Degradation mechanism of fiber-reinforced plastics and its implications to prediction of long-term behavior

L. PRIAN*, A. BARKATT
Department of Chemistry, The Catholic University of America, Washington, DC 20064, USA
E-mail: BARKATT@CUA.EDU

Short-term measurements on fiber reinforced plastics (FRPs) appeared to indicate that their degradation in aqueous media has simple (linear or sublinear) kinetics with Arrhenius-type temperature dependence, permitting easy design of accelerated tests and development of long-term predictive models of FRP degradation. However, upon more prolonged exposure, delayed increases in the rate of degradation were observed. Such non-linear effects greatly complicate predictions of long-term behavior. These effects were postulated to result from interface degradation involving alkali leaching from the fibers, enhanced hydrolytic extraction of monomeric acrylic acid from the matrix, fiber/matrix debonding, microcracking, and ensuing enlargement of the effective area of the composite exposed to further attack, leading to enhanced corrosion. Measurements of fiber dissolution as a function of time demonstrated the existence of accelerated degradation phenomena. The pH at the fiber/matrix interface was shown to rise using an indicator. Hydrolytic depolymerization of the matrix surrounding the fibers was demonstrated using Raman spectroscopy and leachate analysis. Direct evidence of interface cracking and matrix degradation during exposure to aqueous media was gathered using environmental scanning electron microscopy (E-SEM). The effects of porosity as well as of the presence of microcracks were demonstrated by measuring the extent of silica dissolution from the fibers embedded in the FRP before and after the porosity had been altered using various thermal treatments. The results of these measurements were integrated to give a coherent interpretation of the observed delayed increases in degradation rates of FRPs exposed to aqueous environments. © *1999 Kluwer Academic Publishers*

1. Introduction

The feasibility of using FRPs in civil engineering applications (e.g., in reinforcing concrete structures or producing chemically resistant piping) is strongly linked to the capability of these materials to maintain their mechanical and chemical properties during service. Understanding the degradation mechanisms of FRPs and reliable prediction of their properties over long service times based on such understanding are essential. Such predictions require development and validation of quantitative models of the effects of various environments on the fibers, the resin matrix, and the interface at the molecular level. In this context, Springer *et al.* [1] carried out studies on the effect of aqueous solutions on the mechanical and chemical properties of glass/polyester composites. The susceptibility of glass fibers to dissolution in alkaline environments was investigated by Diamond [2], GangaRao [3], and Nanni *et al.* [4]. Hydrolytic depolymerization of the matrix has already been observed using Raman spectroscopy [5] and infrared spectroscopy [6].

Measurements of various properties of FRP materials exposed to aqueous media showed the possibility of a sudden decrease, after a certain induction period, of the mechanical properties of composite materials upon exposure [7]. For instance, the matrix-dependent shear strength of E-glass/vinylester composites decreased drastically when the exposure to water at $80\,^{\circ}$C was extended from 112 to 224 days [7]. Previously reported studies of the degradation of FRPs provide several examples of non-linear behavior as a function of time in the degradation process of composite materials. Wet-dry cycling tests have been shown to cause enhanced damage per cycle as the number of cycles increased [8]. Microcrack nucleation and propagation has been observed in these cycling tests as well as in immersion tests [9]. An abrupt increase in the glass transition temperature was observed in epoxy/graphite composites

in the course of aging at elevated temperature [10]. In general, in order to predict the changes in properties or the rate of degradation of a material over a long period of time it is necessary to evaluate critically the applicability of extrapolation of results obtained in service-condition tests. Because of the limited time available for service-condition tests relative to the required service life, such tests have to be supplemented, in most cases, by accelerated tests, which simulate the much higher levels of damage experienced by a material over its lifetime. Ghosh and Bose [11] used elevated temperatures to accelerate the degradation of composite materials and Gerritse [12] proposed to use exposure to highly concentrated solutions as a means of accelerating the degradation.

Based on the establishment of reliable correlations between the results of accelerated tests and service-condition tests, respectively, the long-term behavior of materials can be predicted.

The common expression used to describe changes in the properties of a material with time is $R = kt^{\alpha}$ [13], where R is the rate of change, t is the time of exposure, k is the rate constant, and α is a material constant.

For instance, the extent of dissolution of silicate glasses in basic solutions is a constant-rate process, i.e., a process in which the amount dissolved is linear with time ($\alpha = 0$). In such cases the behavior over a long period of time can be simply extrapolated from the results of short-term tests.

In the case of degradation following a sublinear time dependence ($\alpha < 0$), (e.g., formation of a protective layer on the surface of the material that decreases the rate of degradation), a linear extrapolation of the results would overestimate the changes occurring under service conditions. This is often the case when silicate glasses are exposed to de-ionized water at high dilution (i.e., a low surface-to-volume ratio). In such cases, linear extrapolation provides a conservative, upper bound estimate of the extent of degradation.

The most serious case can be represented by a supralinear time dependence ($\alpha > 0$) where the degradation process is associated, for example, with significant changes in the macrostructure of the material (e.g., cracking) [14, 15]. Linear extrapolation of the results would lead to erroneous predictions that could lead to premature failure of the material in service. In this case, the microscopic mechanisms of degradation have to be understood in order to characterize and bound the extent of rise in degradation rates which may be encountered in the course of contact with a corrosive environment.

2. Experimental
2.1. Materials
Two different types of commercial E-glass/vinylester rods (VGR I and VGR II) were selected for this study. Both the materials had unidirectional E-glass fibers, a diameter of 6.35 mm, and they were manufactured using the pultrusion process. A commercial E-glass/polyester composite (PG) was also tested. The volume fractions of fibers in these composites were

obtained using burnout tests according to the ASTM D-2584 procedure (1996). The volume fractions of fibers in the VGR I, VGR II, and PG were (61 ± 2)%, (62 ± 2)%, (56 ± 3)%, respectively. Further information concerning the components and manufacturing of these three composites was given in earlier publications [16, 17].

2.2. Analytical techniques
2.2.1. Dissolution of silica under conditions of frequent leachant exchange
Each set of samples was placed in a volume of 50 ml of de-ionized water in a 125-ml polymethylpentene (PMP) container. Each container held three FRP samples, each 2.5-cm long. The samples were cut from portions of the rods using a low speed saw. The temperatures of exposure were 23, 40, 60 and 80 °C, respectively. The water was removed twice weekly and replaced with the same amount of de-ionized water. The leachates were analyzed for dissolved silica using molybdenum blue colorimetry. The accuracy of this method was found to be ± 5% using standard silica solutions. The normalized dissolution or leach rate (NLR) was calculated in each case using the following equation:

$$NLR = \frac{(C - C_0)}{f * (S/V) * \Delta t}$$

where

$NLR =$ Rate of *glass* dissolution (based on silica) per unit area of *composite* per unit time;
$C =$ concentration in leachate, g/m^3;
$C_0 =$ concentration in blank, g/m^3;
$f =$ fraction of silica in the fibers;
$S/V =$ surface-to-volume, m^{-1};
$\Delta t =$ time, days.

Each experiment was carried out in duplicate, accompanied by two blank tests.

2.2.2. Optical and environmental scanning electron microscopy
Optical microscopy at low magnification ($<100\times$) was performed using an optical microscope (Nikon Stereoscopic Microscope). Environmental scanning electron microscopy was performed using an E3 ElectronScan E-SEM. In the test involving E-SEM measurements, the specimens were potted in epoxy molds and then polished following a procedure recommended for polymer matrix/graphite composites [18] before being exposed to corrodents and subsequently to examination by means of E-SEM.

2.2.3. Raman spectroscopy
The part of the sample analyzed by Raman spectroscopy was the interface between the fibers and the resin in the exposed cross-sectional area. A Renishaw Corp.

780 nm laser source and a 50× objective, which gives a spot size of about 1 μm, were used in the measurements.

2.2.4. Differential scanning calorimetry

The thermal properties of the materials included in this study were measured using a Perkin-Elmer DSC 7. For the purpose of the current study the instrument was programmed to heat the sample from an initial temperature of 50 °C to a final temperature of 150 °C at a heating rate of 10 °C/min. Sample preparation consisted of cutting out a section of the material with a knife or with a low speed rotating blade cooled by water. The weight of the samples analyzed was in the 20–30 mg range.

3. Results and discussion
3.1. Short-term tests
3.1.1. Mechanical and thermochemical tests

As reported in previous papers [7, 19], a combination of test methods that included mechanical tests and thermochemical (weight change and TGA) tests was applied to specimens previously exposed for short periods of time to various aging environments. The results of these tests showed that raising the temperature can be generally concluded to be a valid technique of accelerating the corrosion rates in the studies of the degradation of FRP materials. It was observed that the changes in properties, upon exposure for short periods of time, were in general approximately linear with time, and the dependence of such changes on temperature followed an Arrhenius-type behavior. It was also shown that the effects of changing the chemical environment on the properties of the FRP materials were very similar whether the tests were carried out at 23 °C, 50 °C, or at 80 °C [19]. This indicated that over this temperature range the degradation mechanism remained essentially unchanged. Furthermore, differences in susceptibility to environmental degradation among various materials were also unchanged within this temperature range [19]. However, all these conclusions were based on the results of short-term tests.

3.1.2. Dissolution of silica under conditions of frequent leachant exchange

A set of experiments was conducted to determine the concentrations of silica in the aqueous solutions to which the composite materials were exposed as a function of time under conditions of frequent exchange of the aqueous phase. In these experiments, specimens of two different E-glass/vinylester rods (VGR I and VGR II) were tested. In these tests, that lasted up to 74 days, the temperature dependence in the leachant-exchange tests appeared to be Arrhenius-like (see Fig. 1a). The corresponding activation energy (see Fig. 1b) was of the order of 70–75 kJ/mol, similar to the value obtained when the exposed samples were subjected to TGA tests [7, 19]. This value is also within the range of activation energies usually observed in silicate glass dissolution [20].
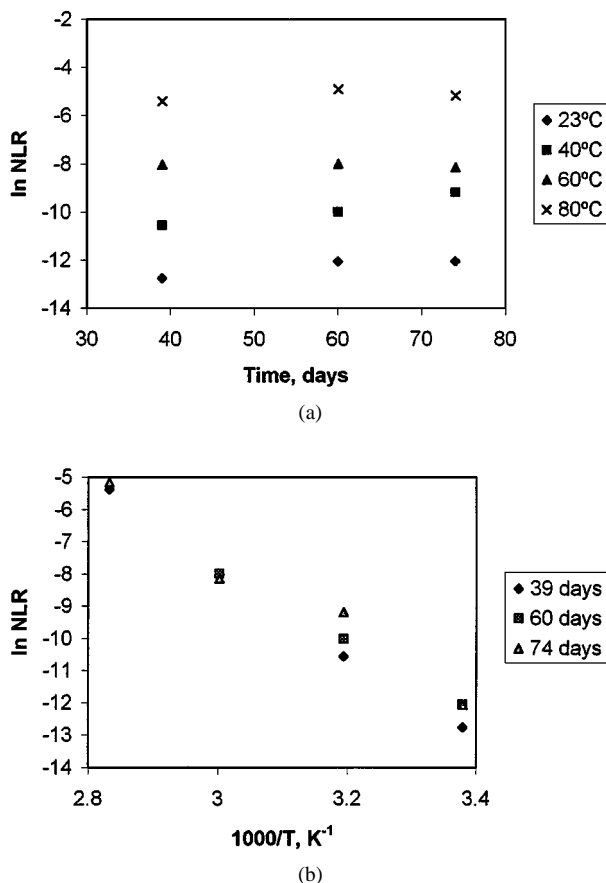

(a)

(b)

Figure 1 Dissolution of VGR II in de-ionized water as a function of time and temperature: (a) NLR as a function of time and (b) arrhenius plot.
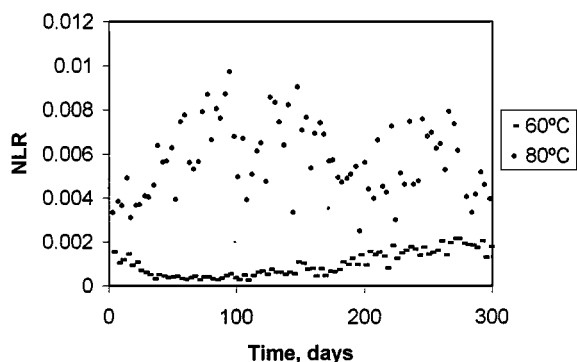

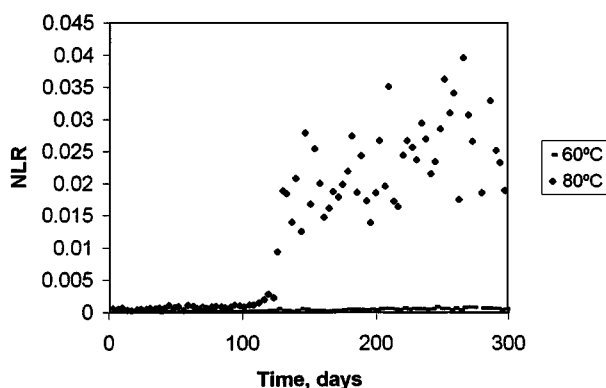*Figure 2* Normalized dissolution rates of silica in leachates from exposure of VGR I to de-ionized water.

Figure 3 Normalized dissolution rates of silica in leachates from exposure of VGR II to de-ionized water.

3.2. Long-term tests
3.2.1. Dissolution of silica under conditions of frequent leachant exchange

In the present study, the measurements described in the previous paragraph were extended over periods of up to 1 year.

Figs 2 and 3 show the normalized leach rates (NLR) in the cases of VGR I and VGR II, respectively, as a function of time. However, the results obtained upon prolonging the test duration over periods of up to 1 year indicate that in the case of specimens exposed at 80 °C an increase in the rate of dissolution of silica is observed after a 90–100 day period. After a long induction period (about 200 days) an increase in the rate of dissolution also appears to start in the case of the specimens exposed at 60 °C.

Figure 4 Optical micrographs of VGR I exposed to phenol red solution at room temperature for 40 min, X68.
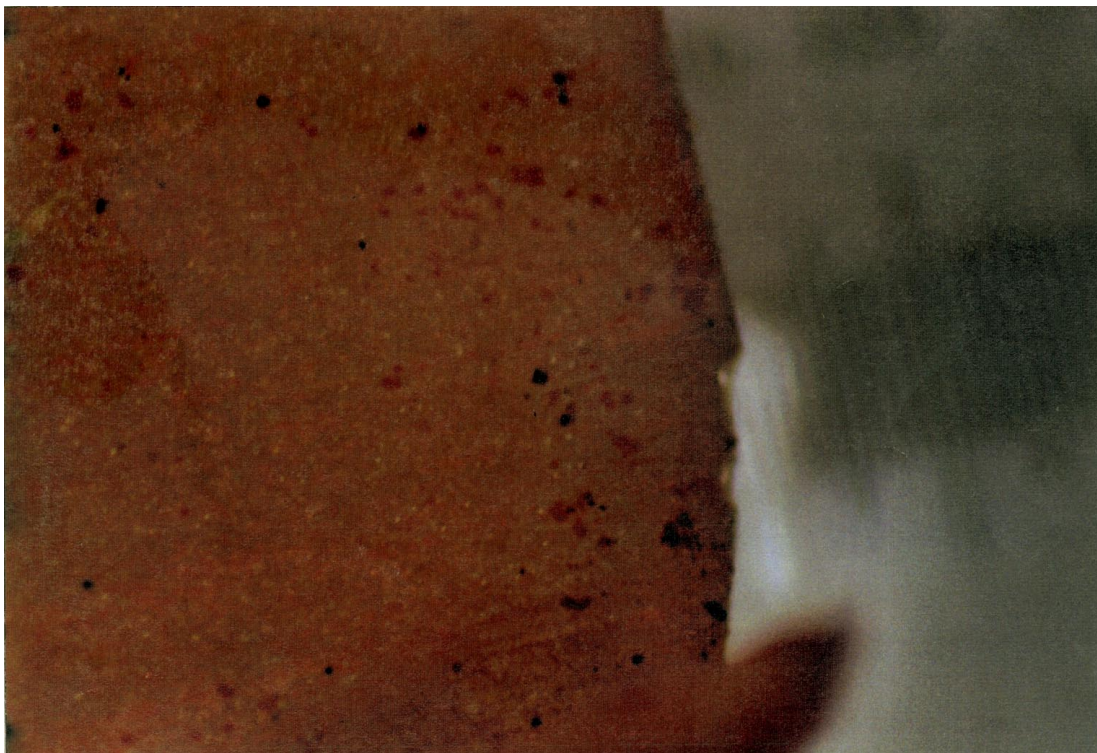

Figure 5 Optical micrographs of VGR I exposed to phenol red solution at 60 °C for 3 weeks, X68.

The rise of the silica dissolution rates observed after the initial induction period cannot be simply attributed to the absorption of water by the composite during immersion. In fact, as indicated in earlier publications [16, 17], diffusion tests performed on the same material (VGR II) showed that at 80 °C the time required to reach 50% saturation with respect to water was approximately 3 days and the time required to reach 90% was approximately 25 days. Furthermore, the water absorption curves follow, as expected, a smooth parabolic $t^{1/2}$ dependence as a function of time, while the dissolution rate excursion observed for the same composite in Fig. 3 is very sharp and almost vertical.

The rise in silica dissolution rates at the end of a longer period of time indicates that despite the agreement of the short-term results with linear time dependence and a simple Arrhenius-type model (Fig. 1), serious complications may arise upon attempting to use the results of such short-term tests in predictions of long-term behavior. Thus, better understanding of the degradation process is required. In order to gain such understanding the experiments described in the following sections were performed.

3.3. pH at the matrix/fiber interfaces
In order to determine the changes in the pH in the area immediately surrounding the fibers, several specimens of VGR I (more translucent than VGR II) were exposed to a phenol red solution ($pK_a = 7.8$) at 60 °C for

3 weeks. The results of the experiment can be seen upon comparing Figs 4 and 5, which show optical micrographs of cross sections of specimens exposed to the indicator solution for 40 min and for 3 weeks, respectively. The micrographs were taken after the samples were allowed to cool to room temperature. It can be seen that prolonged exposure to water causes the pH to rise, as indicated by the change of color from yellow to purple. The purple coloration in Fig. 5 confirms that the dissolution mechanism of the E-glass fibers follows the mechanism proposed by Charles [21] for silicate glass dissolution. According to this mechanism, selective leaching of alkaline components from a silicate glass causes the concentration of OH^- ions in the aqueous medium to rise. The hydroxide ions break up the silica network without being consumed. Thus, in a confined volume, the rate of dissolution of silicate glasses can be expected to rise with time. Indeed, such a rise has been observed in certain cases [22, 23]. As reported by Chateauminois [24], enhanced leaching at the fiber/matrix interfaces can accelerate de-bonding and open channels for the penetration of the attacking medium.

3.4. pH of the exposure solutions
A further series of pH measurements were performed using a glass electrode on the solutions obtained upon subjecting VGR I and VGR II samples to immersion in de-ionized water at temperatures ranging between
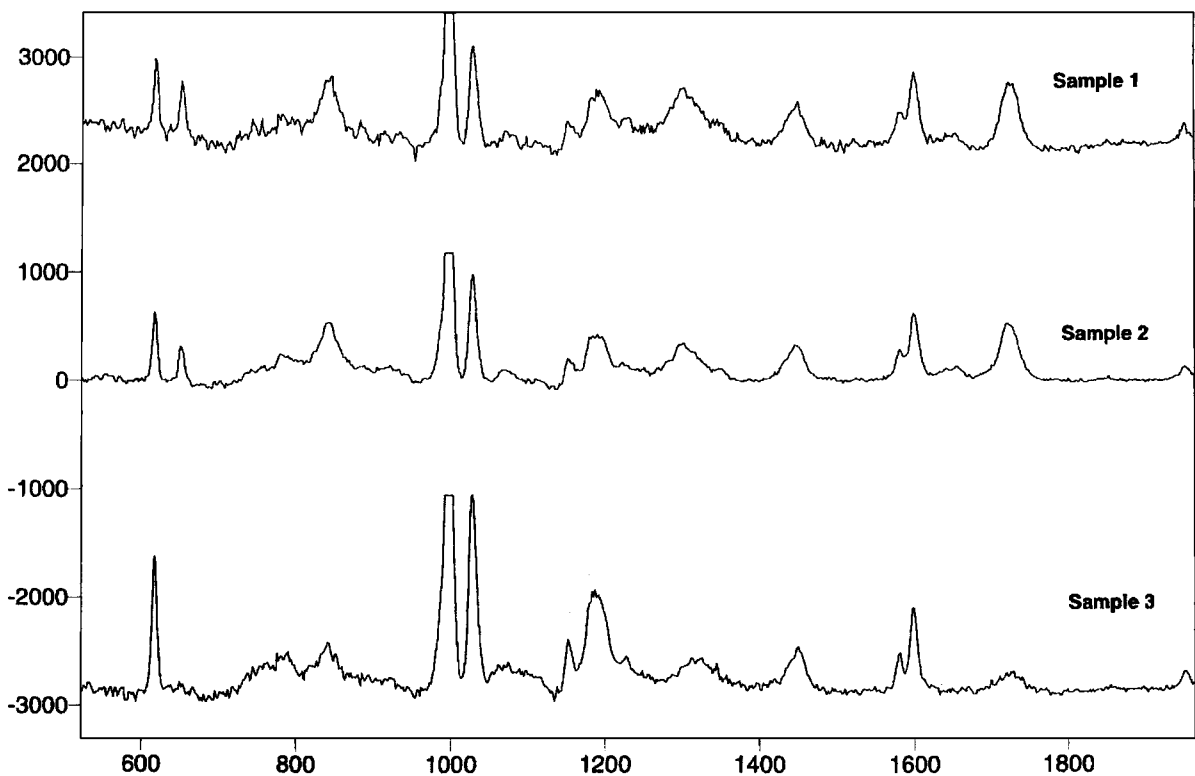
Counts / Raman Shift (cm-1)
File # 2 : BASELINE
Sample 2 interface

Stacked Y-Zoom CURSOR
7/1/97 1:00 AM Res=None

Figure 6 Raman spectroscopy results for E-glass/vinylester rods (VGR II) exposed to various environments.

Duration of exposure (days)	23 °C		40 °C		60 °C		80 °C	
	VGR I	VGR II	VGR I	VGR II	VGR I	VGR II	VGR I	VGR II
7	5.0	5.2	5.1	5.4	4.4	5.3	3.6	4.6
14	4.6	5.1	5.1	5.4	4.3	5.0	3.7	4.5
21	4.7	4.8	4.3	4.8	4.0	4.7	3.4	4.3
28	5.5	5.8	5.4	5.7	4.2	4.8	3.1	4.6
42	5.8	5.7	5.5	5.4	4.2	4.8	3.3	4.3
48	5.7	5.6	5.4	5.5	4.2	5.1	3.4	4.3

23 and 80 °C. Three composite samples, with a total surface area of $(3.1 \pm 0.2) \times 10^3$ mm^2, were placed in each case in a volume of 50 ml of de-ionized water. The water was removed every 3 or 4 days and replaced with the same amount of de-ionized water. The results are shown in Table I.

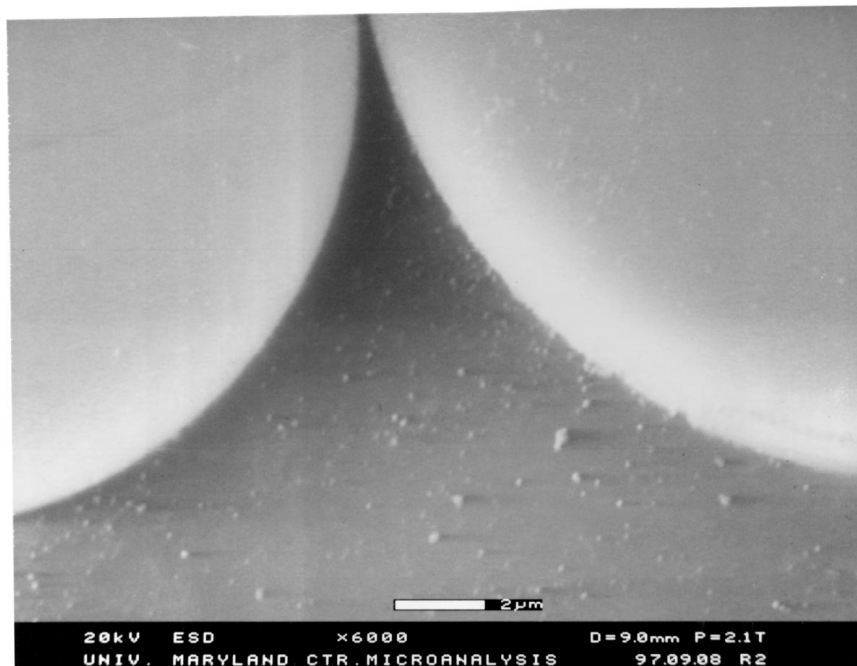Vinylesters are a family of thermoset resins produced by esterification of a polyfunctional epoxy
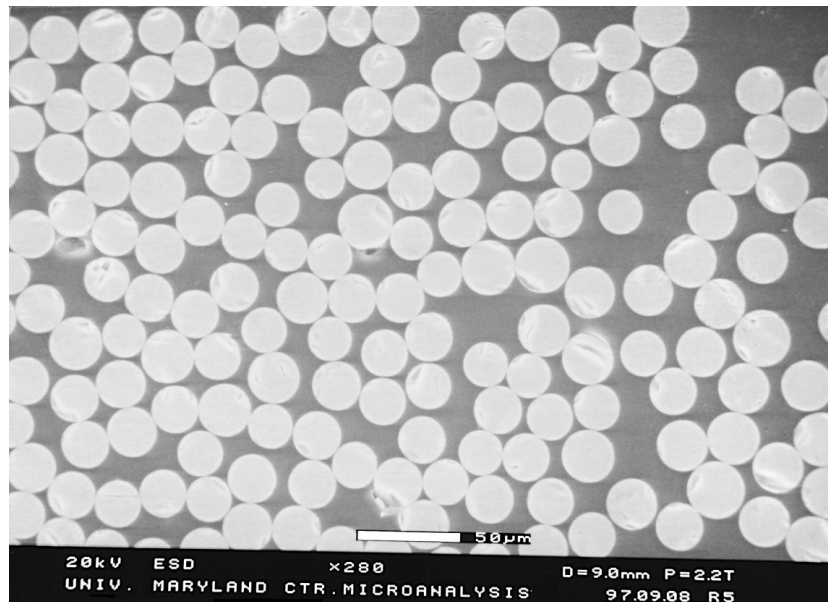
(a)
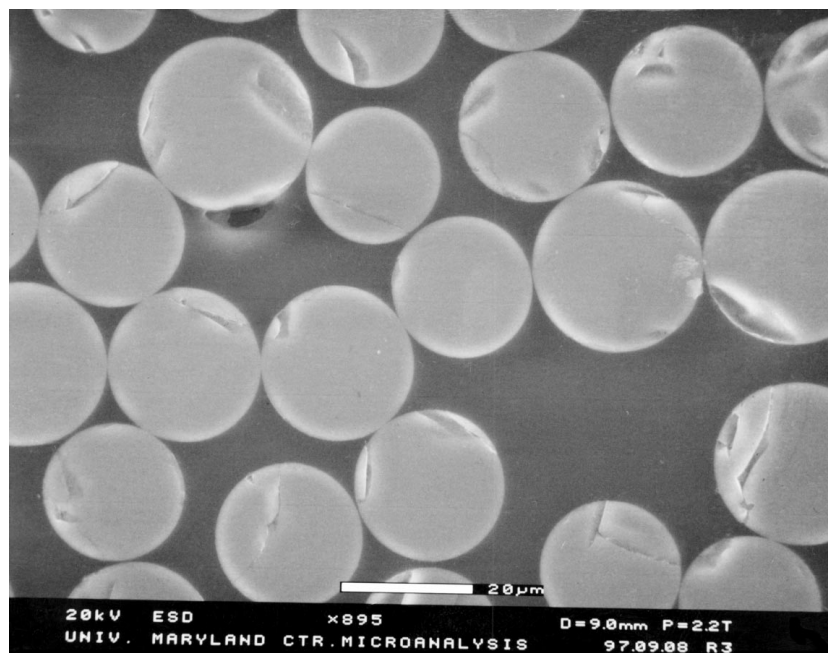
(b)

Figure 7 E-SEM micrographs of cross-section of untreated VGR II: (a) untreated VGR II, X280, (b) untreated VGR II, X895, and (c) untreated VGR II, X6000. (*Continued*)

(c)

Figure 7 (*Continued*).

resin with an unsaturated monocarboxylic acid, usually acrylic or methacrylic acid [25]. In order to identify the acid released by the composite materials in de-ionized water, the leachate solutions were titrated with a 0.01N NaOH solution. Similar titrations, performed on aqueous solutions of acrylic and methacrylic acids at a concentration of 0.00067 M each, showed that the pK_a and the shape of the titration curve obtained with the FRP extracts was very similar to those obtained with dilute acrylic acid. The measured pK_a of the FRP extracts was 4.3 ± 0.1 while the reported pK_a of acrylic acid is 4.25 [26]. This supports the assumption that the increased acidity of the leachate solutions was due to the release of acrylic acid from the FRP. As might be expected, Table I shows that the concentrations of extracted acrylic acid rise upon increasing the temperature of exposure. Furthermore, at similar temperatures of exposure, a larger extent of hydrolysis is observed for the matrix of VGR I than for VGR II, as reflected in the TGA results [7, 19]. Thus, it is possible that as a result of exposure to aqueous media the pH at the internal fiber/matrix interfaces will rise, leading to enhanced attack on the fibers. At the same time, the pH of the aqueous medium in contact with the composite,
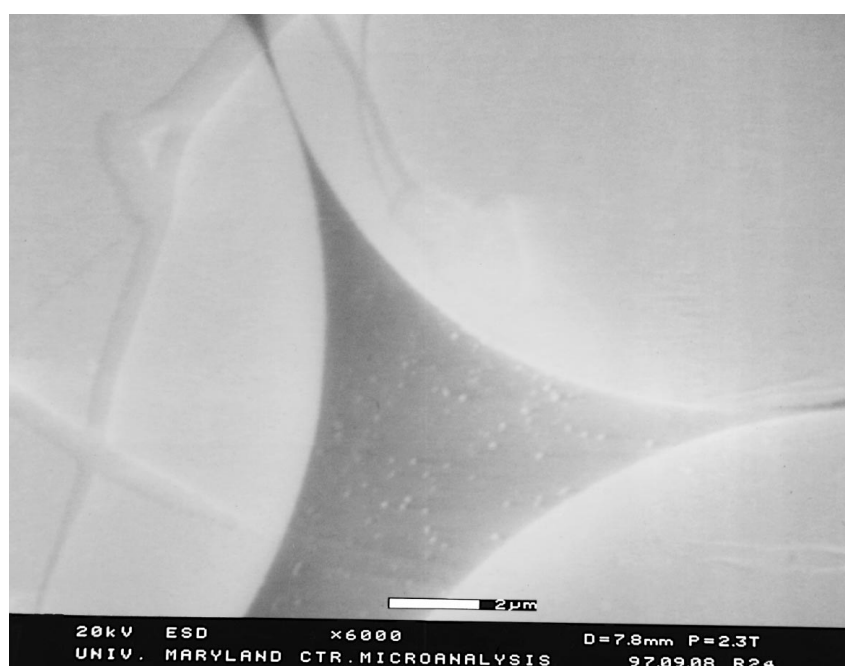

Figure 8 E-SEM micrographs of cross-section of VGR II following exposure to de-ionized water at 23 °C, X6000.

3983

which always has an outer layer of polymeric matrix, will decrease, as a result of hydrolysis of the matrix. Furthermore, the susceptibility of the acrylic acid component of the matrix to hydrolysis, demonstrated here, can be expected to be significantly enhanced by the alkali extracted from the fibers in the interface region. This is one more reason why this region can be expected to undergo more rapid attack than the bulk matrix.

3.5. Raman spectroscopy

Fig. 6 shows the Raman spectra of E-glass/vinylester rods (VGR II). Sample 1 is an untreated specimen. Samples 2 and 3 had been exposed, respectively, to water or 3% ammonia at 80 °C for 28 days. The part of the sample analyzed was the interface between the fibers and the resin in the exposed cross-sectional area. The analysis indicates that there are two bands around 650 cm^{-1} and 1730 cm^{-1} which have decreased markedly in intensity in the sample exposed to 3% ammonia solution. These peaks are associated with the presence of carbon double bonds and carbonyl groups, respectively, in the untreated matrix. The peaks observed in the range of 800–1600 cm^{-1} correspond to aliphatic hydrocarbon units present in the backbone of the vinylester resin. This observation supports the findings discussed above, showing that the depolymerization of the resin proceeds
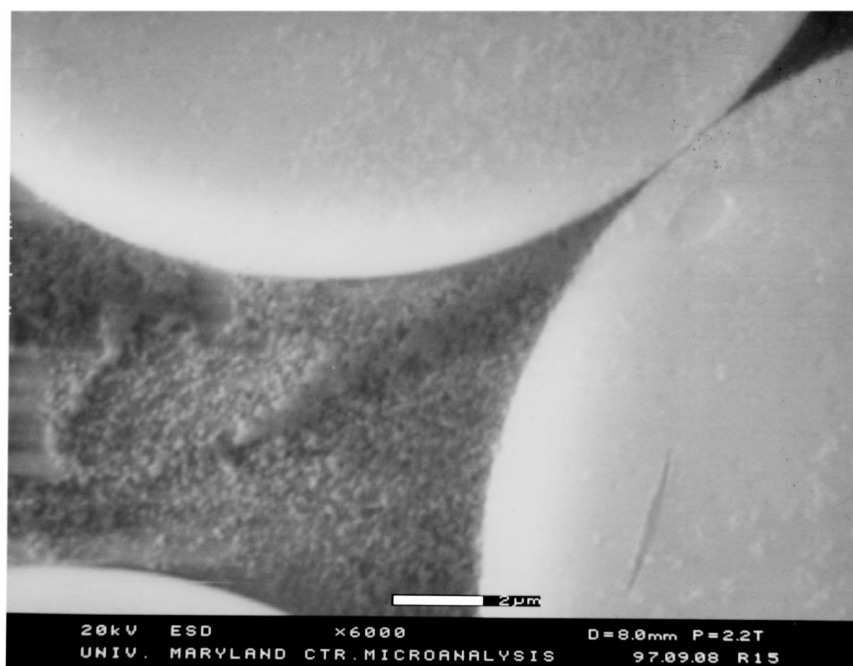

Figure 9 E-SEM micrographs of cross-section of VGR II following exposure to de-ionized water at 50 °C, X6000.
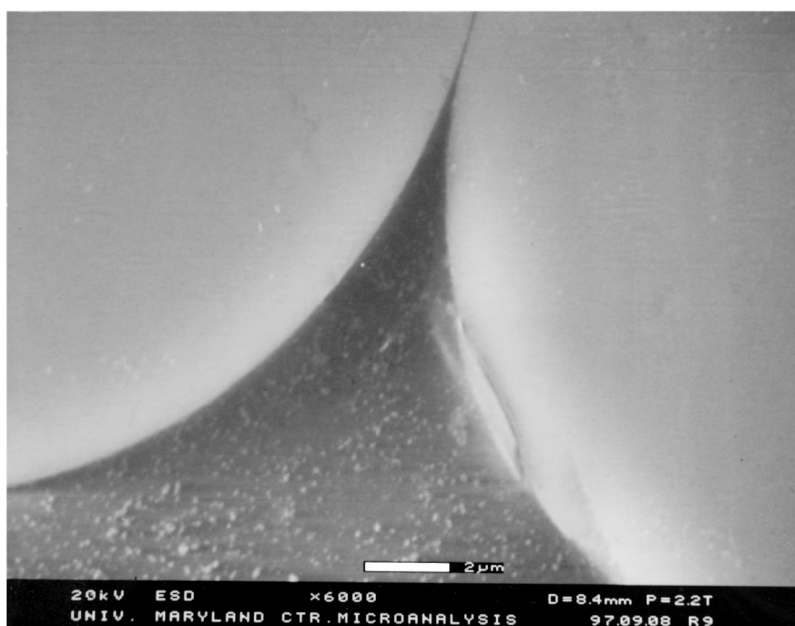

Figure 10 E-SEM micrographs of cross-section of VGR II following exposure to acetic acid buffer at 50 °C, X6000.

with the cleavage of the unsaturated part of the polymeric chain leading to the loss of acrylic acid from the matrix. In addition, the Raman spectroscopy studies indicate that the loss of acrylic acid is even more severe in basic media than in water, in agreement with the conclusions of the previous Section. The degradation of the mechanical properties is also more rapid in basic solutions [7, 19]. The results of the Raman spectroscopy studies combined with the pH data reported in the previous Section indicate that elevated pH causes a rapid attack not only on the fibers but also on the matrix. Elevated pH in the interface region can arise due to selective leaching of alkaline ingredients from the glass fibers even when the aqueous medium is initially neutral (see above).

## 3.6. Environmental scanning electron microscopy

In order to obtain direct observations of the effects of environmental exposure on the FRP materials used in the current study, a series of electron microscopy analyses were performed using environmental scanning electron microscopy (E-SEM).

Specimens of VGR II, 2-cm long, were exposed for 2 weeks to de-ionized water, acetic acid buffer (pH 4.93), or 3% ammonia, respectively. Exposure to each of these three media took place at room temperature or at 50 °C. Micrographs of cross sections of the samples are presented in Figs 7–11.

The effect of increasing the temperature from 23 to 50 °C is evident upon comparing Figs 8 and 9,
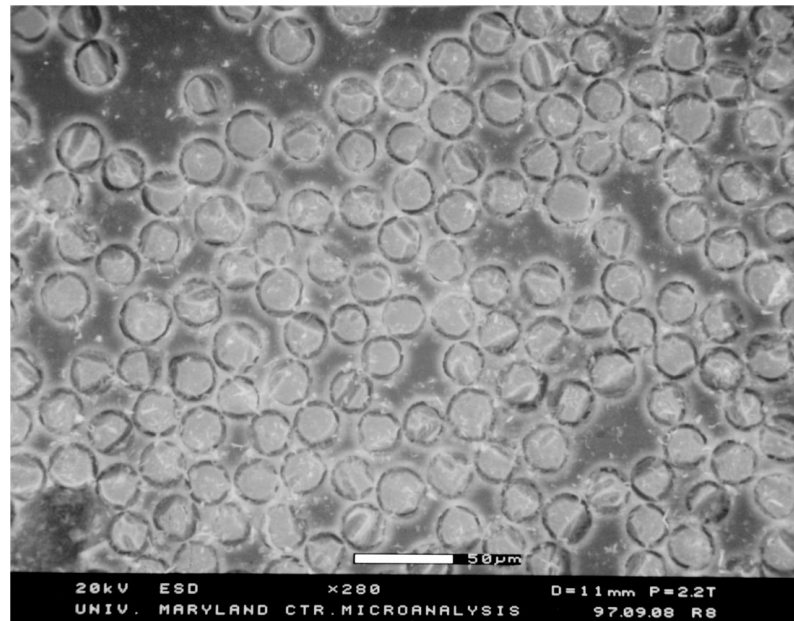
(a)
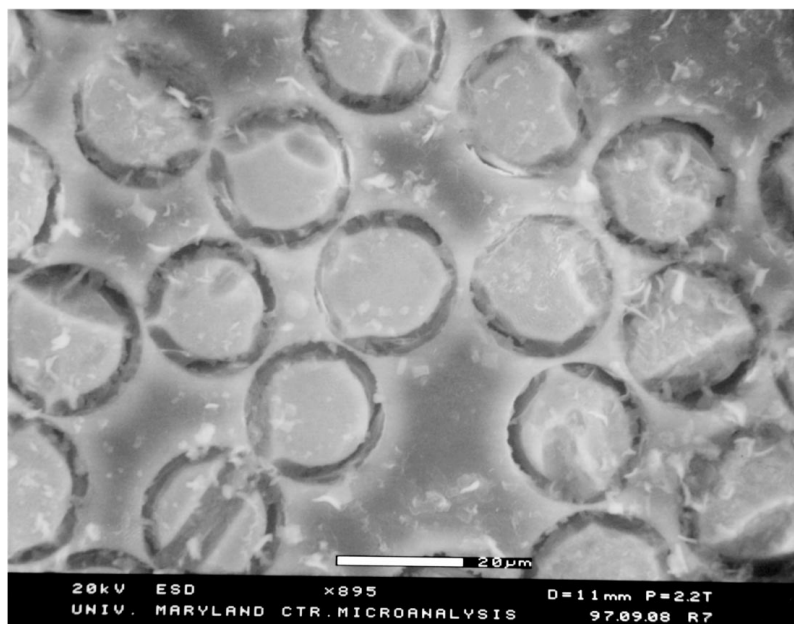
(b)

Figure 11 E-SEM micrographs of cross-section of VGR II following exposure to 3% ammonia solution at 50 °C: (a) VGR II exposed to 3% ammonia solution at 50 °C, X280, (b) VGR II exposed to 3% ammonia solution at 50 °C, X895, and (c) VGR II exposed to 3% ammonia solution at 50 °C, X6000. (*Continued*)

(c)

Figure 11 (*Continued*).

respectively. Indications of the degradation of the polymeric matrix are evident in the cases of all the specimens exposed to a higher temperature (50 °C). Matrix degradation is indicated by the roughening of the surface of the matrix as seen in Fig. 9. The extent of roughening is observed to depend on the composition of the aqueous medium. The specimen exposed to the acetic acid buffer appears to have less surface roughness, apparently due to suppression of significant changes in pH by the buffer during the exposure (Fig. 10).

The effect of the 3% ammonia solution at 50 °C on the matrix/fiber interfaces is very dramatic. The dark area surrounding the edges of each fiber (Fig. 11) is indicative of interfacial debonding resulting from the dissolution of the silica network. As expected, this degradation of the interface due to attack on the fibers is much more severe in the case of the high-pH ammonia solution than in the other two solutions. The E-SEM results provide a direct confirmation of the conclusions reported in the previous sections, viz. that the susceptibility of FRPs to hydrolytic attack is largest at elevated pH. Accordingly, upon exposure to neutral water, such attack is expected to become more pronounced in the interface region due to leaching of alkalis from the fibers.
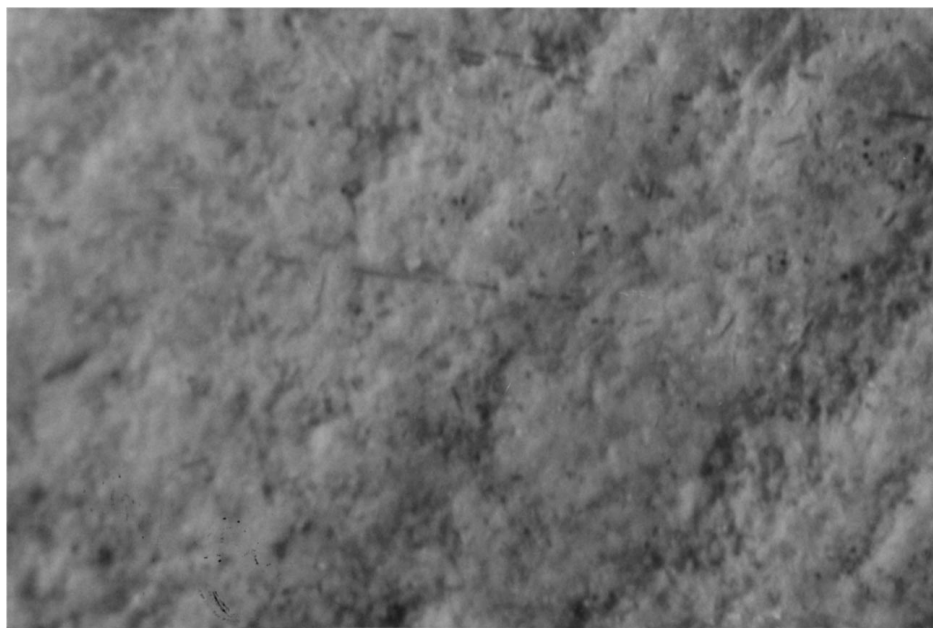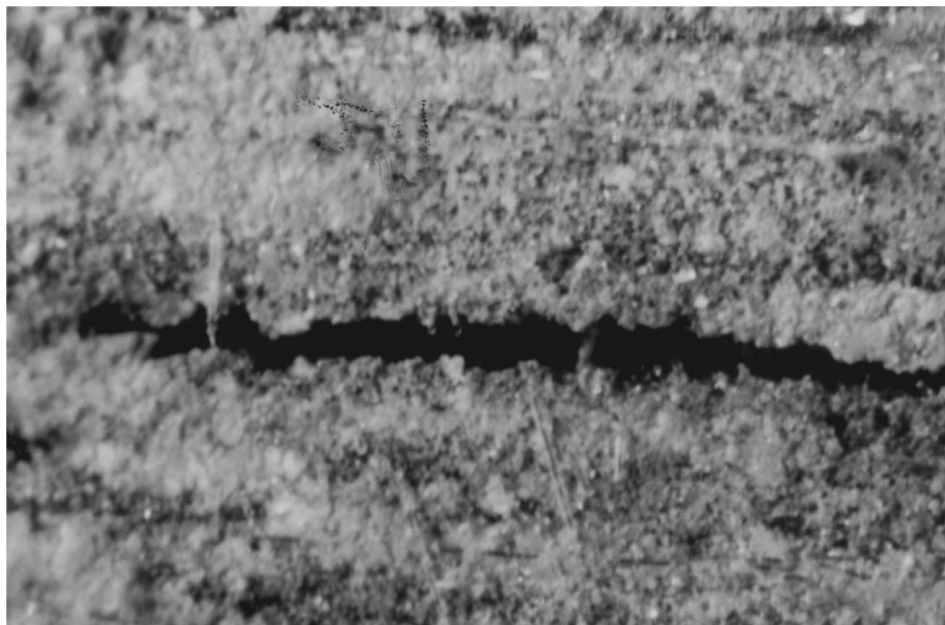

(a)

Figure 12 Effect of thermal exposure on the surface of an E-glass/polyester composite: (a) Untreated sample, X68, (b) sample heated at 150 °C, X68, and (c) sample heated at 250 °C, X68. (*Continued*)
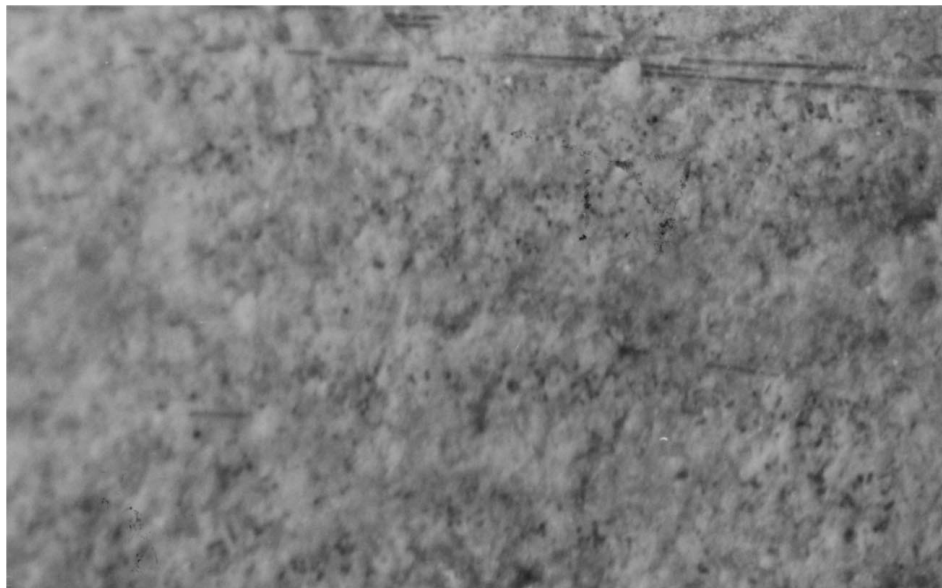
(b)

(c)

Figure 12 (*Continued*).

The interface degradation and debonding observed as a result of the exposure to ammonia provide a direct picture of the microscopic processes leading to the rapid degradation of the mechanical properties of FRPs.

3.7. Effects of porosity

In order to study the effect of porosity on the properties of FRP materials, a number of specimens of E-glass/polyester material were heated in air at 150 or 250 °C for two weeks. The effects of thermal exposure are shown in Fig. 12. The specimen preheated at 250 °C shows on the surface a larger number of microcracks that are indicative of a larger porosity than that of the samples pre-heated at 150 °C or not pre-heated at all.

Following the thermal exposure, the specimens were exposed to de-ionized water at 40 °C. Fig. 13 shows the normalized dissolution or leach rate (NLR) based on measurements of the concentrations of dissolved silica.

The FRP samples pre-heated at 250 °C, which have a larger porosity than the other samples (see above), exhibit a higher effective NLR (Fig. 13). The lower effective NLRs obtained with the specimen pre-heated at 150 °C are apparently due to a post-curing effect involving an increase in the number of cross-linkages between the polymer chains as indicated by an increase in the glass transition temperature, T_g (Table II).

TABLE II Effect of various temperatures on the glass transition temperature of E-glass/polyester

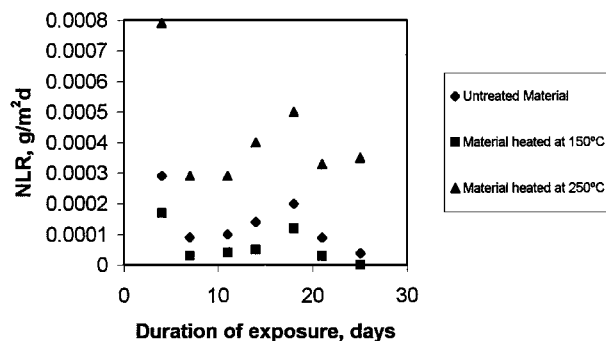|	23 °C	150 °C	250 °C
T_g (°C)	82.5 ± 1.3	88.9 ± 1.5	89.3 ± 1.5

Figure 13 Normalized dissolution rate of silica upon exposure of heat-treated samples of an E-glass/polyester composite to de-ionized water at 23 °C.

This enhanced cross-linking reduces the susceptibility of the material to hydrolysis and to leaching out of low-molecular-weight units. The observation that higher porosity gives rise to a higher effective dissolution rate supports the hypothesis that as prolonged exposure leads to the formation of microcracks and open pores, the resulting increase in surface area exposed to the aqueous medium will cause an increase in the effective dissolution rate of the composite. It should be noted that water absorption studies [16, 17] on the composites used in the present work showed an increase in moisture content after attaining the saturation level, indicating that once the material becomes saturated it begins to degrade at an accelerated rate. This is also probably due to the effects of the formation of microcracks and pores.

4. Conclusions

A series of measurements were performed in order to obtain insight into the degradation mechanisms that occur upon prolonged exposure of composite materials to aqueous environments. Even when the surrounding aqueous medium is initially neutral, the pH at the fiber/matrix interface eventually increases due to leaching out of alkaline components from the silicate glass fibers. The increase in local pH in the interface region was directly demonstrated by observing the color change of a pH indicator infused into the region immediately surrounding the fibers. This increase in local pH leads to enhanced nucleophilic attack on the fibers in the interface region. The correlation between increased pH and rapid interface degradation is demonstrated by the results of the E-SEM studies. Elevated pH causes rapid fiber dissolution, followed by interface de-bonding. Elevated pH also causes enhanced matrix hydrolysis and extraction of acrylic acid. Such release was demonstrated by pH measurements and analysis of aqueous media contacted with FRP materials. The hydrolytic depolymerization of the matrix was directly confirmed by Raman spectroscopy studies that showed that exposure to aqueous media leads to loss of acrylic acid from the matrix. This loss was most extensive in cases of severe degradation of the fiber/matrix interfaces, i.e., in basic environments and at elevated temperatures. Measurements of the concentration of dissolved silica in leachates resulting from

exposure of FRPs of various porosities indicated that the presence of microcracks in the matrix can enhance the rate of degradation. The opening up of new routes, resulting from thermal treatment or from the dissolution of the glass fibers in basic environments, increases the amount of hydrolytic attack on the polymer, accelerating the degradation processes. As proven by the results of measurements of dissolved silica concentrations under conditions of frequent leachant exchange, the rate of dissolution of silica can increase with time as a result of the formation and propagation of cracks in the matrix.

Short-term testing that included mechanical tests and thermochemical tests on specimens following exposure to various aging environments showed that over short periods of time the degradation process was generally linear. Moreover, Arrhenius-type behavior was observed for the temperature dependence. Accordingly, based on the results of such short-term tests, it appeared that the degradation kinetics is simple and that raising the temperature would be a valid technique of accelerating the corrosion rates in tests on FRP materials. However, the present work showed that dramatic increases in degradation rates may be observed in some cases of environmental exposure after a certain induction period. This study identified the fundamental mechanisms that account for such excursions. It was shown that leaching of alkaline components out of the fibers and the consequent increase in the pH around the fibers cause enhanced degradation of the fiber/matrix interfaces, involving both accelerated fiber dissolution and loss of acidic components from the matrix. The deterioration and opening up of the interface region allows further water penetration, promoting enhanced hydrolytic depolymerization of the matrix. Eventually the degradation, concentrated in and around the interface regions, can lead to the formation of microscopic cracks and voids that further facilitate penetration and attack by aqueous media.

The mechanism detailed above, which was demonstrated in its various stages in the present study, accounts for the observation of delayed rises in degradation rates in the course of exposure of FRPs to aqueous media. These rate excursions can occur weeks or months after the start of the exposure even at elevated temperatures (corresponding to months or years at service temperatures). In order to determine the service life of FRPs it is imperative to take into account these excursions and to evaluate their extent quantitatively. This requires detailed understanding of the degradation mechanisms of each FRP material as well as extensive testing under accelerated conditions.

References

1. G. S. SPRINGER, B. A. SANDERS and R. W. TUNG, *J. Compos. Mater.* **14** (1980) 213.
2. S. DIAMOND, *Cement and Concrete Research* **11** (1981) 383.
3. H. V. S GANGARAO, D. S. ALTIZER, P. V VIJAY, N. DOUGLASS and R. PAUER, presented at the 1996 Spring Convention of the American Concrete Institute, Denver, Colorado.
4. A. NANNI, S. MATSUBARA and HASUO, in "Advanced Composite Materials in Bridges and Structures," edited by K. W. Neale and P. Labossiere (CSCE, Montreal, 1992) p. 101.
5. A. BARKATT, L. C. BANK, T. R. GENTRY, L. PRIAN, R. SHAN, J. C. SING and R. POLLARD, in Proceedings of the NACE International Annual Conference and Corrosion Show '95 (NACE International, Houston, 1995) p. 138/1.
6. I. GHORBEL and D. VALENTIN, *Polymer Composites* **14** (1993) 324.
7. L. PRIAN and A. BARKATT, in Proceedings of the NACE International Annual Conference and Corrosion Show '98 (NACE International, Houston, 1998) p. 455/1.
8. B. GUETTA, A. R. BUNSELL, C. BELINSKY and F. LALAU KERALY, *Composites* **20** (1989) 461.
9. R. E. ALLRED, *J. Comp. Mater.* **15** (1981) 117.
10. J. MIJOVIC, *ibid.* **19** (1985) 178.
11. P. GOSH and N. R. BOSE, *J. Mater. Sci.* **26** (1991) 4759.
12. A. GERRITSE, in "Advanced Composite Materials in Bridges and Structures," edited by K. W. Neale and P. Labossiere (CSCE, Montreal, 1992) p. 129.
13. L. HOLLAND, "The Properties of Glass Surfaces" (Chapman & Hall, London, UK, 1966).
14. A. A. BARKATT, S. A. OLSZOWKA, W. SOUSANPOUR, M. A. ADEL-ADADI, R. ADIGA, A. A. BARKATT, G. S. MARBURY and S. LI, in Proceedings of Materials Research Society Symposium, 1991, Vol. 212, p. 65.
15. A. A. BARKATT, J. C. SANG, S. B. XING, Y. GUO, I. L. PEGG and A. L. BARKATT, in Proceedings of Materials Research Society Symposium, 1994, Vol. 333, p. 123.
16. T. R. GENTRY, L. C. BANK, A. BARKATT and L. PRIAN, *ASTM Journal of Composites Technology and Research*, submitted (ASTM: West Conshohocken, PA, 1997).
17. T. R. GENTRY, L. C. BANK, A. BARKATT, L. PRIAN and F. WANG, in Proceedings of SPI/ICE 97 (Nashville, TN, 1997) Session 5D, p. 1.
18. "Microstructural Analysis Optical Instrumentation" (Buehler, Malvern, PA, 1992).
19. L. PRIAN, R. POLLARD and A. BARKATT, in Proceedings of the ASCE International Annual Conference (ASCE International, Washington, DC, 1996).
20. M. A. RANA and R. W. DOUGLAS, *Phys. Chem. Glasses* **2** (1961) 196.
21. R. J. CHARLES, *J. Appl. Phys.* **29** (1958) 1549.
22. C. T. LEE and D. E. CLARK, *Adv. Ceram.* **20** (1986) 541.
23. M. F. DILMORE, D. E. CLARK and L. L. HENCH, *Ceram. Bull.* **58** (1979) 1111.
24. A. CHATEAUMINOIS, B. CHABERT, J. P. SOULIER and L. VINCENT, *Composites* **24** (1993) 547.
25. L. T. BLANKENSHIP, M. N. WHITE and P. M. PUCKETT, in Proceedings of 34th International SAMPE Symposium, 1989, Vol. 34, p. 234.
26. "CRC Handbook of Chemistry and Physics" (CRC Press, Boca Ranton, FL, 1990).