

Role of hygrothermal ageing temperature and time in degrading the fracture toughness of highly cross-linked epoxy

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Abstract

The evolution of plane strain fracture toughness in highly cross-linked epoxy was assessed for different hygrothermal aging temperatures (25°C, 50°C, 75°C) and durations (0-75 days). Water absorption increased with hygrothermal aging, but at a diminishing rate, without saturating. Some absorbed water persisted despite prolonged drying. Thermogravimetric analysis (TGA) revealed that the epoxy decomposition temperature decreased with hygrothermal ageing. ¹³C solid-state NMR revealed an increase in the de-shielding of carbon atoms in the vicinity of electronegative elements like oxygen, with increasing hygrothermal ageing severity, indicating the development of intermolecular hydrogen bonding. X-ray photoelectron spectroscopy (XPS) tracked the chemical bonding state of carbon using a narrow scan on the C1s binding energy region. It is observed that with hygrothermal ageing there was a decrease in C-C/C=C groups indicating main chain scission through hydrolysis and an increase in the C-O species indicating formation of alcohols as hydrolysis reaction products. Thus, the retained water was involved in hydrogen bonding and chemical reactions with the epoxy. With increasing hygrothermal ageing severity, the fracture toughness decreased. This was consistent with the fracture surface images that showed higher distance amongst crack stretch marks (formed on the fracture surface through crazing) in specimens with lower toughness.

Keywords: Epoxy; hygrothermal ageing; fracture toughness; crazing

1. Introduction

The mechanical properties of carbon fiber reinforced thermosetting plastics (CFRP) is known to degrade with an increase in the harshness of the service environment specially when exposed to high humidity at an elevated temperature[1–9]. While carbon fibers (CF) are not affected by moisture and can easily withstand temperatures above 100°C[1], the primary cause of the decline in mechanical properties in Carbon Fiber CFRPs is due to the hygrothermal degradation of the epoxy matrix, deterioration at the interfaces between the fibers and the matrix, and non-uniform swelling within the composite, where certain regions have microscopically higher epoxy content [3–5]. In this study we restrict our attention to the degradation of a laminating grade epoxy subjected to hygrothermal ageing. The evolution of uniaxial tensile and compressive strength (damage resistance ability) with hygrothermal ageing has received limited attention and a few recent studies have attempted to link the structural changes happening in the epoxy during hygrothermal ageing with the evolution of mechanical properties[10–12]. The assessment of epoxy's damage tolerance, particularly regarding how plane

strain fracture toughness evolves during hygrothermal aging, has only been explored in a limited number of studies with relatively short aging durations [13,14].

The intake of water into the epoxy matrix is described as a combination of diffusion and reaction process [13,15–17]. Capiel et al.[18,19] have studied the degradation caused in thin anhydride cured epoxy specimens when subjected to long duration (1 months to ~ 2 years) of hygrothermal ageing at elevated temperature. They have identified that the epoxy's main chain undergoes hydrolysis leading to formation of carboxylic acids and alcohols. The reaction products, catalyse further reaction and make room for more water intake. Hence, this diffusion + reaction mechanism prevents water saturation even after long duration of hygrothermal ageing. Zhou and Lucas [20,21] utilizing the nuclear magnetic resonance (NMR) spectroscopy along with thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) have identified that water molecules can exist in epoxy in different states. A portion of the absorbed water gets easily removed on ambient drying while some water molecules may be retained in the epoxy matrix and exist in two type of bonding states with different mobility. Water that is bonded in Type I, formed typically through simple hydrogen bonding, can be readily eliminated through oven drying. Type I bonded water is known to cause plasticization in the epoxy matrix [20–22]. which is accompanied by the formation of low molecular components and a subsequent drop in the glass transition temperature. Additionally, Type II bonded water engages in intricate hydrogen bonding with the epoxy's polar groups, promoting the development of a secondary cross-link network [20–24]. Longer periods of hygrothermal aging at higher temperatures result in an increased presence of Type II bonded water. These structural alterations in epoxy during hygrothermal aging are likely to affect its strength and toughness.

Salah and Singh [13] studied the effect of moisture and temperature on the fracture properties of epoxy with non-fluorinated clay nano fillers. They hygrothermally aged the specimens in boiling water for 24 hours and dried them in an oven at 110°C for 6 hours and tested specimens in the as-cast condition, moist condition and after drying the moist specimen. They observed that the fracture toughness and the flexural modules decreased for the moist specimens as compared to the as cast conditions. If the moist specimens were oven-dried before the test, a fraction of the decrease in fracture toughness and flexural modulus was recovered. They also observed the formation of a network of micro-cracks on the fracture surface of moist and dried specimens and speculated that water acted as a crazing agent, weakening the matrix and triggered the formation of micro-crack network even far ahead of the pre-crack region. Quino et al. [14] studied the fracture toughness of epoxy using compact tension specimen following the ASTM D5045 test method after ageing the specimens in a climate chamber maintained at 70°C and 90% relative humidity for a maximum duration of 20 days [25]. Because of the short duration of hygrothermal ageing after which the specimens were extracted for testing and a large specimen thickness of 7.5 mm, the moisture distribution was not uniform. Hence Quino et al. [14] resorted to a post processing method of determination of the local content of moisture ahead of the crack tip. Hence, they followed a diffusion + reaction water transport scheme similar to El Yagoubi, Jalal, et al.[13] and determined the moisture present in a region just ahead of the crack tip. The diffusion + reaction water transport model by El Yagoubi, Jalal, et al.[13] describes water movement to be a competition between diffusion and the reaction, wherein the local diffusivity and solubility of moisture is a function of the how the reaction advances locally. Quino et al. [14] observed a two stage behaviour in the evolution of fracture toughness with hygrothermal ageing. In the first stage, the fracture toughness decreased rapidly where as in the second stage, the fracture toughness remained

constant. Although, it is evident that the fracture toughness does decrease with hygrothermal ageing, both the studies lacked long duration of hygrothermal ageing, hygrothermal ageing at different temperatures and progressive investigation.

In the present study, we have provided a systematic investigation of the evolution of plane strain fracture toughness with varying hygrothermal ageing time (0 -75 days) and temperature (25°C, 50°C and 75°C) for low crack tip strain rates where disentanglement crazing based fracture is expected to dominate. The structural changes in epoxy have been examined using nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) techniques. The findings suggest that as the severity of hygrothermal aging increases, the fracture toughness continues to decrease. These changes in fracture toughness are associated with the structural modifications in the epoxy and the morphology of the fractured surface.

2. Materials and methods

2.1. Specimen preparation

In this study, we utilized an epoxy-hardener system provided by Fine Finish Organics Pvt. Ltd, India. Specifically, 100 units by weight of a DGEBA (Bisphenol A diglycidyl ether) based epoxy (EPOFINE ® - 5052) was combined with 38 units by weight of an amine-based hardener (FINEHARD TM – 5052). The mixture was stirred meticulously to achieve thorough and uniform mixing while minimizing the presence of trapped air. In order to eliminate any trapped air, the mixture was placed in a vacuum chamber for 30 minutes to undergo degassing. Following the degassing process, the solution was poured into molds constructed from silicone rubber. The first step of curing happened in controlled lab environment with temperature at 25°C and relative humidity at < 30% for a period of 24 hours followed by the second step of curing in a vacuum oven at 100°C for a period of 2 hours. The mold preparation was such that the epoxy specimens were cast directly in the single edge notch bend (SENB) configuration suitable for fracture toughness testing with a prior machined notch as detailed in Mishra et al.[26]. The weight measurements and time schedule as supplied by the vendor were rigorously followed during the epoxy specimen preparation to ensure proper curing. The glass transition temperature(T_G) of the as prepared specimen was measured using the differential scanning calorimetric (DSC) technique and determined to be 105°C. The value of the T_G was exactly same to the T_G reported in the material specification sheet provided by Fine Finish Organics Pvt. Ltd.

2.2. The hygrothermal ageing setup

Hygrothermal aging was conducted by placing the as prepared specimens into deionized (DI) water baths maintained at three distinct temperatures: controlled ambient temperature (25°C), 50°C, and 75°C. The weight of the specimens was recorded at periodic intervals to track the change in specimen weight due to water intake as the hygrothermal ageing progressed. Before measuring the weight, the specimen underwent a thorough wiping with tissue paper to eliminate any surface moisture. The specimens' weight was then determined using a digital weighing balance with a precision of 0.0002 g. The change in mass percentage was calculated using the formula below.

Equation 1

$$M_t \text{ (in \%)} = (W_t - W_0)/W_0$$

Where, M_t is the % change in mass of the specimen at time 't' with respect to the initial mass of the specimen. W_t and W_0 is the measured weight of the specimen at time 't' and the measured initial weight respectively.

A predefined number of specimens was removed from each bath at predefined intervals of hygrothermal ageing, dried until there was no change in specimen mass over a period of 72 hours. The structural changes were examined and the plain strain fracture toughness was evaluated. The specimens were removed from the hygrothermal ageing batch after 7, 15, 30, 45, 60 and 75 days of hygrothermal ageing. Specimens hygrothermally aged at room temperature (25°C), 50°C and 75°C shall be referred to as HTART, HTA50C and HTA75C respectively. The change in weight of the specimens during the desorption cycle was done using a process similar to that of the absorption cycle.

A specific number of specimens were taken from each bath at predetermined intervals during hygrothermal aging. These specimens were then dried until their mass remained unchanged over a 72-hour period. Subsequently, their structural changes were examined, and their plane strain fracture toughness was assessed. The specimens were retrieved from the hygrothermal aging process after being subjected to it for 7, 15, 30, 45, 60, and 75 days. The specimens shall be referred to as HTART, HTA50C, and HTA75C, corresponding to their hygrothermal ageing temperatures of room temperature (25°C), 50°C, and 75°C, respectively. The change in weight during the desorption cycle was determined using a method similar to that employed in the absorption cycle.

2.3. Fracture toughness testing

The plane strain fracture toughness testing was conducted on SENB specimens that have been hygrothermally aged in the three hygrothermal ageing baths for pre-defined intervals of time. The schematic of the specimen used for the plane strain fracture toughness testing is presented in **Figure 1**. The specimens' dimensions were in accordance with ASTM D5045-14 standard [25]. The specimen thickness (B) of 5 mm ensured that the thickness was sufficiently large to ensure that the fracture toughness tests were conducted under a plane strain condition.

Prior to plane strain fracture toughness testing, the SENB specimens were pre-cracked to an a/W ratio between 0.45 to 0.55 by tapping a sharp razor blade at the root of a machined notch. The details of the pre-cracking process followed are available in Mishra et al.[26].

The pre-cracked specimens were then subjected to plane strain fracture toughness testing using the 3-point bend fixtures on an Instron E1000 electrically plus pneumatically actuated UTM (Universal Testing Machine) having a maximum capacity of 1 kN. The specimens were tested at a cross-head velocity of 0.1 mm/min. The selected cross-head velocity (CV) was such that the micro mechanism of fracture would be dominated by disentanglement crazing [26,27]. During the test, the load and cross-head displacement were recorded and the candidate fracture toughness was determined using the following formulae.

Equation 2

$$K_Q = \left(\frac{P_Q}{BW^{\frac{3}{2}}} \right) f\left(\frac{a}{W}\right)$$

Equation 3

$$f\left(\frac{a}{W}\right) = \frac{6 \left(\frac{a}{W}\right)^{0.5} \left[1.99 - \left(\frac{a}{W}\right) \left(1 - \left(\frac{a}{W}\right)\right) \left(2.15 - 3.93 \left(\frac{a}{W}\right) + 2.7 \left(\frac{a}{W}\right)^2 \right) \right]}{\left[\left(1 + 2 \left(\frac{a}{W}\right)\right) \left(1 - \left(\frac{a}{W}\right)\right)^{1.5} \right]}$$

Where ‘K_Q’ is the ‘candidate fracture toughness’ in MPa√m, ‘P_Q’ is the load value in kN at which specimen failed, ‘B’ is the thickness of the specimen in cm and ‘W’ is the width of the specimen in cm.

The candidate fracture toughness (K_Q) qualifies as K_{IC} on satisfying all the conditions as per ASTM D5045-14 standard [25]. At least four specimens were subjected to testing under a specific hygrothermal aging condition and duration.

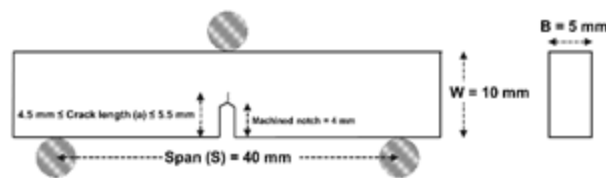


Figure 1 Schematic showing the dimensions of the SENB specimen used for plane strain fracture toughness study

2.4. Fracture surface analysis

Fracture surface analysis of fracture toughness tested specimens was carried out using a Hitachi S3400N Scanning Electron Microscope (SEM) equipped with a tungsten filament. To avoid electrical charging during image capture, the fracture surface was coated with carbon black before SEM imaging.

2.5. Structural characterization

2.5.1. Nuclear magnetic resonance (NMR) spectroscopy

¹³C solid state (CP MAS probe) NMR was conducted on both unaged and hygrothermally aged specimen using a JEOL ECZR Series 600 MHz NMR spectrometer. NMR tests were conducted to track the development of inter molecular hydrogen bonding that is speculated to happen during hygrothermal ageing [20,21]. Both unaged and hygrothermally aged specimens were carefully machined into fine powder prior to NMR analysis. Care was taken that all the hygrothermally aged specimens were completely dried (to the maximum extent possible) prior to NMR testing. The data was collected in the range of 230-0 ppm and each sample was scanned multiple times. JEOL Delta NMR analysis software was used for analyzing the NMR data.

2.5.2. Thermogravimetric analysis (TGA)

The TGA analysis was performed using TA instruments TGA setup on both unaged and hygrothermally aged specimens to track the degradation caused in the epoxy. The specimens were heated from room temperature to 400°C at 10°C/minute and the % change in mass with temperature was recorded. Care was taken that all the hygrothermally aged specimens were completely dried (to the maximum extent possible and to the point of saturation) prior to TGA.

2.5.3. X-ray photoelectron spectroscopy (XPS)

The XPS scans were conducted on both unaged and hygrothermally aged specimens. First the wide scans (Low resolution scans) were taken for all the specimens over the entire range of binding energy (0 -1200 eV). This was followed with narrow (high resolution, 0.1 eV step size) scans performed over the carbon (1s) peak for identifying the relative change in the volume fractions of chemical species and identify the formation of any new species. The XPS data was analyzed using CasaXPS software package. A Shirley background type was used for background identification. The C1s spectra was fitted with component peaks having a Gaussian-Lorentzian line shape (10 percent Lorentzian). The full width half maxima (FWHM) were fixed at the same value for all the component peaks.

3. Results and Discussion

3.1. Water absorption and desorption

Figure 2 illustrates the water absorption and desorption behavior of specimens that underwent various durations of hygrothermal aging under HTART, HTA50C, and HTA75C conditions. Notably, the HTA75C specimens, which experienced the highest temperature during aging, displayed the greatest water intake percentage. In the desorption cycle, the specimens did not return to the initial mass and hence the specimens were desorped for longer durations (exceeding 30 days) and until their mass remained unchanged over a 72-hour span. The fraction of water that was retained in the specimen is shown in **Figure 3** and taken from one of our previous studies for the exact same hygrothermal ageing condition[28]. A detailed analysis of the water absorption/desorption kinetics and diffusion coefficient measurements is available in a previous work [28].

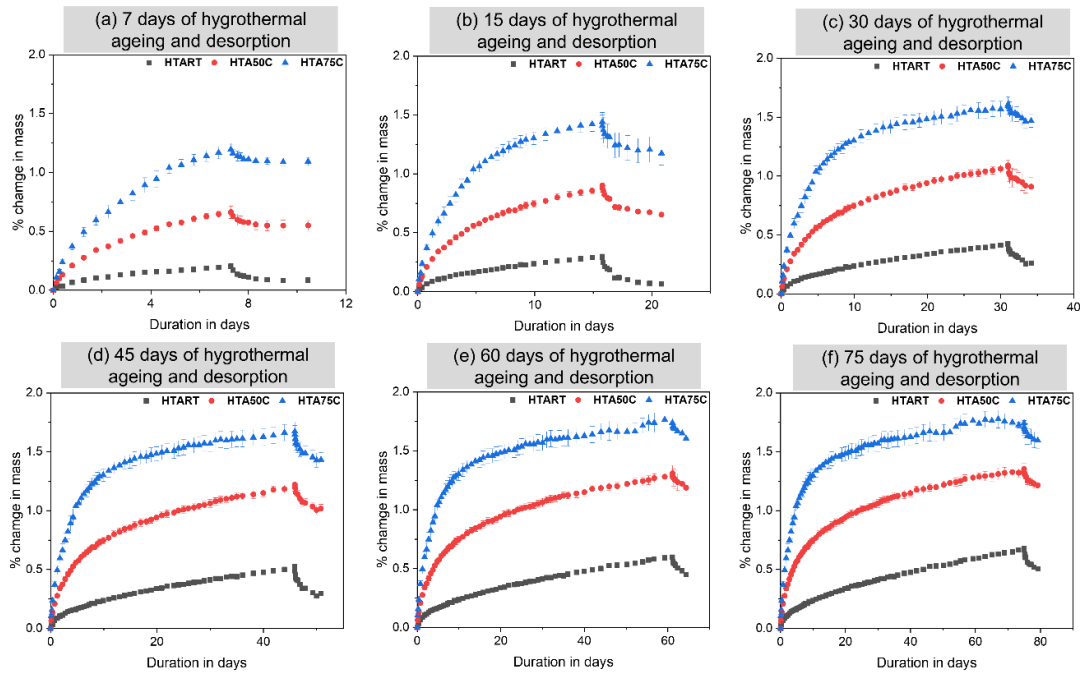


Figure 2 % Change in mass with water absorption and desorption for varying durations of hygrothermal ageing

Figure 3 presents the water retained in the epoxy after long term (in excess of 30 days) desorption for specimen hygrothermally aged for different durations. In case of HTART, there was no retention of water for 7 days and 15 days of hygrothermal ageing while the % retained water increased thereafter to a maximum of ~ 60%. In case of HTA50C ~60% of the absorbed water was retained even after 7 days of hygrothermally ageing which gradually increased to ~86% at the end of 75 days of hygrothermal ageing. HTA75C specimen showed the highest fraction of water retention of ~ 80% at the end of 7 days of hygrothermal ageing which slowly increased to ~90% of the end of 75 days of hygrothermal ageing.

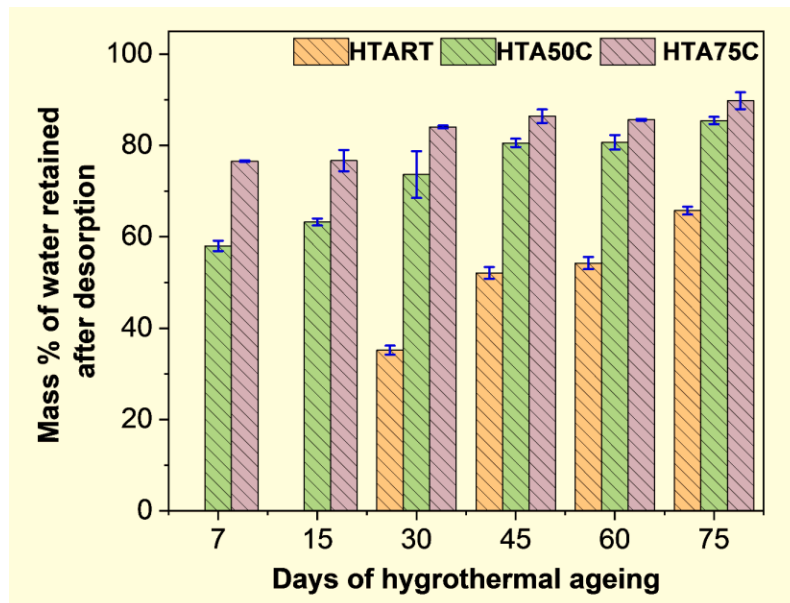
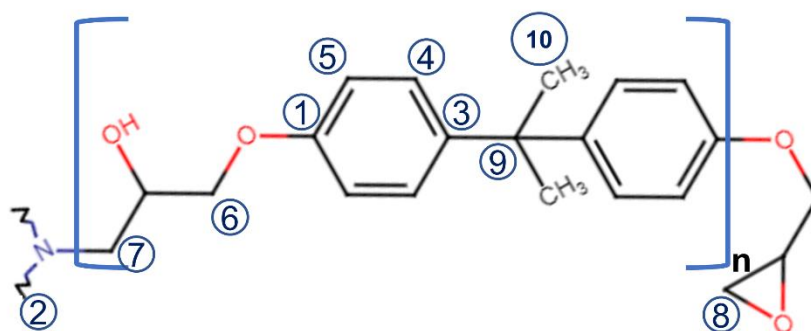


Figure 3 % absorbed water that is retained after long duration desorption taken from Mishra and Singh [28]

Considering that the HTA75C specimens retain the highest fraction of absorbed water, it is anticipated that the prevailing bonding state of water molecules, especially over extended periods of hygrothermal aging, will be predominantly characterized by Type II bonding. The Type I bonded water would lead to weakening of the epoxy matrix. To assess the degree of hydrogen bonding between water molecules and the epoxy, NMR spectroscopy was conducted on both unaged and hygrothermally aged specimens.

3.2. Nuclear magnetic resonance (NMR) spectroscopy

Figure 4 presents the NMR spectra of amine-cured epoxy in the unaged conditions. All the carbon atom and their respective peak positions on the NMR spectra have been identified and marked. As stated by Zhou and Lucas [20,21], water molecules forms hydrogen bonding both simple (Type I) and complex (Type II) with the polar groups present on the epoxy structure. To qualify the hydrogen bonding we have identified carbon atom marked as number '6' on **Figure 4** and the chemical shift of the same has been tracked with increasing hygrothermal ageing time and temperature. **Figure 5** presents the NMR spectra of hygrothermally aged specimens for HTART, HTA50C and HTA75C specimens that were dried at the end of 45 days and 75 days of hygrothermal ageing. We observe that the peak of carbon atom marked as number '6' on **Figure 4** shifts down field (or gets de-shielded) with increase in severity of hygrothermal ageing. As water is the only species that is increasing in the epoxy, the shifting of peaks or de-shielding of carbon atom '6' is trigger by water molecules. Moreover, as the NMR was conducted only after the specimens were completely dried, the de-shielding would result from the bonded water. **Figure 6** presents the down field chemical shifts or de-shielding of carbon atom '6' with hygrothermal ageing time and temperature. It is observed that the de-shielding is highest for HTA75C and lowest for HTART. Such kind of de-shielding usually happens when an intermolecular hydrogen bonding network develops. Hence, it can be concluded that the de-shielding results from intermolecular hydrogen bonding and the extent of intermolecular hydrogen bonding increases with hygrothermal ageing time and temperature.



Unaged

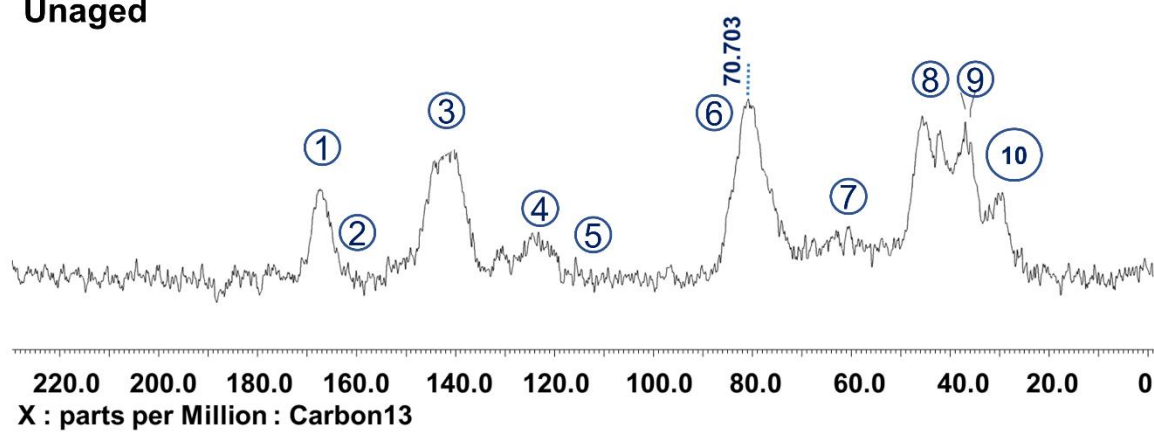


Figure 4 ¹³C solid state NMR spectrum of amine-cured epoxy before hygrothermal ageing

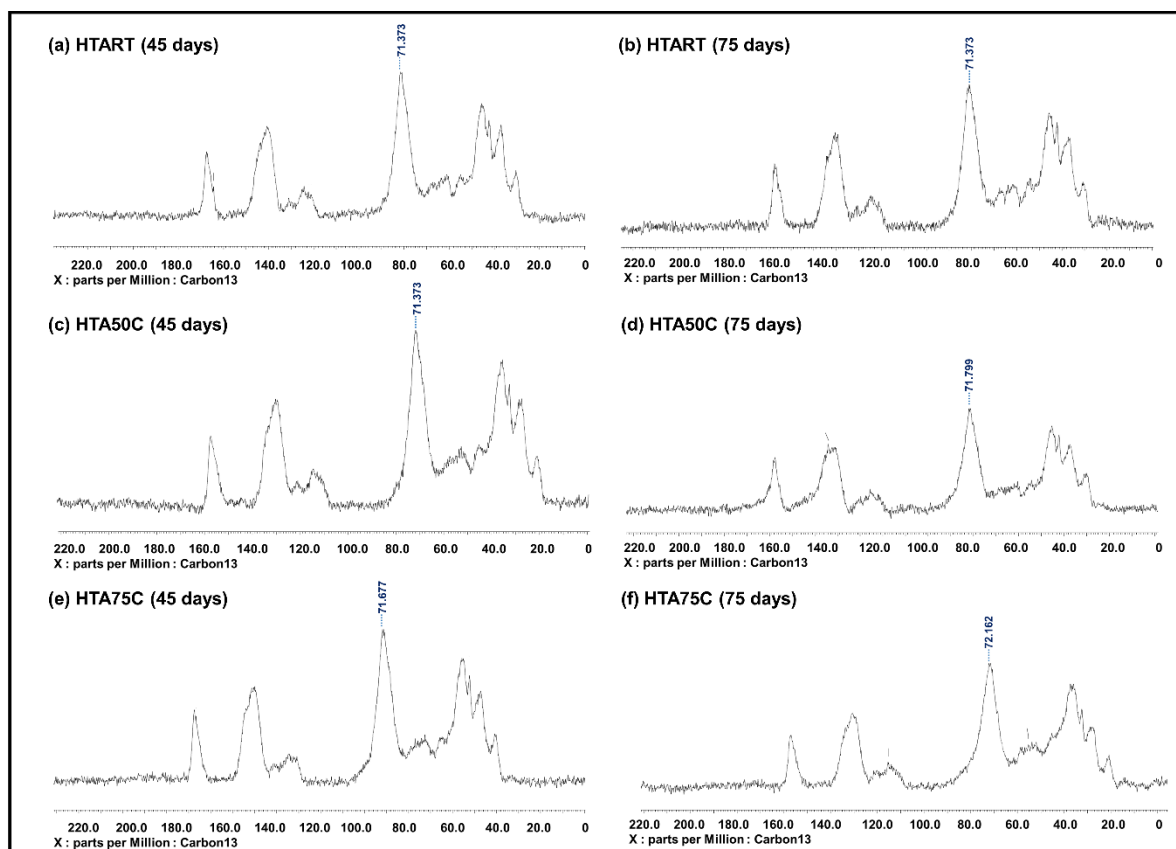


Figure 5 ^{13}C solid state NMR spectrum of hydrothermally aged amine cured epoxy after hydrothermal ageing (a) HTART (45 days) (b) HTART (75 days) (c) HTA50C (45 days) (d) HTA50C (75 days) (e) HTA75C (45 days) (f) HTA75C (75 days)

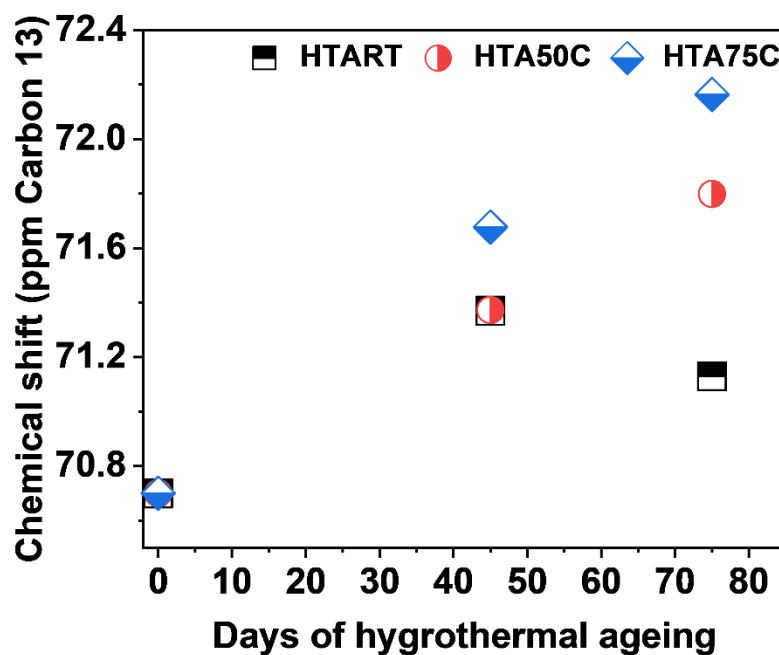


Figure 6 Variation of carbon shift of carbon atom number 6 (as marked on **Figure 4**) in ppm for HTART, HTA50C and HTA75C hydrothermal ageing condition

3.3. Thermo-gravimetric analysis (TGA)

Figure 7(a) presents the % mass loss with increasing temperature for Unaged, HTART (45 days and 75 days), HTA50C (45 days and 75 days) and HTA75C (45 days and 75 days) specimens. It is observed that the decomposition of hygrothermally aged specimens starts much earlier than the 'Unaged' specimen. **Figure 7(b)** presents the rate of change of % mass loss with temperature where two clear peaks, one between 50°C - 200°C and the other between 275°C - 400°C is observed. The peak between 50°C - 200°C could be due to the removal of loosely bonded water (Type I). The other region starts after 250°C which could be due to the removal of strongly bonded water (Type II) and the start of the decomposition of the epoxy matrix. First the second peak between 275°C - 400°C is discussed.

Figure 7(c,d) presents the zoomed in region showing the rate of percentage mass loss with temperature between 275°C -400°C for the three hygrothermal ageing conditions subjected to 45 days and 75 days of hygrothermal ageing respectively. The degradation temperature decreases by ~ 40°C with hygrothermal ageing. The shift in the degradation temperature is very similar and for all the hygrothermal ageing conditions. However, a shoulder (marked on **Figure 7(c,d)**) develops on the curve as the hygrothermal ageing severity increases. Such a shoulder is not seen in case of the 'Unaged' specimen and HTART (45 days) specimen. In case of specimens hygrothermally aged for 75 days, the development of the shoulder region becomes more prominent and is also seen for HTART specimen (**Figure 7(d)**). The development of the shoulder in **Figure 7(c,d)** could possibly indicate the development of a 'second region' that decomposes at a lower temperature. The second region could correspond to the Type II bonded water which had a prior complex hydrogen bonding with the polar groups in the epoxy and hence is less mobile and requires a higher temperature for removal than Type I bonded water. It's crucial to highlight that this "second region" emerges exclusively when hygrothermal aging is extended over longer periods and conducted at elevated temperatures. The formation of Type II bonded water typically occurs after prolonged hygrothermal aging and at higher temperatures [20,21]. Consequently, the content of Type II water within the epoxy rises as the severity of hygrothermal aging increases.

Figure 7(e,f) presents the zoomed in region showing the rate of percentage mass loss with temperature between 50°C - 225°C for all the three hygrothermal ageing conditions subjected to 45 days and 75 days of hygrothermal ageing respectively. This temperature is usually associated with the removal of loosely bonded water (Type I water). The 'Unaged' condition shows the lowest mass change between 50°C-225°C signifying that the mass loss between 50°C- 225°C in hygrothermally aged specimens is caused by the loss of loosely bonded water. For 45 days of hygrothermal ageing, the amount of water removal (computed by area under the graph) was highest for the specimens aged in HTA75C followed by HTA50 and HTART. However, after 75 days of hygrothermal ageing, HTART showed the highest amount of water removal followed by HTA50C and was lowest for HTA75C. For long durations of hygrothermal ageing and for higher hygrothermal ageing temperatures, the retained water would exist more as Type II water molecules rather than Type I and hence would require a higher temperature for removal. Hence, for HTART (75 days) mass removed at loosely bonded (Type I) water molecules would be highest between 50°C-225°C. To track the formation of new chemical species and change in the fraction of existing species due to degradation of water, XPS analysis was performed on 'Unaged' and hygrothermally aged specimens as presented in the next section.

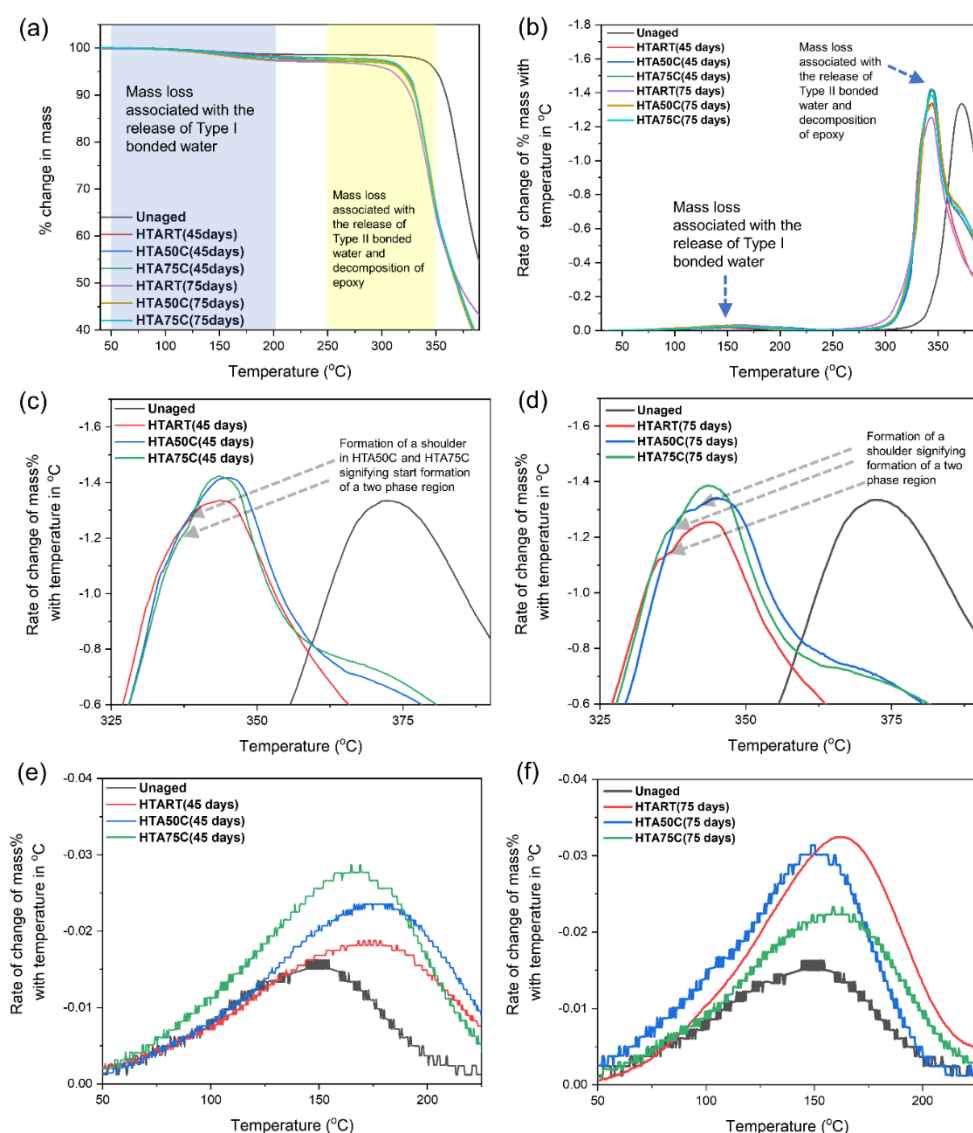


Figure 7 TGA data analysis plots for the ‘Unaged’ condition and specimens hygrothermally aged for 45 and 75 days. (a) % mass loss with temperature for ‘Unaged’, HTART (45 days and 75 days), HTA50C (45 days and 75 days) and HTA75C (45 days and 75 days). (b) show the rate of change of % mass loss with temperature for ‘Unaged’, HTART (45 days and 75 days), HTA50C (45 days and 75 days) and HTA75C (45 days and 75 days). (d) show the rate of change of % mass loss with temperature for ‘Unaged’, HTART (45 days), HTA50C (45 days) and HTA75C (45 days). (e) show the rate of change of % mass loss with temperature for ‘Unaged’, HTART (75 days), HTA50C (75 days) and HTA75C (75 days). (e,f) show the rate of change of % mass loss with temperature for 45 days and 75 days of hygrothermal ageing for ‘Unaged’, HTART, HTA50C and HTA75C over a temperature range of 50 to 225°C.

3.4. X-ray photoelectron spectroscopy (XPS)

Figure 8(a) presents the wide scan (at a larger step size) for the Unaged specimen over the entire binding energy range and **Figure 8(b)** presents the narrow scan (0.1 eV step size) over the C1s binding energy range for the unaged specimen. In (b) the peaks have been deconvoluted as per specifications mentioned in

Section 2.5.4. After the deconvolution, it is identified that there are three species; the C-C/C=C, the C-O- group and the carbon attached to a more electron withdrawing group (C=O). The C-C/C=C species and C-O- species concentration has been tracked for varying hygrothermal ageing temperature (**Figure 9**) and for varying hygrothermal ageing days (**Figure 10**).

Figure 9(a-c) presents the deconvoluted C1s spectra for specimens hygrothermally aged up to 75 days at different hygrothermal ageing conditions while **Figure 9(d)** shows the percentage change in concentration of C-C/C=C and C-O- with hygrothermal ageing temperature for 75 days of hygrothermal ageing. It is observed that the concentration of C-C/C=C goes on decreasing with increasing severity of hygrothermal ageing temperature while the concentration of C-O- goes on increasing with increase in hygrothermal ageing temperature. **Figure 10(a-c)** presents the deconvoluted C1s spectra for specimens hygrothermally aged at HTA75C condition for varying days of hygrothermal ageing while **Figure 10(d)** shows the percentage change in concentration of C-C/C=C and C-O- with varying hygrothermal ageing time for HTA75C hygrothermal ageing condition. Similar to **Figure 9(d)** (variation with respect to the hygrothermal ageing temperature), here also the C-C/C=C species concentration decreases and C-O- species concentration increases with increasing hygrothermal ageing days keeping the hygrothermal ageing condition same at HTA75C. However, the concentration of both C-C/C=C and C-O do not change after 45 days of hygrothermal ageing at 75°C. This indicates that the reactions happening in HTA75C condition had reached equilibrium after 45 days of hygrothermal ageing. The decrease in C-C/C=C is indication of main chain hydrolysis while the increase of C-O- is indicative of formations of alcohols as reaction product of hydrolysis. The XPS results further support the fact that water absorption in epoxy leads to main chain hydrolysis and the severity of the main chain hydrolysis increases with hygrothermal ageing temperature and time.

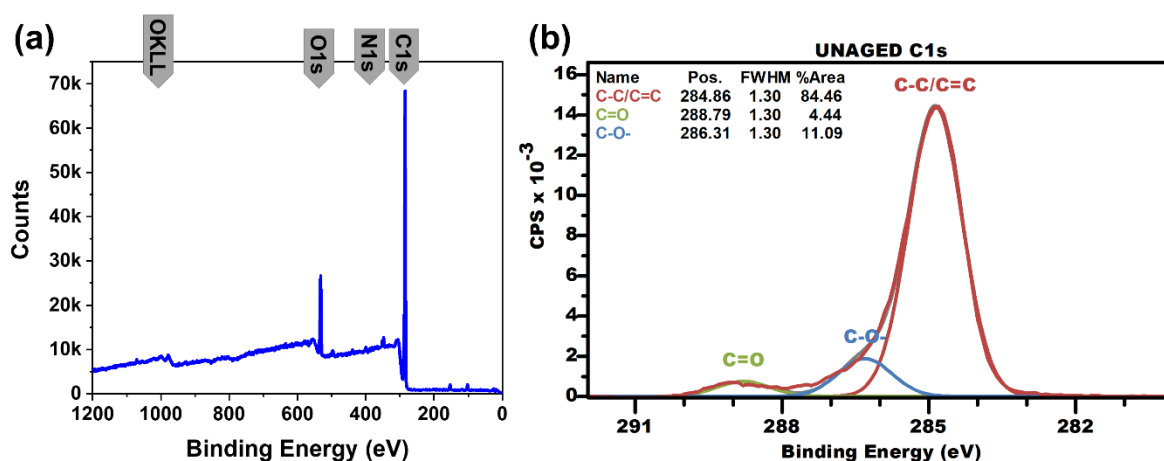


Figure 8 (a) Low resolution survey spectra for 'Unaged' specimen. (b) high resolution XPS scan for C1s for Unaged specimen and its deconvoluted peaks.

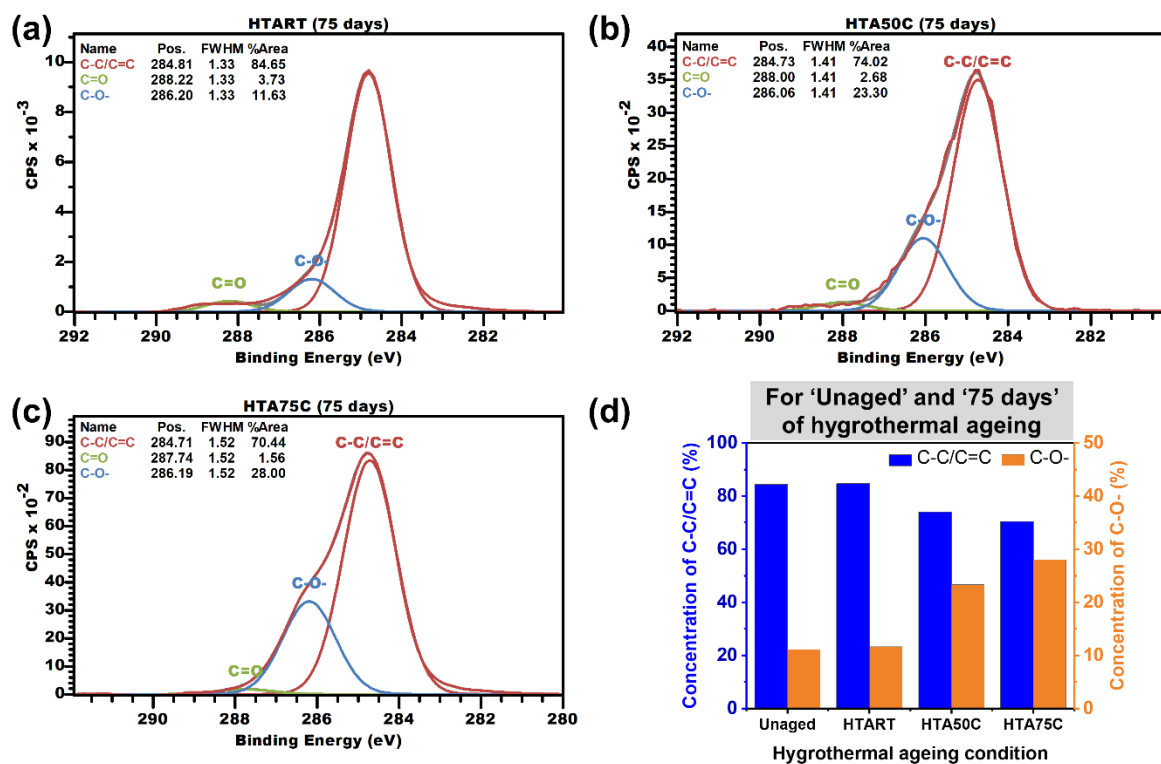


Figure 9 Deconvoluted C1s spectra for specimens hydrothermally aged up to 75 days at different hydrothermal ageing condition (a) HTART (b) HTA50C (c) HTA75C. (d) Change in concentration of C-C/C=C and C-O- with hydrothermal ageing temperature for 75 days of hydrothermal ageing.

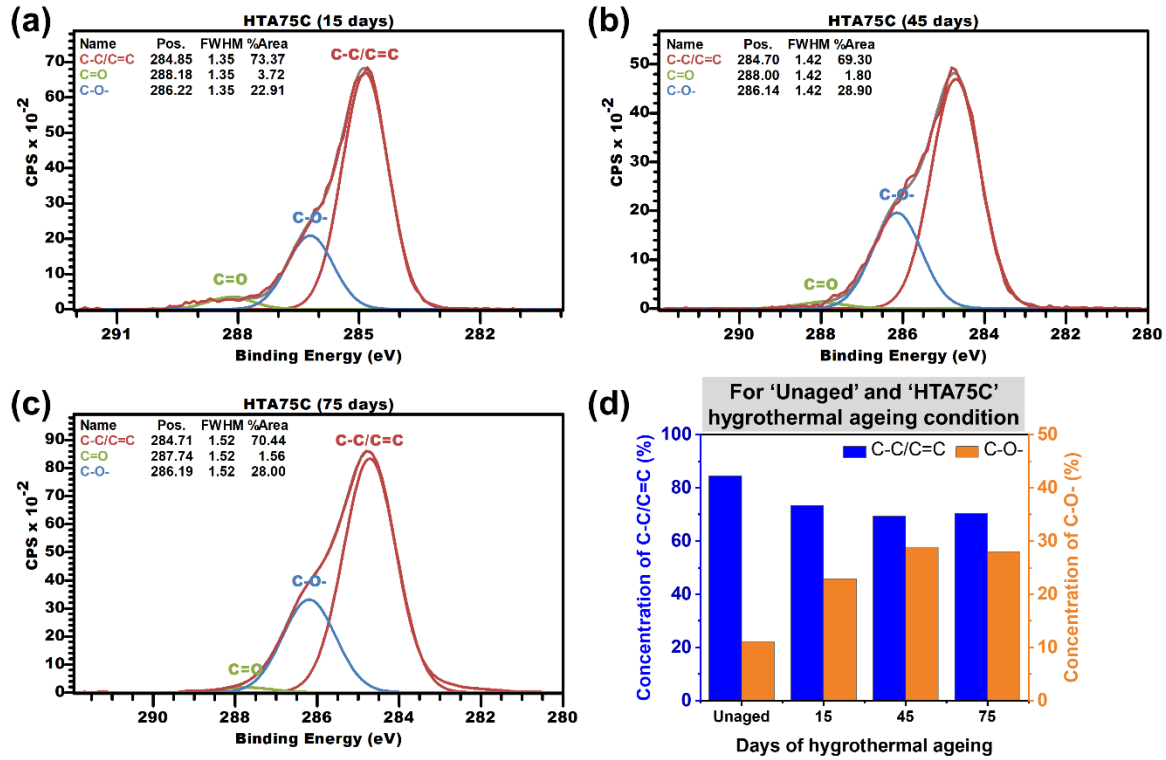


Figure 10 Deconvoluted C1s spectra for specimens hydrothermally aged at HTA75C condition for varying days of hydrothermal ageing (a) 15 days (b) 45 days (c) 75 days. (d) Change in concentration of C-C/C=C and C-O- with increasing hydrothermal ageing time for HTA75C hydrothermal ageing condition.

3.5. Plane strain fracture toughness test

Figure 11 shows the variation in the plane strain fracture toughness (K_{IC}) with hydrothermal ageing time and temperature. For the unaged condition, the K_{IC} is $\sim 1.23 \pm 0.03 \text{ MPa-m}^{0.5}$. The K_{IC} goes on decreasing with hydrothermal ageing time for all the three hydrothermal ageing conditions. In case of HTART, there is no decrease in K_{IC} over the first 15 days of ageing but there after the K_{IC} goes on decreasing as hydrothermal ageing progresses. No decrease in K_{IC} for HTART up to 15 days of ageing could be due to no retention of absorbed water over 15 days of hydrothermal ageing (**Figure 3**) and hence no degradation is caused to the epoxy matrix. After 15 days of hydrothermal ageing, water retention happens for HTART and the K_{IC} decreases. For HTA50C, the decrease in K_{IC} is larger over the first 15 days of ageing ($\sim 20\%$ decrease) and becomes sluggish thereafter. In case of HTA50C, water is retained in the epoxy matrix even after 7 days of hydrothermal ageing and hence there is an immediate decrease in K_{IC} . Thereafter, the water retention increases slowly for HTA50C and the value of K_{IC} follows suit. In case of HTA75C, the decrease in K_{IC} is $\sim 30\%$ over the first 7 days of hydrothermal ageing and there after the rate of decrease of K_{IC} for HTA75C becomes much slower. In case of HTA75C, water retention is $\sim 80\%$ at the end of 7 days of hydrothermal ageing and increases to $\sim 90\%$ for 75 days of hydrothermal ageing. Here also the decrease in K_{IC} value is proportional to the increase in water retention.

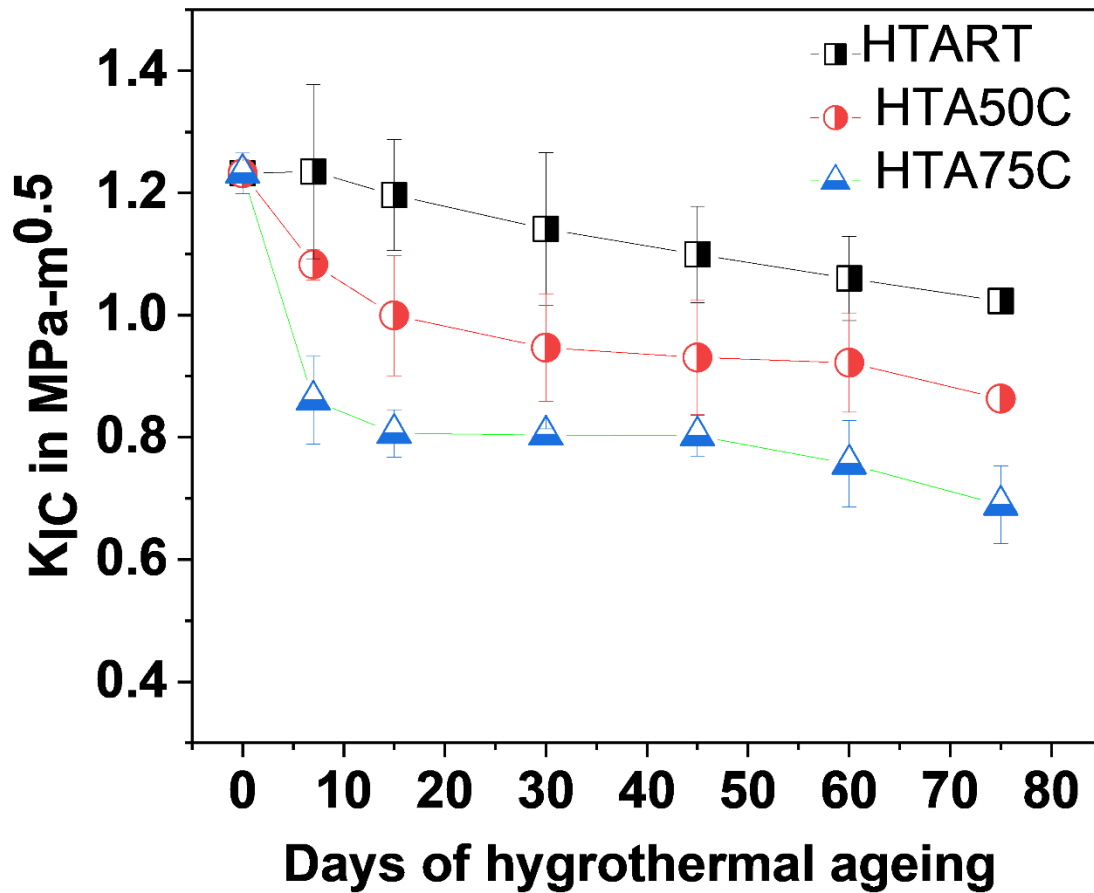


Figure 11 Variation of plane strain fracture toughness with hygrothermal ageing time and temperature for both high and low crack tip strain rate .

3.6. Fracture surface analysis

Figure 12(a-h) display the fracture surface of specimens subjected to fracture toughness testing at low crack tip strain rates, with variations in both hygrothermal ageing time and temperature. **Figure 12(b)** presents a schematic of the region over which the fractography was performed. A more detailed methodology of selecting the region for fractography is available in Mishra et al [26]. The fracture surface of the fracture toughness specimens consists of crack stretch marks which run parallel to the crack propagation direction. The crack stretch marks consist of what remains of a bunch of stretch and broken craze fibrils [26]. In the case of the "Unaged" specimen, the crack stretch marks are evenly distributed across the entire surface (**Figure 12(a)**). However, as hygrothermal ageing progresses the crack stretch marks are formed in bunches of two or more especially for HTA50C and HTA75C. The gap between each cluster of crack stretch marks expands as the duration and temperature of hygrothermal aging increases. The formation of a bunch of crack stretch marks and an increase in the spacing between the bunches of crack stretch marks indicates that not all regions in the epoxy matrix ahead of the sharp pre-crack are participating the deformation process, that is, the deformation becomes more localized. A measure of the change in the spacing between the crack stretch marks is presented in **Figure 13**. Previously, in-situ SEM-based tensile tests were employed to determine that the crack stretch marks

occurring in front of a sharp crack are a result of the remnants of stretched and fractured craze fibrils [26]. As the severity of hygrothermal aging increases and the spacing between the crack stretch marks widens, it can be deduced that the degraded areas are unable to participate in the deformation process. Specific areas with lower levels of degradation are the ones actively involved in the crazing process, which consequently reduces the material's ability to accommodate strain and leads to a decrease in K_{IC} .

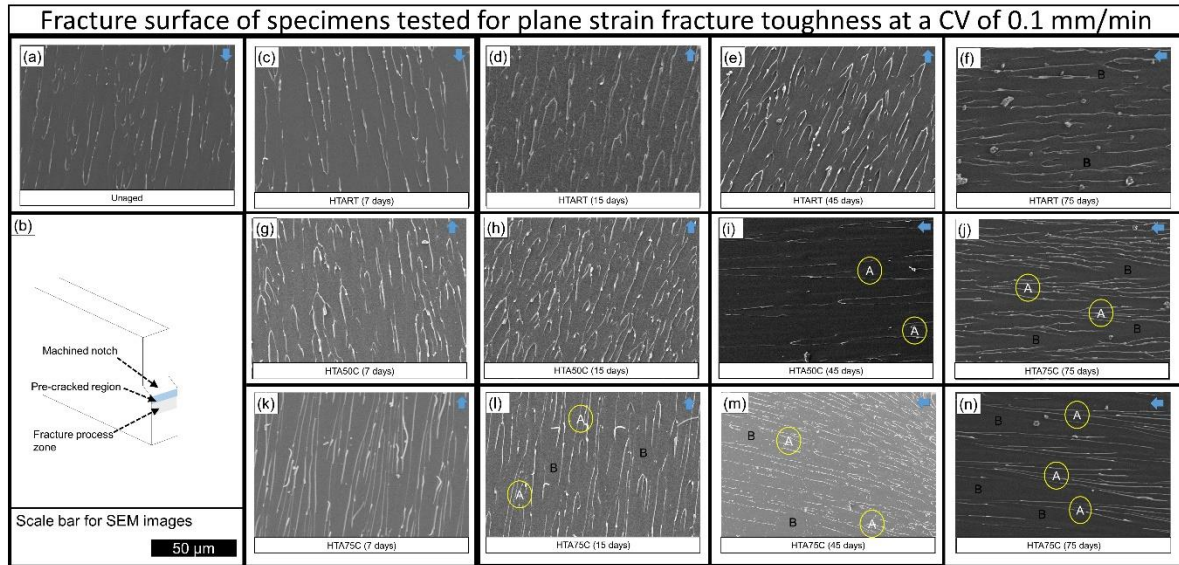


Figure 12 SEM micrographs of the fracture surface of specimens tested for plane strain fracture toughness at low crack tip strain rate. (a) Fracture surface for the ‘Unaged’ condition, (b) shows a schematic of the region selected for fracture toughness imaging. (c), (d), (e) and (f) fracture surface of specimen aged at HTART at the end of 7, 15, 45 and 75 days of hygrothermal ageing. (g), (h), (i) and (j) fracture surface of specimen aged at HTA50C at the end of 7, 15, 45 and 75 days of hygrothermal ageing. (k), (l), (m) and (n) fracture surface of specimen aged at HTA75C at the end of 7, 15, 45 and 75 days of hygrothermal ageing. The arrows on the fracture surface indicate the crack propagation direction. The circled regions indicate the formation of benches of crack stretch marks and regions marked as ‘B’ indicate regions which do not participate in the deformation process.

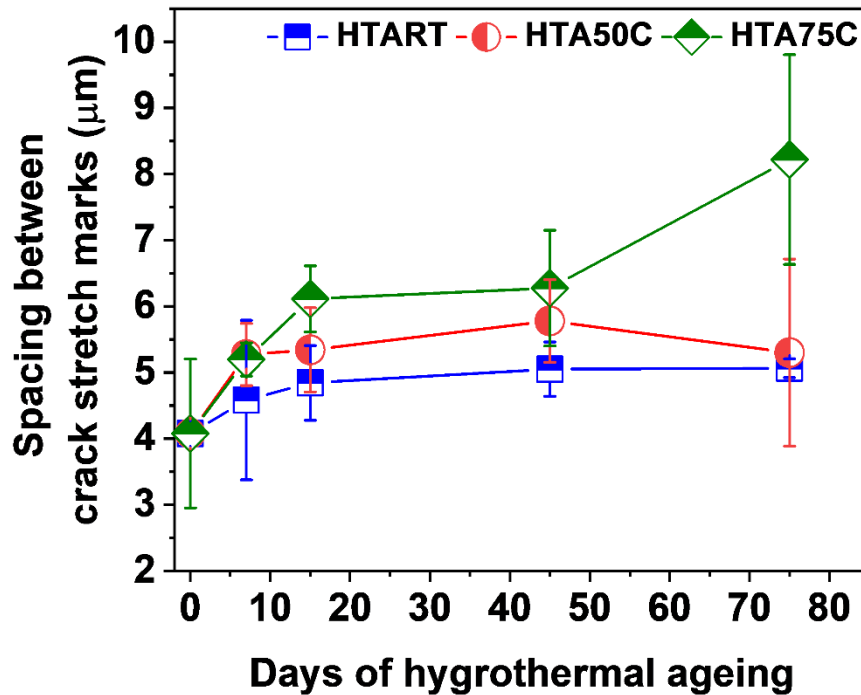


Figure 13 Change in spacing between crack stretch marks of fracture toughness tested specimens with hygrothermal ageing time and temperature

4. Conclusion

We have hygrothermally aged highly cross-linked epoxy specimens in DI water maintained at three different temperatures and tested for plane strain fracture toughness both for low crack tip strain rates. Basing on the results of the mechanical testing and structural characterization using NMR, TGA and XPS, the following conclusions were drawn

- 1) Specimens hygrothermally aged at the highest temperature absorbs the highest amount of water and no saturation in terms of mass absorption is observed.
- 2) A fraction of absorbed water is retained in the epoxy matrix even after the specimens achieve a saturation in mass during the drying cycle after hygrothermal ageing. NMR results indicate that the retained water forms hydrogen bonding with the polar group present in the epoxy which is indicated by de shielding of NMR peaks of carbon atoms bonded to oxygen.
- 3) During extended periods of hygrothermal aging, the Type I (loosely) bonded water molecules is higher for low hygrothermal ageing temperature, whereas, the fraction of Type II (strongly) bonded water molecules is higher for specimens being aged at higher temperatures.
- 4) The thermal decomposition temperature of epoxy decreases as both the duration and temperature of hygrothermal aging increase.
- 5) The low crack tip strain rate plane strain fracture toughness (K_{ICL}) decrease with hygrothermal ageing time and temperature and the rate of decrease in K_{ICL} is proportional to the rate of increase in water retention post desorption.
- 6) The fracture surface of specimens subjected to low crack tip strain rate plane strain fracture toughness testing displays crack stretch marks, which result from the stretching and breaking of craze fibrils

through disentanglement crazing. Over hygrothermal ageing time and with increasing hygrothermal ageing temperature, the spacing between these crack stretch marks expands, ultimately resulting in a reduction in K_{IC} due to deformation being concentrated in localized regions.

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