DEGRADATION MECHANISM ANALYSIS OF FRP WITH EPOXY MATRIX SUBJECTED TO CONCENTRATION CYCLING

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ABSTRACT

The roof of a fiber-reinforced plastic (FRP) chemical tank failed by accident after it had been operated for less than its expected lifetime. A detailed analysis of the durability cyclic solution concentration of the material is required, as this could be the cause of failure. In this research, an amine-cured epoxy-glass fiber composite was exposed to 35 mass % of HCl and 0 mass% (water) alternately at the same temperature condition of 40°C to replicate cyclic concentration exposure in both the vapor and liquid phases. The mass uptake, strength loss, and penetration depth of HCl is investigated. Mass uptake result showed that HCl penetrates the epoxy at a faster rate than water, this might be due to the amine salt generation reaction. There was less acceleration in the vapor phase compared to the continual immersed in 35mass% of HCl in the liquid phase. Three-point bending test is conducted to examine the flexural strength for its mechanical properties. The result showed that the flexural strength is decrease with increasing exposure time. The reduction of flexural strength is linearly proportional to mass uptake of solution and the reason is mainly due to the effect of plasticization. The penetration depth of Cl in specimens was obtained from elemental mapping of cross-section using SEM (Scanning electron microscope)/EDS (Energy-dispersive X-ray spectroscopy). For vapor phase condition, the result showed that after 1 cycle exposure to cyclic concentration, Cl penetrates into the center part of specimen. Meanwhile, for the liquid phase condition, Cl penetration is only in the outside part and not so much Cl detected in the center part, this might be due to salt layer making in the outside part of the specimen. After 3 cycle exposure to cyclic concentration, not much Cl was detected in the inside part of the specimen, but still making salt layer in the outside part, for vapor phase condition. On the other hand, for liquid phase condition, free Cl detected. This may occur as a result of cleansing by water penetration after a second or third dipping. The center of the specimen can be cleaned more thoroughly with water, resulting in a lower HCl concentration in the core of the specimen. The Fourier-transform infrared (FTIR) spectroscopy observation is conducted to collect the evidence of swelling behaviour that occurred on the surface specimens by monitoring acid diffusion and reaction with cured epoxies. The result revealed that no significant chemical degradation processes were found. As a result, the HCl acid degradation of this amine-cured epoxy system occurs through a physical degradation mechanism caused by swelling.

1 INTRODUCTION

Glass Fiber Reinforced Plastic (GFRP) composites have been utilized in a wide range of engineering applications in chemical plant field, including the manufacturing of pipelines and chemical storage tanks that containing severe chemical solutions, due to their high chemical durability, water resistance, corrosion resistance, and deliver good mechanical strength [1]. GFRP provides outstanding performance, high acid and alkali corrosion resistance, a low cost, and superior designability [2].

From the perspective of the end users, the durability of FRP applications is of the utmost importance to guarantee that it will have a long lifetime. The expected service lifetime of the FRP material, such as chemical tank is about 20-25 years. On the other hand, an accident has been reported where the FRP

chemical storage tank has failed at the roof part during the checking the pipes on the roof to remove it after being used for 15 years which occurred shorter time than the expected service life. The roof failure of FRP chemical tank leads to the question that why the performance of material in vapor phase was weakened more than wall-side which directly exposed to liquid solution. The failure showed that material exposed to the vapor phase was weaker than material exposed to the liquid phase. However, most of the study which is related to the influence of water or chemical solution suggested that material in the liquid solution would weaken the performance of material more than vapor phase [3].

The roof failure of FRP chemical tank has a big gap of understanding of material exposed to chemical solution in the vapor phase. Explanation for this phenomenon needs to consider dynamic effects on the tank such as daytime and night-time temperature cycles. Condensation and evaporation can easily occur because of this temperature cycle, resulting in concentration changes of chemical being in contact with the material exposed to the vapor phase and could lead to the reason of roof tank failure.

2 LITERATURE REVIEW

The key elements investigated in FRP chemical tank failure are exposure period, solution concentration and temperature under isothermal settings, temperature gradient condition, and their influence on solution penetration into corrosion barrier layer or polymeric material. According to a few researchers, components in the liquid phase of the solution would endure harsher circumstances than those in the vapor phase. The earlier investigation of the accelerated failure of unsaturated polyester resin in water, hydrochloric acid (volatile acid) solution, and sulfuric acid (non-volatile acid) solution suggested that the strength of the material in the liquid phase was more destructive than in the vapor phase [4]. Unsaturated polyester resin was studied in 20 mass% HCl in an isothermal environment and cyclic solution. The findings demonstrated that at 80°C isothermal conditions, the rate of mass uptake was higher than under cyclic temperature conditions [5]. The diffusion of hydrochloric acid into an amine-cured epoxy system utilizing simultaneous gravimetric analysis and element analysis was examined. The mass uptake behaviour was observed to differ significantly from that of water diffusion, being an order of magnitude faster. Material characterization studies have revealed that the dominant degradation mechanism is physical in nature, with the formation of surface cracks driven by the swelling stresses resulting from the core shell swelling behaviour in highly concentrated hydrochloric acid, resulting in an erosion-type degradation phenomenon [6].

The degradation behaviour under the wide range of temperature conditions was already observed in many studies. Changes in temperature between day and night could lead to a dynamic state in the vapor phase that could lead to the failure of a chemical tank. At a greater temperature, gases will begin to evaporate, and at a lower temperature, they will condense into a liquid. At a temperature close to the dew point of the saturated condition, gases will begin to condense on the surface of the material. In a polymer network, the absorbed solution may also dew. After the dew condensation occurs, concentration is significantly changed. For the volatile solution, concentration of chemicals in the vapor phase is relatively higher than in liquid phase. For this reason, study of a cyclic solution concentration is needed to extend knowledge of material degradation behaviour. An investigation of the acid and water degradation behaviour of glass fiber epoxy composite in cyclic solution concentration condition has not been reported. Thus, the short-term experimental investigation which can greatly affect mechanical property is necessary. To achieve this purpose, in this research, new accelerated experimental methods has been developed, such as cyclic solution, in which the concentration change are investigated to evaluate the solution penetration in the liquid phase and vapor phase condition.

3 EXPERIMENTAL PROCEDURES

3.1 Specimen preparation

Bisphenol A-diglycidyl ether (DGEBA, R140) epoxy resin with poly(oxypropylene) diamine as a hardener (Jeffamine D230) was employed. Specimen of epoxy was prepared by mixing with hardener (curing agent) at a mass ratio of 100:30.6. After mixing and defoaming process, it was poured into the glass fibre on pre-heated steel mould and cured using a hot press at a schedule of 60˚C for 6 hours for

the first curing and 110 ˚C for 12 hours for the second curing. After finishing the curing procedure in a hot press, cooling to room temperature, and the cured epoxy plates were removed from the mould. The specimen was precisely cut into small pieces at dimensions of 60x20x2 mm (length x width x thickness), as shown in Fig. 1. To remove mould release and other material that could interfere with surface adsorption, all specimens were cleaned with water, then dried in a room temperature for 1-2 days.

Figure 1. Final specimen of glass-fiber epoxy

3.2 Cyclic exposure condition

The specimens are prepared for vapor phase and liquid phase. Specimens are exposed to various solution concentrations at different times. Specimens are changed from higher HCl concentration to lower concentration or water alternately. The concentration of chemical solutions is 35 mass% HCl and 0 mass% (water), and the temperature will be constantly kept at 40˚C. For HCl 35% condition, specimens were put inside of the glass beaker as shown in Fig. 2.

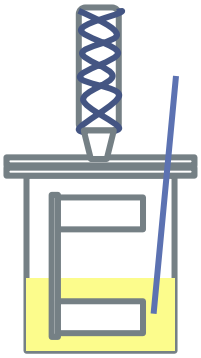

Figure 2. Schematic of 35 mass% HCl exposure condition

For 0 mass% (water) exposure condition, the specimens in glass beaker were put inside of the water bath as shown in Fig. 3.

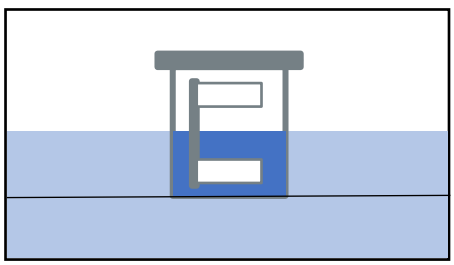

Figure 3. Schematic of water exposure condition

One cycle is the period when the specimen went through two different solution concentrations (35 mass % and 0 mass%), exposure for one concentration lasted for 5 days (half cycle). The total exposure time is decided to be 30 days or 3 cycles, as depicted in Fig. 4.

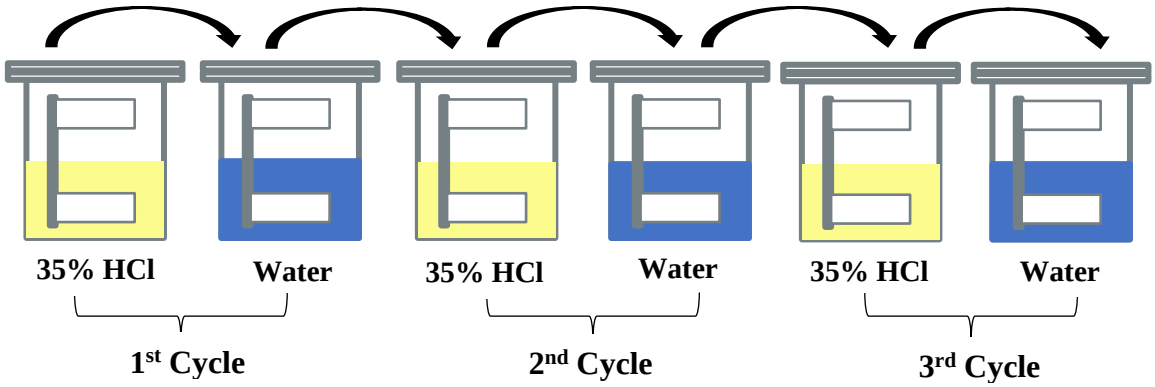

Figure 4. Schematic of cyclic solution concentration

3.3 Mass uptake and dimensional measurements

Each specimen was removed from the solution and patted dried by towel/tissue, and then the mass uptake was measured on a digital balance with a precision ± 0.0001 g. Gravimetric analysis was used to estimate the amount of penetrated acid solution. The change in mass of the specimens was calculated based on Eq. 1, where M_t is mass of specimen at time t, and M_0 is mass of specimen at initial time.

$$Mass\ Uptake\ (\%) = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

For dimensional measurement, were measured digital caliper with a precision ± 1μm. The changes in thickness, length, and width calculated based on Eq. (2-4).

$$Thickness\ Change\ (\%) = (h_t - h_0)/h_0 \times 100 \quad (2)$$

$$Length\ Change\ (\%) = (l_t - l_0)/l_0 \times 100 \quad (3)$$

$$Width\ Change\ (\%) = (w_t - w_0)/w_0 \times 100 \quad (4)$$

Where h is thickness of specimen at time t, and h_0 is thickness of specimen at initial time, l_t is length of specimen at time t, and l_0 is length of specimen at initial time, and w_t is width of specimen at time t, and w_0 is width of specimen at initial time.

3.4 Mechanical properties

Three-point bending test is conducted to examine the flexural strength for its mechanical properties. The bending test was conducted using Shimadzu Autograph AGS-1KNJ machine with cross-head speed at 2 mm/min and performed according to ASTM D790. The specimens were prepared for the three-point bending test after finishing through exposure conditions.

3.5 SEM/EDS observation

Following the bending test, the specimen cross-section surface in the vapor phase and liquid phase was observed. SEM/EDS is used to determine the chemical composition of materials and to create element composition maps, which can be used to determine the penetration depth of Cl in the specimen from the cross-section surface.

3.6 FTIR observation

Fourier-transform infrared (FTIR) spectra were obtained using an FTIR-ATR (Shimadzu AIM-8000R) at a resolution of 4 cm-1 and a minimum of 60 scans averaged per spectrum. To ensure consistent patterns in the data, spectra from at least three sites on a specimen were averaged. FTIR observation is conducted to collect the evidence of swelling behaviour that occurred on the surface specimens by monitoring acid diffusion and reaction with cured epoxies while immersed in 35 mass% HCl.

4 RESULTS AND DISCUSSIONS

4.1 Mass uptake and dimensional change during exposure to cyclic concentration

In the early stage of the cycle, the mass uptake data for sample exposed to liquid phase showed faster diffusion rate than that of vapor phase as depicted in Fig. 5. During exposure to high HCl concentration, a large amount of HCl penetrated into the specimens caused by amine salt generation reaction, resulting in increased mass uptake. During exposure to low HCl concentration in the subsequent half-cycle, mass uptake decreased might occur due to leaching of some part of resin.

As shown in Fig. 5, after specimens through immersion condition under cyclic solution concentration for 2 cycles which is 20 days (480 h), the result of mass uptake in liquid phase is reached minus (negative). This might happen because the material is already degraded. Meanwhile, for vapor phase, the degradation of material is occurred after specimens through immersion condition under cyclic solution concentration for 30 days at final stage. These results considered that the material of glass fiber epoxy is more severe in the liquid phase rather than in vapor phase.

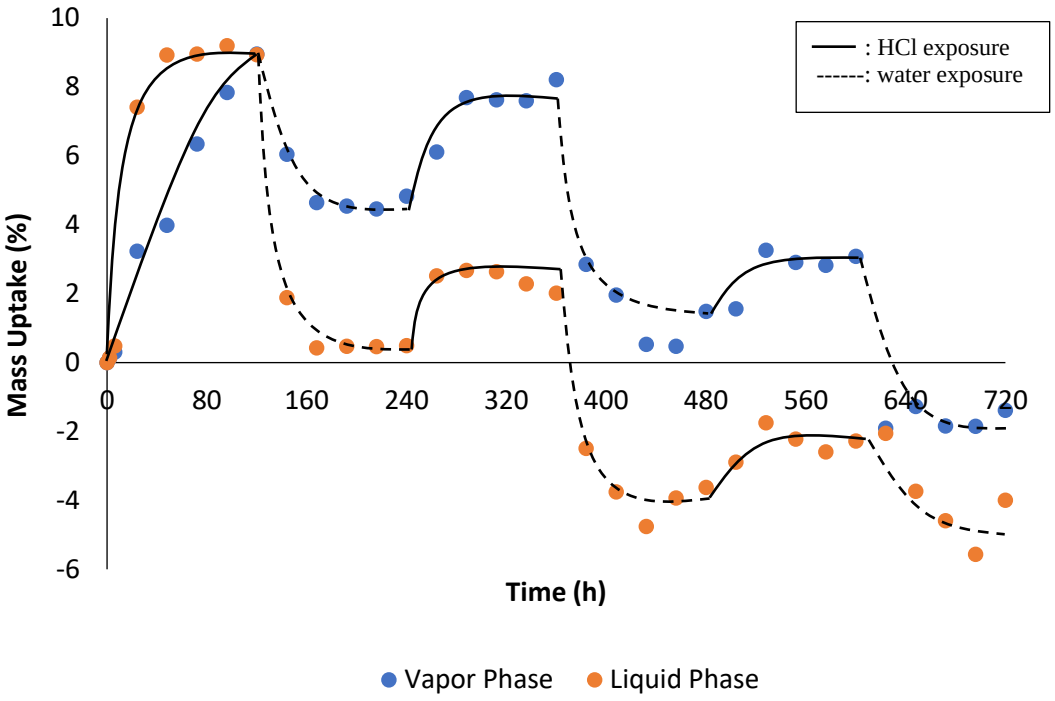

Figure 5. Mass uptake of glass fiber epoxy specimen in 35 mass% HCl and 0 mass% (water) under cyclic solution concentration

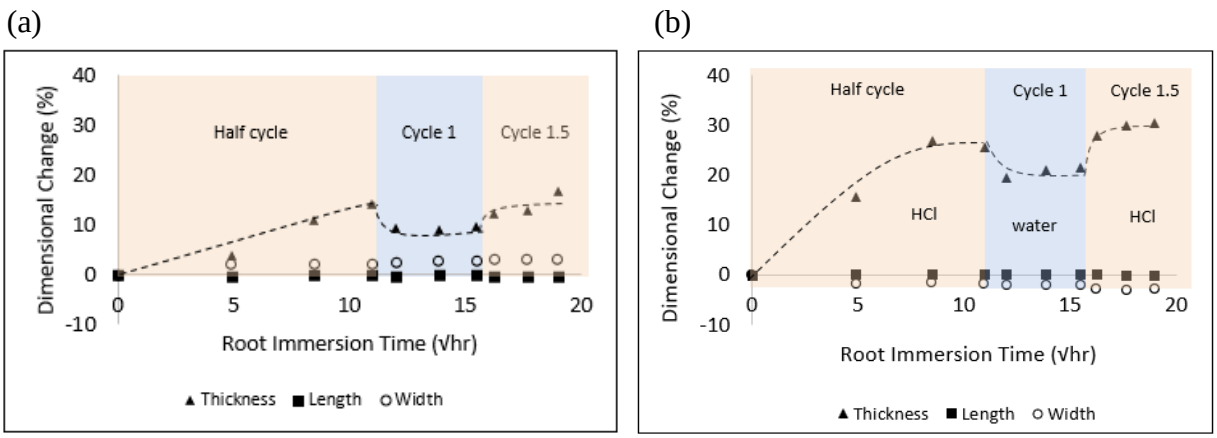

Figure 6. Dimensional change of glass fiber epoxy specimen in 35 mass% HCl and 0 mass% (water) under cyclic solution concentration at (a) vapor phase condition (b) Liquid phase condition

Besides mass uptake measurement, dimensional change is also examined. Fig. 6 shows the thickness, length, and width changes for vapor phase and liquid phase. The results show that the change in thickness is much greater than the change in length and width. This result indicates that inside the material has not changed so much for the size, but the surface penetration may occur. In FRP case, the width and length are limited to deform. Only the direction of thickness is changed, this might occur because the specimens contained glass fiber. The thickness change in liquid phase is higher rate than vapor phase. The result indicates swelling behavior may occur much bigger inside of liquid phase material.

4.2 Mechanical properties

After the mass uptake and dimensional change analyzed, the specimen of vapor phase and liquid phase is examined by three-point bending test to investigate the mechanical property from the flexural strength data. The flexural strength of glass fiber epoxy in 35 mass% HCl and water under cyclic solution concentration at 40˚C shown in Fig. 7. The result shows that flexural strength decreases with increasing exposure time. The reduction of flexural strength is linearly proportional to mass uptake of solution. The reduction of the flexural strength was mainly due to the effect of plasticization. Matrix plasticization in the wet state accompanies the penetration of environmental liquid, reducing the laminate's modulus and strength. Additionally, decreases in flexural strength occurred as water penetrated the resin in the deterioration process.

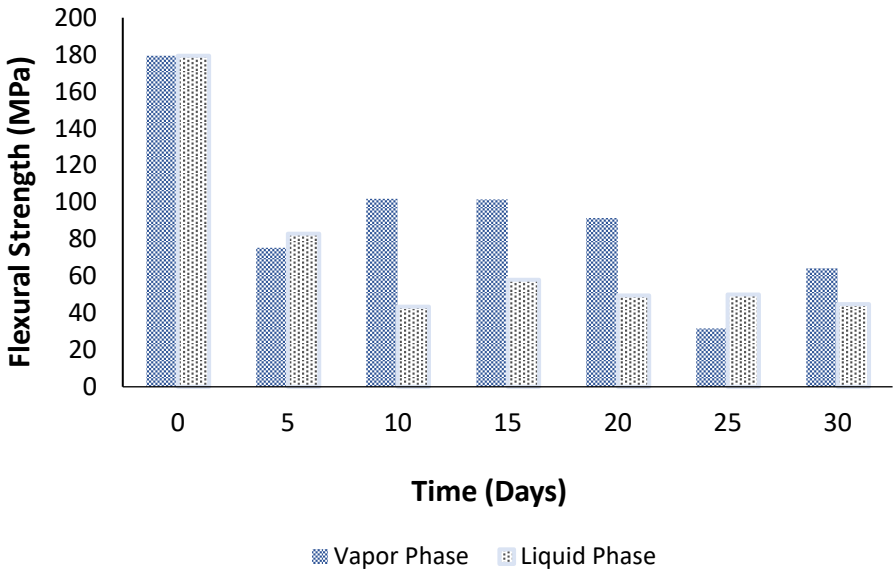

Figure 7. Flexural strength of glass-fiber-epoxy specimen in 35 mass% and 0 mass% (water) under cyclic solution concentration

4.3 Penetration depth of Cl

The penetration depth of Cl in specimens was obtained from elemental mapping of cross-section using EDS. From fig. 8 (a), (c), (e), penetration of Cl for vapor phase condition can be seen. After 1 cycle exposure to cyclic concentration solution depicted in Fig. 8 (a), Cl penetrated to the center part of the specimen. However, after 3 cycles exposure to cyclic concentration solution, there is not so much

HCl inside of the specimen. It can be seen from Fig. 8 (e), the outside part is making of the salt layer, meanwhile, free Cl is detected in the inside part of specimen.

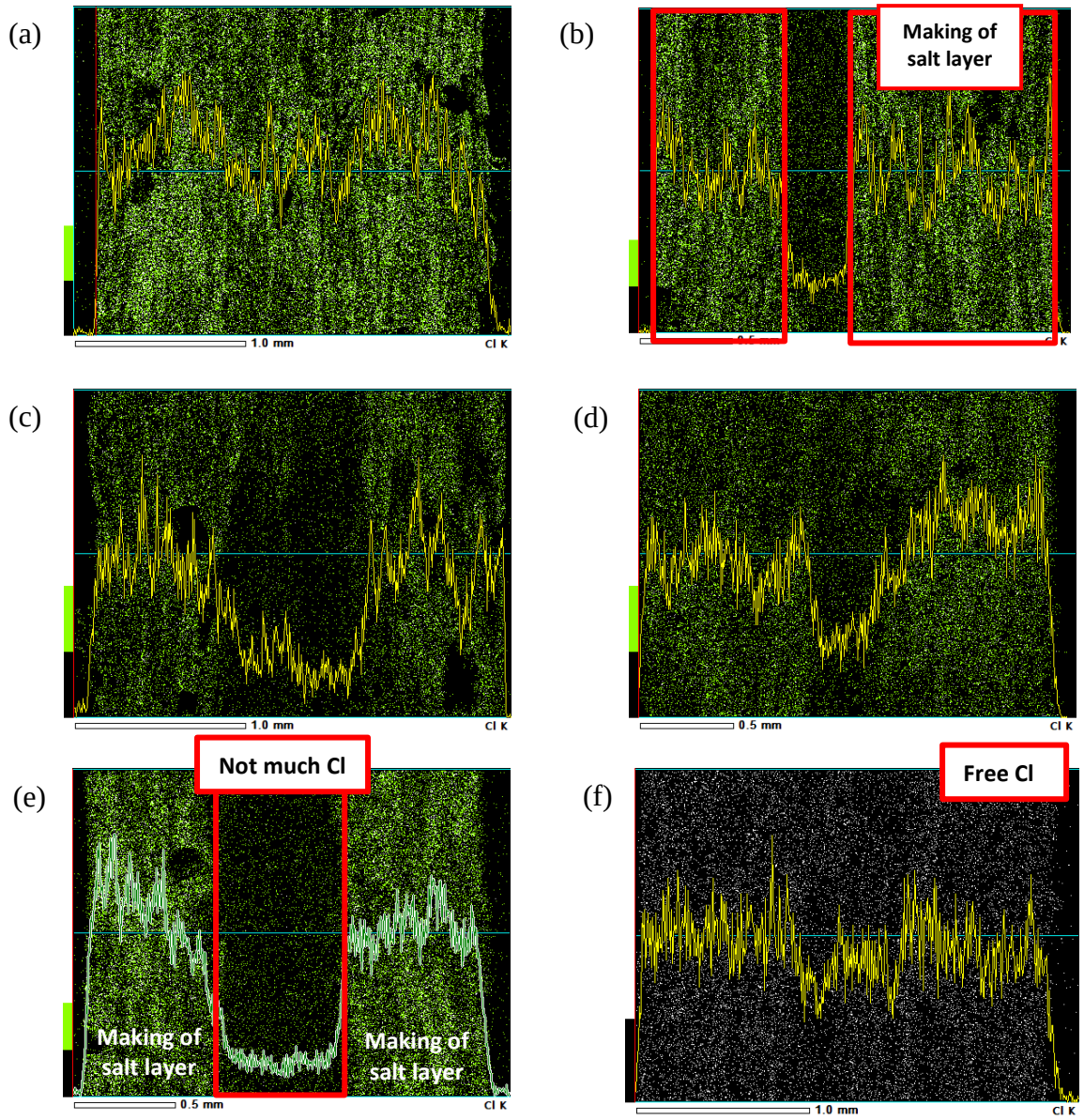

Figure 8. EDS Cl mapping of cross section glass-fiber-epoxy specimen in (a) vapor phase after 1 cycle (b) liquid phase after 1 cycle (c) vapor phase after 2 cycles (d) liquid phase after 2 cycles (e) vapor phase after 3 cycles (f) liquid phase after 3 cycles.

Penetration of Cl for liquid phase condition can be seen from Fig. 8 (b), (d), and (f). After 1 cycle exposed to cyclic concentration solution, salt layer is made in the outside part of specimen, meanwhile, there is not so much Cl detected in the inside part, this might be due to penetration of Cl is not reached to center part of the specimen yet. On the other hand, after 3 cycles exposure to cyclic concentration solution, it can be seen in Fig. 8 (f), free Cl is detected. This might happen due to cleaning out by the water penetration after secondary or three times water dipping. The center part of the specimen can be more clearly cleaned by water and makes the center of the specimen have a low HCl concentration.

4.4 FTIR observation

FTIR observation is conducted to collect the evidence of swelling behavior that occurred on the surface specimens by monitoring acid diffusion and reaction with cured epoxies while immersed in cyclic solution concentration. FTIR analysis for initial condition shown in Fig. 9. The absorbance peak at 1510 cm^{-1} attributed to the stretching mode of the aromatic ring in the epoxy monomer was identified as the invariant band. The absorbance peak at around 700-1000 cm^{-1} is attributed to silicon ring that formed from glass fiber. The absorbance of the band 1105 cm^{-1} corresponds to the ether function of the amine (curing agent for epoxy) part.

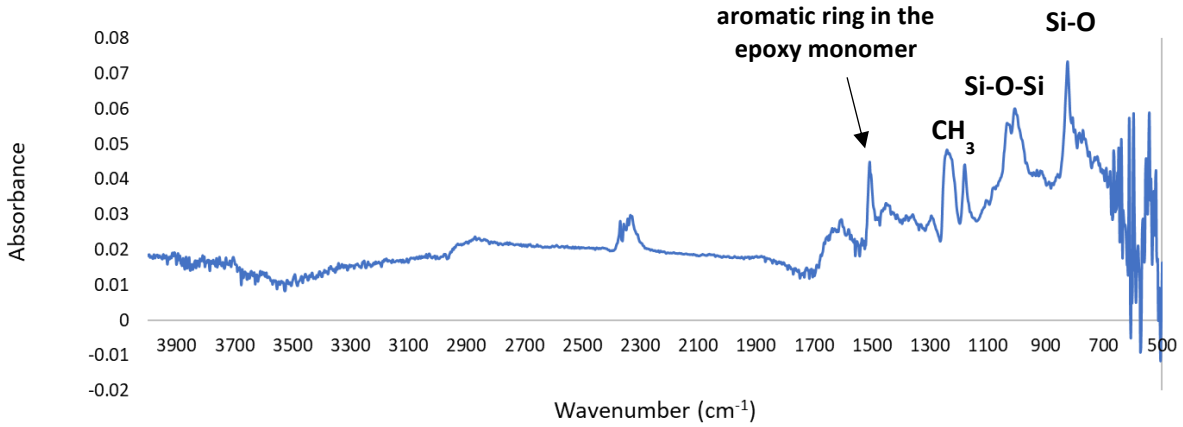

Figure 9. FTIR observation for cyclic solution concentration at initial condition

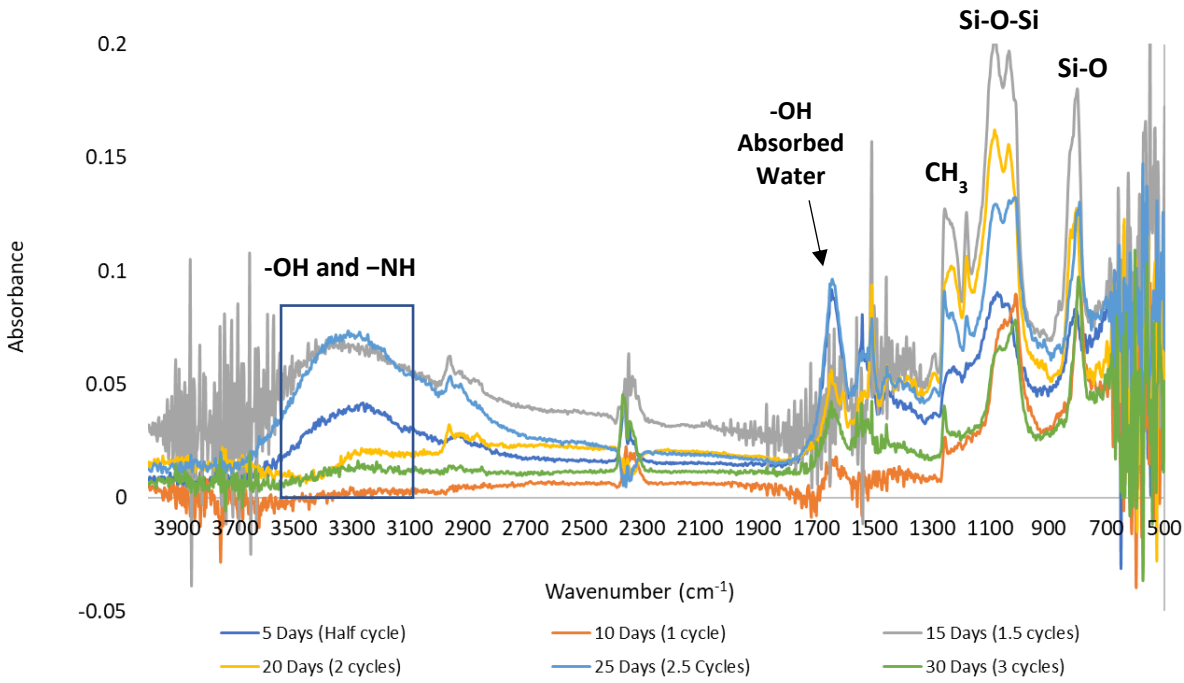

Figure 10. FTIR observation on vapor phase condition after exposure to cyclic solution concentration

As shown in Fig. 10, during exposure in 35 mass% HCl, the broad peaks corresponding −NH bands in the 3500−3200 cm^{-1} region were observed could be attributed to the ionic bonding between HCl and tertiary amine moieties within the epoxy network to form an ammonium chloride salt complex. The formation of salts disrupts the noncovalent polar interactions within the amine-cured epoxy matrix and facilitates further plasticization by HCl. IR spectra absorbed water in the range of 3700-3000 cm^{-1} an increasing intensity of –OH variant band as water diffuses into the epoxy networks.

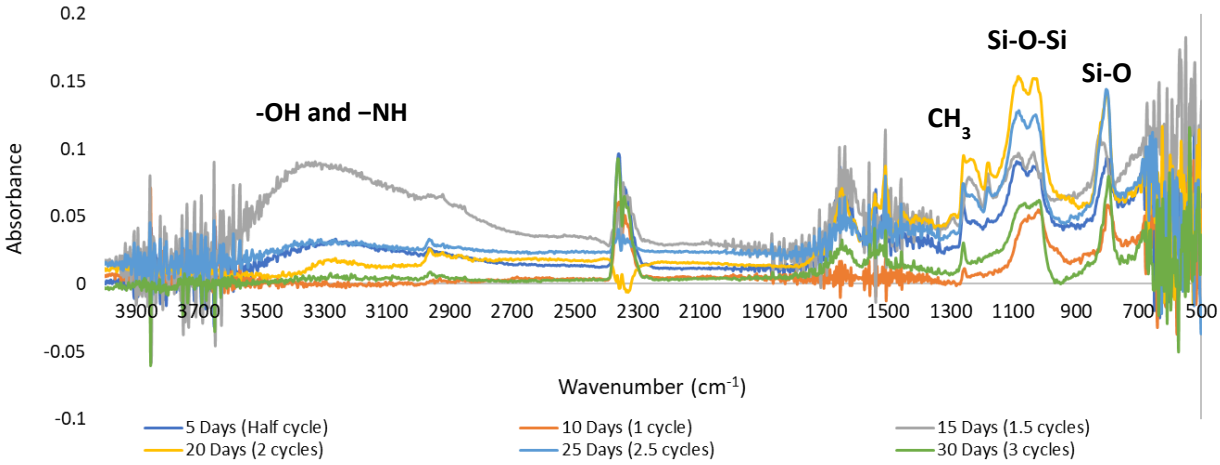

Figure 11. FTIR observation on liquid phase condition after exposure to cyclic solution concentration

The broad plateau shown in Fig. 11, attributed to HCl hydrates and ammonium chloride salt complex remains despite being lower in intensity, evident of the strong binding between HCl and tertiary amine moieties. Other than the polar interactions indicated by the broad peak 3500−3200 cm^{-1} region as explained earlier, no significant chemical degradation reactions were observed. Thus, it can be concluded that the HCl acid degradation during the experiment of this amine-cured epoxy system proceeds via a physical degradation mechanism due to swelling.

5 CONCLUSIONS

In this research, an accelerated experimental method such cyclic solution concentration, has been developed to acknowledge the cause of the tank roof failure. The evaluation of solution penetration and degradation behaviour of glass fiber-epoxy amine cured exposed to 35 mass% HCl and 0% (water) alternately under cyclic solution concentration on vapor phase and liquid phase condition is studied. Degradation behaviour is analysed from the mass uptake, mechanical properties, penetration depth of Cl and FTIR observation. The conclusion of this research as follows:

(1) Mass uptake result showed that HCl penetrates the epoxy at a faster rate than water, this might be due to the amine salt generation reaction. There was less acceleration in the vapor phase compared to the continual immersed in 35mass% of HCl in the liquid phase.
(2) Three-point bending test is conducted to examine the flexural strength for its mechanical properties. The result showed that the flexural strength is decrease with increasing exposure time. The reduction of flexural strength is linearly proportional to mass uptake of solution and the reason is mainly because of plasticization. Additionally, decreases in flexural strength occurred as water penetrated the resin in the deterioration process.
(3) The penetration depth of Cl in specimens was obtained from elemental mapping of cross-section using SEM/EDS. The result showed that there is salt making layer in the outside part of the

specimens for both vapor phase and liquid phase condition. After 3 cycle (30 days) exposure to cyclic concentration, not much Cl was detected in the inside part of the specimen, but still making salt layer in the outside part, for vapor phase condition. On the other hand, for liquid phase condition, free Cl detected. This may occur because of cleansing by water penetration after a second or third dipping. The center of the specimen can be cleaned more thoroughly with water, resulting in a lower HCl concentration in the center of the specimen.

(4) FTIR observation is conducted to collect the evidence of swelling behavior that occurred on the surface specimens by monitoring acid diffusion and reaction with cured epoxies while immersed in cyclic solution concentration. During exposure in 35 mass% HCl, −NH bands in the 3500−3200 cm^{-1} region were observed could be attributed to the ionic bonding between HCl and tertiary amine moieties within the epoxy network to form an ammonium chloride salt complex. The generation of salts resulted in plasticization by HCl in the specimen. There are no significant chemical degradation reactions observed both in the vapor phase and liquid phase condition. Thus, it can be concluded that the HCl acid degradation of this amine-cured epoxy system proceeds via a physical degradation mechanism due to swelling.

The effect of dynamic concentration change under cyclic solution was confirmed. Water or acid penetrating into the epoxy matrix makes the network enlarge and swell, thus the strength of the composites decreases and lead to the material's degradation.

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