at the adhesive-solid filler interface and within the bulk of the adhesive itself and is similar to the deteriorative mechanism described earlier in glass fiber reinforced composites.¹²

To better understand the moisture uptake kinetics of the adhesive desorption of film samples (~ 0.5 mm thick), these were cut from the central part of moisture specimens after 36 months immersion in various conditions at 60°C. As can be seen in Figure 2, the desorption curves are Fickian in nature. Diffusion coefficients for desorption determined using

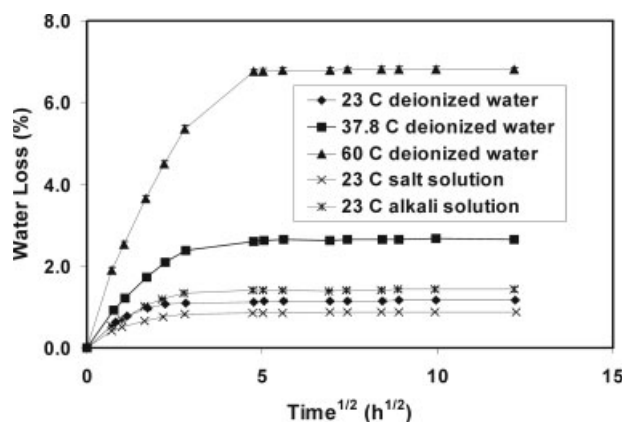


Figure 2 Desorption curves.

TABLE II
Diffusion Parameters Related to Desorption

Immersion conditions	D (mm^2/s)	M_m (%)
23°C Deionized water	4.49×10^{-6}	1.14
37.8°C Deionized water	2.05×10^{-6}	2.64
60°C Deionized water	1.31×10^{-6}	6.81
23°C Salt solution	4.01×10^{-6}	0.86
23°C Alkali solution	2.81×10^{-6}	1.41

$$m = m_0 - m_0 \left(1 - \frac{1}{1 + M_m} \right) \times \left\{ 1 - \exp \left[-7.3 \left(\frac{Dt}{h^2} \right)^{0.75} \right] \right\} \quad (3)$$

following Ref. 10, where m is the weight at drying time, t , m_0 is the original weight of the wet film (corresponding to a drying time of 0), and M_m is the equilibrium desorbed moisture content, which are listed in Table II. As shown in Table II, the diffusion coefficients resulting from the five immersion conditions are of the same order of magnitude, indicating that there is not much difference in the moisture diffusing rate for these samples at 60°C. The difference between the equilibrium water content resulting from the desorption test (M_m) and the maximum water uptake (M_{max}) from absorption is in line with the existence of tightly bond water molecules within the material prior to immersion, which can only be removed at higher temperatures.⁶

Distribution of water uptake in the adhesive was studied via TGA on film samples (~ 0.5 mm thick) cut from both the skin and core of moisture specimens after 36 months of immersion in different conditions. The water contents of skin and core samples immersed in different conditions are listed in Table III, indicating the obvious differences arising from the skin and core for samples immersed in deionized water, salt solution, and alkali solution at 23°C and in deionized water at 37.8°C. The difference in water content between the skin and core is in line with results reported for two-stage diffusion¹³ and used by Bao et al.⁸ in proposing the use of Eq. (1) to characterize parameters associated with stage 1 dif-

TABLE III
Water Content of Skin and Core Regions

Conditions	Water content (%)	
	Skin	Core
Ambient	0.35	0.25
23°C Deionized water	2.45	0.90
23°C Salt solution	1.54	0.88
23°C Alkali solution	3.66	1.62
37.8°C Deionized water	4.55	2.38
60°C Deionized water	6.50	5.93

fusion. It should be noted that the moisture content of core samples from TGA is comparable to that from characterization through desorption. For these conditions, the much larger water content of skin samples indicates that water uptake had not reached equilibrium even after 36 months of immersion. In contrast, the difference between the water content in the skin and core of the samples immersed in deionized water at 60°C is small, with the level in the samples from the skin region being just slightly higher than that of the core, indicating that the uptake is nearing true saturation at the end of the 36-month period of immersion studied in this investigation.

It is noted that the water content of both the skin and core samples for the coupons immersed in the salt solution are the lowest among the three aqueous solutions at 23°C, which is consistent with the previous absorption and desorption results from the bulk material.

Characterization of viscoelastic response

DMTA was performed to determine the influence of hygrothermal ageing on the viscoelastic response of the adhesive. The loss factor curves for all specimens aged in aqueous solutions, with the exception of those aged in the alkali solution, show a split in the $\tan \delta$ peaks as a result of immersion. Figure 3 compares typical loss factor ($\tan \delta$) curves for unaged specimens and those immersed in deionized water at 60°C. It is noted that at the end of the period of investigation the upper and lower peaks for specimens in deionized water at 23°C were 78.1°C and 96.9°C, respectively (with standard deviations of 0.26°C and 0.17°C, respectively), while the corresponding values for samples aged in deionized water at 37.8°C were 84.7°C and 111.9°C, respectively (with standard deviations of 0.46°C and 1.06°C, respectively) and those aged in deionized water at 60°C showed values of 85.5°C and 118.4°C, respectively (with standard deviations of 1.31°C and 0.84°C, respectively). Samples aged in salt solution over the same period showed upper and lower peaks at 79.1°C and 101.9°C, respectively (with standard deviations of 0.40°C and 0.74°C, respectively). The lack of a split in the alkali solution aged specimens despite the higher levels of water uptake as compared to the specimens aged in deionized water and salt solution again suggest a domination of interface related deterioration, rather than plasticization. The split of $\tan \delta$ peaks has been frequently reported for water/moisture aged polymers and/or polymer composites^{10,14–17} with the split being attributed either to the drying effect of the DMTA on specimens^{10,16,17} or to heterogeneous plasticization.^{14,15} To elucidate the mechanisms in the current investiga-

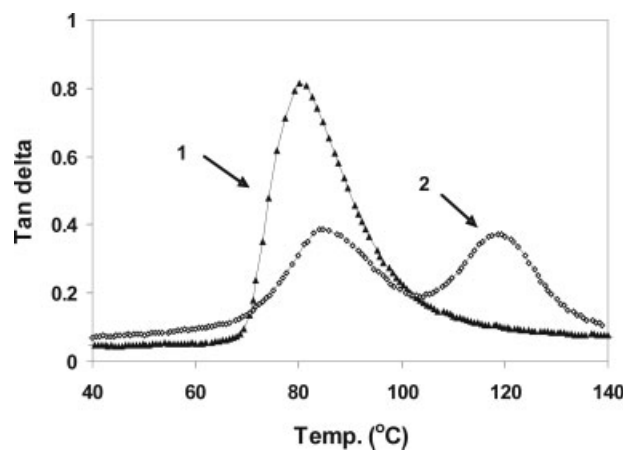


Figure 3 DMTA $\tan \delta$ spectra: (1) before aging, (2) after immersion in deionized water at 60°C for 24 months.

tion, DMTA tests were performed additionally on specimens vacuum dried at 60°C. As shown in Figure 4, after vacuum drying at 60°C, the hygrothermally aged specimens show a well defined $\tan \delta$ peak, the position of which is very close to the upper $\tan \delta$ peak of the wet specimens. Based on this the lower temperature $\tan \delta$ peak is believed to be due to the water-plasticized fraction of the specimen, while the upper $\tan \delta$ peak is due to the dried fraction of the specimen. This supports the drying effect mechanism proposed in Refs. 10 and 16. The upper T_g therefore represents the dried fraction of the specimen and reflects the crosslinkage of epoxy adhesive. Increasing immersion temperatures prompts a post-curing effect, leading to the higher glass transition temperatures. It should be noted that the specimens hygrothermally aged in deionized water at 37.8 and 60°C showed insignificant variation in T_g after 6 months of immersion, suggesting completion of the slow temperature induced postcure at that time.

It is, however, of interest to note that unlike in earlier studies reporting this phenomena^{10,14–17} where the upper T_g had a value similar to that of unexposed samples, thus representing the less plasticized phase (or more dried structure), the adhesive specimens show a lower T_g that is close to the T_g of unexposed samples. To understand this phenomenon, specimens placed under controlled conditions of 23°C and 30% relative humidity for periods longer than 28 months were vacuum dried at 60°C until their weight stabilized and were then tested by DMTA. It is of interest to note that the T_g of these vacuum dried control specimens, which is around 103°C, is much higher than the T_g of control specimen tested as it is, which is around 86°C (Fig. 5). It should be noted that the T_g of vacuum dried control samples is close to upper T_g , indicating that the adhesive in this study is hydrophilic and has an initial apparent moisture content, which remains even

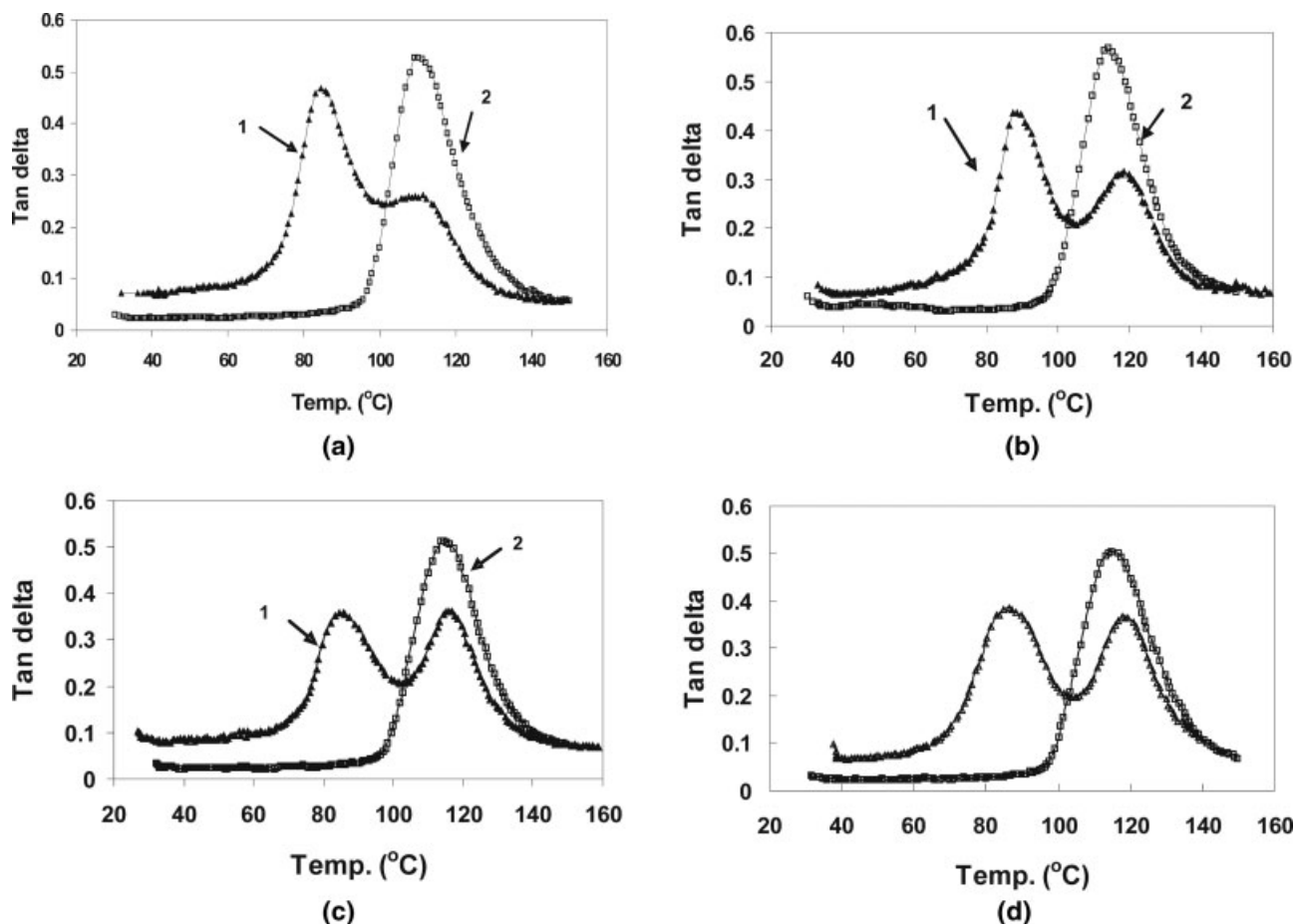


Figure 4 DMTA $\tan \delta$ spectra of specimens immersed in deionized water at 60°C; (1) tested immediately after removal from immersion; (2) tested after drying in vacuum; (a) 6 months; (b) 12 months; (c) 18 months; (d) 24 months.

under the low relative humidity of the control conditions. The shift of T_g to lower temperature is caused by this apparent moisture content. The existence of moisture in samples under ambient conditions had earlier been indicated through mass loss via the TGA (Table III).

Over the period of investigation, the unexposed specimens show an increase in T_g from an initial value of 80.9°C to a high of 86.3°C due to slow progression of cure, a majority of which occurs in the first 6 months. Specimens immersed in deionized water, salt solution, and alkali solution at 23°C show a slight decrease (5%, 4% and 5.4%, respectively) in the first 6 months after which there is insignificant further change, indicating that the effects are only due to the initial plasticization. For samples aged in deionized water at 37.8°C and 60°C, the lower T_g s increase after the first 6 months by about 9% and then level off after a very small decrease, indicating that the initial effect of elevated temperature exposure causes the effect of post-cure to dominate over that of plasticization. It should be noted that the initial period of decrease matches with the initial time period over which stage 1 diffusion occurs as shown in the moisture uptake

curves in Figure 1. The role of absorbed water as a plasticizer can be further characterized in terms of decreases in storage modulus E' in the glassy state (taken at a constant level of T_g 40°C) at the same period of time as shown in Figure 6.

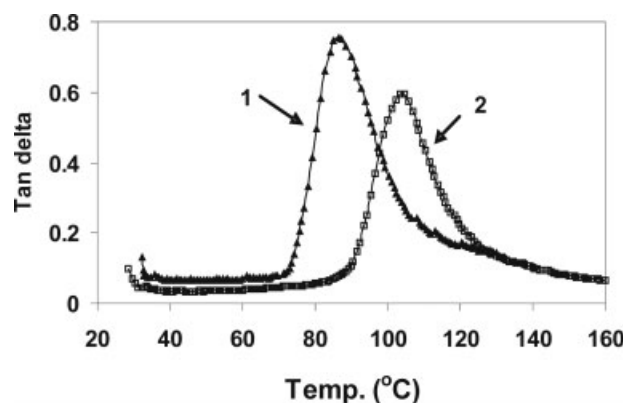


Figure 5 $\tan \delta$ trace after 24 months in controlled conditions (23°C, 30% humidity); (1) tested immediately after removal from conditioning; (2) tested after drying in vacuum.

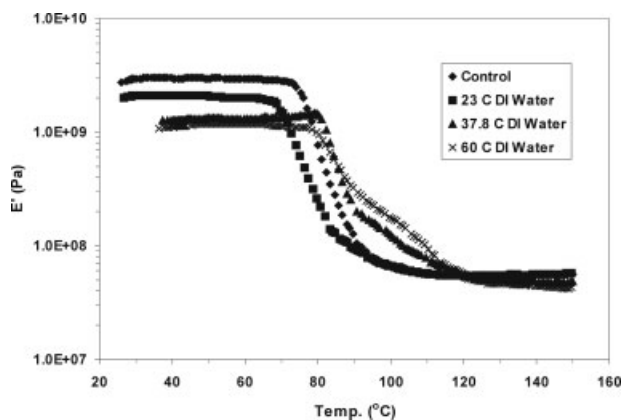


Figure 6 Effect of 6-months exposure on the flexural storage modulus.

The loss tangent as determined through DMTA testing is defined as the ratio of the loss modulus to the storage modulus. The variation of $\tan \delta$ over time can be complicated by aspects such as progression of cure, moisture induced plasticization, extraction of low molecular weight species through leaching under conditions of prolonged immersion in specific solutions, overall materials degradation, and interface deterioration.^{18,19} Figure 7 plots the variation of $\tan \delta$ values at lower T_g over time for samples in different conditions, again indicating that the maximum change occurs over the first 6 months of immersion, which coincides with the period of phase 1 diffusion. As can be seen, immersion in aqueous solutions causes a decrease in value, with the maximum decrease resulting from immersion in deionized water at the two higher temperatures.

To date there is very little guidance on the required relation between the glass transition temperature of a cured adhesive system and the expected service temperature for a strengthened system. Considering that

the efficiency of the externally bonded FRP is inherently dependent on the integrity of the bond between the FRP and the concrete, any change in the response of the adhesive could translate to changes in the structural response of the strengthened system. The Federal Aviation Authority (FAA) recommends that the wet glass transition temperature of an adhesive be at least 30°F higher than the maximum operation temperature.²⁰ Using the commonly used maximum temperature for bridge structures of 60°C (140°F), the requirement for the adhesive would be 76.7°C (170°F), which is not substantially below the value achieved at phase 1 and phase 2 equilibrium for the material, indicating that although the adhesive meets this requirement, a retardation of cure, or incomplete initial cure could result in the requirement not being met. Also, considering that full equilibrium under stage 2 diffusion had not been achieved over the period of study, there is a likelihood that the glass transition temperature could be further depressed.

Composition

TGA scans were conducted on specimens cut from hygrothermally aged samples between 25 and 750°C. As can be seen from Figure 8, the epoxy adhesive experienced three major weight losses. The onset temperatures of each weight loss for different conditions are summarized in Table IV. The first weight loss can be assigned to the evaporation of the water in the adhesive since the onset temperature of the first deviation of the TGA curve is close to 100°C. TGA results on vacuum dried samples (samples after reaching equilibrium in the desorption test) indicating no further weight loss till after 100°C further supports this. The onset temperature of the second weight loss is around 330°C, and this is attributed to

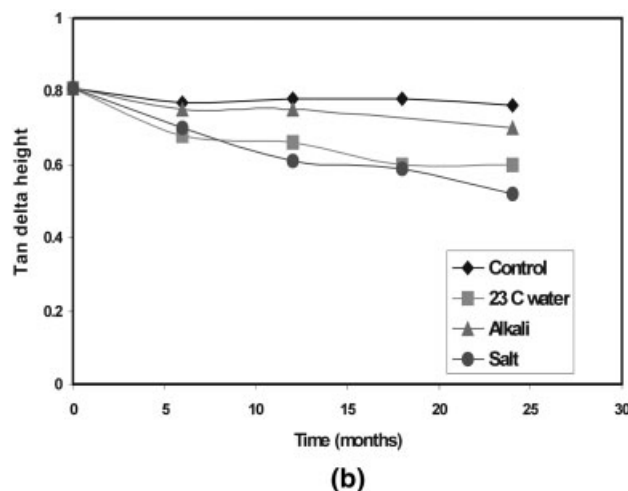
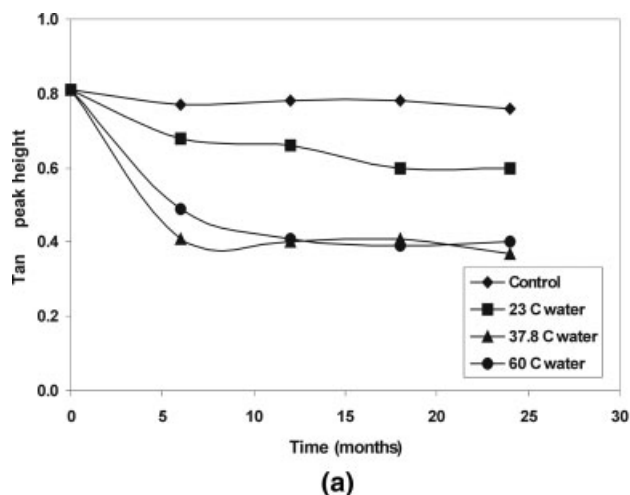


Figure 7 Change in $\tan \delta$ value (determined at the lower T_g) as a function of ageing time based on (a) the temperature of immersion in deionized water and (b) the type of aqueous solution at 23°C.

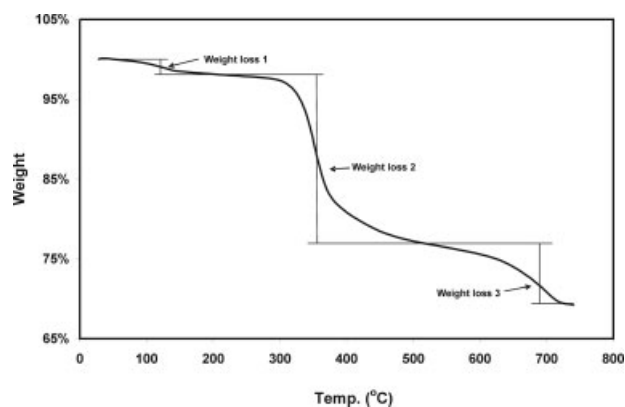


Figure 8 Representative TGA trace of the epoxy adhesive showing three major weight loss transitions between 25 and 750°C.

the decomposition of the aromatic hydrocarbon component. This was confirmed by a separate TGA scan conducted on the two components, A and B, used to make this adhesive. A transition due to mass loss was noted around 330°C for component A. Although the exact nature of the transition due to the third weight loss in the TGA scan is uncertain, it is noted that the temperature of the transition is beyond the range of the organic polymer decomposition (usually between 150 and 500°C) and close to that for the onset of decomposition of the inorganic fillers used in the adhesive.

Cure

The characterization of the extent, and progression, of cure is important to the study of durability of polymeric adhesives, since cure not only affects moisture uptake and sensitivity to deterioration but also the thermal and mechanical properties, and consequently the durability of polymeric materials.¹ The cure of the epoxy adhesive was studied through the nonisothermal multiple-heating-rate method using DSC following the procedure recommended by Kissinger.^{21,22} The multiple-heating-rate method assumes that the conversion value is constant at the peak exotherm temperature in a DSC analysis and is independent of

the heating rate.^{23,24} Following the Kissinger method, the activation energy E can be obtained as²⁵:

$$E = -R \frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} \quad (4)$$

where ϕ is the heating rate, T_p is the peak exotherm temperature, and R is the universal gas constant (8.3 J/mol K). Since curing reactions are complex, generally involving multiple mechanisms, the value of the activation energy, E , obtained by the use of Eq. (3) must be understood as a representation of the overall activation energy of all the complex reactions that occur during curing. It should also be noted that although the Kissinger method assumes that the DSC peak exotherm is iso-conversional and hence its value is not dependent on the heating rate, this assumption is not necessarily valid for all systems and has to be verified.²⁶

Figure 9 shows relative heat flow traces from dynamic DSC tests of the epoxy adhesive run at rates of 2, 5, 10, and 20°C/min. It is evident that the peak of the exotherms occurred at increasingly higher temperatures as the heating rate was increased. Analysis of the exotherms using Eq. (4) result in an activation energy of 50.5 kJ/mol. The linear relationship between $\ln(\phi/T_p^2)$ and $1/T_p$, depicted in Figure 10, confirms the validity of the assumption necessary for use of the Kissinger method. In addition, the peak conversion values obtained at the peak exotherm for the different heating rates, as listed in Table V, are extremely close, further confirming the validity of the use of the Kissinger method for the epoxy adhesive under study.

Cure progression of the epoxy adhesive in the first week is shown in Figure 11 with the percentage of conversion (α_t) and T_g determined from the corresponding DSC runs being listed in Table VI. It can be seen that the level of cure, α_t , only reaches 90% in 24 h, and exceeds 95% only after a period of a week, indicating that an extended period of time is necessary to completely cure the adhesive under room temperature conditions. DSC scans run over extended periods of time show a very slow further increase in α_t beyond this level, with full cure being achieved in about

TABLE IV
Onset Temperatures from TGA

Conditions	Weight loss 1 T_{onset} (°C)	Weight loss 2 T_{onset} (°C)	Weight loss 3 T_{onset} (°C)
Control	86.1	332.8	629.2
23°C Deionized water	85.7	332.0	660.7
37.8°C Deionized water	88.8	330.4	683.5
60°C Deionized water	91.2	331.3	629.2
23°C Salt solution	86.8	326.9	636.5
23°C Alkali solution	86.4	329.2	644.6

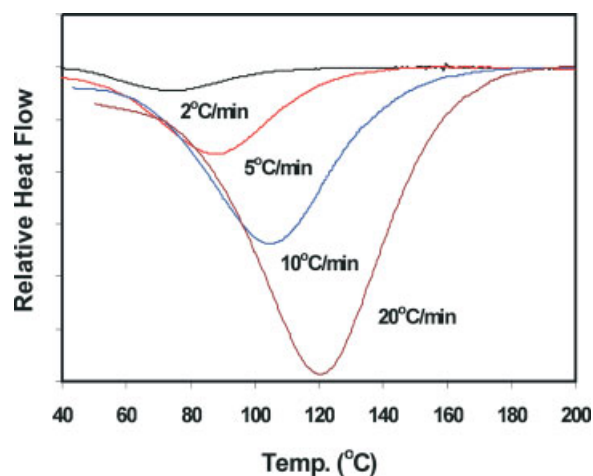


Figure 9 DSC cure exotherms at different rates of heating. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

12 months, indicating the potential for retardation of cure (or incomplete cure) due to moisture uptake under ambient conditions during this period.

Tensile characteristics

As seen in Figure 12(a–d), the results of tensile testing of the adhesive samples show that progression of cure in the control samples results in a slight increase of 17% in the modulus over the first 12 months, while there the change in the tensile strength is only of the order of about 7%. It is noted that there is insignificant further change beyond this point, although the scatter in data appears to increase with time. Immersion in deionized water causes a significant decrease in both strength and modulus, with the effect of the highest temperature of immersion (60°C) being the greatest, with very little difference in effect between the other two temperatures. The retention in tensile strength at the end of

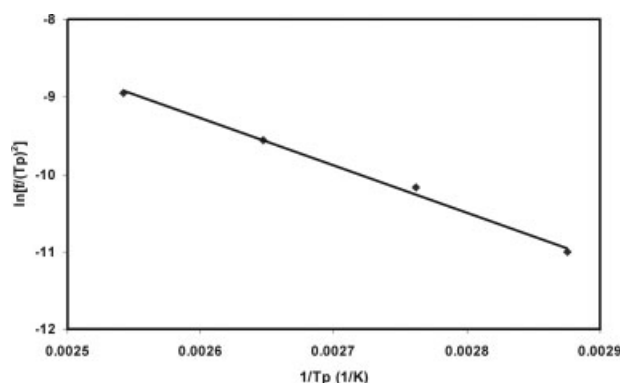


Figure 10 Determination of the activation energy following the Kissinger method.

TABLE V
Conversion at the Peak Exotherm for Different Heating Rates

Heating rate (°C/min)	Peak temperature (°C)	Peak conversion (%)
2	74.80	49.61
5	89.06	49.84
10	104.80	49.29
20	120.38	49.68

the 24-month period of immersion in deionized water was 57%, 55.5%, and 31%, respectively, and the retention in tensile modulus was 63.8%, 60%, and 31.7%, respectively. This corresponds with moisture absorption/desorption results wherein the water uptake of adhesive samples immersed in 60°C deionized water was much higher than that under the other conditions. This suggests a greater level of damage development within the bulk adhesive and at the interfaces with fillers resulting in matrix microcracking. It is noted that a significant amount of the overall deterioration took place within the first 6 months of immersion, corresponding to phase 1 diffusion. Overall between 59 and 65% of the drop in modulus was in this period, whereas that in strength ranged from 55% at the lower temperature to 77% at the highest temperature. Thus, both changes in tensile characteristics and glass transition temperature are primarily determined within the phase 1 diffusion period with further changes being gradual, as was noted earlier by Popineau et al.²⁷

A comparison of trends in Figure 12(b,c) shows that initial rates of decrease for the samples in salt solution are lower than those in deionized water and alkali solution (which are almost identical) over the 24-month period of immersion the samples in alkali solution show the maximum deterioration in both tensile strength and modulus. The retention in tensile strength at the end of the 24-month period of immersion at 23°C is 57%, 63.9%, and 47.4%, respectively,

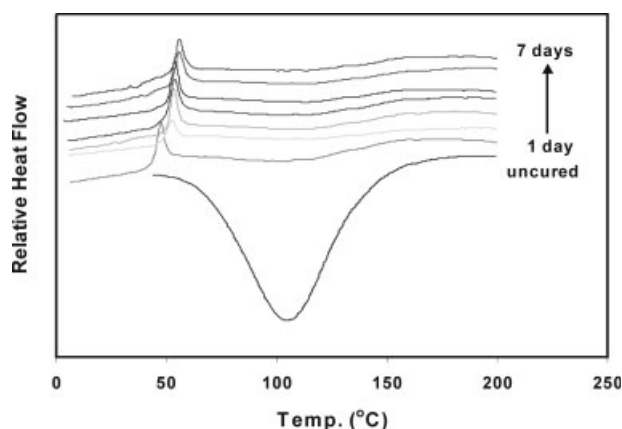


Figure 11 Cure progression of the epoxy adhesive.

TABLE VI
 T_g from DSC during Cure Progression of the Epoxy Adhesive

Cure time (days)	1	2	3	4	5	6	7
Percentage of conversion (α_t)	90.92	92.01	92.94	93.67	94.20	94.69	95.07
T_g ($^{\circ}\text{C}$)	45.7	49.7	51.4	51.8	52.2	53.9	54.2

for samples in deionized water, salt solution, and alkali solution, respectively, whereas the level of retention in tensile modulus at the end of the same period of immersion is 63.8%, 70.0%, and 50.2%, respectively. Correlations between levels and rates of water uptake and mechanical property degradation for these immersion conditions are obvious with an increasing order of water uptake for the three different immersion conditions being salt solution, deionized water, and alkali solution respectively.

SUMMARY AND CONCLUSIONS

Water uptake in the adhesive appears to follow the two-stage diffusion model with the uptake in stage 1 correlating well with a significant portion of the deg-

radation in the characteristics of the adhesive. Specimens immersed in deionized water, salt solution, and alkali solution at 23 $^{\circ}\text{C}$ show a slight decrease in T_g in the first 6 months, which corresponds to the period during which stage 1 diffusion occurs, after which there is insignificant further change, indicating that the effects are only due to the initial plasticization. It is noted that the hygrothermally aged materials show a glass transition temperature that is not significantly higher than the level recommended by the FAA for safe use, indicating that although the adhesive meets the requirement, a retardation of cure or incomplete initial cure could result in the requirement not being met, thereby raising concern regarding the long-term integrity of the strengthening system. It is seen that immersion in deionized water causes a significant decrease in both strength

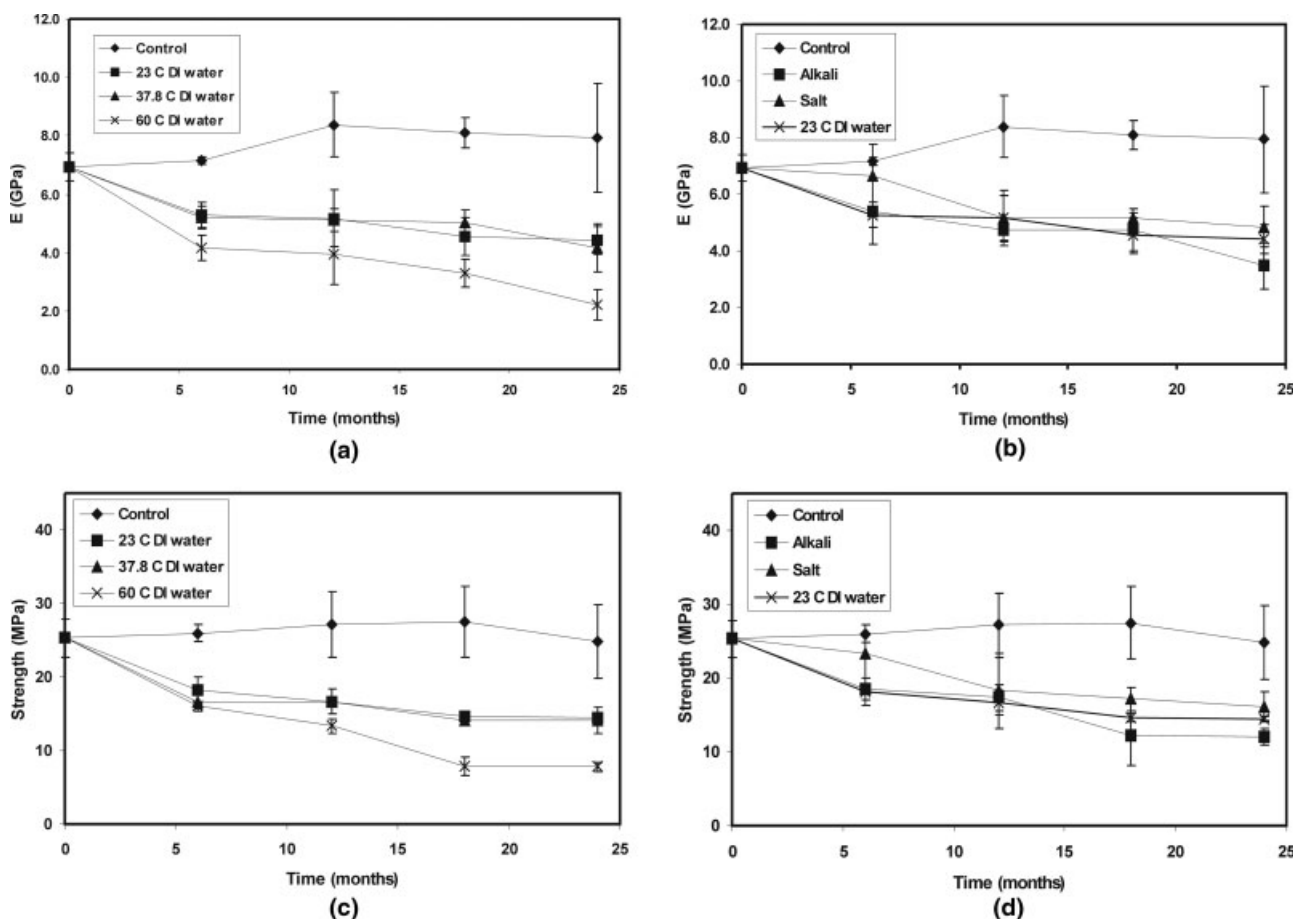


Figure 12 Change in tensile characteristics as a function of ageing time. Tensile modulus based (a) on the temperature of immersion in deionized water and (b) on the type of aqueous solution at 23 $^{\circ}\text{C}$. Tensile strength based (c) on the temperature of immersion in deionized water and (d) on the type of aqueous solution at 23 $^{\circ}\text{C}$.

and modulus, with a significant amount of the overall deterioration taking place within the first 6 months of immersion, corresponding to phase 1 diffusion. While initial rates of decrease for the samples in salt solution are lower than those in deionized water and alkali solution (which are almost identical) over the 24-month period of immersion, the samples in alkali solution show the maximum deterioration in both tensile strength and modulus. Correlations between levels and rates of water uptake and mechanical property degradation for these immersion conditions are obvious with an increasing order of water uptake for the three different immersion conditions being salt solution, deionized water, and alkali solution respectively.

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