ANISOTROPIC ACID PENETRATION IN TRIANGULAR BAR REINFORCED EPOXY COMPOSITE

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1 Introduction
Polymer composites are commonly used as barrier coating or lining in chemical equipment due to slow diffusion of fluid through the composite. The impermeable fillers suspended inside the polymer matrix of the composite reduce fluid diffusion by decreasing the area available for transport and increasing the path length of the diffusing fluid [1-4]. Polymer composites are usually categorized according to the shape of the reinforcing fillers [5-7]. Composites reinforced with fibers and whiskers are one dimensional; those reinforced with flakes, platelets, disks, and ribbons are two dimensional; and with spheres and beads are three dimensional. Among the types of polymer composites, two dimensional composites are advantageous as barrier materials due to the capability of their fillers for planar reinforcement [6,7].

Diffusion of fluids in polymer composites is anisotropic and highly dependent on the orientation of suspended fillers in the polymer matrix. In the case of flake-filled polymer composites, if the impermeable flakes are uniformly oriented orthogonal to the direction of fluid diffusion, overall diffusion is slow compared to unfilled polymer [1-4]. However, if the impermeable flakes are oriented parallel to the direction of fluid diffusion, overall diffusion is faster than polymer filled with orthogonal flakes [1-4,8-10]. Overall diffusion resistance of the polymer composite is a function of filler alignment. When flakes are oriented perpendicular to diffusion direction, the effective diameter of flakes greatly reduces the area available for diffusion and increases the diffusing species path length. When flakes are oriented parallel to diffusion direction, only the flake thickness reduces the diffusion area and the diffusing species path length is similar to that of the unfilled polymer. This orthogonal relationship between diffusion resistance and filler orientation is also evident in other polymer composites, such as polymer matrices reinforced with aligned impermeable fibers.

A previous work [11] investigated water diffusion in a permeable polymer matrix reinforced with a layered assembly of semi-permeable triangular bars. The polymer matrix is made of acid anhydride cured epoxy resin, while the reinforcing triangular bar fillers are made of cured vinyl ester. Acid anhydride cured epoxy absorbs more water than cured vinyl ester due to their chemical structure. After the composite specimens were prepared, they were immersed in deionized water for 1200 h, vacuum dried for 300 h, and re-immersed again for another 300 h at 80°C. The weight changes in specimens were monitored with time, and diffusion coefficient values during water immersion, vacuum drying, and re-immersion were calculated from experimental data. Based from the results, overall water diffusion was observed to be fast when water diffuses from the pointed/sloped side of the polymer composite; and slow when water diffuses from the base/flat side of the material. The result from the previous work is illustrated in Fig. 1. The pointed/sloped side of the material behaves like a polymer reinforced with tipped flakes; the base/flat side of the material behaves like a polymer reinforced with orthogonal flakes. This functionality is possible due to the asymmetric shape of the triangular filler. While effective diffusion in flake polymer composites is orthogonally dependent, effective diffusion in triangular bar reinforced composite was observed to be uniaxial and direction-dependent.

This work further investigated the expected anisotropic diffusion behavior of fluids in triangular bar reinforced polymer composites. Epoxy composite specimens were manually fabricated and immersed in acid solution at constant temperature.
Acid penetration depths in epoxy composite specimens were measured versus time. Effect of triangular bar filler orientation (pointed/sloped side versus base/flat side) and alignment (parallel versus staggered) were discussed based from the experimental results.

2 Experimentation

2.1 Material Selection

Bisphenol A type epoxy resin (Epoxy Epomik R140, Mitsui Chemical Co., Ltd.) cured with polypropylene oxide diamine curing agent (Jeffamine D230, Huntsman Co.) was chosen as the polymer matrix of composite specimens. Cured bisphenol A vinyl ester resin (Ripoxy R-804, Showa Highpolymer Co., Ltd.) was the material used for the triangular bar fillers of the composite. Fig. 2 shows the chemical structure of bisphenol A type epoxy resin, polypropylene oxide diamine curing agent, and vinyl ester resin. Amine cured epoxy resin is selected as the permeable polymer matrix of the composite specimens due to its high absorption of acid solutions at high temperature as reported in literature [12-15]. During acid diffusion, tertiary amine salts are formed resulting from the coordination of acid ions and amine groups present on the polymer network. On the other hand, cured vinyl esters and polyesters are quite resistant to dissolution and diffusion of acid solutions [16,17].

2.2 Composite Specimen Fabrication

Triangular bar fillers made of cured vinyl ester were prepared following the procedures in the previous study [11]. For a batch of triangular bar fillers, 50 g of vinyl ester resin was mechanically mixed with 0.2 g of methyl ethyl ketone peroxide and 0.2 g of 6% cobalt naphthenate. The resulting polymer mixture was degassed and poured into a special mold assembly as shown in Fig. 3 (sprayed with mold release agent Daifree GA-7500, Daikin Industries, Ltd.) specifically fabricated for curing triangular bar fillers with base, height, and length of 5 mm, 1.6 mm, and 120 mm, respectively. The metal mold assembly consists of attaching two corrugated cover plates to a smooth middle plate by screws. The mold was then placed inside a convection oven and was heated for 2 h at 50°C, followed by 3 h at 100°C for post-curing. A batch could produce a maximum of 42 cured triangular bars. It was noted that it was somewhat difficult to produce defect-free triangular bar fillers due to trapped air in the small triangular channels of the special mold assembly. The trapped air usually results to voids inside the triangular bar fillers after curing. The brittle nature of cured vinyl ester resin also contributes to preliminary cracks and early breakage of some triangular bar fillers. Those triangular bar fillers that were fully cured with minimal defects were selected and trimmed to a final length of 10 mm for filler assembly.

The triangular bar fillers were manually assembled as shown in Fig. 4. The arrangement of triangular bars per layer was guided by a pattern laid out in 1-mm grid paper. Unlike in the previous study [11] where two separate 3-layer structures were assembled and bonded to form a 6-layer symmetrical structure, the triangular bar fillers in this study were continuously placed in a layer-wise fashion until a 6-layer asymmetrical structure was formed. The triangular bar fillers were bonded at their ends using cyanoacrylate adhesive (Aron Alpha Extra 2000, Toagosei Co., Ltd.). Each layer of the resulting asymmetrical structure was composed of 15 triangular bars with 1 mm spacing. The filler assembly was used to reinforce a 100 x 100 x 10 mm composite specimen.

Two types of filler alignment were used during manual filler assembly, as illustrated in Fig. 5. Composite specimens with parallel alignment were labeled AB5-1, while those with staggered alignment were labeled CD5-1.

The 6-layer asymmetrical filler structure was then placed inside a 190 x 190 x 10 mm metal mold. The metal plates were lined with thin polyester sheets, and all contact surfaces of the mold setup were applied with mold release agent (QZ 13, Nagase Chemtex Corp.) The polymer matrix was prepared by mechanically mixing 300 g of epoxy resin and 96 g of diamine curing agent. The degassed polymer mixture was slowly added to the mold with the filler assembly fixed inside. Afterwards, the mold was closed with a metal plate and was taken to a thermal press for curing. The amine epoxy matrix was cured using the following steps: 5 h at 80°C and 10 h at 120°C.

2.3 Edge Sealing of Specimens

The cured epoxy composite reinforced with the asymmetrical triangular bar filler structure was cut
into a 100 x 100 mm square plate. Edges were polished with waterproof abrasive paper before storing in a convective air oven at 50°C for at least 100 h. While composite specimens in [11] used stainless steel foil in sealing the edges of specimens before the experiment, composite specimens in this study used cured vinyl ester. The application of vinyl ester lining around the edges of the specimens was performed using a simple setup shown in Fig. 6. The surfaces of the square plate specimen (excluding the edges) were wiped with mold release agent (QZ 13, Nagase ChemteX Corp.) before placing it in a metal pan (approximately 150 x 120 x 15 mm; also wiped with mold release agent). About 100 g of vinyl ester resin, mechanically mixed with 0.40 g of methyl ethyl ketone peroxide and 0.40 g of 6% cobalt naphthenate and then degassed, was poured in the pan. A cylindrical metal weight (90 x 45 mm, 2300 g) was used to fix the specimen on the pan. The metal pan was then put on a convection air oven for curing of vinyl ester lining. The excess cured vinyl ester resin was cut to leave a lining of 1-2 mm thickness around the edges of the composite specimens. The cured vinyl ester lining in the edges of the composite specimens was needed to ensure through-the-thickness diffusion and penetration of acid solution in the composite specimen. After curing the vinyl ester lining around the edges, the composite specimens were again stored in a convective air oven at 50°C for at least 100 h before proceeding to acid immersion experiments. Aside from composite specimens, pure amine epoxy specimens were also prepared for testing and comparison and were labeled as EP-AM.

2.4 Optical Microscopy
Excess material taken from AB5-1 and CD5-1 specimens after they were cut into 100 x 100 x 10 mm square plates were analyzed under an optical microscope to take images of their cross-section and to view the actual alignment and spacing of triangular bar fillers inside the composite specimens. Images of the physical state of specimens were also taken after exposure to acid solution.

2.5 Acid Immersion and Penetration Depth
Pure epoxy EP-AM and its composite specimens AB5-1 and CD5-1 were immersed in 10 wt% H₂SO₄ solution maintained at 80°C. After a certain time of exposure, specimens were taken out of acid immersion and were cut to observe the composite structure by optical microscope and to measure the penetration depth of sulfate ions in the specimens by energy dispersive x-ray spectroscopy (EDS). The method of using EDS to measure the acid solute penetration depth in specimens as a function of exposure time [12-15] involves the sulfur line concentration profile as a guide. The acid penetration depth in specimens during acid immersion was manually measured from the surface of the specimen in contact with the acid solution.

3 Results and Discussion
3.1 Cross-Sectional Images of Composites
Fig. 7 shows the cross-section optical images of polymer composite specimens AB5-1 and CD5-1. In both optical images, the pointed/sloped side of reinforcing triangular bar fillers is oriented on one surface of the specimen, while the base/flat side is oriented on the opposite surface. The actual composite structure of specimens is composed of 6 layers of triangular bar fillers with an overall specimen thickness of 10 mm. The estimated height and base of each triangular bar filler is 1.6 x 5 mm; the estimated gap size between triangular bar fillers in the same layer is 1 mm. The said composite structure is fabricated in this study for the purpose of viewing the penetration of diffusing acid solution in the composite specimen from both sides during acid immersion. As also shown in Fig. 7, triangular bar fillers in AB5-1 specimen are arranged in parallel alignment, while fillers in CD5-1 specimen are arranged in staggered alignment. Small misalignment in the arrangement of triangular bar fillers is observed since the fillers are manually assembled by hand.

3.2 Acid Penetration during Immersion
Fig. 8 shows the EDS images of acid penetration in EP-AM and AB5-1 (from the pointed/sloped side and base/flat side) specimens after 50 h of immersion in 10 wt% H₂SO₄ solution at 80°C. The sulfur line concentration profile indicates the presence and penetration of acid solution in the specimen during acid immersion. The same EDS image was also observed for CD5-1 specimens during early acid immersion.
The acid penetration depth in specimens is measured from the EDS image as shown in Fig. 8. A solid line is drawn in the EDS image to indicate the position of the acid penetration front. The distance of the acid penetration front from the exposed surface of the specimen is measured and recorded as the acid penetration depth.

Fig. 9 shows the acid penetration depth in EP-AM specimen as a function of immersion time in 10 wt% H$_2$SO$_4$ solution at 80°C. The measured acid penetration depth in EP-AM specimen increases linearly with square root immersion time, as also observed in [12-15]. From this result, it is possible to predict the acid penetration depth in pure amine cured epoxy as a function of acid immersion time, given in this study by Eq. 1:

$$y = 0.159x$$

where $y$ is the acid penetration depth in EP-AM specimen and $x$ is the square root of acid immersion time.

Fig. 10 shows the acid penetration depth in EP-AM and AB5-1 specimens during early acid exposure as a function of immersion time. Side A corresponds to the AB5-1 specimen surface where pointed/sloped side of aligned triangular bars is oriented; side B corresponds to the surface of AB5-1 specimen where base/flat side of aligned triangular bars is oriented. The acid penetration depth of EP-AM is given by Eq. 1. At 50 h and 100 h of acid immersion, acid penetration is observed to be faster in side A than in side B. The difference in acid penetration between sides A and B is due to difference in exposed permeable epoxy matrix area for sulfuric acid penetration. The resistance to acid penetration offered by side B is similar to orthogonal flakes, where only a small area of epoxy matrix is exposed to the penetrating acid solution. However, in side A, the resistance to acid penetration is small due to large area exposed to acid penetration. This behavior is somewhat similar to the diffusion resistance offered by a polymer composite reinforced with parallel or tipped flakes.

Aside from filler orientation (pointed/sloped versus base/flat sides), Fig. 10 also shows the effect of triangular bar filler reinforcement (EP-AM versus AB5-1) in acid penetration. After 50 h of acid immersion, acid penetration is observed to be lower in AB5-1 than in EP-AM. Similar to flakes, the triangular bar fillers decrease the permeable area and increase the path length of penetrating acid solute within the composite specimens. However, after 100 h of acid immersion, the acid penetration in side A of AB5-1 specimen is higher than in EP-AM; acid penetration in side B of AB5-1 specimen is lower than in EP-AM. The observed high acid penetration in side A of AB5-1 specimen than in EP-AM is due to filler/matrix interface degradation, as shown in Fig. 11. After 100 h of acid immersion, the area of exposed fillers due to epoxy matrix degradation is large in side A compared in side B due to difference in concentration of filler/matrix interfaces. Side A has more filler/matrix interfaces than side B. During early acid immersion, the triangular bar fillers are acting as barrier fillers, creating a tortuous path for acid penetration through the polymer composite. After most of the filler/matrix interfaces are degraded, the acid solution prefers to penetrate at the interfaces. At this time, the degraded interfaces around triangular bar fillers are acting as conduits for faster acid penetration within the polymer composite.

The mechanism of tortuous acid penetration coupled with accelerated acid transport at the degraded filler/matrix interfaces is also observed in polymer composites reinforced with untreated glass flakes [15,18].

Fig. 12 shows the acid penetration depth in EP-AM and CD5-1 specimens during early acid exposure as a function of immersion time. Side C corresponds to the CD5-1 specimen surface where pointed/sloped side of aligned triangular bars is oriented; side D corresponds to the surface of CD5-1 specimen where base/flat side of aligned triangular bars is oriented. Similar to AB5-1 specimen, acid penetration is observed to be faster from the pointed/sloped side than from the base/flat side. Moreover, after 100 h of acid immersion, acid penetration from the pointed/sloped side of CD5-1 specimen is higher than EP-AM which indicates filler/matrix interface degradation.

From Figs. 10 and 12, acid penetration in the composite specimens at 50 h of acid immersion is observed to be independent of filler alignment. At this time of exposure, the acid solution has not completely penetrated the first layer of the reinforcing composite structure. In polymer composites reinforced with orthogonal flakes [1-4,8-
10,18], the effect of filler alignment is evident after the diffusing fluid reaches the second layer of reinforcing fillers. Staggered fillers offer higher diffusion resistance than parallel fillers due to “wiggling” or increased tortuosity in staggered fillers. After 100 h of immersion, accelerated acid transport at the degraded filler/matrix interfaces has governed the overall acid penetration behavior in the polymer composite specimens.

4 Conclusion
The results from this work show anisotropic acid penetration behavior in amine cured epoxy composites reinforced with aligned triangular bars made of cured vinyl ester. Acid penetration is faster from the sloped side of the polymer composite than from the flat side; hence, uniaxial and direction-dependent. The experimental observation suggests the mechanism of tortuous acid penetration in triangular bar reinforced polymer composites coupled with accelerated local acid transport at the degraded filler/matrix interfaces. Acid penetration is found to be independent of filler alignment during early acid immersion of polymer composite specimens.

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References
Fig. 1. Anisotropic fluid diffusion in triangular bar reinforced polymer composite

Fig. 2. Chemical structure of bisphenol A type epoxy, polypropylene oxide diamine, and vinyl ester

Fig. 3. Special mold assembly for curing triangular bar fillers, showing the surfaces of corrugated cover plate and smooth middle plate
Fig. 4. Layer-wise manual assembly of triangular bar fillers into a 6-layer structure. The resulting 6-layer asymmetrical filler structure is fixed inside a mold for curing the polymer composite specimen.

Fig. 5. Parallel filler alignment in composite specimen AB5-1 and staggered filler alignment in composite specimen CD5-1.

Fig. 6. Setup for applying cured vinyl ester lining at the edges of specimen.

Fig. 7. Cross-section optical images of AB5-1 and CD5-1 epoxy composite specimens.
Fig. 8. EDS images of acid penetration in EP-AM and AB5-1 specimens during immersion in 10 wt% H₂SO₄ solution at 80°C.

Fig. 9. Acid penetration depth in EP-AM specimen as function of square root immersion time in 10 wt% H₂SO₄ solution at 80°C.

Fig. 10. Acid penetration depth in EP-AM and AB5-1 specimens as function of immersion time in 10 wt% H₂SO₄ solution at 80°C.
Fig. 11. Filler/epoxy matrix degradation in sides A and B of AB5-1 composite specimen during 100 h of immersion in 10 wt% H$_2$SO$_4$ solution at 80°C.

Fig. 12. Acid penetration depth in EP-AM and CD5-1 specimens as function of immersion time in 10 wt% H$_2$SO$_4$ solution at 80°C.