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Degradation kinetics of glass-reinforced polyesters in chemical environments

Part I *Aqueous solutions*

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Glass-reinforced polyesters (GRPs) are attractive in structural applications due to their strength-to-weight ratio and resistance to chemical attack. For marine and processing applications, in particular, GRPs must withstand long-term exposure to brine and either highly acidic or basic aqueous solutions. In this work, we report on the degradation of two GRP laminates, a pultruded isophthalic polyester (IPE) and a hand-moulded vinyl ester (VE), in brine (5% w/v NaCl) and a 10% w/v NaOH(*aq*) solution over the course of 270 days at 25 °C. Tensile and flexural strengths have been measured as a function of immersion time and reveal that the IPE resin is more susceptible to water permeation and fibre–resin debonding than the VE. While the IPE laminate undergoes dramatic tensile strength deterioration in NaOH(*aq*) within the first 30 days of immersion, the VE resin is far more resistant to degradation in either solution. These measurements are consistent with surface features imaged with electron microscopy. Incorporation of polyethylene terephthalate (PET) or C-glass surface veils into these laminates is not generally beneficial for property retention, since the veils produce more interfaces and enhance water absorption through wicking.

1. Introduction

Commercial interest in glass-fibre reinforced polyester (GRP) composites has grown tremendously in recent years due principally to the attractive strength-to-weight ratio afforded by these materials. While the importance of this ratio is well-established (particularly in the aerospace and automotive industries), these materials have also become the focus of efforts undertaken to inhibit structural degradation (e.g., corrosion) in adverse solution environments. The marine environment, for instance, is considered to be one of the most naturally aggressive, capable of corroding steel at rates of up to 0.75 mm per year. For this reason, marine vessels, as well as oil and natural gas pipelines, are typically coated with a protective composite layer to reduce the extent of corrosion [1]. In marked contrast to the kinetics of steel degradation, the physical properties (e.g., tensile strength) of some GRP composites have been found [2] to decrease by less than 20% after 3 years of incessant exposure to brine (3.5% NaCl).

Alkaline solutions constitute another highly corrosive environment commonly encountered in a variety of chemical processing industries. Alkaline emulsions are often used to remove organic constituents from recycled cleaning chemicals, while large volumes of caustic soda (i.e., sodium hydroxide, NaOH) are produced upon sodium hypochlorite decomposition in wood pulp bleaching processes [1]. Upon prolonged exposure to concentrated NaOH (*aq*) solutions, the tensile strength of GRP laminates has been found to decrease by as much as 75% [3]. Degradation of these composites occurs when the solution either (i) diffuses through the surface polyester layer and reaches the underlying glass laminates [4, 5] or (ii) penetrates into the laminate core through microcracks or other surface imperfections resulting from moulding and shrinkage [6, 7]. It has been suggested that, since free segmental motion is restricted in chemically crosslinked polymers, microvoids develop in the polymer as it is cured and cooled through its glass transition [6]. Penetration of solution through the polyester is consequently facilitated by both capillary effects through the matrix [7] and wicking along the polymer–glass interface [8].

Once the solution contacts the glass mats within the laminate core, catastrophic degradation ensues as the solution reacts chemically with individual glass fibres. When exposed to alkaline, acidic or even neutral aqueous solutions, glass fibres containing alkaline modifiers (such as Na^+ or K^+) are subject to chemical attack. In low-pH and slightly basic solutions

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(pH < 9), the primary reaction governing glass degradation is dissociation of the Si–O–R bond (R = Na or K) [9, 10]:

$$\text{Si–O–R} + \text{H}^+ \rightarrow \text{Si–OH} + \text{R}^+ \qquad (1)$$

Depending on factors such as the concentration of alkaline modifiers in the glass and the initial solution pH, the final solution pH can increase substantially due to an increase in alkali. When the solution pH exceeds ≈9, Si–O–Si bonds, as well as Si–O–R bonds, are affected, resulting in [10]

$$\text{Si–O–Si} + \text{NaOH} \rightarrow \text{Si–O–Na} + \text{Si–OH} \quad (2)$$

Since catastrophic degradation of a GRP composite commences when the solution contacts the vulnerable interior glass mats, a reasonable course of action to delay material degradation (and consequently increase application life) is to hinder solution penetration into the laminate core. Recent efforts by Cowley and Robertson [11] have suggested that this can be achieved in commercial polyester composites comprised of isophthalic polyester (IPE) or vinyl ester (VE) by incorporating a nonreactive surface layer (a veil). This layer, consisting of either a more chemically resistant glass (C-glass, rather than the E-glass used in interior mats) or a semicrystalline thermoplastic (e.g., polyethylene terephthalate, PET), would serve to produce a dense polyester-rich surface. [Note that the E-glass fibres in nonveiled composites are often exposed at the surface.] In this work, we examine the role of surface veils by monitoring the morphological and strength evolution of veiled and nonveiled GRP composites during long-term (270 day) exposure to brine and NaOH aqueous solutions. The objectives here are two-fold: (i) to compare the degradation kinetics of pultruded IPE and hand-laid VE GRP composites, and (ii) to ascertain the efficacy of PET and C-glass veils on degradation resistance.

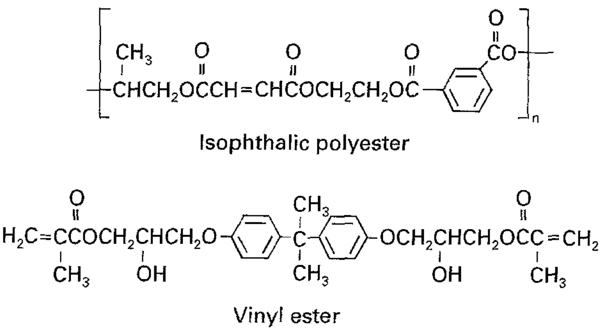

Figure 1 Chemical structures of the isophthalic polyester (IPE) and vinyl ester (VE) resins used to produce the glass-reinforced polyester (GRP) laminates examined in this work.

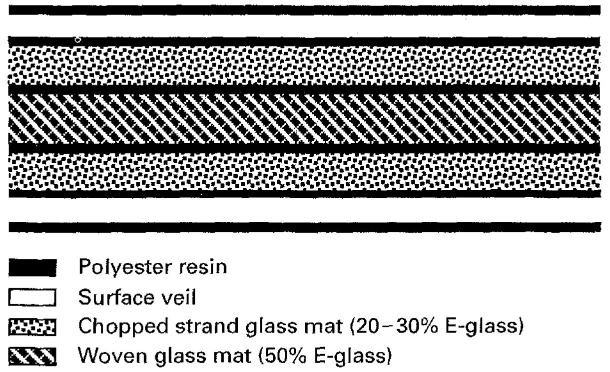

Figure 2 Illustration of a veiled GRP laminate in cross-section. Note that the veil is sub-surface, residing below a polyester-rich layer. The laminate components are labelled in the key.

2. Experimental methods

2.1. Materials

The chemical structures of the two matrix esters employed in this study, IPE (Dion® 31031, Reichhold Chemicals Inc.) and VE (Dion® 9100NP, Reichhold Chemicals Inc.), are shown in Fig. 1, and the glass in the primary glass-fibre rovings was E-glass. The veils examined here were either PET or C-glass. Large quantities (4.5 L) of two aqueous solutions, one 5% (w/v) NaCl (Fisher Scientific) and the other 10% (w/v) NaOH (Fisher Scientific), were also prepared.

2.2. Methods

Composites were either pultruded (IPE) or hand-moulded (VE) to form both veiled and nonveiled laminates. These material/method pairs permitted evaluation of GRP laminates used in products of uniform thickness, such as pipes (pultruded IPE), as well as in large-scale products, such as storage tanks (hand-molded VE). A cross-sectional view of a veiled composite is schematically depicted in Fig. 2. Rectangular coupons measuring 10 cm long × 2.5 cm wide × 0.375 cm thick were cut from the laminates and edge-coated with bisphenol fumurate polyester resin (Atlac® 4010A, Reichhold Chemicals Inc.) to reduce solution penetration through the exposed sides. Samples were immersed in the two solutions and stored in non-reactive Qorpak glass bottles (946 mL maximum capacity) at 25 °C. To minimize solution evaporation over the course of the study, the bottles were sealed with Teflon tape. Seven coupons were placed at random orientation in each bottle: three for flexural tests, three for tensile tests and one for morphological/chemical testing.

Samples were removed at specific time intervals up to 270 days, rinsed with distilled water and air-dried for 30 min prior to storage or analysis. To determine the tensile strength (σ_t), the coupons were ground into a dog-bone shape (for stress concentration) and tested on an ATS 1105C unit operated at a crosshead speed of 0.2 cm min^{-1}. Flexural strengths (σ_f) were measured by the four-point method. These tests were conducted in accordance with ASTM standards D 638–89 and D 790–86, respectively. After sputter-coating with *ca.* 20 nm of Au, sample surfaces were imaged, and elemental maps obtained, with a Hitachi S530 scanning electron microscope (SEM) operated at 25 kV and equipped with an energy-dispersive X-ray (EDX) detector.

3. Results and discussion

3.1. Degradation in brine

3.1.1. Effect of polyester

The derogatory effect of brine on GRP composite properties is due principally to the presence of water, which permeates into the composite core, carrying with it Na^+ and Cl^- ions [12]. Water permeation during the course of study is evidenced by an increase in sample mass. Fig. 3 shows the mass uptake of non-veiled IPE and VE composites (averaged over 5 samples) and clearly demonstrates that the IPE composites absorb more water than do the comparably constructed VE samples. The shapes of the curves help to elucidate two important permeation characteristics: (i) the diffusive mechanism and (ii) the ester-dependent solubility. An initially sigmoidal (*S*-shaped) curve is representative of non-Fickian diffusion, which is expected here *a priori* due to the glassy, as well as layered, nature of both polyester matrices [13]. Close comparison of the IPE data collected here with those reported by Jones [14] for diffusion of distilled water in IPE at 50 °C (see the inset of Fig. 3) reveals an inconsistency with respect to the mechanism of diffusion (i.e., the data obtained with distilled water are suggestive of Fickian diffusion). In the case of Fickian diffusion, the diffusion coefficient of a penetrant species through a polymeric medium can be deduced from the linear portion of the curve obtained by plotting mass uptake as a function of $\text{time}^{1/2}$. Diffusion coefficients reported for water in IPE and VE composites are approximately 6.7×10^{-9} and 4.0×10^{-9} $cm^2 s^{-1}$, respectively [15]. In the event that diffusion is non-Fickian (as it is in the present work), this approach is invalid and cannot be used to estimate *D*.

Whether Fickian or non-Fickian, the diffusion fronts perpetuating from both exposed surfaces of the sample coupons continue to penetrate toward the sample interior where they meet and an equilibrium solubility is established. While diffusion is a kinetic phenomenon, solubility is a measure of matrix-penetrant thermodynamic interactions and thus depends strongly on environmental conditions and resin chemistry [7]. Both of these factors are discussed in detail below. It is important to immediately recognize from Fig. 3, however, that the solubility of brine in IPE is more than double that in VE. Subramaniam *et al.* [16] have found that the equilibrium absorption of water in neat phenolic resins and carbon–fibre phenolic composites is nearly independent of temperature (unless degradation of the laminate takes place), whereas the time to reach equilibrium is, as expected, faster at elevated temperatures. Again comparing the data obtained here to those provided by Jones [14] indicates that the NaCl salt does not seem to appreciably change the solubility of water in IPE. In contrast to this result, Tai and Szklarska-Smialowska [17, 18] report that an increase in NaCl concentration (from 0.01 to 3.5%) yields a reduction in the solubility of water in epoxy adhesives. While the brine data in Fig. 3 suggest that the equilibrium mass uptake may be slightly lower than that of distilled water, the accuracy of the data collected here cannot permit such subtle differentiation. In addition, the mass uptake data displayed in Fig. 3 have been acquired at 25 °C, whereas those of Jones [14] correspond to 50 °C. The temperature difference is again seen to have little effect on the equilibrium solubility of water in IPE. It must be remembered, however, that these comparisons involve data differing in both salt concentration and temperature, reflecting a coupled effect on water solubility.

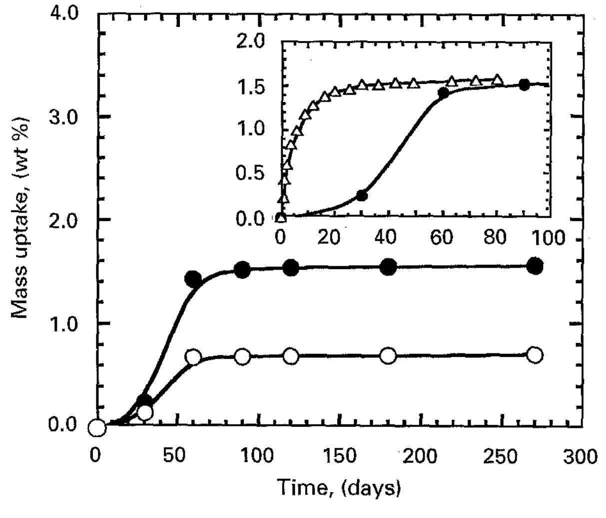

Figure 3 Mass uptake as a function of time for brine (5% NaCl solution) permeating through VE (○) and IPE (●) laminates. Shown in the inset are the data of Jones [14] for distilled water through IPE (△).

Bellenger *et al.* [19] have demonstrated that the water equilibrium concentration is independent of temperature and packing density in vinyl esters, but have correlated water solubility with the concentration of hydroxyl, ether and ester polar functionalities. According to their data, solubility increases with the number of carbonyl groups, which weaken intramolecular hydrogen–bonding and therefore promote intermolecular hydrogen bonds between the water and polyester. Once water molecules diffuse into a polyester matrix, they readily hydrogen–bond with the crosslinked polymer at the polar ester linkages [14]. As seen in Fig. 1, the IPE investigated here possesses four ester linkages per repeat unit, in contrast to the VE which has only two ester linkages per repeat unit. Thus, based on previous results [19], brine is expected to be more soluble in IPE than VE due to the greater concentration of hydrogen bonding sites. Consistent with this expectation, Harper and Naeem [15] have shown that IPE samples immersed in distilled water exhibit higher water solubilities than do comparable VE samples. According to Morel *et al.* [20], the equilibrium water uptake may also be envisaged as a measure of inter-molecularly bonded hydroxyl groups; i.e., an increase in the concentration of such bonds yields a reduction in water solubility. From Fig. 1, the VE is seen to possess two hydroxyl groups per repeat unit, whereas the IPE has none.

Fig. 4 shows the percentage retention of tensile strength (σ_t) with time for the two polyesters examined here. Retention is defined here as $1 - M(t)/M(t = 0)$, where $M(t)$ is a material property measured at time *t*.

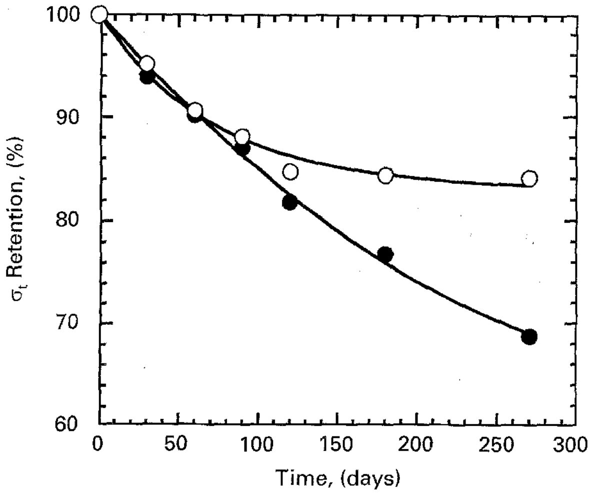

Figure 4 Variation of tensile strength (σ_t) retention with immersion time for VE (○) and IPE (●) GRP laminates in brine at 25 °C.

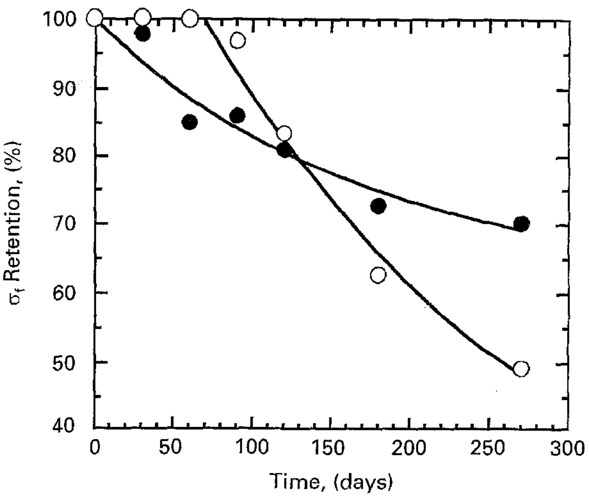

Figure 5 Time evolution of the flexural strength (σ_f) for VE (○) and IPE (●) laminates in brine at 25 °C.

In both cases, σ_t is seen to decrease substantially, by about 16% in the VE and 31% in the IPE at 270 days. The observed reduction in σ_t can be most likely attributed to fibre–resin debonding. This explanation is consistent with the results of Chua *et al.* [21], who report that the force required to extract an E-glass fibre from IPE decreased by about 40% when the composite was immersed for 100 h in water at 60 °C. A moisture-induced 30% reduction in σ_t has also been recorded [22] for graphite/epoxy laminates upon prolonged exposure to air at 100% relative humidity. In addition to fibre–matrix debonding due to water clustering, such strength reduction may reflect water-induced polyester plasticization [16, 23, 24], which would further facilitate debonding (see Fig. 4). Even in this case, however, retention of nearly 69% of the initial IPE σ_t indicates that penetrated brine has little, if any, effect on the glass fibres. Similar results have been reported by Karloshov *et al.* [12], who found that σ_t retention in carbon/epoxy composites is about 94% in a 3% NaCl solution after 30 days at 90 °C. Note that their data are virtually identical to the short-time data displayed in Fig. 4.

In contrast to the σ_t retention data in Fig. 4, the IPE laminate is seen in Fig. 5 to exhibit greater flexural strength (σ_f) retention than the VE analogue upon long-term exposure to brine. This behaviour seems counter-intuitive, especially considering that the IPE has absorbed almost twice as much water than the VE. The presence of water, which plasticizes the IPE resin, may, however, help to promote "crack blunting" [14], in which permeated water molecules cluster together within the matrix and hinder propagation of a crack tip. In the study conducted by Jones [14] (see Fig. 3), crack blunting commences when the water concentration reaches a critical value ($\approx$0.32%). Since water clusters possess finite size, they prefer to settle in less densely packed sites, such as voids or microcracks [8, 25], thereby changing the mechanical response of the surrounding plastic zone and inducing an increase in the fracture surface energy [14]. Thus, the increased water absorption in the IPE laminate investigated here promotes greater matrix plasticization and, consequently, more flexibility than the comparable VE laminate. In a separate study, Morii *et al.* [26] have recorded a σ_f retention of 45% for a VE laminate immersed in distilled water for 125 days at 80 °C. From Fig. 5, however, the σ_f retention for the present VE laminate in brine is much greater ($\approx$80%) after 125 days. While no explanation is offered here for this variation, it must be remembered that the two studies were conducted at different temperatures and salt concentrations.

Examination of the post-immersion laminates by SEM reveals that the sample and fracture surfaces of the IPE laminates are similar to those of the VE samples after 270 days. Fig. 6 consists of a pair of secondary electron micrographs obtained from an IPE laminate (Fig. 6a) and a VE laminate (Fig. 6b). The sample surfaces of both materials exhibit long crack lines that appear to follow glass fibres. Such cracks are not unexpected: as the concentration of permeated water within the laminates increases, the polyester resin swells, resulting in both fibre–resin debonding and resin cracking. Note that, according to images such as the ones in Fig. 6, the IPE laminate possesses more and wider surface cracks than the VE analogue, which is consistent with the tensile and flexural data presented in Figs 4 and 5. That is, the IPE composites absorb more water and undergo greater fibre–resin debonding (significant σ_t reduction rate) and more plasticization (less pronounced σ_f reduction) than the VE composites at long times. At short times, the flexural strength does not change appreciably for the VE laminates up to about 60 days, suggesting that an induction period exists during which time water absorption is relatively slow (see Fig. 3).

A micrograph of an IPE fracture surface (produced during the tensile tests) is provided in Fig. 7 and clearly demonstrates that, after 270 days of immersion in brine, the IPE laminate fails due to fibre–resin debonding, since the E-glass fibres remain relatively intact beyond the point of polyester fracture. Since the fibres do not crack along the same plane as the matrix, it can be concluded that the fibres have not degraded

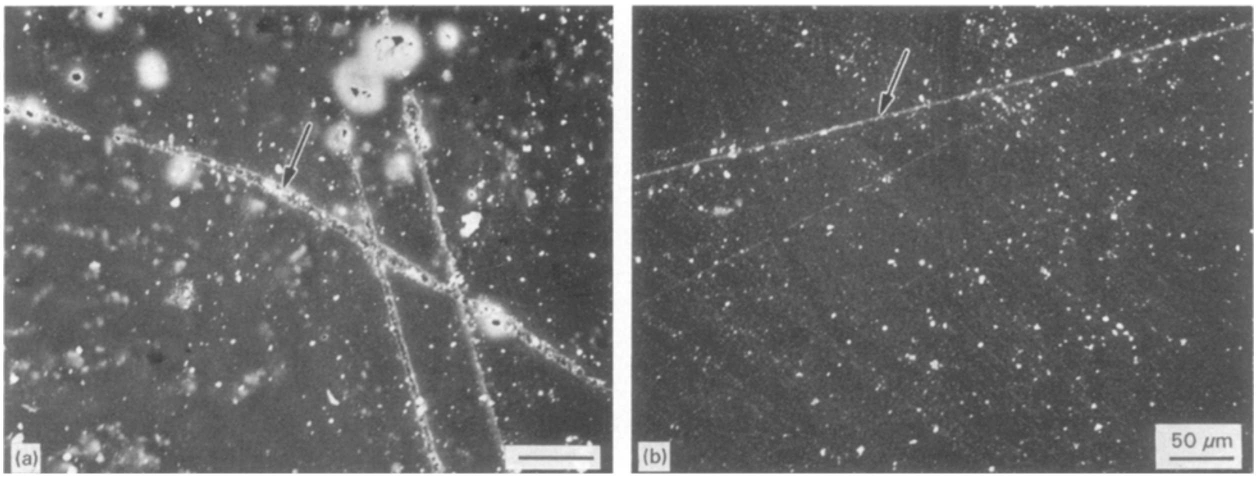

Figure 6 SEM micrographs of the (a) IPE and (b) VE laminate surfaces upon immersion in brine for 270 days. Note the presence of cracks that appear to follow glass fibres (arrows).

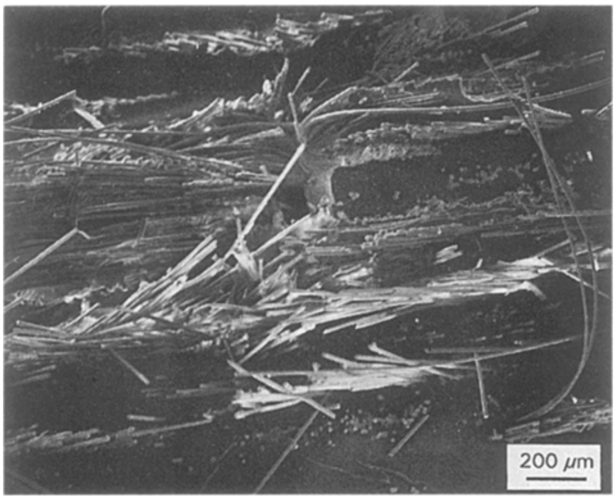

Figure 7 Fracture surface of the IPE laminate after being exposed to brine for 270 days. Many of the glass fibres remain intact, extending from the polyester matrix, suggesting that failure occurred by fibre–resin debonding.

appreciably, again in agreement with the tensile and flexural strength retention discussed earlier. Energy-dispersive X-ray maps obtained from fracture surfaces of the IPE and VE composites (data not shown here) demonstrate that (i) Cl is present throughout the laminate, signifying that brine is not restricted to the surface layer, and (ii) the spatial distribution of Cl from NaCl correlates only marginally with that of Si from the E-glass fibres.

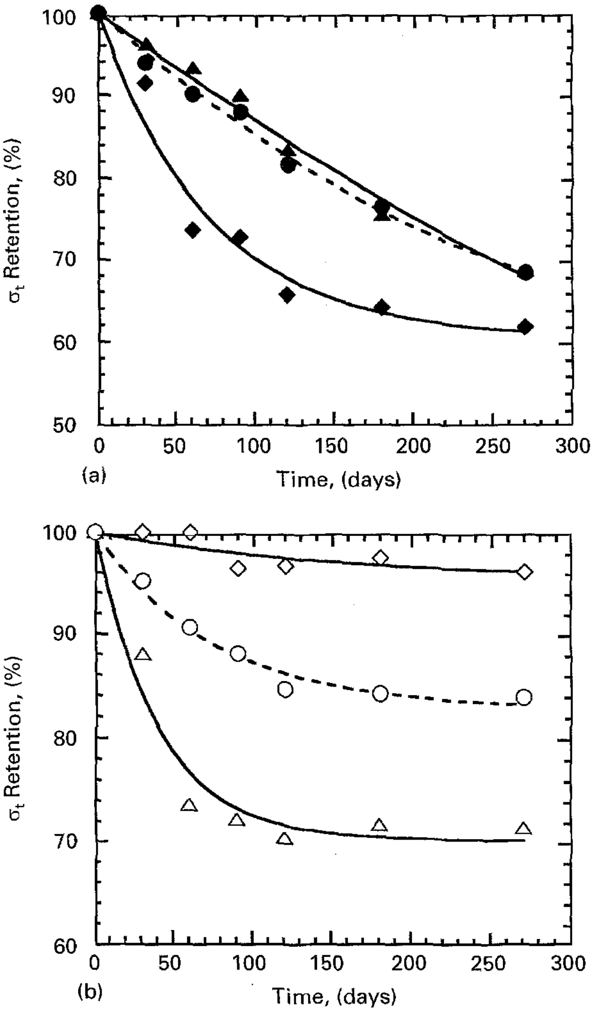

Figure 8 σ_t retention as a function of immersion time in brine for (a) IPE and (b) VE laminates with no veil (circles), a PET veil (diamonds) or a C-glass veil (triangles).

3.1.2. Effect of surface veil

If a protective veil is incorporated into either the IPE or VE laminate, a *ca.* 0.23 cm thick polyester-rich surface is obtained. This layer, along with the chemically resistant veil, are anticipated to hinder diffusion/wicking of a liquid penetrant into the laminate core, thereby reducing the rate at which degradation of the vulnerable E-glass mats (or the fibre–resin interface) occurs. In this work, two veils have been examined: a three-dimensional woven composed of PET and a pressed mat comprised of C-glass. Their efficacy in the presence of brine can be compared in Fig. 8, which shows σ_t retention for IPE (Fig. 8a) and VE (Fig. 8b) laminates. In Fig. 8a, the time evolution of σ_t retention for the nonveiled and C-glass-veiled IPE laminates is virtually identical, suggesting that the mechanism responsible for strength reduction is the same in each case. In both cases, σ_t retention decreases monotonically and does not exhibit any evidence of reaching a limit over the course of the 270-day study. In contrast, the strength retention of the PET-veiled IPE laminate undergoes a substantial initial reduction at short times (< 120 days) and then exhibits a limiting value of about 62–64% at long times. This observation implies that the presence of a PET surface veil initially accelerates degradation in brine by enhancing water permeation via wicking and, consequently, fibre–resin debonding. At times beyond 270 days, it is unclear whether the σ_t of the unveiled and C-glass-veiled laminates will continue to decrease monotonically, in which case the PET-veiled laminates would exhibit greater strength retention.

In Fig. 8b, the σ_t retention of all three VE laminates is seen to initially decrease with immersion time and then level off to about 84% (nonveiled), 71% (C-glass) and 96% (PET-veiled). A comparison of Fig. 8(a, b) immediately reveals that the benefit of adding a surface veil differs substantially for IPE and VE laminates in brine. Incorporation of the PET veil, for instance, results in the most pronounced strength reduction in the IPE laminates, but the greatest strength retention in the VE laminates. In the case of the VE composites, the PET veil (possessing ester linkages) serves to hinder both brine permeation into the E-glass core and subsequent fibre–resin debonding. Unlike the IPE laminates, however, addition of a C-glass veil to the VE composites promotes the most significant reduction in σ_t. While the PET veil does not substantially affect the tensile strength of either laminate, the C-glass veil contributes greater strength to the laminate, as well as four resin–fibre interfaces at which water molecules may aggregate. Since absorbed water interacts more effectively with IPE than with VE, water molecules may cluster more readily along the C-glass fibres in the VE laminates (and expedite fibre–resin debonding sooner) than in the IPE laminates.

In all cases, however, the long-term brine-induced loss in σ_t is clearly seen to be substantially greater for the IPE laminates than for any of the VE analogues. This difference is again attributed to the greater permeation of water through the IPE resin. It is, however, important to remember at this juncture that the IPE and VE laminates were processed differently, and so generalizations regarding their comparative performance must be necessarily limited. Improved adhesion between the VE and PET veil during the course of hand-moulding, for example, is expected to decrease the extent of wicking, while surface imperfections in the C-glass-veiled laminates could facilitate brine penetration. Thus, processing differences must be explicitly considered in (i) the analysis of the data presented in this work and in a related study [27] and (ii) the rational design of veiled GRP composites for commercial applications.

Flexural strength retention data, shown in Fig. 9a for the IPE laminates, reveals that the veil-induced mechanisms responsible for tensile strength reduction (Fig. 8a) are also responsible for flexural strength reduction. Fig. 9a demonstrates that the nonveiled and C-glass-veiled laminates respond similarly to long-term exposure to brine, whereas the flexibility of the PET-veiled IPE laminates degrades more rapidly. Concurrent reductions in σ_t and σ_f suggest that the PET veil facilitates both water solubility (plasticization) and fibre–resin debonding. The VE laminates, on the other hand, respond differently due to the greater hydrophobicity of the matrix resin. In Fig. 9b, σ_f retention is greatest at short times for the unveiled laminate (due to less water absorption). The flexural strength of the C-glass- and PET-veiled VE laminates decreases at a comparable rate over the course of the study, indicating that both veils promote water absorption. As mentioned earlier, glass fibres can strongly interact (and chemically react) with water, and the PET veil consists of ester linkages which can serve to entrap water molecules through hydrogen bonds. Gopalan *et al.* [28] have reported that water absorption in epoxy composites reinforced with Kevlar® (which is a strong hydrogen–bonding polyamide) is greater than in an epoxy reinforced with E-glass continuous strand mat. Aditya and Sinha [29], as well as Wright [30], have observed similar increases in water uptake when the reinforcing fibre is more absorbent than glass. Since the contribution of the PET veil to tensile strength is minimal (much less than the C-glass veil), water-enhanced polyester plasticization

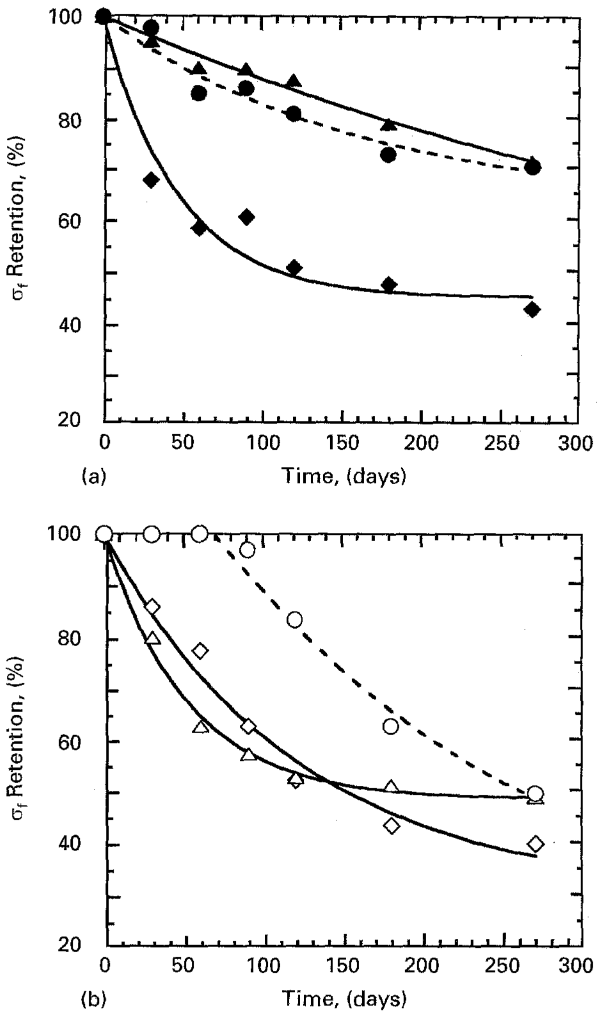

Figure 9 Dependence of σ_f on immersion time in brine for (a) IPE and (b) VE laminates with no veil (circles), a PET veil (diamonds) or a C-glass veil (triangles).

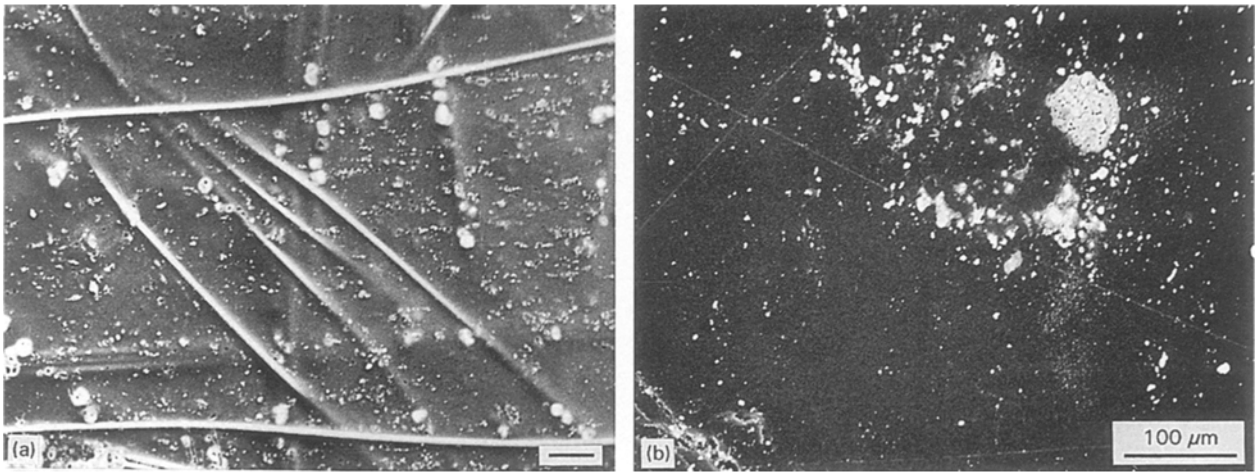

Figure 10 SEM micrographs of the (a) IPE and (b) VE laminates with C-glass veil, illustrating that their surfaces exhibit cracks which could lead to reductions in either σ_t and/or σ_f.

due to incorporation of a surface veil can be more accurately ascertained through flexural testing.

Electron micrographs of the C-glass-veiled IPE (Fig. 10a) and VE (Fig. 10b) laminates reveal that their surfaces exhibit cracks and, to a lesser extent, fibres extending from the surface. As in the nonveiled specimens, degradation occurs predominantly as cracks that follow individual glass fibres. According to Fig. 10a, entire glass fibres, as well as coincident cracks, are evident on the IPE surface after 270 days of immersion in brine. The VE specimen displayed in Fig. 10b exhibits markedly fewer fibres and less cracking on its surface (due to less water absorption and, hence, less swelling) than the IPE laminate. Fig. 10b also illustrates that discrete flaws arise on the VE surface due to prolonged exposure to brine. Micrographs of the PET-veiled IPE and C-glass-veiled VE laminate surfaces are similar in appearance to those presented in Fig. 10 and are not included here for that reason.

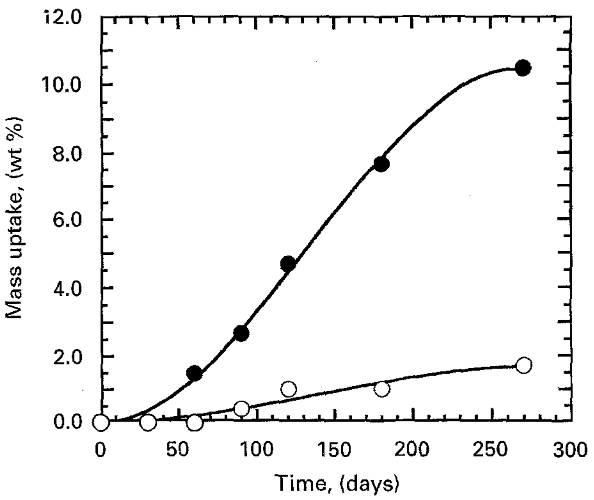

Figure 11 Mass uptake of NaOH(aq) in VE (○) and IPE (●) laminates as a function of immersion time.

3.2. Degradation in NaOH solution

3.2.1. Effect of polyester

Shown in Fig. 11 is the mass uptake that occurs in each of the nonveiled GRP laminates upon immersion in NaOH aqueous solution. As in the case of brine (Fig. 3), absorption is more pronounced (by as much as $\approx 9\%$) in the IPE laminate than in the VE analogue, and the S-shaped curve is again representative of non-Fickian diffusion. While the explanations provided earlier to account for the greater brine-induced weight change of IPE (as compared to VE) remain pertinent in describing NaOH(aq) permeation, the reactive nature of a high-pH solution must also be considered (see Equation 2). Hojo *et al.* [31] have investigated the degradation of both epoxy and polyester resins at different NaOH concentrations and at varying temperatures. At their highest temperature (80 °C), diffusion of alkali from a 20% NaOH(aq) solution into epoxy resin initially induces a weight increase, but is soon followed by a reduction in weight due to dissolution and hydrolysis of the resin (i.e., sample erosion). A remarkable increase in weight then ensues after 100 h of exposure due to absorption of alkali. At 50 °C, they only observe a monotonic decrease in sample mass, due presumably to erosion of the laminate. In the present study (conducted at 25 °C in a 10% NaOH solution), degradation of both polyesters is observed in Fig. 11 to occur without evidence of an erosion-induced reduction in specimen weight. Though a comparison of the results from these studies is not straightforward due to the temperature difference (which strongly affects chemical reactivity), such a comparison implies that (i) the degradation mechanism of GRP laminates in NaOH(aq) at elevated temperature may not be the same at ambient temperature and (ii) extrapolation of data from accelerated high-temperature degradation studies to lower temperatures may be entirely invalid.

Fig. 12 shows the time evolution of σ_t retention for IPE and VE laminates in the aqueous NaOH solution. The tensile strength of the IPE laminate decreases dramatically (by as much as 85%) over the first 30 days of exposure and then reaches a limit of about 10% after 270 days of immersion. As in the case of brine, water diffuses into the laminate and leaches out water–soluble alkaline components (e.g., sodium,

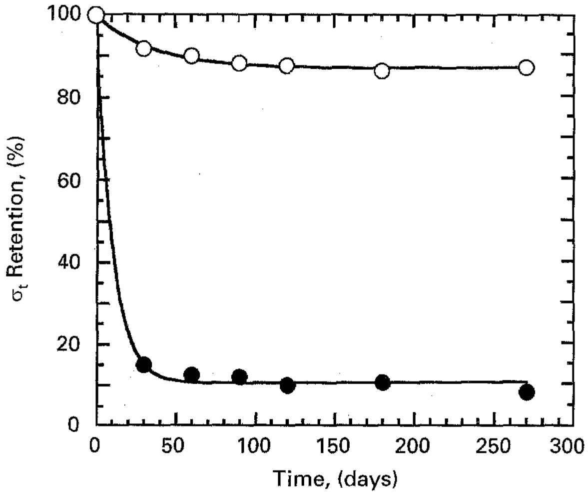

Figure 12 σ_t retention as a function of immersion time for VE (○) and IPE (●) GRP laminates in NaOH(*aq*) at 25 °C.

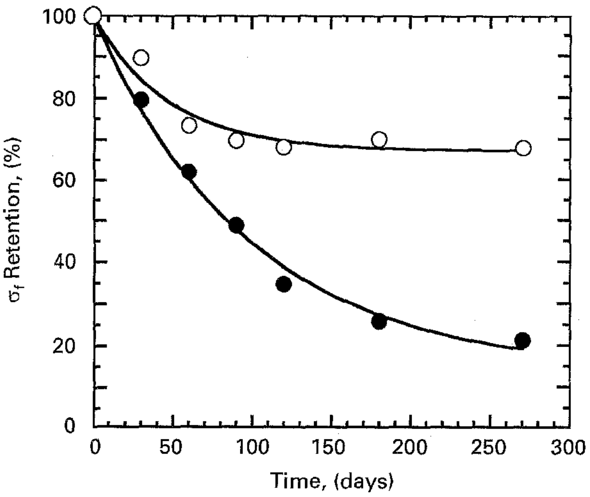

Figure 13 Time evolution of σ_f for VE (○) and IPE (●) laminates in 10% NaOH(*aq*) at 25 °C.

calcium and magnesium ions) present in the E-glass fibres that serve to reinforce the laminate [32]. This mechanism has been examined by Barkett *et al.* [7], who determined the types of oxides leached from E-glass, as well as the rate at which leaching occurs, by analysing the composition of the deionized water in which GRP VE samples were stored for 450 days. As leaching proceeds, alkaline ions present in the glass are replaced by protons, resulting in an increase in tensile stress along the fibre and a corresponding reduction in the tensile strength of the fibre [5]. Moreover, the high-pH NaOH(*aq*) solution is also capable of breaking the SiO_2 bond (see Equation 2) and hydrolysing the polyester resin, causing almost total destruction of the IPE laminate. In fact, alkali resistance is a principal deficiency of IPE resins, since their ester linkages are prone to hydrolysis in the presence of an alkali [33].

The VE laminates, on the other hand, are considerably less affected by the NaOH(*aq*) solution than the IPE laminates. In contrast to the rapid 85% reduction in σ_t for the IPE laminates, the reduction in σ_t for the VE laminates is only about 14% after 270 days of exposure (see Fig. 12). It is of interest to note that this result is in close agreement with the 16% reduction in σ_t measured for the VE laminate in brine (see Fig. 4). The observed reduction in σ_t for the VE laminates can therefore be attributed to the same mechanism responsible for degradation of the laminates in brine, namely, water-induced plasticization of the resin, followed by fibre–resin debonding. Unlike the IPE resin, VE consists of phenyl ether linkages, which are more resistant to hydrolysis, especially in alkaline solutions. Moreover, since the VE is terminated by methacrylate groups (see Fig. 1), the pendant methyl groups are effective in sterically shielding the two ester linkages [34].

The chemical effect of NaOH on the IPE and VE resins also helps to explain the decrease in σ_f seen in Fig. 13. While both polyesters exhibit a more dramatic reduction in NaOH(*aq*) than in brine (Fig. 5), the VE laminates are again less affected by immersion in NaOH(*aq*) than are the IPE laminates (32% versus 79% after 270 days). This trend is to be expected, since the IPE is susceptible to chemical attack in an alkaline environment, and is consistent with data provided by Matzeg and Santrach [3], who report a σ_f retention of 49% for VE GRP (E-glass) laminates after 300 days of immersion in NaOH(*aq*) at 25 °C. The difference in the magnitudes of σ_f retention at long times may be attributed to process-related specimen variation. Upon comparing Figs 12 and 13, the VE specimens are also found to exhibit a greater decrease in σ_f than in σ_t, reflecting a combination of resin plasticization (as in the case of brine) and fibre–resin debonding. Note, however, that degradation of the load–bearing E-glass fibre mats in the VE laminate, unlike those in the IPE laminate, appears almost negligible, even after 270 days of immersion.

Electron micrographs of the IPE and VE sample surfaces after 270 days in NaOH(*aq*) are presented in Fig. 14(a, b), and show a distinct change in topology. The IPE laminate seen in Fig. 14a at relatively low magnification consists of highly degraded resin and large gaping cracks that expose the E-glass fibres comprising the laminate core. At higher magnification (see the inset of Fig. 14a), the degraded surface resin appears as spherical bundles of resin that resemble yarn. Degradation of the E-glass fibres in the IPE laminates is apparent from the SEM micrograph obtained from a cross-fractured IPE specimen (after 270 days of immersion) and displayed in Fig. 15. In contrast to the fracture surface shown in Fig. 7 for an IPE laminate exposed to brine, the micrograph in Fig. 15 reveals that the E-glass has become embrittled upon long-term exposure to NaOH(*aq*), cracking primarily along the fracture plane of the matrix resin. Note that very little fibre–resin debonding is evident in this micrograph. In the VE laminates, on the other hand, degradation is not as rampant, since large cracks or extending glass fibres are not characteristic of the surface topology (see Fig. 14b). Only resin degradation is clearly evident in these specimens after 270 days of immersion. Micrographs of cross-fractured VE laminates (data not shown) indicate that failure in these composites occurs primarily by fibre–resin debonding.

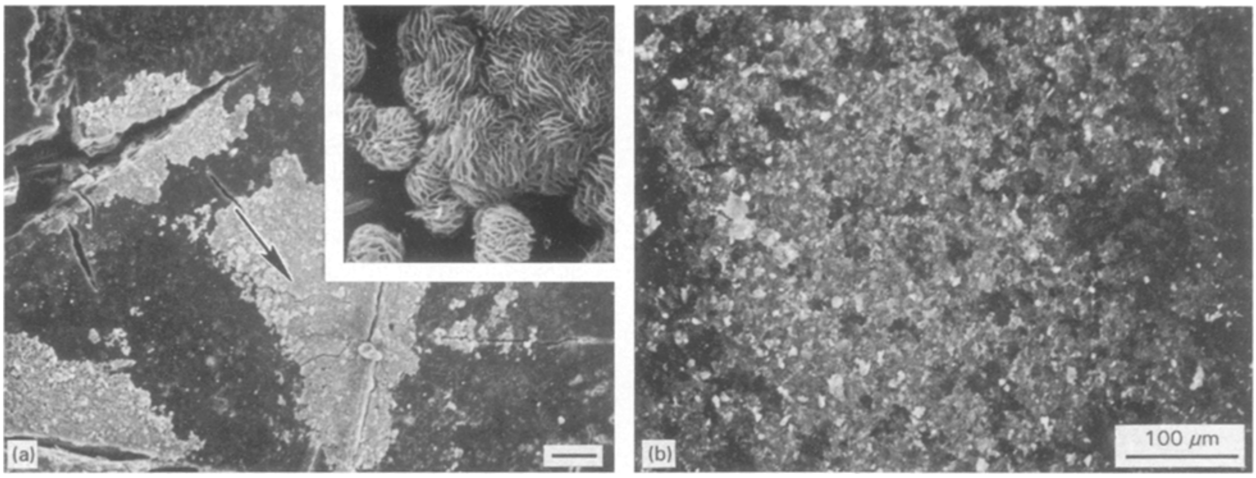

Figure 14 SEM micrographs of the (a) IPE and (b) VE laminate surfaces after 270 days of immersion in NaOH(aq). The inset in (a), enlarged by 31 ×, corresponds to the highly degraded region (arrow).

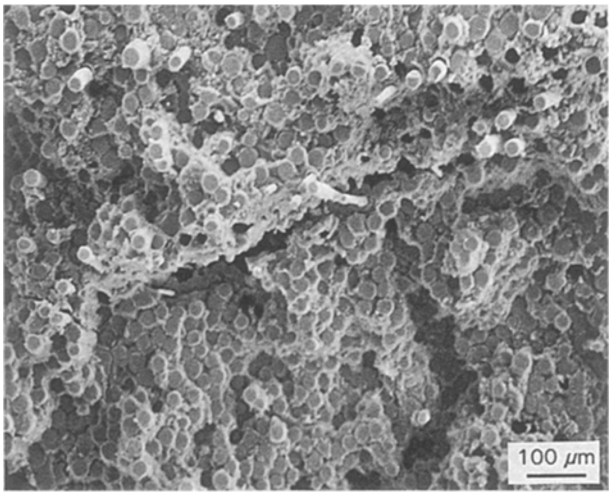

Figure 15 Electron micrograph of a cross-fractured IPE laminate showing that the E-glass fibres break along the fracture plane of the resin, indicating that they have chemically degraded after 270 days in NaOH(aq).

3.2.2. Effect of surface veil

According to Duffy [35], if the GRP resin is not resistant to the solution in which the laminate is immersed, incorporation of a chemically resistant surface veil will provide no discernible benefit, and structural degradation will remain extensive. This conclusion is drawn from a study in which a chlorendic anhydride-based polyester resin was supposed to be exposed to a 5% aqueous NaOH solution at 65 °C for a period of 360 days, but was removed prior to completion due to extreme sample deterioration. Fig. 16 shows the effect of C-glass and PET veils on σ_t retention in the IPE (Fig. 16a) and VE (Fig. 16b) laminates investigated in the present work. In Fig. 16a, incorporation of either veil serves to reduce the rate at which σ_t decreases with time of immersion in the 10% NaOH aqueous solution. Since the σ_t retention curves each start at 100% at $t = 0$ days and exhibit a limit of $\approx 6.5\%$ at $t = 270$ days, they can be fitted to an empirical function of the form $100 - A[1 - \exp(-kt)]$, where A is a limiting constant and t denotes immersion time, to compare the relative degradation rate constants (k). Linear regression of the data yields the following values of k (in days^{-1}): 0.075 for the nonveiled IPE, 0.037 for PET-veiled IPE and 0.033 for C-glass-veiled IPE.

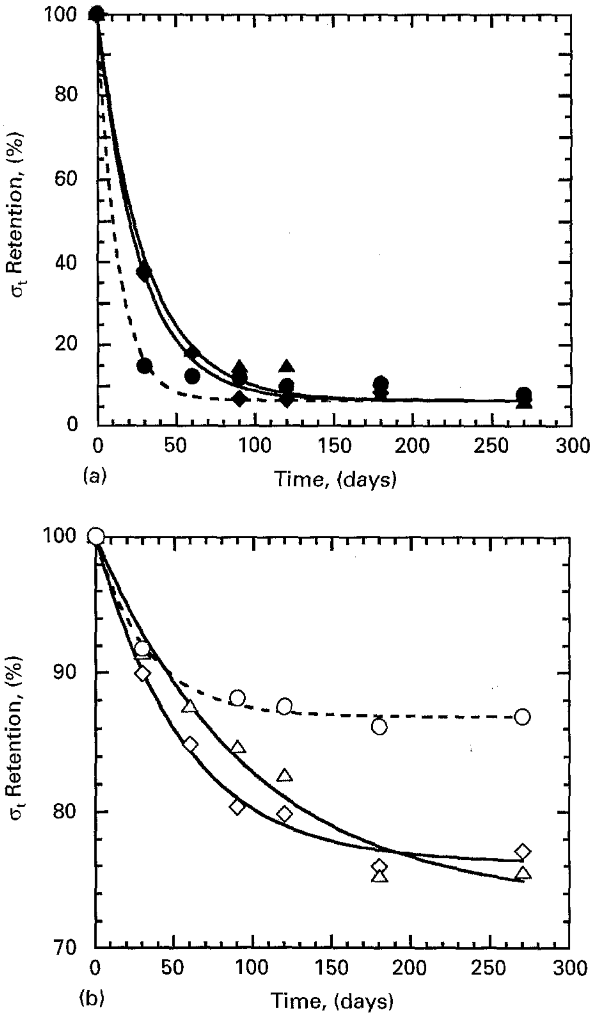

Figure 16 σ_t retention as a function of immersion time in NaOH(aq) for (a) IPE and (b) VE laminates with no veil (circles), a PET veil (diamonds) or a C-glass veil (triangles).

Thus, the PET and C-glass veils are nearly equally effective in reducing the rate at which the IPE

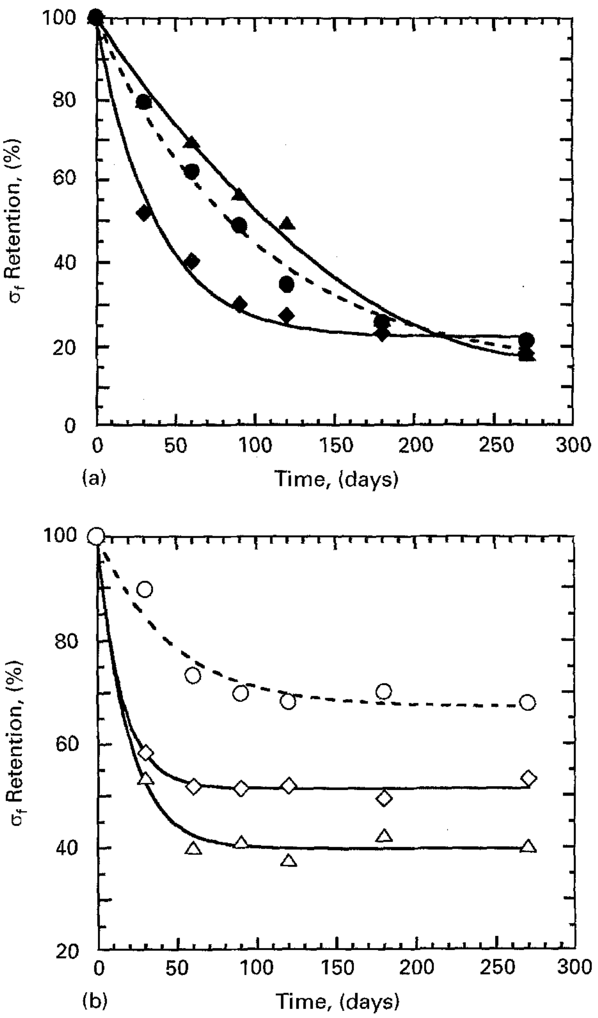

Figure 17 Dependence of σ_f on immersion time in NaOH(*aq*) for (a) IPE and (b) VE laminates with no veil (circles), a PET veil (diamonds) or a C-glass veil (triangles).

laminates degrade. However, degradation of the IPE laminates with either surface veil added is still dramatic, and is comparable to that of the nonveiled IPE laminates, indicating that the veils are not very effective in a resin that is itself susceptible to chemical degradation (in agreement with the conclusion reached by Duffy [35]). In marked contrast, the nonveiled VE laminates appear to be more resistant to σ_t reduction than either the PET- or C-glass-veiled VE laminates. According to the data in Fig. 16b, retention of σ_t for nonveiled laminates reaches a limiting value of about 87% after 270 days, whereas the σ_t retention decreases to less than 80% for the PET- and C-glass-veiled laminates. The similarity in the PET and C-glass curves suggests that these veils promote a comparable degradation mechanism which results in quicker degradation of the load-bearing glass fibres. Since the VE laminate is relatively resistant to NaOH degradation, incorporation of either veil into the VE laminate increases the rate of structural degradation, presumably by facilitating NaOH wicking through the VE resin. It should be realized, however, that all of the VE laminates, with and without added surface veil, clearly outperform all of the IPE laminates in terms of σ_t retention.

As seen in Fig. 17a, the time evolution of σ_f (like σ_t in Fig. 16a) in the IPE GRP does not depend strongly on added surface veil, although σ_f of the PET-veiled laminate appears to decrease at a slightly quicker rate than the nonveiled or C-glass-veiled materials. After 270 days of exposure to aqueous NaOH, the σ_f retention of all three IPE composites is comparable ($\approx 20\%$), once again indicating that the PET and C-glass veils are of little benefit to a resin that is prone to chemical degradation in a solution environment. In contrast, the nonveiled VE laminate is seen in Fig. 17b to exhibit superior σ_f retention over the PET- and C-glass-veiled VE laminates. While the regressed rate constants (k) are comparable in magnitude for the laminates with added PET and C-glass veils, the limiting values of σ_f retention in these materials at long times differ by about 12%. According to the tensile and flexural tests performed, the nonveiled VE laminate is more resistant to NaOH degradation than any of its veiled variants. This observation can be attributed to the number of existing interfaces. Since interfaces are particularly vulnerable to water clustering and concurrent alkali leaching, an increase in the number of interfaces is anticipated to reduce σ_f. Moreover, enhanced solution permeation via wicking results in an increase in glass fibre degradation and a corresponding reduction in σ_t.

O'Hearn and Kitchen [36, 37] have studied the effect of 5% NaOH(*aq*) solution on VE laminates reinforced with C-glass and PET veils at 80 °C. They report that laminates with the C-glass veil exhibit a 13% greater retention in σ_f than the PET-veiled laminates after 180 days of exposure, in contrast to the data shown in Fig. 17b. Duffy [35] has also examined the benefit of these veils using a similar VE in a 5% NaOH(*aq*) solution maintained at 65 °C. After 105 days, the C-glass is more effective in reducing the extent of degradation than the PET veil by exhibiting a 4% greater σ_f retention than the PET-veiled laminate. This difference decreases to 3% after 360 days. Based on these previously reported results, the C-glass veil appears to be more effective in retaining σ_f than the PET veil in aqueous NaOH solutions at elevated temperatures. Such behaviour is consistent with chemical reactivity considerations: as the temperature is increased, the rate of alkaline-induced hydrolysis of the PET veil also increases, thereby reducing the benefit of the veil [38]. Even though the present study employs a 10% (rather than 5%) NaOH(*aq*) solution, the σ_f retention of a C-glass-veiled VE laminate, relative to that of a laminate possessing the PET veil (designated $\Delta\sigma_f$ retention), is presented as a function of temperature in Fig. 18. From the interpolated curve, the C-glass veil appears to be more effective at temperatures above about 58 °C. Below this temperature, PET-veiled laminates retain greater σ_f than those with the C-glass veil.

Scanning electron micrographs of the surfaces of IPE laminates with different veils are topologically similar, exhibiting deep cracks with little evidence of resin degradation. Shown in Fig. 19a is a micrograph of the IPE laminate with PET veil after 270 days of immersion in aqueous NaOH. The surfaces of

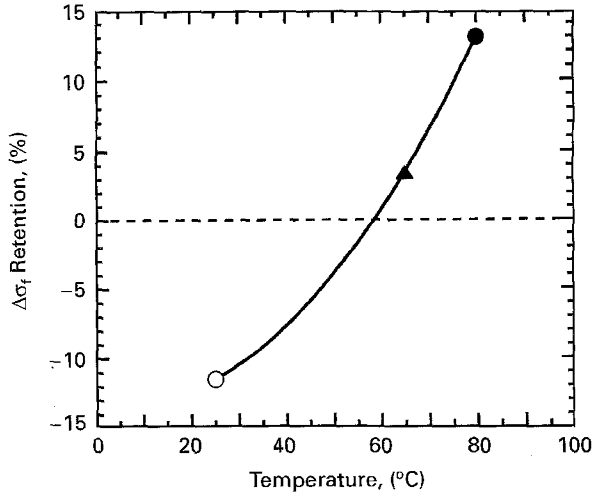

Figure 18 Difference in σ_f retention between C-glass-veiled and PET-veiled VE as a function of temperature. The data from O'Hearn and Kitchen [36, 37] and Duffy [35] are designated as (●) and (▲), respectively.

laminates possessing the C-glass veil exhibit more resin degradation, resembling the surfaces of the nonveiled laminates (see Fig. 14a), as well as discrete blisters. Blisters are the result of oxides leached from E-glass fibres into solution during chemical degradation of the fibres in the presence of NaOH(*aq*). As the concentration of oxides in solution increases, the osmotic pressure of the solution also increases, in which case more water must permeate through the laminate to dilute the solution. Blistering occurs when the local pressure of water builds up due to insufficient available volume within the laminate. Such topological features are commonly seen on graphite/epoxy laminates used in marine applications [25, 39, 40]. In contrast to the IPE laminates examined here, micrographs of the VE laminates with PET or C-glass veils are, for the most part, featureless after 270 days of exposure to NaOH(*aq*). The one shown in Fig. 19b (VE laminate with C-glass veil) reveals that the resin has degraded, but no macroscopic cracks are evident, which is consistent with the remarkably high σ_t retention seen in Fig. 17b.

4. Conclusions

While GRP laminates have received tremendous attention as structural materials due to their attractive weight-to-strength ratio, they also show promise as chemically resistant materials in chemically aggressive environments. In this work, we have investigated the degradation behaviour of pultruded isophthalic polyester and hand-moulded vinyl ester laminates, with and without PET and C-glass surface veils, as a function of immersion time in both brine and a 10% NaOH aqueous solution. Tensile and flexural analyses have provided fundamental insight into fibre–resin debonding, fibre degradation, and resin plasticization. In the case of brine, diffusion into either resin appears non-Fickian, while solubility is greater in the IPE resin due to the higher concentration of ester linkages available for hydrogen–bonding with permeated water. At short times, the reduction in tensile strength for the two neat resins is similar, but addition of a veil can result in greater or lesser strength retention, depending on water solubility in, and water diffusion through, the polyester resin. Flexural strength provides a measure of surface plasticization of the resin, decreasing as water molecules cluster along existing interfaces. The trends reported here for brine-induced degradation in the nonveiled and veiled GRP laminates correspond principally to physical mechanisms involving permeation and capillarity.

The same cannot be said for degradation of the laminates in aqueous NaOH. In this case, the isophthalic polyester and PET veil, as well as the E-glass load-bearing fibres, are susceptible to simultaneous physical and chemical (e.g., hydrolysis) degradation, which results in a greater reduction in both tensile and flexural strength after 270 days of immersion. Since both the resin and glass fibres are prone to chemical attack by NaOH, the PET and C-glass veils do not prove to be very beneficial in protecting the vulnerable E-glass fibres in the laminate core, resulting in a dramatic reduction in tensile strength over just 30 days. The nonveiled vinyl ester laminates, on the other hand, degrade the same way in NaOH(*aq*) as they do in brine; i.e., the solubility of NaOH(*aq*) in the vinyl ester is relatively low (compared to that in the

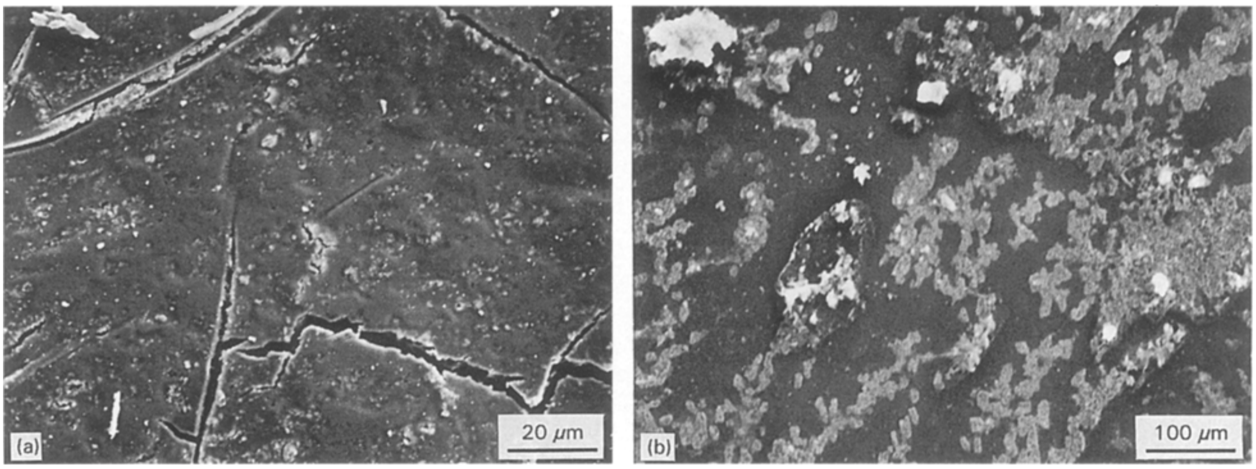

Figure 19 SEM micrographs of the (a) IPE laminate/PET veil and (b) VE laminate/C-glass veil, showing that surface cracks are prevalent on the IPE surface after 270 days in NaOH(*aq*).

isophthalic polyester), in which case degradation occurs by a combination of fibre – resin debonding and resin plasticization. Upon incorporation of a surface veil into a vinyl ester laminate, strength retention decreases due to an increase in the number of interfaces, at which permeated water molecules and oxides leached from the E-glass fibres may accumulate and further promote fibre–resin debonding and resin plasticization. In the vinyl ester laminates, the C-glass veil is found to be more effective in reducing flexural strength retention at elevated temperatures than the PET veil. The converse is true at temperatures below ≈60 °C.

Acknowledgments

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References

1. ASM International Handbook Committee, "Metals Handbook: Corrosion" 9th ed. (ASM International, Metals Park, 1987) Vol. 13, pp. 893–1371.
2. M. SCHUMACHER, "Seawater Corrosion Handbook" (Noyes, Park Ridge, 1979) pp. 461–2.
3. R. MATZEG and D. SANTRACH, *Sampe Q.* **23** (1991) 12.
4. B. D. CADDOCK, K. E. EVANS and D. HULL, *J. Mater. Sci.* **22** (1987) 3368.
5. R. F. REGESTER, *Corrosion-NACE* **25** (1969) 157.
6. W. R. VIETH, "Diffusion in and through Polymers" (Hanser, New York, 1991) pp. 1–85.
7. A. BARKETT, L. C. BANK, T. R. GENTRY, L. PRIAN, R. SHAN, J. C. SANG and R. POLLARD, presented at *Corrosion 95 (NACE)*, Orlando, Florida, March, 1995.
8. H. V. S. GANGARAO, P. V. VIJAY and P. K. DUTTA, *ibid.*
9. M. H. LEWIS, "Glasses and Glass–Ceramics" (Chapman & Hall, New York, 1989) pp. 1–342.
10. A. M. FILBERT and M. L. HAIR, in "Advances in Corrosion Science and Technology" edited by M. G. Fontana and R. W. Staehle (Plenum, New York, 1976) Vol. 5, pp. 1–54.
11. T. W. COWLEY and M. A. ROBERTSON, *Mater. Perform.* **30** (1991) 46.
12. A. V. KARLASHOV, E. M. BABENKO, G. M. BOROZENETS, V. V. CHERNYAK and K. V. MARKEVICH, *Sov. Mater. Sci.* **3** (1990) 369.
13. L. W. CAI and Y. WEITSMAN, *J. Compos. Mater.* **28** (1994) 130.
14. F. R. JONES, *J. Strain Anal. Eng. Des.* **24** (1989) 223.
15. J. F. HARPER and M. NAEEM, *Mater. Des.* **10** (1989) 297.
16. N. SUBRAMANIAM, F. D. BLUM and L. R. DHARANI, *Polym. Eng. Sci.* **33** (1993) 1204.
17. R. C. L. TAI and Z. SZKLARSKA-SMIALOWSKA, *J. Mater. Sci.* **28** (1993) 6199.
18. *Idem. ibid.* **28** (1993) 6205.
19. V. BELLENGER, J. VERDU, M. GANEM and B. MORTAIGNE, *Polym. Polym. Compos.* **2** (1994) 17.
20. E. MOREL, V. BELLENGER, M. BOCQUET and J. VERDU, *Polymer* **30** (1989) 69.
21. P. S. CHUA, S. R. DAI and M. R. PIGGOTT, *J. Mater. Sci.* **27** (1992) 919.
22. C.-H. SHEN and G. S. SPRINGER, *J. Compos. Mater.* **11** (1977) 2.
23. S.-B. LEE, T. J. ROCKETT and R. D. HOFFMAN, *Polymer* **33** (1992) 3691.
24. T. MORII, T. TANIMOTO, H. HAMADA, Z.-I. MAEKAWA, T. HIRANO and K. KIYOSUMI, *Polym. Polym. Compos.* **1** (1993) 37.
25. W. C. TUCKER and R. BROWN, *J. Compos. Mater.* **23** (1989) 389.
26. T. MORII, T. TANIMOTO, H. HAMADA, Z.-I. MAEKAWA, T. HIRANO and K. KIYOSUMI, *Polym. Compos.* **15** (1994) 206.
27. S. P. SONAWALA and R. J. SPONTAK, *J. Mater. Sci.* (submitted).
28. R. GOPALAN, B. R. SOMASHEKAR and B. DATTAGURU, *Polym. Degradation Stab.* **24** (1989) 361.
29. P. K. ADITYA and P. K. SINHA, *J. Reinf. Plast. Compos.* **11** (1992) 1035.
30. W. W. WRIGHT, *Composites* **12** (1981) 102.
31. H. HOJO, K. TSUDU, K. OGASAWARA and T. TAKIZAWA, *Polym. Mater. Sci. Eng.* **53** (1985) 475.
32. A. PAUL, "Chemistry of Glasses" (Chapman & Hall, London, 1982) pp. 108–47.
33. "Plastics-Thermosets and Thermoplastics" 8th ed. (D.A.T.A., San Diego, 1986) pp. 1–1398.
34. I. I. RUBIN, editor, "Handbook of Plastic Materials and Technology" (Wiley & Sons, New York, 1990) pp. 905–18.
35. M. J. DUFFY, in Proceedings of the 41st Annual Conference of Reinforced Plastics/Composites Institute (Society of Plastics Industry, New York, 1986) pp. 1–5.
36. T. P. O'HEARN and K. E. KITCHEN, *Plast. Eng.* **44** (1988) 35.
37. *Idem.*, in Proceedings of the 41st Annual Conference of Reinforced Plastics/Composites Institute (Society of Plastics Industry, New York, 1988) pp. 1–7.
38. S. H. ZERONIAN, H.-Z. WANG and K. W. ALGER, *J. Appl. Polym. Sci.* **41** (1990) 527.
39. F. CHEN and A. W. BIRLEY, *Plast. Rubber and Compos. Process Appl.* **15** (1991) 161.
40. *Idem. ibid.* **15** (1991) 169.

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