JOURNAL OF MATERIALS SCIENCE 31 (1996) 4757–4765

Degradation kinetics of glass-reinforced polyesters in chemical environments

Part II *Organic solvents*

S. P. SONAWALA, R. J. SPONTAK*
Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695-7907, USA

Numerous studies have been conducted to elucidate the mechanism(s) by which glass-reinforced polyesters (GRPs) degrade in aqueous solutions varying in salt concentration, pH and temperature. In this work, we examine the degradation kinetics of two GRPs in two organic solvents, 1,1,1-trichloroethane (TCE) and toluene, to ascertain if these laminates could be utilized in fuel or solvent storage and transportation applications. The tensile strength of isophthalic and vinyl ester laminates is not significantly affected ($> 85\%$ retention) by TCE after 270 days of immersion. While incorporation of a polyethylene terephthalate (PET) or C-glass surface veil does not improve tensile strength retention and, in fact, reduces the flexural strength of the vinyl ester GRPs, these veils preserve surface finish by reducing blistering. In toluene, the GRPs behave quite differently. A marked increase in toluene absorption into the vinyl ester laminate is accompanied by a substantial reduction in tensile strength retention (with or without a surface veil). From these results, a two-stage degradation mechanism for vinyl ester in toluene is proposed in which the first stage corresponds to diffusion-limited plasticization and the second reflects matrix relaxation/swelling.

1. Introduction

Since glass–fibre reinforced polyester (GRP) laminates can be readily processed into complex shapes without expensive tooling and panel beating (which are often necessary in the fabrication of steel and metal components [1]) and since their properties can be tailored by judicious choice of design factors such as fibre, resin and composition, they are ideal candidates for commercial products such as pipes and storage tanks. These materials possess high strength-to-weight ratios relative to metals such as steel and aluminium, and can subsequently impart greater fuel efficiency (and less environmental pollution) in transportation applications. Another important characteristic of many GRP laminates is that they degrade less and therefore require less maintenance when exposed to chemically aggressive environments for prolonged time intervals. While metals typically require organic coatings and paints to inhibit corrosion in liquid environments, some GRP laminates exhibit surprisingly good chemical resistance to both aqueous solutions and organic solvents. For this combination of reasons, GRP composites continue to remain a subject of tremendous interest in the aerospace and automobile industries.

If a GRP composite is immersed in a nonreactive aqueous solution for an extended period of time, water from the solution may permeate through, hydrogen-bond with and plasticize the polyester resin [2]. As a result of surface plasticization, the flexural strength (σ_f) of the laminate is expected to decrease. Water molecules will also hydrogen-bond to the load–bearing glass fibres, forming a thin (*ca.* 2 nm) film around each fibre, and eventually promote fibre–resin debonding. In this case, the tensile strength (σ_t) decreases and premature failure under an applied stress ensues [3]. If the aqueous solution is highly alkaline (e.g., NaOH) or acidic (e.g., HCl), it can chemically react with both the polyester resin and the internal glass fibres, inducing GRP degradation by concurrent chemical and physical means. While numerous studies have been conducted to elucidate the kinetics and mechanisms(s) of GRP degradation in nonreactive aqueous solutions such as brine (3–5% NaCl) and reactive solutions such as HCl and NaOH [4–10], fewer efforts have been undertaken to understand the long-term response of GRP composites to nonreactive organic liquids.

Since GRP laminates are presently employed in high-volume commercial applications wherein the polyester matrix is continually exposed to organic liquids (e.g., valve covers, as well as oil and fuel pumps), an understanding of the stability of the laminates under these conditions is necessary to estimate long-term performance and time-to-failure. In under-the-hood automotive applications, for instance, GRPs

---

* To whom correspondence should be addressed.

0022–2461

have proven extremely valuable in reducing part weight by about 30%, as well as cost by more than 30%, when compared to conventional aluminium castings [5]. In such applications, however, the composites must be able to tolerate prolonged exposure to organic liquids such as oil and antifreeze. Springer *et al.* [6] have examined the properties of isophthalic polyester (IPE) and vinyl ester (VE) composites immersed in a variety of organic liquids (No. 2 diesel fuel, lubricating oil, antifreeze and indolene) at 23°C and 93°C. According to their results, the antifreeze and indolene are, at 93°C, the most destructive of the liquids studied. When a GRP composite is immersed in an organic liquid such as these, the liquid permeates through (and swells) the polyester until it reaches the glass fibres comprising the laminate core.

The concentration of liquid that permeates into the crosslinked polyester matrix depends on the free energy of mixing (ΔG_{mix}) of the polymer–solvent system. Here, ΔG_{mix} is a function of parameters such as composition, polyester chain length, temperature, and the Flory–Huggins (χ) interaction parameter between the penetrating solvent and polyester matrix. If an organic liquid is a good solvent for the polyester (i.e., $\chi < 0$), its solubility within the polyester will be relatively high, and mixing considerations result in a decrease in ΔG_{mix}. Incorporation of solvent into the laminate also induces swelling of the crosslinked polyester, yielding a decrease in conformational entropy and a corresponding increase in ΔG_{mix}. Equilibrium is achieved when these two driving forces are balanced [11]. Since the concentration of permeated liquid in the polyester matrix of the laminate is non-negligible, its effect on GRP properties must be ascertained. A liquid that promotes surface plasticization and fibre–resin debonding will cause undesirable reductions in both σ_f and σ_t.

In this work, we examine the flexural and tensile properties of the same two GRPs employed in our companion study [4] of GRP degradation in brine and NaOH(*aq*). Pultruded IPE and hand-moulded VE laminates containing E-glass fibres and, in some cases, a polyethylene terephthalate (PET) or C-glass surface veil to hinder the penetration of liquid into the laminate core are studied.

2. Experimental methods

2.1. Materials

The chemical structures of the isophthalic polyester and vinyl ester employed in this work are given in Part I of this study [4], as is additional information regarding the PET and C-glass veils. Reagent-grade toluene (C_7H_8), an aromatic (bulky molecule), non-polar liquid, and 1,1,1-trichloroethane (CH_3CCl_3, designated hereafter as TCE), a relatively small-molecule, polar liquid, were purchased from Fisher Scientific.

2.2. Methods

The experimental procedures followed in this work are identical to those described in detail in Part I of this series [4].

3. Results and discussion

3.1. Degradation in trichloroethane

3.1.1. Effect of polyester

When a crosslinked polymer is immersed in a good solvent, the individual segments of the polymer become solvated and the polymer swells. Since the presence of covalent crosslink sites prevents the solvent molecules from dissolving the polymer, a swollen gel results. Flory [12] has related the chemical potential of the solvent in the gel to the crosslink-induced gel elasticity to derive an expression by which to ascertain χ for a polymer–solvent system from a sol–gel analysis. While such an analysis of swollen polyester laminates is beyond the scope of the present work, evaluation of polymer–solvent interactions remains a critical consideration. Assuming positive deviation from Raoultian solution behaviour, χ is also related to tabulated solubility parameters (δ) through

$$\chi \approx \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \qquad (1)$$

where v_1 is the molar volume of the solvent, R is the gas constant, T denotes absolute temperature, and the subscripts 1 and 2 on the solubility parameters refer to solvent and polymer, respectively. Note that, as the solubility parameters converge, $\chi \to 0$, the solution becomes ideal (i.e., $\Delta H_{\text{mix}} \to 0$) and $\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}}$. Since ΔS_{mix} in the limit of ideal mixing is necessarily positive, $\Delta G_{\text{mix}} < 0$ and mixing will occur over the entire composition range.

The solubility parameters for TCE, IPE and VE are estimated to be about 9.3, 10.7 and 9.8 H, respectively [13]. Since they are comparable in magnitude, the solubility of TCE in the polyester matrices of the GRP laminates examined here is expected to be relatively high. This is confirmed in Fig. 1, which shows sample weight change as a function of exposure time for the IPE and VE laminates. Both curves in this figure are sigmoidal (*S*-shaped) at short times, indicating that TCE diffusion into the laminate is non-Fickian. Similar results have been obtained [4, 14] for the permeation of brine and NaOH(*aq*) into comparable laminates. The extent of TCE solubility in the laminates is, however, substantially greater than that of brine (which, like TCE, is nonreactive) due to greater chemical compatibility between TCE and the polyester resins. Another feature exhibited by the curves in Fig. 1 is that they both appear to increase at 270 days, rather than level off (a limiting mass uptake value would be dictated by polyester–TCE thermodynamic interactions). Thus, it can be concluded that, after 270 days, the equilibrium solubility of TCE in these laminates is not yet achieved.

Figure 1 also reveals that the absorption of TCE is consistently greater in the IPE laminates than in the VE laminates. This observation is attributed to the polar nature of the IPE resin, which possesses a greater concentration of ester linkages per repeat unit than the VE resin. As provided elsewhere [4], the VE resin consists of only two sterically hindered ester linkages, as well as two ether linkages, per repeat unit. Recall that 1,1,1-TCE is comprised of an odd number

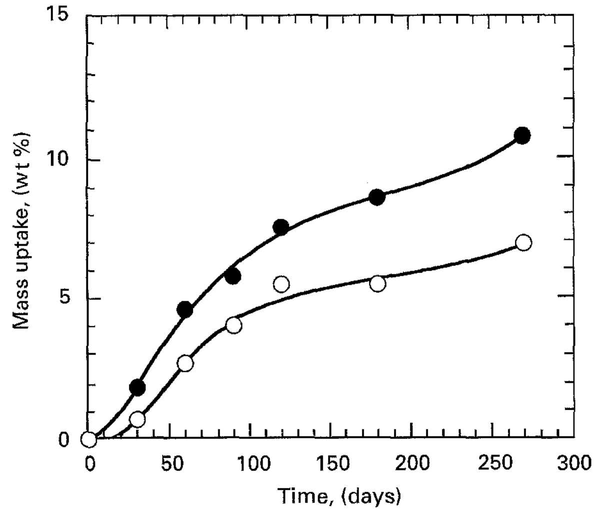

Figure 1 Mass uptake as a function of time for 1,1,1-trichloroethane (TCE) permeating through VE (○) and IPE (●) laminates.

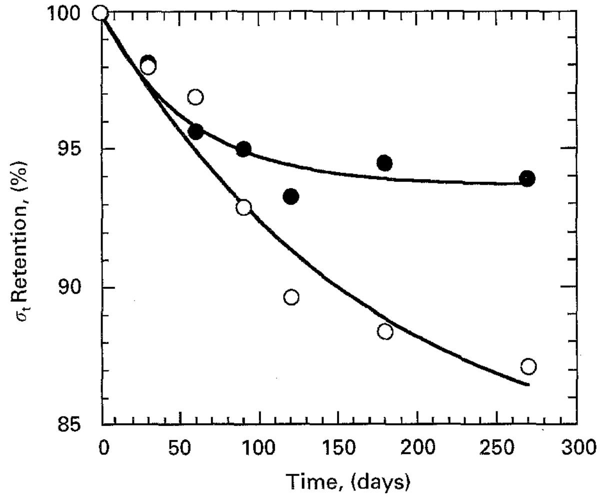

Figure 2 Variation of tensile strength (σ_t) retention with immersion time for VE (○) and IPE (●) GRP laminates in TCE at 25 °C.

of electronegative Cl atoms bonded to one carbon atom, yielding a highly asymmetric linear molecule with an uneven charge distribution. Due to its polarity, TCE is expected to interact more with the IPE resin rather than with the VE resin, resulting in a more pronounced increase in IPE mass uptake with TCE immersion time (see Fig. 1).

As TCE permeates into the GRP laminates, the tensile strength (σ_t) retention is seen in Fig. 2 to decrease, but not by very much ($< 15\%$) over the course of the study (270 days). The percentage retention shown in figures such as Fig. 2 is defined here as $100\% \times [1 - M(t)/M(t = 0)]$, where $M(t)$ is a material property (σ_t or σ_f) measured at time t. The tensile strength provides a measure of glass–fibre integrity, since the E-glass fibres within the IPE and VE laminates are primarily responsible for supporting the applied tensile load, and likewise reveals the extent of fibre–resin debonding due to the accumulation of a penetrant liquid. According to the data shown in Fig. 2, σ_t retention is greater for the IPE composite than for the VE analogue, despite the earlier observation that TCE is more soluble in, and is more likely to plasticize, the IPE composite. If this is the case, the near-negligible 6% reduction in σ_t evident in Fig. 2 for the IPE laminate indicates that the load–bearing E-glass fibres and the fibre–resin interfaces are virtually unaffected by the presence of TCE. Thus, the TCE molecules must be highly distributed throughout the IPE resin. In contrast, since TCE should not affect the strength of the E-glass fibres (through, e.g., oxide leaching [15]), the data in Fig. 2 also imply that TCE promotes more fibre–resin debonding in the VE laminate than in the IPE laminate. This conclusion is consistent with the mass uptake data presented in Fig. 1. If the TCE is less soluble in VE resin, it is reasonable to deduce that, upon penetration into the laminate, it would migrate to, and accumulate at, available interfaces, thereby promoting debonding. In this case, laminate degradation occurs by a physical, rather than chemical, mechanism [16].

The flexual strength (σ_f) is more sensitive to surface changes, as well as resin plasticization, than σ_t. Hojo *et al.* [9] have examined the degradation of E-glass-reinforced IPE exposed to methanol (a polar alcohol) at 50°C, and report that the σ_f retention decreased to about 40% after 42 days. A less dramatic reduction in σ_f is observed in this study using TCE. In Fig. 3, σ_f retention is presented as a function of immersion time for the IPE and VE laminates, and demonstrates that the VE resin is affected more quickly by TCE penetration than the IPE resin. After 60 days of immersion, however, σ_f reaches a lower limit of *ca.* 72% and becomes independent of immersion time. According to Fig. 1, though, the mass uptake of TCE in VE increased beyond 60 days, suggesting that TCE resides at existing fibre–resin interfaces. The σ_f retention of the IPE composite, on the other hand, is seen in Fig. 3 to decrease steadily over the course of the study. After 270 days, σ_f is reduced by about 34%. The greater reduction in σ_f for the IPE resin suggests that penetrated TCE increasingly plasticizes the IPE, in agreement with the data in Figs 1 and 2.

Scanning electron micrographs of the IPE and VE laminates after 270 days of immersion in TCE are presented in Fig. 4(a, b). Fig. 4a reveals that the IPE

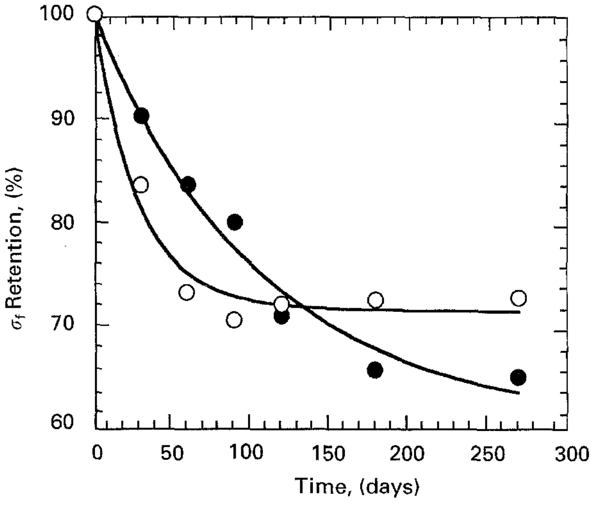

Figure 3 Time evolution of the flexural strength (σ_f) for VE (○) and IPE (●) laminates in TCE at 25 °C.

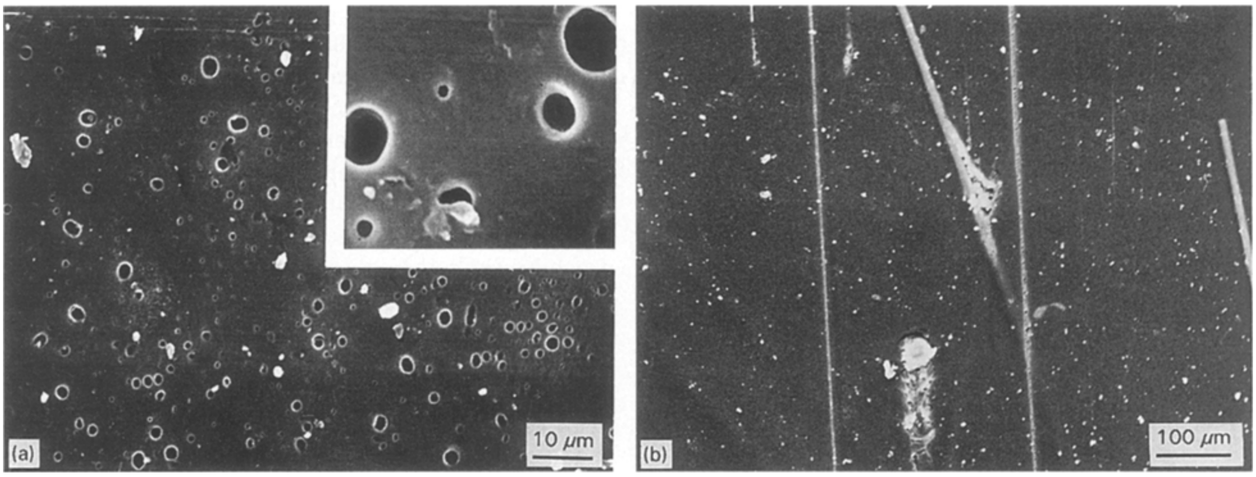

Figure 4 SEM micrographs of the (a) IPE and (b) VE laminate surfaces upon immersion in TCE for 270 days. The inset is a 6 × enlargement of several of the ruptured blisters seen in (a).

sample surface possesses a large population of holes. These holes, measuring as much as 2.5 μm in diameter, are absent in non-immersed IPE samples and are therefore not considered process-related imperfections. Upon absorption into the laminate, the TCE swells the IPE matrix resin and produces localized pockets of high solvent concentration (i.e., blisters). If these pockets swell too much, the blisters rupture, leaving behind surface holes which induce a reduction in σ_f. Thus, the holes seen in Fig. 4a provide additional evidence of substantial TCE absorption into the IPE resin, and suggest that a critical absorption may be required for blister rupture. In contrast, the micrograph of the VE laminate displayed in Fig. 4b shows that, upon long-term immersion in TCE, surface swelling occurs to a lesser extent, but is responsible for E-glass fibres extending from the surface. Microscopical examination of fracture surfaces upon tensile failure reveals that, even after 270 days in TCE, the glass fibres remain intact, and laminate failure occurs by fibre pull-out (data not shown). These results are consistent with those of Christianson and Shortall [17], who report that chloroform and acetone (both polar organic liquids) degrade phthalate-based ester resin within several days at 25 °C. Energy-dispersive X-ray analysis of cross-fractured specimens demonstrates that Cl (from TCE) diffuses through the polyester matrix so that TCE is uniformly distributed throughout each of the GRP laminates.

3.1.2. Effect of surface veil

Shown in Fig. 5 are σ_t retention data for IPE (Fig. 5a) and VE (Fig. 5b) laminates with PET and C-glass veils. In Fig. 5a, incorporation of the PET veil into IPE laminates results in a negligible reduction ($< 5\%$) in σ_t over the course of 270 days in TCE. At short times, the nonveiled IPE and C-glass-veiled laminate exhibit almost identical behaviour. When the immersion time exceeds 180 days, the specimens with the C-glass veil undergo a more marked reduction in σ_t retention. This can be explained by recalling that the C-glass not only separates the polyester-rich laminate surface and the vulnerable E-glass core, but also

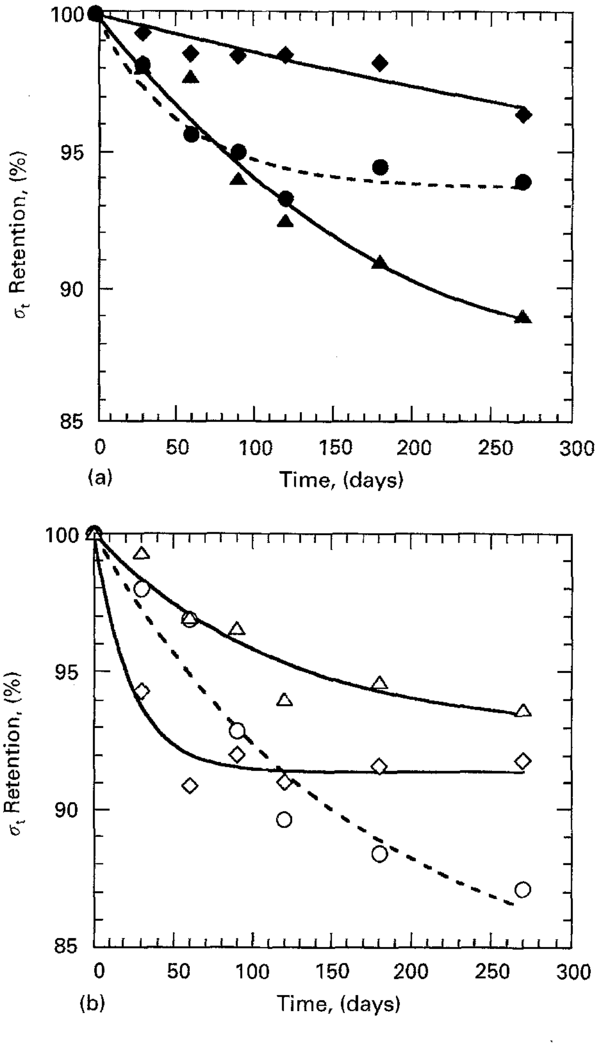

Figure 5 σ_t retention as a function of immersion time in brine for (a) IPE and (b) VE laminates with no veil (circles), a PET veil (diamonds) or a C-glass veil (triangles).

serves as a load-bearing member of the composite. Rapid plasticization of the IPE surface is anticipated to promote fibre–resin debonding with the C-glass fibres, which, in turn, would result in a more pronounced decrease in σ_t retention. In the case of the VE resin, σ_t retention at short times does not differ very much for any of the VE laminates with different veils

(Fig. 5b). After 270 days of exposure to TCE, however, composites possessing either a PET or C-glass veil undergo less σ_t degradation than the nonveiled laminate. It is interesting to note that the efficacy of the two veils in VE is opposite to that in IPE; i.e., incorporation of a PET veil into VE laminates is not as effective as in the IPE laminates.

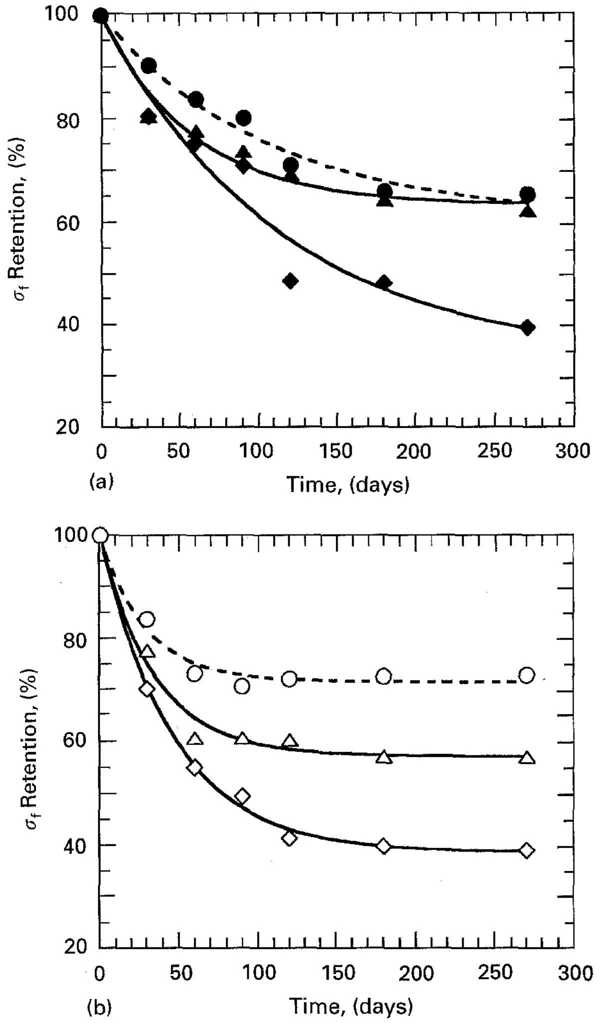

Figure 6 Dependence of σ_f on immersion time in brine for (a) IPE and (b) VE laminates with no veil (circles), a PET veil (diamonds) or a C-glass veil (triangles).

This last observation may reflect a veil-induced increase in TCE uptake, since PET consists of ester linkages which could interact with TCE. If this is the case, VE plasticization should be the most extensive, and σ_f retention should be the lowest, of the series examined here. Flexural retention data are provided for comparison in Fig. 6(a, b) for the IPE and VE GRPs, respectively. As seen in both figures, the PET-veiled laminates exhibit the greatest reduction in σ_f retention ($\approx 60\%$ for both IPE and VE), which is consistent with the view that the PET veil enhances TCE solubility. The σ_f retention data for the nonveiled and C-glass-veiled IPE laminates in Fig. 6a are comparable, suggesting that the C-glass veil does not immensely benefit σ_f retention. Incorporation of C-glass into the VE laminates, on the other hand, yields a more pronounced reduction in σ_f, as compared to the nonveiled laminate. Thus, in the case of TCE, improved σ_f retention is achieved with a C-glass, rather than PET, veil. Similar results have been reported by O'Hearn and Kitchen [18, 19], who studied the degradation of VE GRPs in methanol at 48 °C.

Scanning electron micrographs of the surfaces of the veiled IPE and VE laminates are presented in Fig. 7(a, b) respectively, and are strikingly reminiscent of micrographs obtained from these same laminates after long-term immersion in brine [4]. Glass fibres are occasionally observed on sample surfaces after 270 days of exposure to TCE, but there is no evidence of surface cracking or, in the case of the IPE laminate, blister-induced holes. Thus, while the PET and C-glass surface veils do not appear to benefit σ_f retention (see Fig. 6) in these GRPs, they prevent formation of surface blemishes (e.g., holes), which could be detrimental to surface finish and appearance.

3.2. Degradation in toluene

3.2.1. Effect of polyester

All the studies discussed above, including those reported in Part I of this series, have focused on the degradation kinetics of IPE and VE GRP laminates in either aqueous solution or polar organic liquids. Since these IPE and VE resins are also polar (due to the

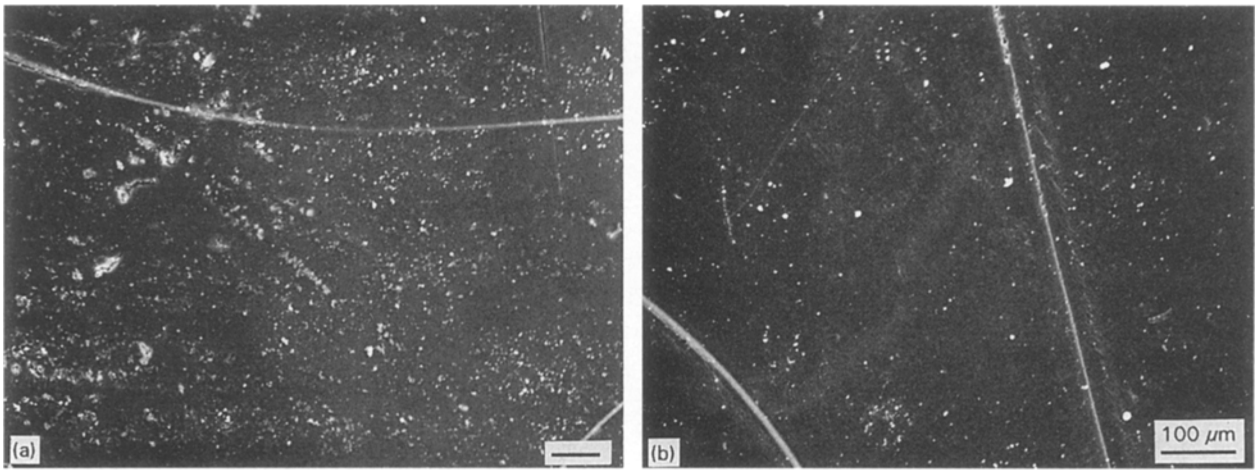

Figure 7 SEM micrographs of the (a) IPE and (b) VE laminates with the C-glass veil, illustrating that their surfaces are relatively featureless (no evidence of gross degradation) after 270 days in TCE.

presence of ester, ether and hydroxyl functionalities in their repeat units), absorption of water or a polar organic liquid necessarily transpires [20]. In this part, we turn our attention to another organic liquid, toluene, which is nonpolar and unable to hydrogen bond with polyester resin. Toluene, an aromatic molecule, also constitutes a good model for complex (nonpolar) fuel mixtures such as gasoline. Polymer–solvent interactions in this case are the result of nonpolar chemical compatibility, which again can be accurately described in terms of χ or, equivalently, pure-component solubility parameters. The solubility parameter of toluene is 8.9 H, and recall from the previous section that the solubility parameters for IPE and VE are about 10.7 and 9.8 H, respectively. From these values, it is expected *a priori* that toluene is more soluble in VE than in IPE.

Figure 8 shows the mass uptake of toluene in both GRPs. As expected from the discourse presented above, the equilibrium solubility of toluene (discerned as the limit from long-time mass uptake) is observed to be significantly greater in the VE laminate than in the IPE laminate. At short times (< 90 days), the two mass uptake curves in Fig. 8 appear *S*-shaped (indicating non-Fickian diffusion) and are virtually indistinguishable. Beyond 90 days of immersion time, however, the two curves diverge, with the curve corresponding to the VE laminate increasing monotonically up to about 22% after 270 days and the IPE curve exhibiting a plateau at 10% after only 60 days of immersion. The plateau in the IPE curve signifies that the toluene has reached its equilibrium solubility in IPE at 25 °C, whereas the absence of a plateau in the VE curve indicates that, over the course of 270 days, equilibrium has not yet been established between toluene and the VE GRP.

Figure 9 reveals that σ_t retention decreases for both GRPs upon prolonged exposure to toluene. As seen previously in the mass uptake curves (Fig. 8), the σ_t retention data for the VE and IPE laminates are almost identical up to about 90 days of immersion time. During this time interval, σ_t reduces by about 14–18%. At long times, the reduction in σ_t is much greater in the VE laminate than in its IPE counterpart. This feature, which is evident again later, suggests that the mechanisms of σ_t reduction in the IPE and VE laminates are identical when the concentration of toluene in each is comparable (see Fig. 8). When the VE absorbs more toluene at longer immersion times, σ_t in the VE GRP decreases further. Since toluene is not expected to interact chemically with E-glass fibres and since σ_t is a measure of (load–bearing) fibre integrity and fibre–resin adhesion, the significant decrease in σ_t retention seen for the VE in Fig. 9 can be inferred to mean that toluene-induced resin plasticization promotes fibre–resin debonding in VE GRPs.

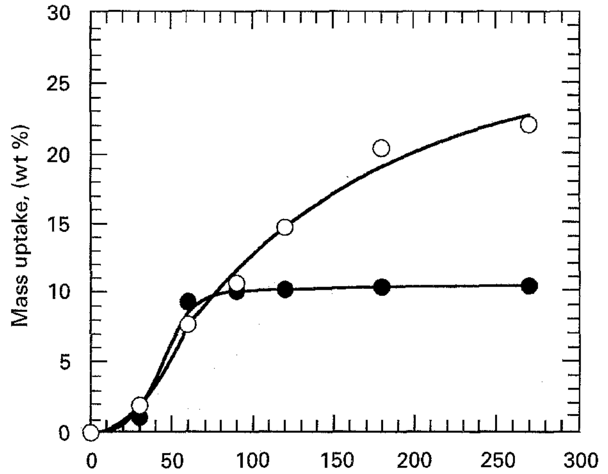

Figure 8 Mass uptake of toluene in VE (○) and IPE (●) laminates as a function of immersion time.

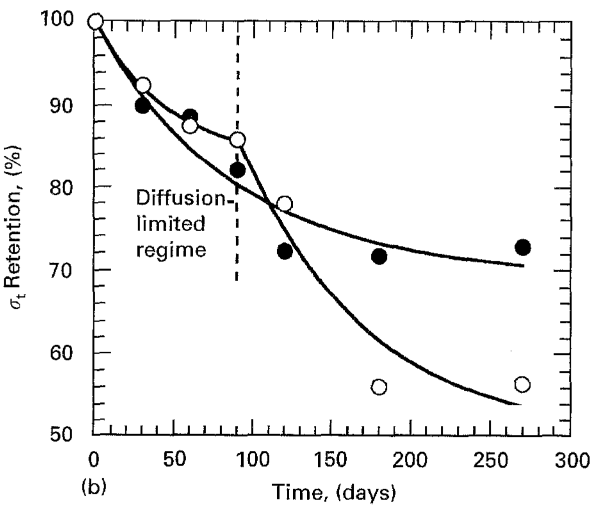

Figure 9 σ_t retention as a function of immersion time for VE (○) and IPE (●) GRP laminates in toluene at 25°C.

This explanation is consistent with the conclusions drawn by Laoubi *et al.* [21], who investigated the degradation behaviour of epoxy resin coatings in toluene at ambient temperature. They report that the toluene plasticizes and softens the resin as it advances through the laminate, and propose that subsequent diffusion through the plasticized zone is facilitated due to an increase in available free volume within the resin matrix. Fibre–resin debonding due to toluene-induced resin plasticization is evident in the SEM micrograph presented in Fig. 10 for a cross-fractured IPE laminate after 270 days of immersion in toluene. Note that the E-glass fibres are relatively free of surface debris, implying poor local fibre–resin adhesion, and that the IPE matrix and fibre bundle are distinctly separated, suggesting large-scale fibre–resin debonding at failure.

As mentioned earlier, σ_f provides an accurate measure of polyester plasticization. Shown in Fig. 11 is the time evolution of σ_f retention for IPE and VE laminates exposed to toluene. It is interesting to see in this figure that the σ_f retention decreases almost identically (to about 30% after 270 days) for the two GRPs, even though their mass uptake (Fig. 8) and σ_t retention (Fig. 9) responses differ considerably. The similarity of results in Fig. 11 suggests that both polyester resins at the laminate surfaces are saturated (to their solubility limit) with toluene even after relatively short times so that the extent of surface plasticization (and flexibility) appears comparable for the two polyesters. If this is the case, the trend seen in Fig. 11

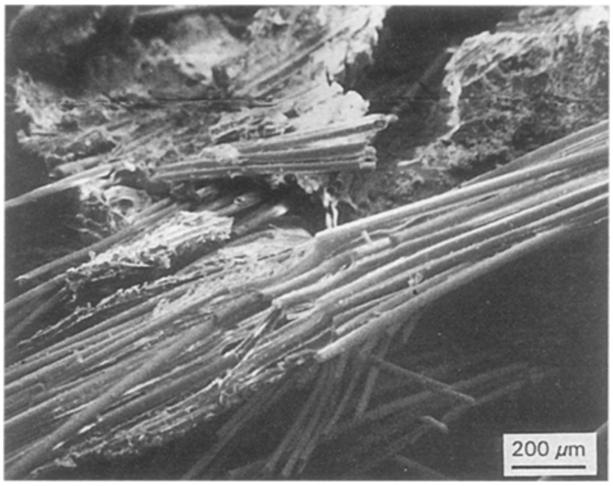

Figure 10 Fracture surface of the IPE laminate after being exposed to toluene for 270 days. The glass fibres remain intact and are relatively free of surface debris, revealing that failure occurred by fibre–resin debonding.

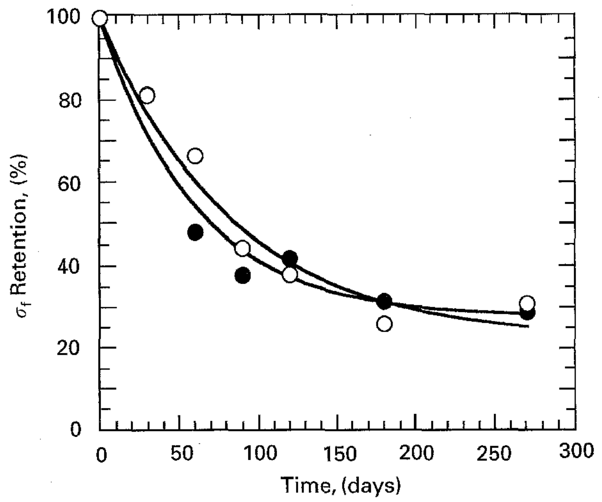

Figure 11 Time evolution of σ_f for VE (○) and IPE (●) laminates in toluene at 25°C.

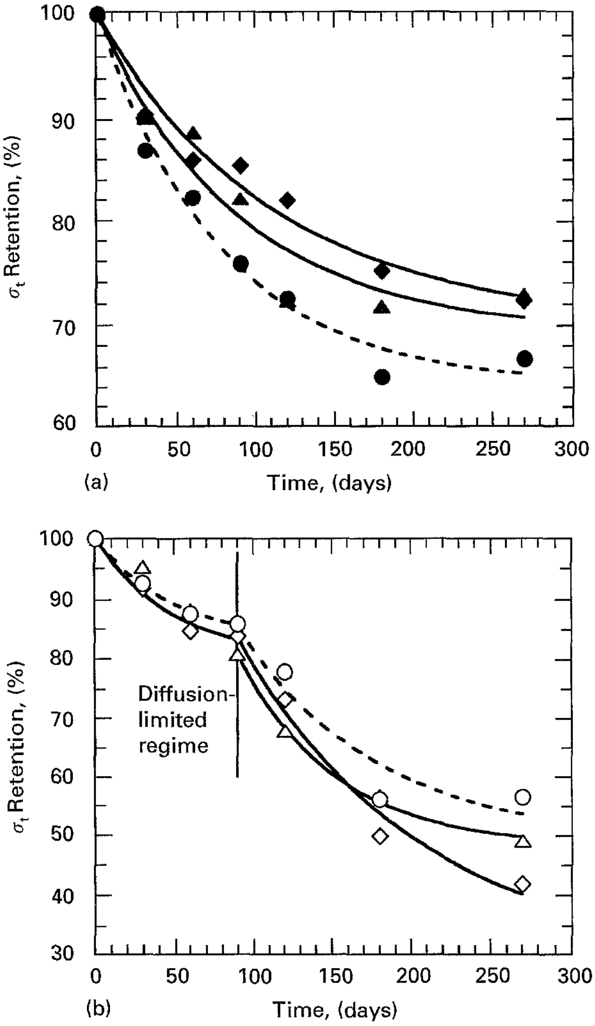

Figure 12 σ_t retention as a function of immersion time in toluene for (a) IPE and (b) VE laminates with no veil (circles), a PET veil (diamonds) or a C-glass veil (triangles).

supports the conclusion reached by Laoubi *et al.* [21] that toluene advances as a constant–concentration front through the polyester matrix. While this explanation is reasonable based upon the data collected, it is interesting to note that the greater toluene solubility in VE, as compared to IPE, does not appear to strongly influence the (normalized) σ_f retention. In a related study, Lehmann–Burgel [5] has examined the degradation of a VE composite in a hydrocarbon-based motor oil at 160 °C and reports that the σ_f decreased by 26% after 180 days, with most of the degradation occurring during the first 30 days of immersion. In this work, σ_f retention after 180 days in toluene is much lower, about 25–30%.

3.2.2. Effect of surface veil

Figure 12 shows the effect of surface veil on the σ_t retention in IPE (Fig. 12a) and VE (Fig. 12b) laminates. In Fig. 12a, the nonveiled IPE GRP exhibits the greatest reduction in σ_t, indicating that the PET and C-glass veils serve to inhibit toluene penetration into the interior E-glass roves. If these data are fitted to a curve of the form 100-A [1-exp(-kt)], where A is the limiting value at long immersion times, k is a degradation rate constant and t denotes time, these curves exhibit comparable values of k (in day^{-1}): 0.011 (nonveiled), 0.013 (PET-veiled) and 0.010 (C-glass-veiled). This observation suggests that the mechanism responsible for toluene-induced σ_t reduction is most likely the same with and without the presence of a surface veil. The same trend appears to be true for the VE laminates. In Fig. 12b, the initial reduction observed in σ_t for the nonveiled and veiled VE laminates is relatively invariant, and is comparable to that seen in Fig. 12a for the nonveiled and veiled IPE laminates at short immersion times (< 90 days). Beyond this diffusion–limited threshold, the σ_t retention curves corresponding to the nonveiled and veiled VE GRPs remain comparable within experimental scatter, implying that the incorporated surface veils contribute very little toward σ_t retention.

Likewise, the flexural strength data displayed in Fig. 13 show that addition of a PET or C-glass surface veil to the IPE and VE GRPs has little influence on σ_f retention upon long-term immersion in toluene. In

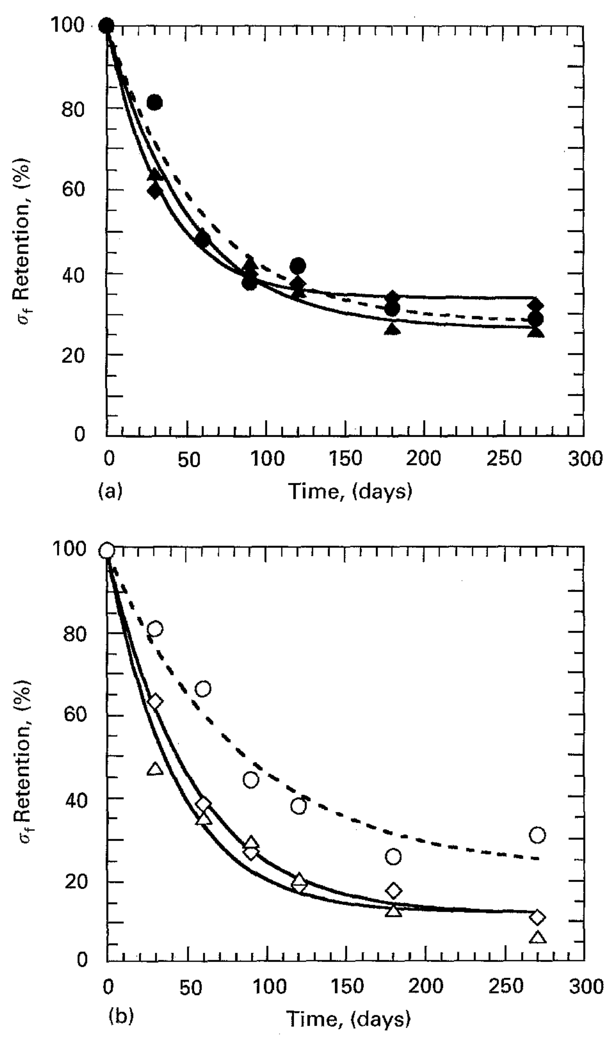

Figure 13 Dependence of σ_f on immersion time in toluene for (a) IPE and (b) VE laminates with no veil (circles), a PET veil (diamonds) or a C-glass veil (triangles).

the case of the IPE laminates (Fig. 13a), there is no discernible difference in σ_f retention between any of the specimens examined. This observation reveals that incorporation of a veil does not promote penetrant accumulation along the more numerous veil–resin interfaces, which would be manifested in a more extensive reduction in σ_f. Fig. 13b demonstrates that the non-veiled VE laminate retains more of its original σ_f than its veiled analogues. These data suggest that the presence of a PET or C-glass veil results is either a greater surface concentration of entrapped toluene (at, e.g., the veil–resin interfaces) or enhanced VE plasticization, as compared to laminates with no veil. Since it is unclear how these veils could promote resin plasticization, the possibility of accumulated toluene presently seems to be a more plausible interpretation of the data in Fig. 13b, although additional work is certainly required to resolve existing uncertainty.

4. Conclusions

Use of glass-fibre reinforced polyesters as structural materials in adverse chemical environments offers an attractive alternative to metals due to strength-to-weight ratio and chemical resistance considerations. While most studies addressing the chemical resistance of isophthalic polyester and vinyl ester laminates have focused on strongly acidic or alkaline aqueous solutions, we have examined here the degradation of such laminates, with and without a protective surface veil, in polar (1,1,1-trichloroethane, TCE) and nonpolar (toluene) organic liquids.

Penetration of TCE into nonveiled isophthalic polyester laminates results in little change in σ_t, but a more pronounced decrease in σ_f, suggesting that the TCE is more highly solubilized within the polyester resin. The opposite is true for TCE penetration into the vinyl ester composite, indicating that TCE accelerates fibre–resin debonding. Incorporation of a PET or C-glass surface veil can increase or decrease σ_t or σ_f retention, depending on the veil/resin combination, in which case pair-independent generalizations cannot (and should not) be inferred from the data presented here. One shared feature between the two GRPs examined in this work is that addition of the PET veil induces a more pronounced long-term reduction in σ_f, due presumably to an increase in polar interactions between TCE and the ester linkages along the PET backbone.

In the case of toluene, vinyl ester GRPs are far more susceptible to greater long-term solvent absorption and plasticization effects than laminates composed of isophthalic polyester. Up to about 90 days, σ_t retention is virtually identical for both GRPs, with and without an added surface veil. Beyond this immersion time, the vinyl ester laminates undergo significantly greater σ_t reduction due to toluene-induced resin swelling and, consequently, fibre–resin debonding. The σ_f of these GRP laminates is also affected by long-term exposure to toluene. In the case of isophthalic polyester laminates, incorporation of a surface veil has no discernible effect on σ_f retention, whereas both PET and C-glass veils promote a decrease in σ_f below that of nonveiled laminates, suggesting that toluene accumulates along the more numerous fibre–resin interfaces in the veiled GRPs.

From the data presented here, it is evident that the end-use application of GRPs such as the ones examined here dictates the combination of resin and veil that must be used to minimize chemical degradation induced by an aqueous solution or organic liquid. For long-term exposure to TCE and toluene, the isophthalic ester GRP with PET veil appears to be more generally resistant to solvent degradation, as measured in terms of σ_t retention. In TCE, however, this veil promotes a greater decrease in σ_f. Thus, property trade-offs must be considered in designing GRPs for optimal chemical resistance in adverse chemical environments.

Acknowledgments

This work was partially supported by the Precision Fabrics Group (Greensboro, NC). We are indebted to Mr. L. Fraser (Precision Fabrics Group), Mr. C. Medlin (Reichhold Chemicals Inc.) and Dr. H. West (NC State Univ.) for their technical assistance during the course of this work.

References

1. P. I. SMITH, "Plastics as Metal Replacements" (Scientific Publications: Broseley, 1968) pp. 189–254.
2. M. S. W. WOO and M. R. PIGGOTT, *J. Compos. Technol. Res.* **9** (1987) 162.
3. P. S. CHUA, S.R. DAI and M. R. PIGGOTT, *J. Mater. Sci.* **27** (1992) 919.
4. S. P. SONAWALA and R. J. SPONTAK, *ibid.* (submitted).
5. U. LEHMANN-BURGEL, *Plast. Rubber Compos. Process Appl.* **16** (1991) 183.
6. G. S. SPRINGER, B. A. SANDERS and R. W. TUNG, *J. Compos. Mater.* **14** (1980) 213.
7. R. MATZEG and D. SANTRACH, *Sampe Q.* **23** (1991) 12.
8. B. D. CADDOCK, K. E. EVANS and D. HULL, *J. Mater. Sci.* **22** (1987) 3368.
9. H. HOJO, K. OGASAWARA, W. L. CHANG, and K. TSUDA, *Adv. Compos. Mater.* **3** (1994) 341 (translated from *J. Jpn. Soc. Compos. Mater.*).
10. S. H. GOODMAN, editor, "Handbook of Thermoset Plastics" (Noyes: Park Ridge, 1986) pp. 52 –121.
11. E. G. RICHARDS, "An Introduction to Physical Properties of Large Molecules in Solution" (Cambridge University Press, New York, 1980) pp. 115 –127.
12. P. J. FLORY, "Principles of Polymer Chemistry" (Cornell University Press, Ithaca, NY, 1952) ch. 13.
13. A. F. M. BARTON, editor, "Handbook of Polymer–Liquid Interaction Parameters and Other Cohesive Parameters" (CRC Press, Boca Raton, 1983) pp. 11– 20, 518 – 520.
14. L. W. CAI and Y. WEITSMAN, *J. Compos. Mater.* **28** (1994) 130.
15. 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.
16. R. HILL, A. COWKING and W. S. CARSWELL, *Composites* **20** (1989) 215.
17. A. CHRISTIANSEN and J. B. SHORTALL, *J. Mater. Sci.* **11** (1976) 1113.
18. T. P. O'HEARN and K. E. KITCHEN, *Plast. Eng.* **44** (1988) 35.
19. *Idem.*, in Proceedings of the 41st Annual Conference of Reinforced Plastics/Composites Institute (Society of Plastics Industry, New York, 1988) pp. 1– 7.
20. R. B. SEYMOUR, in "Macromolecular Solutions Solvent–Property Relationships in Polymers" edited by R. B. Seymour and G. A. Stahl (Pergamon, New York, 1982) pp. 10–13.
21. S. LAOUBI, J. BOUZON and J. M. VERGNAND, *Eur. Polym. J.* **27** (1991) 1437.

Received 31 October 1995
and accepted 15 December 1995