Effects of Water, Salt Solution and Simulated Concrete Pore Solution on the Properties of Composite Matrix Resins Used in Civil Engineering Applications

by

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One of the obstacles hindering the acceptance of polymer composites in civil engineering applications is the susceptibility of the polymeric matrix: to degradation that is initiated by moisture, temperature, and corrosive chemical environments. The objective of this study was to characterize chemical and physical changes in polymer matrix resins following exposure to these environments. Resin systems studied were vinyl ester and isophthalic polyester, both of which are proposed for use in construction applications. Unreinforced free films were exposed to water, alkaline and saline environments at ambient and elevated temperatures for extended periods of time. Changes in strength and thermophysical properties were evaluated through tensile testing. dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). Chemical degradation of the polymers was characterized using Fourier transform infrared (FTIR) spectroscopy. Energy dispersive X-ray (EDX) analysis of specimens following exposure was carried out to determine if ion diffusion into the bulk polymer occurred. Only minor changes in the glass transition temperatures of the polymers were observed after prolonged exposure at elevated temperature, but more substantial changes were noted in tensile strength, particularly in the case of the isophthalic polyester. Examination of the polymers following immersion in salt solution and alkaline solution showed essentially no ionic penetration into the bulk, with the exception of specimens that were visibly degraded. Spectroscopic analysis of chemical structure prior to and following exposure revealed varying degrees of ester hydrolysis.

INTRODUCTION

At the present time, deterioration of the world's infrastructure is motivating the use of advanced materials, such as fiber-reinforced polymer (FRP) composites, in civil engineering applications. Owing to their high specific strength, light weight. fatigue and corrosion resistance, these materials are candidates for use in primary structures as well as in rehabilitation and retrofitting of existing structures. FRP composites are also utilized in the reinforcement of concrete in the form of reinforcing bars and tendons.

Questions concerning the durability of polymer composites in the applications described above are a barrier to the acceptance of these materials in infrastructure and other civil applications. Expected lifetimes of 50 years to 75 years are common for many civil engineering structures such as bridges. At the present time, relatively few studies have been conducted on the long-term effect of moisture, saline and alkaline environments on polymers such as vinyl ester and polyester, which have been touted for use in infrastructure and other civil applications. It is necessary to understand the mechanisms that govern polymer degradation: not only to optimize material performance, but also to provide information that can be used in the design of accelerated aging tests.

Although it is one of the key constituents of a fiber-reinforced polymer composite, the polymer matrix is often considered to be the weak link in the FRP system. Polymer composites in outdoor applications are susceptible to photo-initiated oxidation (1) and are also known to be sensitive to hygrothermal (2), alkaline and saline environments (3).
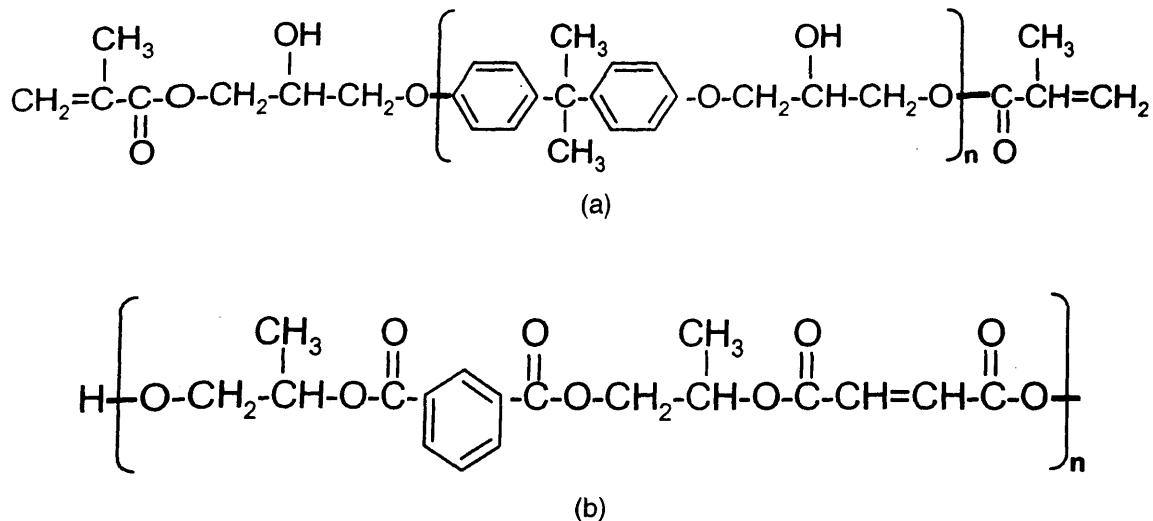
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Fig. 1. Representative chemical structures for (a) vinyl ester resin. and (b) isophthalicpolyester resin Crosslinking with styrene takes place via the unsaturated double bonds to form a crosslinked network.

The objective of this study was to systematically study chemical and physical changes in polymer matrix composites following exposure to moisture, alkaline and saline conditions at ambient and elevated temperatures. Measurement of physico-chemical properties can yield critical information on the mechanisms of degradation and can be used to model mechanical performance. Data obtained at elevated temperatures are important in determining the validity of accelerated aging tests in which temperature is used to accelerate degradation. One of the long-term goals of this research is to identify factors that contribute to matrix resin degradation, and to determine if the mechanisms of degradation are altered at elevated temperature.

EXPERIMENTAL

Specimen Preparation

Commercial vinyl ester and isophthalic polyester (isopolyester)prepolymer resins were selected for this study. Representative chemical structures of the un-crosslinked resins are depicted in *Fig. 1*. Vinyl ester specimens were prepared by hand-mixing the resin, a 3% mass fraction of a methyl ethyl ketone peroxide (MEKP) catalyst and a small amount (less than 0.5% mass fraction) of a silicone defoaming agent until thoroughly blended. A similar procedure was followed or the isopolyester specimens, except that only 2% mass fraction of the MEKP catalyst and no silicone defoamer were used. Because both the vinyl ester and sopolyester resins were already formulated with accelerator and promoter, only the addition of the catalyst was necessary to initiate crosslinking.

Free films were molded between two acrylic plates o minimize styrene evaporation as well as oxygen inhibition of the curing process. Poly(ethylene terephalate) sheets served as release films and also as

spacers for controlling film thickness. Films were allowed to gel at room temperature, followed by a 2 h/150°C postcure. Final film thickness ranged from 230 μm to 260 μm.

Dogbone-shaped tensile specimens were produced for mechanical testing. The procedure for making dogbones is similar to that described above for films, except that a 1.5 mm thick poly(tetrafluoroethylene) dogbone mold was used. Specimens were molded rather than machined or punched due to the tendency of the resin to crack. The gage section of the dogbone specimens was 4 mm wide and 27 mm long, as shown in *Fig. 2*, with thickness ranging from 1.3 mm to 1.5mm.

Exposure Environments

Free films with dimensions 50 mm × 50 mm and dogbone specimens were immersed in distilled water, salt solution (to simulate a seawater environment) and an artificial concrete pore solution (to simulate the alkaline environment of a cementitious material) for 1300 hours at ambient temperature (nominally 22°C), 60°C and 90°C. Specimens were contained in sealed Pyrex jars; jars containing the 60°C and 90°C specimens were placed in circulating air ovens set at the appropriate temperature.

The salt solution was composed of 0.58 mol/L NaCl in distilled water. Concrete pore solution was formulated according to the composition described by Christensen et al. (4) and consists of 0.32mol/L KOH, 0.17 mol/L NaOH and 0.07 mol/L $Ca(OH)_2$ in distilled water. The pH of this solution was approximately 13.5. After immersion, samples were dried for one week under vacuum at 35°C prior to thermal, spectroscopic and tensile measurements, so plasticization by moisture would not contribute to observed changes in properties.
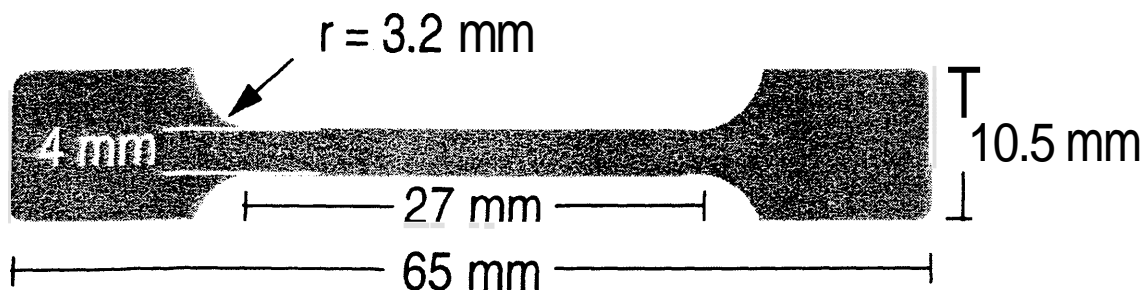
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Fig. 2. Schematic of **dogbone specimen** used for mechanical **testing.**

Uptake Experiments

Vinyl ester and isopolyester films having lateral dimensions of 25 mm X 25 mm were immersed in distilled water, salt solution and concrete pore solution, which were contained in glass jars at temperature, **with** each jar containing one specimen. For uptake experiments at ambient temperature. films were periodically removed from solution, rinsed with distilled water (in the case of salt solution and concrete pore solutions), blotted dry and weighed on a Mettler AT automatic balance.* Water and solution sorption was calculated as the change in mass **with** respect to the initial dry mass of the film. Six films of each polymer were tested in each solution.

For sorption studies at 60°C, the procedure was similar to the one described above **with** the exception that the sealed jars were placed in a **sand bath** maintained at *60°C* ± **2°C.** Mass uptake was determined as previously described. Sorption experiments were not carried out at 90°C, because of the difficulty of maintaining the temperature of the solutions in the jars.

Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA): *12* mm X *35* mm films were tested in tensile mode in a Rheometrics Solids Analyzer (RSA) II at a frequency of 10 Hz and a dynamic **strain** of 0.05%. Analysis was carried out from 30°C to 180°C, with data being recorded in *2°C* increments. During the test, specimens were pre-strained to maintain a constant state of tension throughout the experiment and to prevent film buckling. Three samples were analyzed for each polymer and exposure condition. The glass transition temperature **was** taken as the peak of the loss modulus (E)curve, in accordance with ASTM **D4092.**

Differential Scanning Calorimetry (DSC):twelve-milligram to 15-milligram specimens were sealed in aluminum pans and analyzed in a TA Instruments DSC **2910** differential *scanning* calorimeter equipped **with** a

refrigerated cooling system. Analysis **was** conducted in modulated DSC mode, with a modulation frequency of ± 1.0°C every 60 s. Specimens were heated from **25°C** to 180°C at a rate of 5.0°C/min. Three samples were analyzed for each polymer and exposure condition.

Thermogravimetric Analysis **(TGA)** Thermogravimetric **analysis** was carried out on a **TA** Instruments 2950 thermogravimetric analyzer at a heating rate of 5.0°C/min in a nitrogen atmosphere. Mass loss was characterized in the range from **25°C** to 400°C. Typical sample size was 10 mg and three replicates were analyzed for each polymer and exposure condition.

Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) analysis was performed in transmission mode on a Nicolet Magna-IR *560* infrared spectrometer. Specimens that had been dried under vacuum (as described in the section on **Exposure Environments)** were pulverized, mixed **with** dry, spectroscopic grade potassium bromide **and** pressed into pellets. Spectra were collected in a *dry air* atmosphere and ratioed to a blank background. One hundred scans were collected and averaged at a resolution of 4 cm^{-1}. Changes in peak heights were quantified by ratioing peaks of interest to the aromatic C–H stretching peak at 3027 cm^{-1}, which corresponds to the benzene rings in the resin structures and is assumed not to be altered by exposure to the aqueous solutions.

Tensile Testing

A custom-designed testing device used for determining tensile strengths of the dogbone specimens consisted of a screw-driven linear actuator equipped **with** a **227 kg** (500 lb) load cell and linear voltage displacement transducer (LVDT). Dogbone-shaped specimens were secured in machined aluminum grips that conformed to the shape of the dogbone end tabs and were loaded at the rate of 1 mm/s. Four to six replicates were tested for each polymer and exposure condition. Tensile strengths were normalized to the ultimate tensile strengths of the control specimens.

Energy Dispersive X-ray (EDX) Analysis

To determine if sodium, potassium, calcium or chlorine ions from the salt and pore solutions diffused

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into the interior of the resin specimens, 25 mm diameter rods of vinyl ester and isopolyester were immersed in salt solution and pore solution at ambient temperature and 60°C for 60 days. The rods were then scribed and fractured, yielding a fresh fracture surface for EDX analysis. Spots at the outermost edge of the sample as well in the interior were analyzed with an ISI SX-40 scanning electron microscope equipped with a Noran 5402 EDX detector. Analyzed areas were scanned for sodium, potassium, calcium and chlorine.

RESULTS AND DISCUSSION

Sorption Experiments

As shown in *Fig. 3*, mass uptake plots for vinyl ester and isopolyester at *22°C* in water, salt solution and concrete pore solution show an initial linear region followed by a region concave to the abscissa. Chin *et al.* have previously presented plots of M_t/M_∞ versus $t^{1/2}/\ell$ for these materials which are linear up to or beyond $M_t/M_\infty = 0.6$ (where M_t = mass uptake at time t, M_∞ = equilibrium mass uptake, and ℓ = specimen thickness), thus allowing the sorption to be characterized as Fickian (5).

Figure 4 presents mass uptake as a function of time for vinyl ester and isopolyester in water, salt solution and concrete pore solution at *60°C.* The rate of approach to equilibrium is clearly more rapid at *60°C* relative to that at 22°C, which is an expected result. In addition to the increased rate of uptake, the equilibrium mass uptake for vinyl ester at 60°C, shown in *Table 1*, also appears to be slightly higher than that observed at 22°C, even when the standard deviation
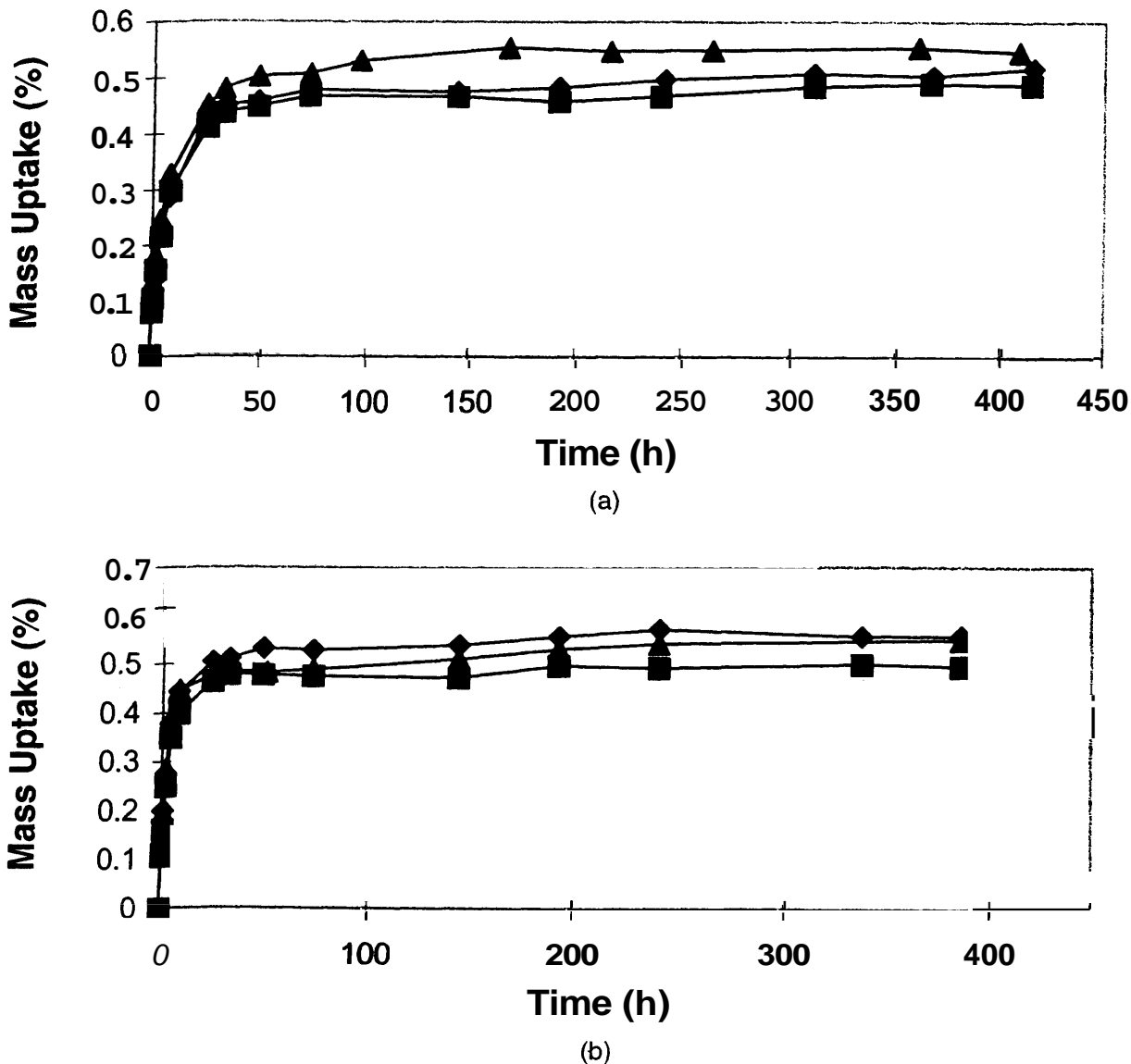

(a)

(b)

Fig. 3. *Mass uptake curves for (a) vinyl ester and (b) isopolyester in water* ● *. salt solution* ▲ *and concrete pore* solution■ *at 22°C (estimated standard deviation is 0.05* mass %).
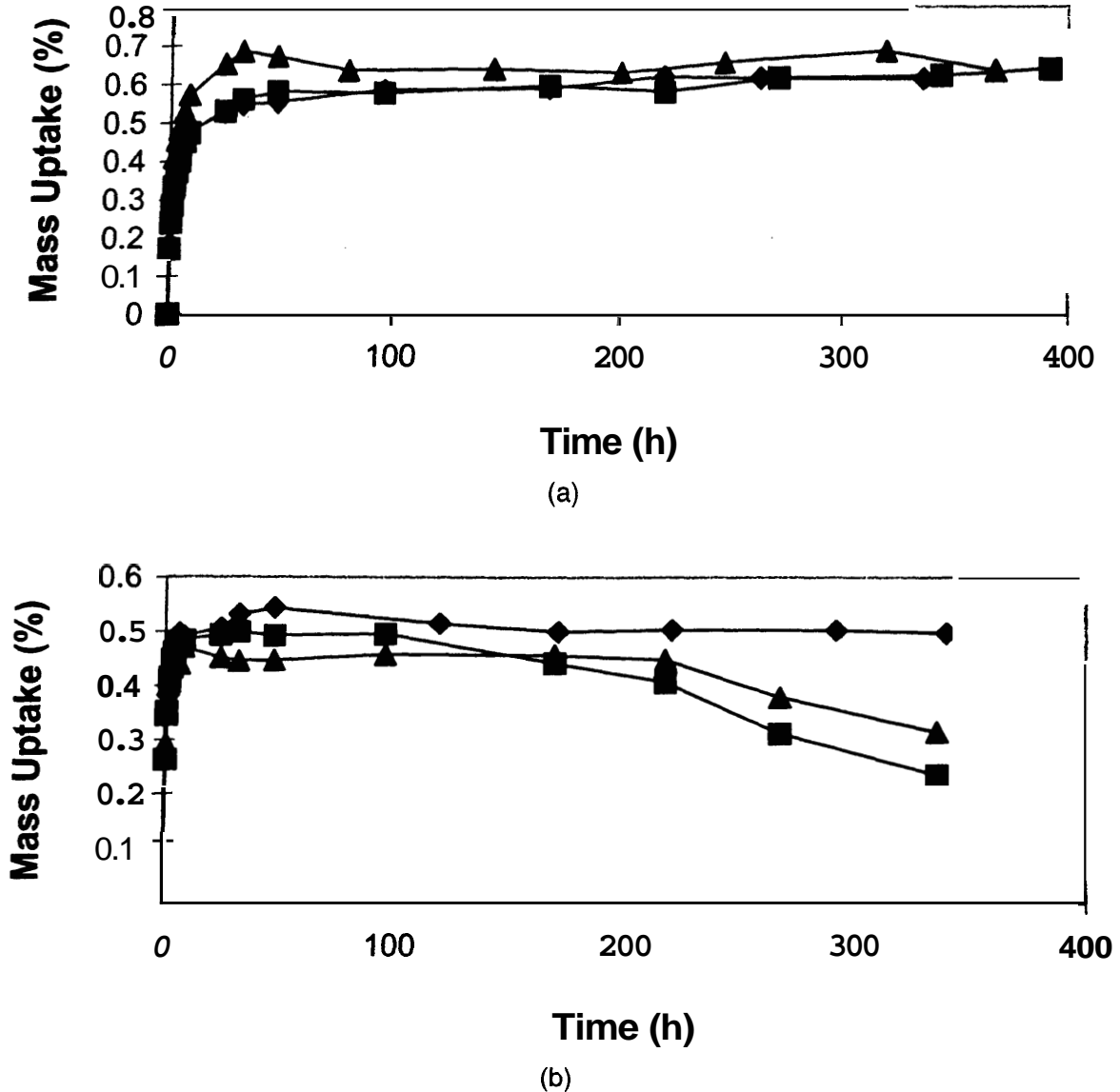
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Fig. 4. Mass *uptake curves* for *(a) vinyl ester and (b) isopolyester in water* ◆, *salt solution* ▲ *and concrete pore solution* ■ *at 60°C (estimated standard deviation is 0.08 mass %).*

of the data is taken into account. This phenomenon could be due to the fact that sorption at room temperature may not have reached equilibrium in the same time frame as sorption at *60°C. Also,* evidence exists to suggest that actual moisture equilibrium in some polymers such as epoxy may take years to achieve (6). Other studies have reported that hygrothermal aging of polymers at elevated temperature may create damage in the form of crazing, microcracking and other types of morphological changes, thus allowing additional sorption to occur *(7)* This observation of higher equilibrium uptake at elevated temperature would need to be accounted for in any aging test in which temperature is utilized to accelerate degradation; that is, not **only** is the rate of diffusion accelerated, but the equilibrium uptake may also be increased.

In the case of the isopolyester water uptake at 60°C, mass loss occurs after 100 hours in pore solution and after approximately 215 hours in salt solution. This mass loss is attributed to the hydrolysis and subsequent dissolution of the isopolyester resin. Morii *et al.* also observed mass loss in certain **types of** glass-reinforced polyester panels that were immersed in *60°C* and *80°C* distilled water (8).It **has also** been shown by Abeysinghe *et al.* that a number of polyesters immersed in *65°C* water exhibited significant mass loss, along with the development of disc-shaped surface cracks (9).It was **also** observed that the most severe degradation occurred following exposure to basic solution. This was attributed to resonance stabilization of the carboxylate ion, which tends to minimize the possibility of the reverse reaction to re-form the ester.

Table 1. Equilibrium Mass Uptake for Epoxy, Vinyl Ester and Isopolyester Films (uncertainties are equivalent to one standard deviation).

Matrix	Sorbent	Equilibrium Mass Uptake (mass %)	
		22°C	60°C
Vinyl Ester	Distilled Water	0.52 ± 0.01	0.62 ± 0.05
	Salt Solution	0.55 ± 0.01	0.69 ± 0.04
	Pore Solution	0.49 ± 0.04	0.64 ± 0.03
Isopolyester	Distilled Water	0.56 ± 0.02	0.5 ± 0.08
	Salt Solution	0.55 ± 0.03	0.45 ± 0.10*
	Pore Solution	0.50 ± 0.04	0.49 ± 0.05″

'Maximum mass uptake prior to mass loss.

Figure 5 shows an infrared spectrum taken of the residue found in the pore solution where an isopolyester specimen had been immersed for **30** days at **60°C**. The pore solution was filtered and evaporated onto a zinc selenide crystal and the resulting residue analyzed via attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The peaks shown in the spectrum are clearly indicative of organic material, as the peaks at 3334 cm⁻¹, 1557 cm⁻¹/1420 cm⁻¹ (doublet) **and** 1019 cm⁻¹ can be attributed to hydrogen bonded O-H stretching, carboxylate stretching (COO-) and O-H bending, respectively. Two small shoulders on the peak centered at **3334** cm⁻¹ fall in the **2900** cm⁻¹ region and provide evidence for C-H stretching.

A similar experiment carried out on vinyl ester showed little or no evidence of organic residue in the pore solution. In general, Vinyl ester has been found to be less susceptible to hydrolysis than polyester, due to the fact that ester functional groups in vinyl esters are terminal and shielded by methyl groups, whereas in isopolyester they are distributed along the main chain, making them more accessible **for** reaction. In a study of vinyl ester model compounds, Ganem *et al.* found that vinyl ester resins are at least one order of magnitude more hydrolytically stable than unsaturated polyesters (10).

Thermal Analysis

Figures 6 and 7 show the glass transition temperatures (T_g) obtained by **DMTA** of the dried **vinyl** ester and isopolyester films as a function of immersion time. The standard deviation **of** the data was estimated from a set of **10** replicates to be approximately 2°C.

For vinyl ester, increases in the T_g occurred following exposure to water, salt solution and pore solution at **60°C** and **90°C**. In all solutions and temperatures, the T_g was observed to increase by up to **4°C**. Increases in T_g of up to **6°C** were also observed for isopolyester following exposure to water, salt solution and pore solution at **60°C** and **90°C**. This observed increase is consistent with hydrolytic degradation and subsequent dissolution: loss of hydrolyzed low
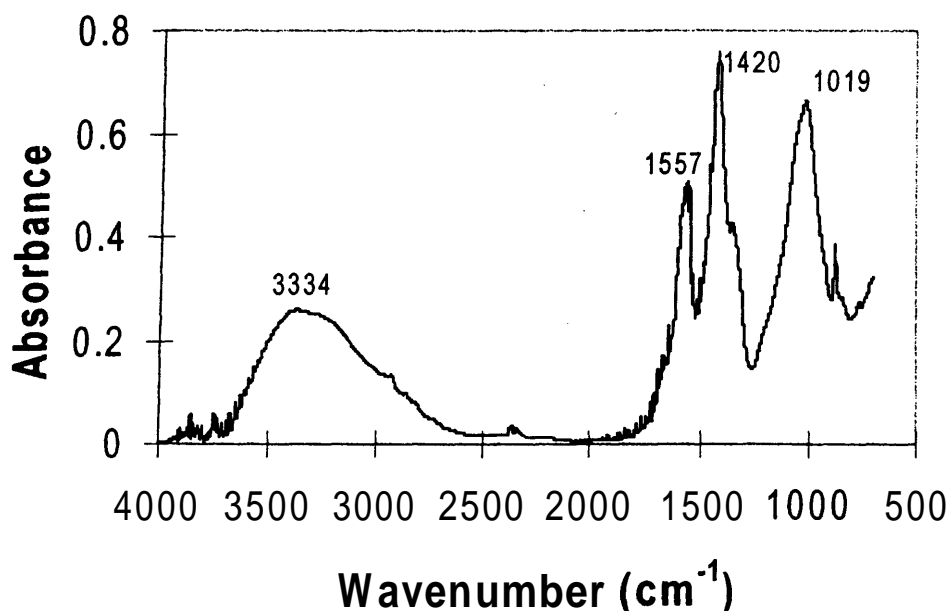

Fig. 5. *FTIR spectrum of concrete pore solution following immersion of iso-polyester at 60°C.*
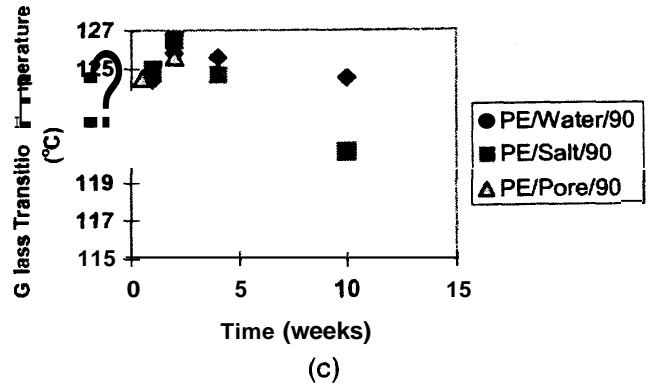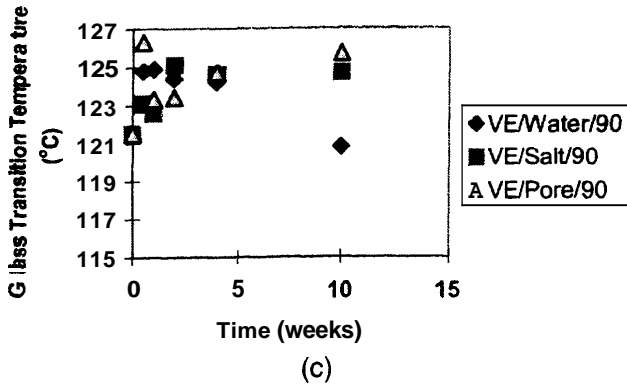
(a)

(b)

(c)

(c)

Fig. 6. Vinyl *ester* **glass** **transition** **temperatures** **determined** by *DMTA following* *exposure* *to water, salt solution and concrete pore solution at (a) ambient temperature. (b)60°C. and (c)* *90°C (estimated standard deviation is 2°C).*
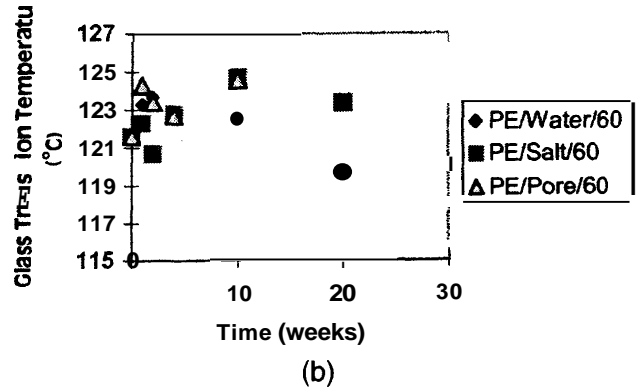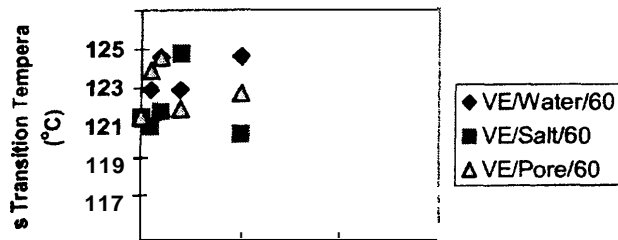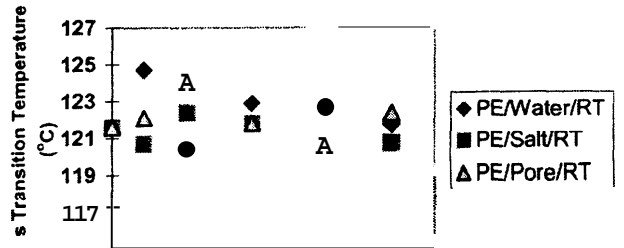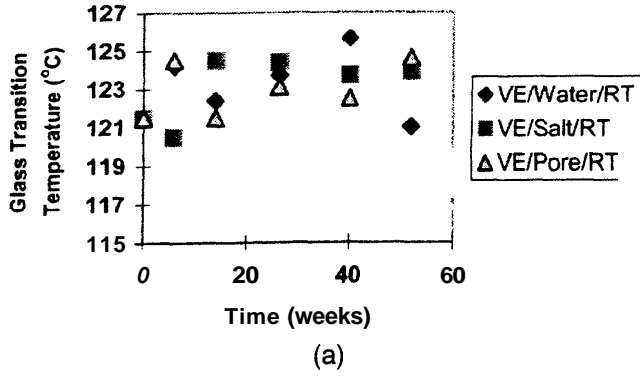
Fig. 7. Isopolyester glass *transition temperatures determined* by *DMTA following* *exposure* *to* **water,** *salt solution and concrete pore solution at* (4 ambient *temperature, (b) 60°C. and (c)* *90°C (estimated standard deviation is 2°C).*

molecular segments is postulated to lead to embrittlement and hence an increase in T_g (**11**). Elevated temperature pore solution was observed to be extremely corrosive to isopolyester; specimens aged in **90°C** pore solution for 10 weeks were too severely degraded for DMTA analysis.

Comparison **of** TGA decomposition profiles is a well-known method **of** assessing the relative thermo-oxidative stability of polymeric materials (12).In particular. mass changes at temperatures between 150°C and

300°C can be correlated to changes in molecular structure and is believed to reflect the extent of matrix-depolymerization which may have occurred (13). Above 300°C, mass loss is rapid and severe for almost all organic materials, and is no longer sensitive to previous environmental history.
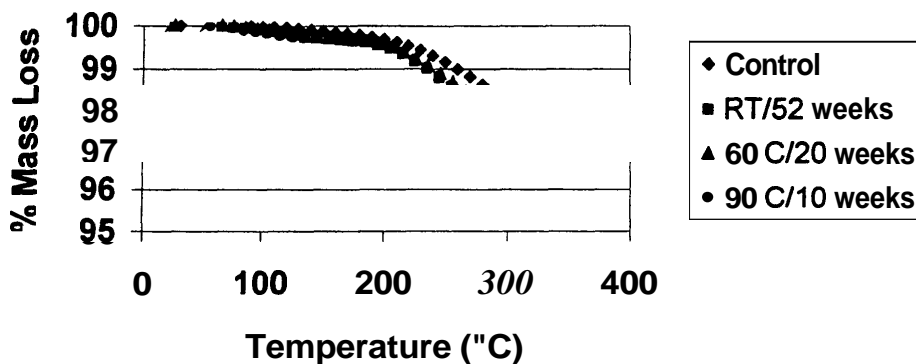
Figure 8 shows **a** representative vinyl ester mass loss profile as a function of temperature as obtained by TGA. Average total mass loss up to 300°C for three specimens **is** charted in *Fig. 10a* (**standard** deviation
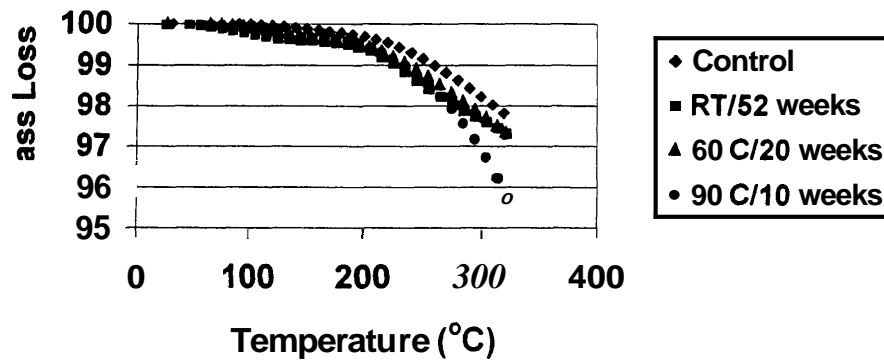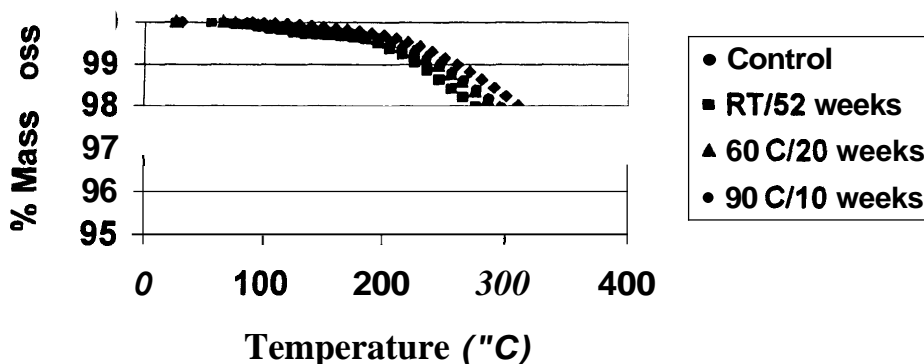
Fig. 8. Representative TGA curves for vinyl ester controls and specimens immersed in (a) water, (b) salt solution and (c) concrete pore solution.

for total mass loss up to **300**°C ranges from **0.2%** to 0.5% mass fraction). Relative to the control, all exposed specimens show slightly greater mass loss beginning at temperatures just above **100**°C and continuing throughout the remainder of the analysis. Specimens exposed to **90**°C water are observed to undergo an increase in the mass loss rate beginning at approximately **270°C.** This increased mass loss rate for specimens exposed to **90**°C water can also be correlated to changes observed in the infrared spectrum of this particular specimen, to be discussed later in this paper.

Representative **TGA** curves for isopolyester are shown in *Fig.* 9, and the average total mass loss for

isopolyester up to **300**°C is presented in *Fig. 10b.* The mass loss curves show that **all** exposed specimens exhibit slightly higher mass loss relative to the control, beginning at approximately **250°C.** In the case **of 60**°C and **90**°C concrete pore solution exposures, **mass** loss is substantial relative to the control and begins at lower temperatures. These observations are consistent with degradation of the polymer network structure.

Tensile Testing

Normalized tensile strengths (reported as percent-*age* of tensile strength retained relative to the control) of vinyl ester and isopolyester specimens **as** a function of exposure time are shown in *Figs.* 11 and *12.* The

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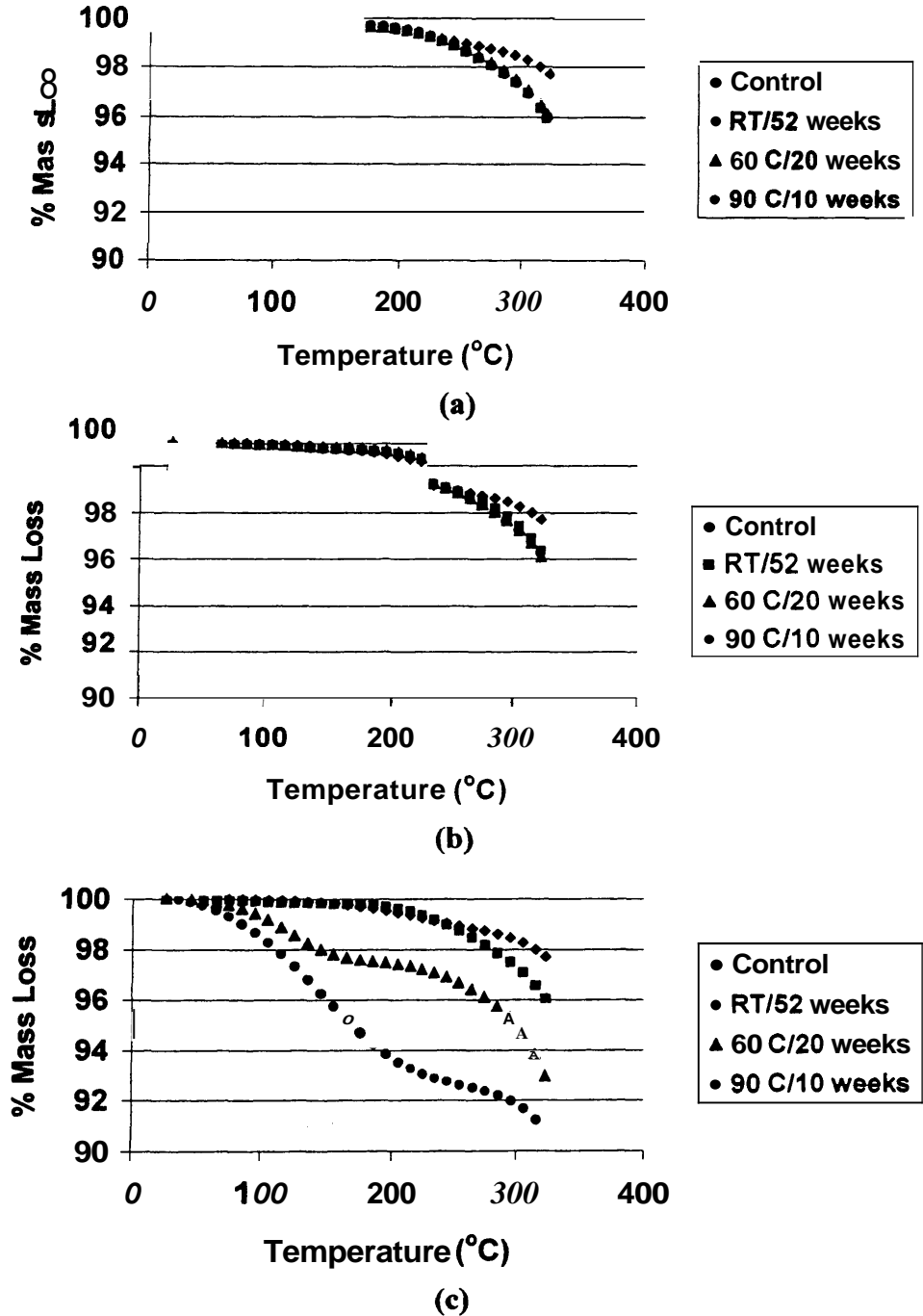

Fig. 9. Representative TGA curves for isopolyester controls and specimens immersed in (a) water. (b) salt solution, and (c) concrete pore solution.

tensile strength of the vinyl ester control was measured to be 68 MPa, which is comparable to values of 76 MPa to 83 MPa provided by the manufacturer. The isopolyester control had a tensile strength of 55 MPa, which also compares well to the value of 59 MPa reported in the product literature. Standard deviation of the unnormalized data is approximately 23%.

An overall decrease in tensile strength with exposure time was observed for all environments and temperatures. Specimens exposed to elevated temperature pore solution exhibited the most severe tensile

strength loss. In the case of isopolyester in 90°C pore solution, specimens were so severely degraded after 10 weeks that they were no longer intact. Degradation in strengths of isopolyester and vinyl ester composites exposed to alkaline environments was also documented by Altizer *et al.* (14) and Sonawala and Spontak (3).

To determine the validity of accelerated *aging* using elevated temperature, a simple Arrhenius analysis was conducted. The Arrhenius relationship expresses the rate constant k of a chemical process as a function of temperature via:
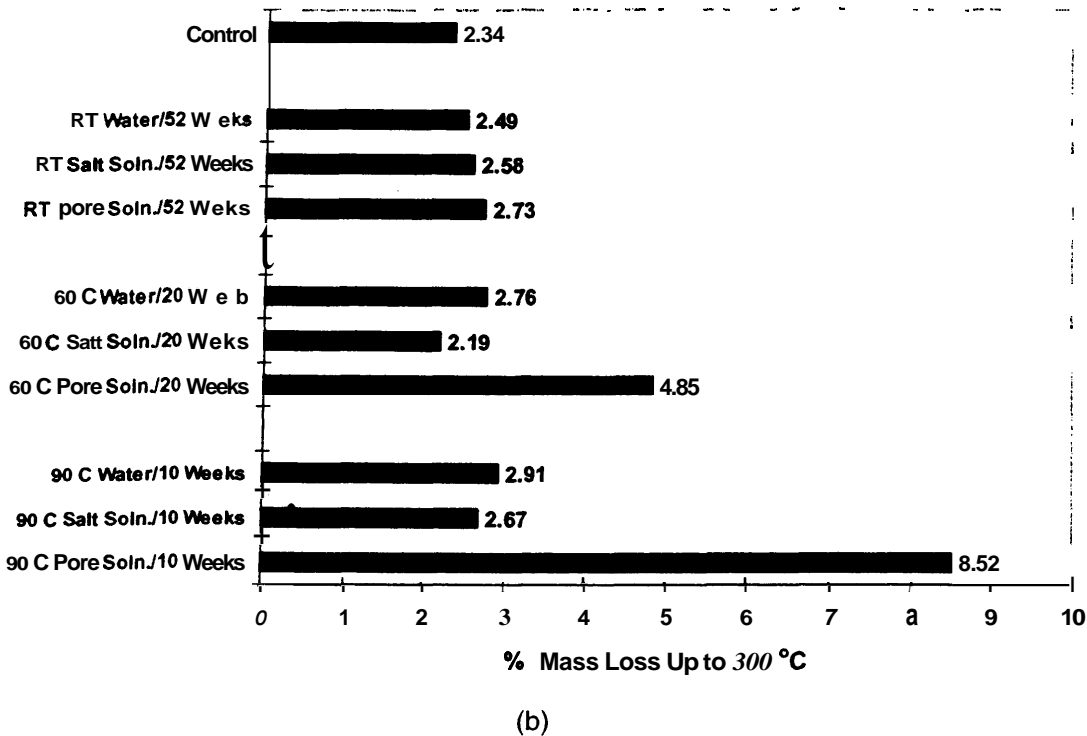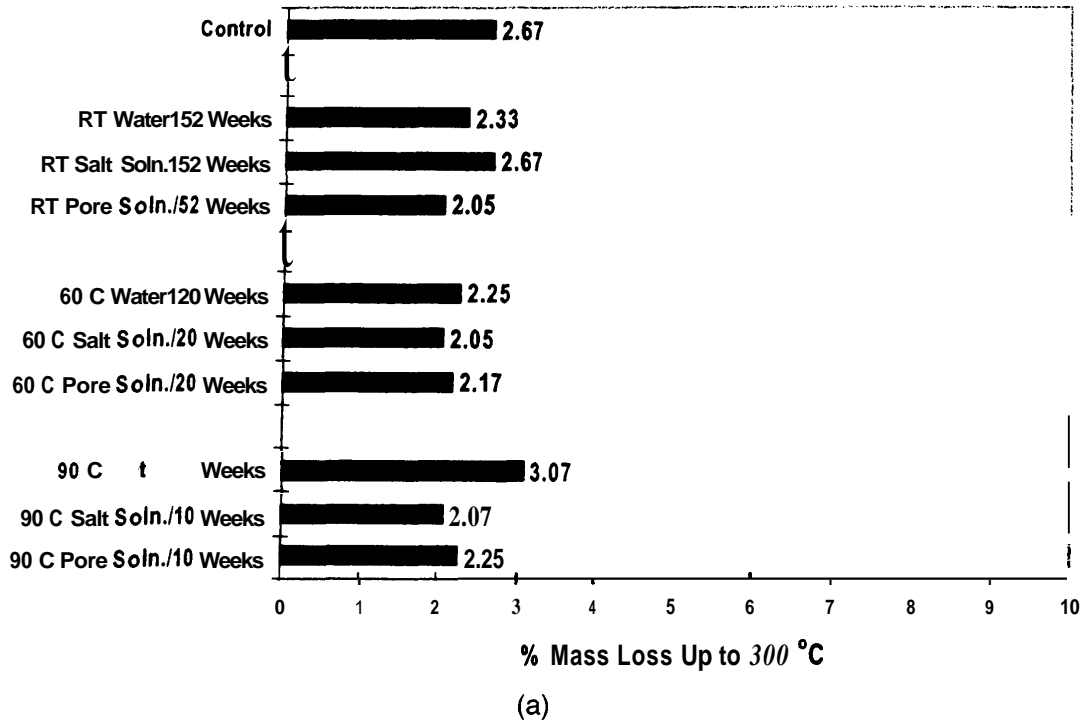
(a)

(b)

Fig. 10. Percent mass loss measured by thermogravimetric analysis between ambient temperature and 300°C for (a) vinyl ester. and (b)isopolyester (estimated standard deviation is 0.5 mass %).

$$k = A \exp[-E_a/RT] \qquad (1)$$

where A is the pre-exponential factor, E, is the activation energy for the process. R is the universal gas constant and T is the Kelvin temperature. k has units of s^{-1} and can be approximated as 1/time (15), thus

allowing the time needed for a material property to fall to a given value to be taken as a measure of the degradation rate. If the degradation process follows first order kinetics, a given material property can be measured as a function of time at a series of temperatures and a plot of the logarithm of the time needed to
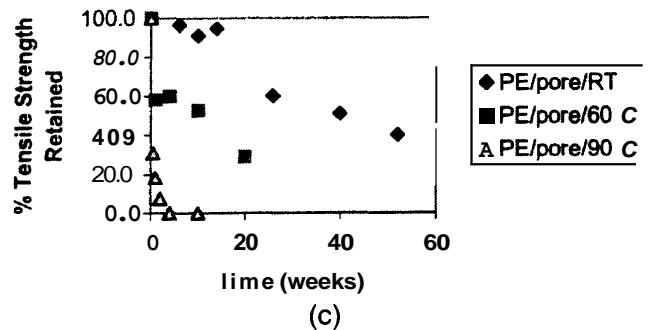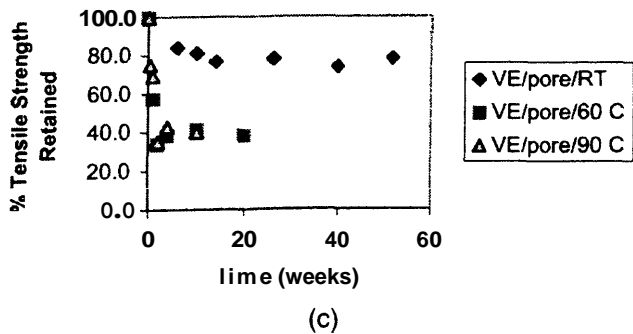
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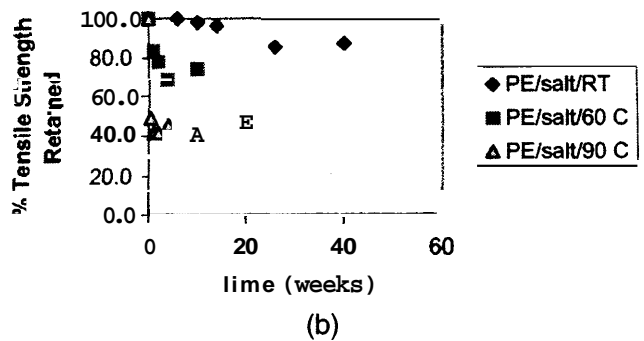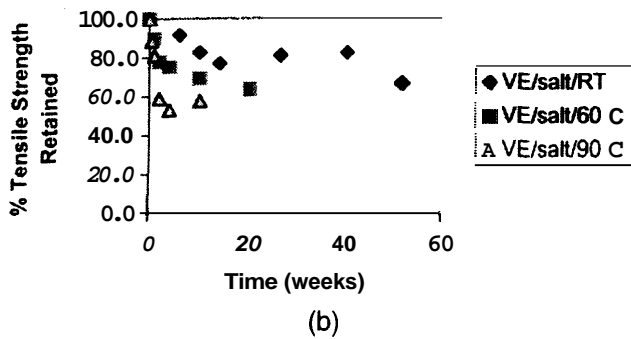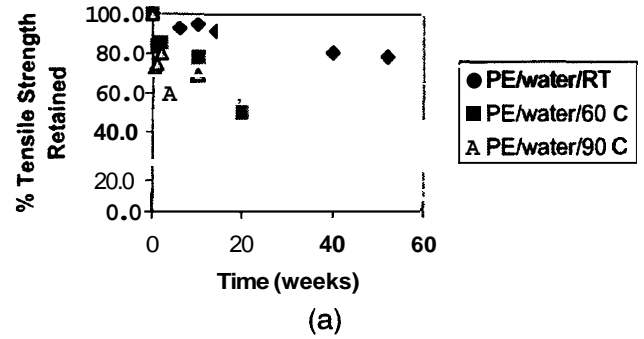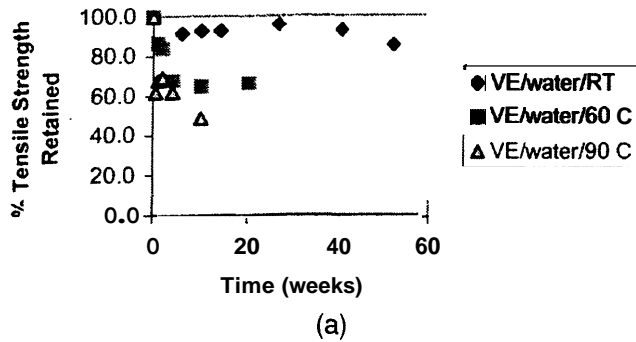
Fig. 11. Percentage of vinyl ester tensile strength retained following exposure to (a) water. (b) salt solution and (c) concrete pore solution at ambient temperature. 60°C and 90°C.

Fig. 12. Percentage of isopolyester tensile strength retained following exposure to (a) water. (b) salt solution, and (c) concrete pore solution at ambient temperature, 60°C and 90°C.

reach a particular value of the property (equivalent property time) vs. $1/T$ will yield a line with slope E_a.

Following the procedure used by Proctor *et al.* (16), *Fig. 13* shows Arrhenius plots generated by plotting the natural log of the time to reach 70% of the original tensile strength vs. $1/T$. Data obtained for vinyl ester and polyester in water and salt solution could be fitted with lines having correlation coefficients of at least 0.95. However, pore solution data for vinyl ester and polyester did not fall on a line, implying that accelerated aging methods utilizing temperature as the accelerating factor may be valid for water and salt solution environments, but not for the harsher pore solution environment in which severe degradation was often observed. It is also pointed out that the slopes of the lines are not equivalent, revealing that degradation of

tensile strength in the various environments have different activation energies and follow potentially different mechanisms. However, the degree of scatter in the tensile strength data makes it difficult to confirm this hypothesis. Additional study in this area is warranted.

Fourier Transform Infrared Spectroscopy

A number of changes were observed in the infrared spectra of vinyl ester specimens exposed to water, salt solution and pore solution, relative to the controls. *Table* 2 shows normalized FTIR peak intensities, which were computed by ratioing the height of the peak of interest to the height of the aromatic **C–H** stretch peak at 3027 cm^{-1} (assuming that this particular functional group is not affected by the exposure conditions in this study). For all exposure conditions
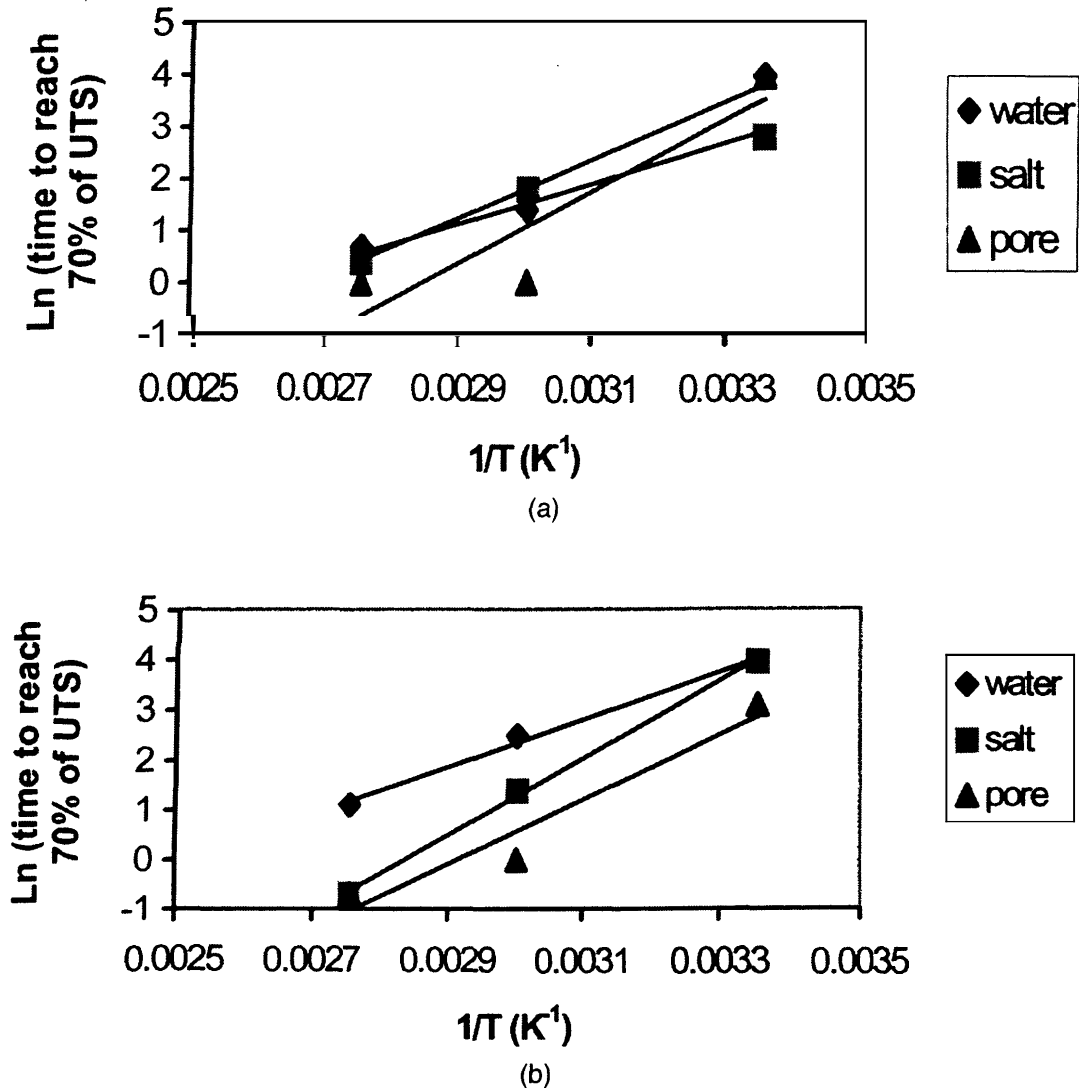
Fig. 13. Arrhenius plots of tensile strength degradation for (a)vinyl ester. and (b) isopolyester.

and temperatures, a small peak at **3740** cm⁻¹ was observed following exposure and is tentatively assigned to acid O–H stretch. All specimens, with the exception of those exposed to **90°C** water, showed an increase in the normalized intensity of the **0 – H** stretching peak at **3473** cm⁻¹, and decreases in the normalized intensities of peaks at **1245 cm⁻¹** (C–O stretching), and **1182** cm⁻¹ (C–O stretching). Only minor changes were observed in the normalized intensity of the $C = O$ peak at **1727 cm⁻¹**. These spectral changes are consistent with ester hydrolysis, in which ester functional groups are converted to hydroxyl and carboxylic acid byproducts. An increase in the concentration of hydroxyl and carboxylic acid groups would also contribute to the increase in intensity of the O–H stretching peak. However, the lack of significant spectral changes indicates that any hydrolysis that occurred is probably minor.

In contrast, significant spectral changes were observed in vinyl ester specimens following exposure to **90°C** water, shown in *Fig.* 14 compared to the vinyl ester control, ambient temperature, and **60°C** water specimens. The 0 – H stretching peak at **3473** cm⁻¹ in the control spectrum is greatly diminished after **10** weeks in **90°C** water, as are the intensities of the **C–H** bending peak at **1509** cm⁻¹, and the C–O stretching peak at **1182** cm⁻¹. In addition, there is a significant increase in the intensity of the carbonyl stretching peak at **1727 cm⁻¹, and** a shift in position of C – 0 stretching peaks originally at **1 182 cm⁻¹ and 1 108 cm⁻¹** to lower wavelengths. The reason for the changes is not known at this time.

A number of spectral changes were **also** observed for the isopolyester specimens. *Figure* 15 shows the spectrum of isopolyester following exposure **to** pore solution at ambient temperature, **60°C** and **90°C.** Significant

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Table 2. FTIR Peak Height Ratios for Vinyl Ester Following Exposure to Water, Salt Solution and Pore Solution, Referenced to Aromatic C–H Stretch at 3027 cm^{-1}.

|	3473 cm^{-1} O–H stretch	1727 cm^{-1} C=O stretch	1245 cm^{-1} C–O stretch	1182 cm^{-1} C–O stretch
Vinyl Ester Control	0.65	1.5	2.4	2.4
Water/RT/52 weeks	0.74	1.4	2.0	2.0
Water/60°C/20 weeks	0.73	1.5	2.1	1.9
Water/90°C/10 weeks	0.39	2.4	2.0	1.7
Salt solution/RT/52 weeks	0.76	1.4	2.0	2.0
Salt solution/60°C/20 weeks	0.77	1.1	1.9	1.9
Salt solution/90°C/10 weeks	0.84	1.5	1.9	1.8
Pore soln./RT/52 weeks	0.74	1.4	2.0	2.0
Pore soln./60°C/20 weeks	0.73	1.4	2.0	2.0
Pore soln./90°C/10 weeks	0.84	1.4	1.8	1.8
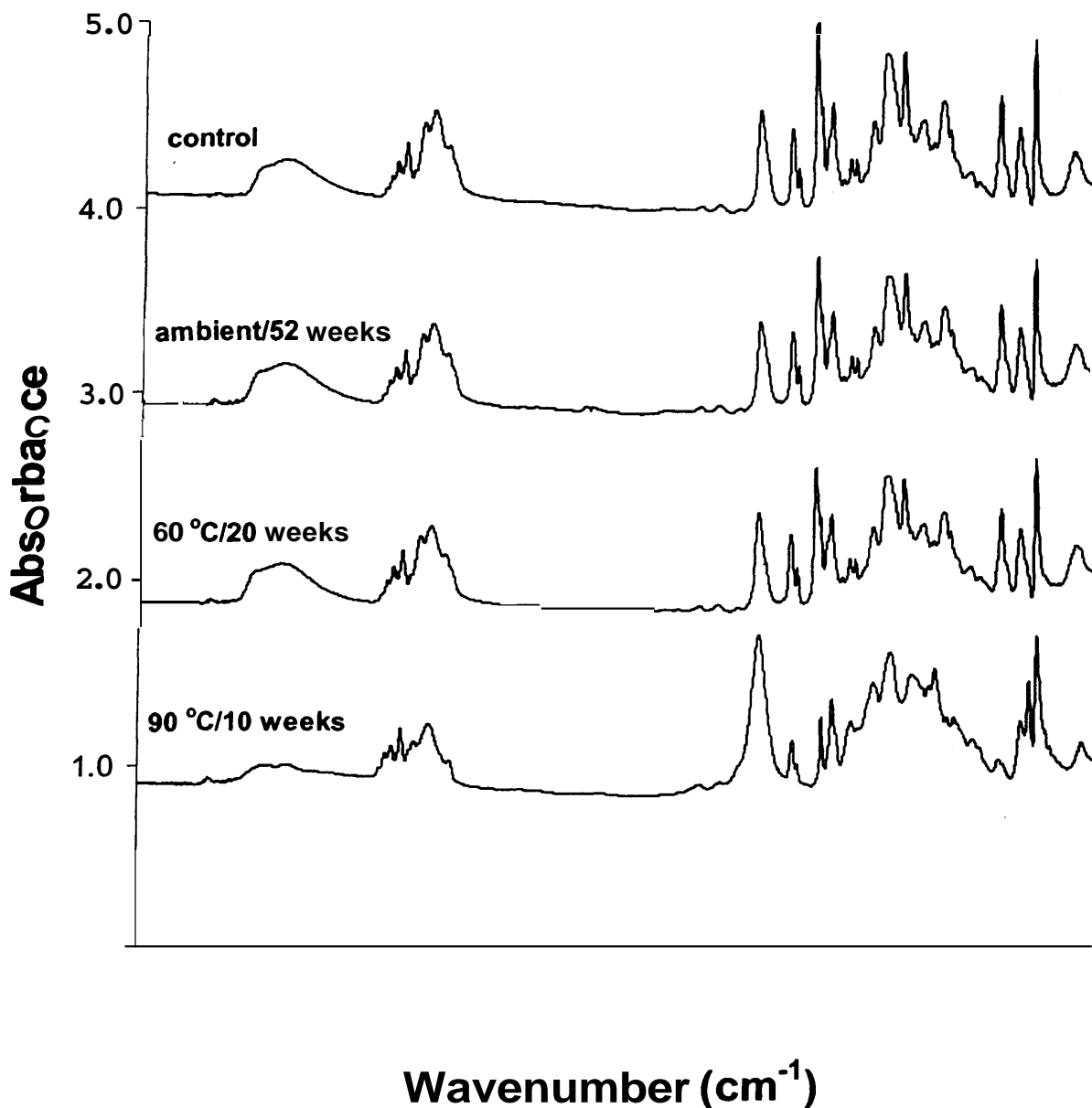
Fig. 14. Infrared spectrum of vinyl ester before and after exposure to water at ambient temperature. 60°C and 90°C.
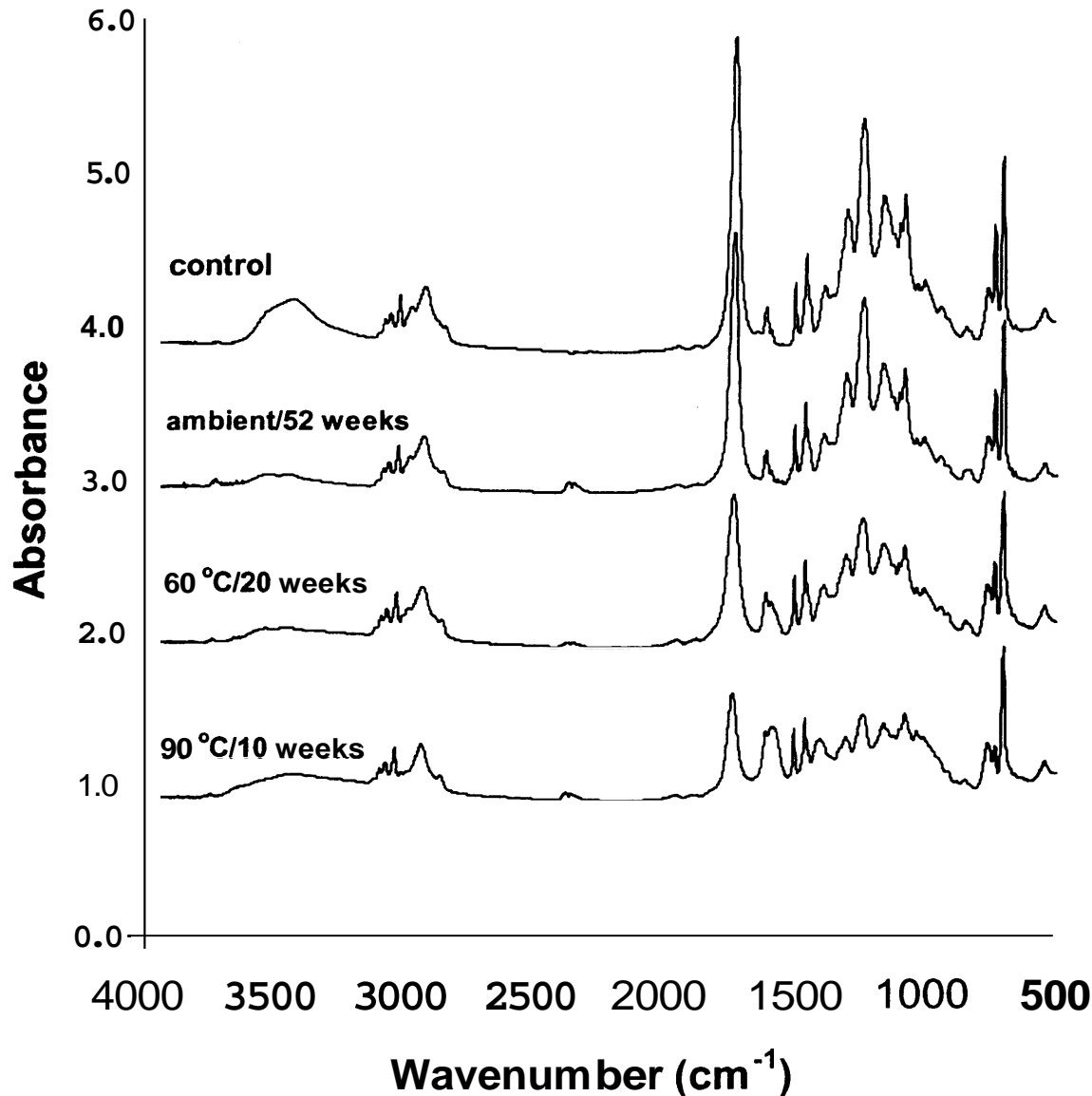
Fig. 15. Infrared spectrum of isopolester before and after exposure to concrete pore solution at ambient temperature, 60°C and 90°C.

changes are seen in the 60°C and the 90°C spectra, which correspond to the specimens that exhibited the greatest mass loss in the **TGA** analysis. Changes include a decrease in intensity and broadening of the O–H stretching peak at **3473** cm^{-1}, a decrease in the intensity of the ester carbonyl peak at 1728 cm^{-1} and the appearance of the carboxylate doublet in the 1584 cm^{-1} to 1600 cm^{-1} region. Normalized peak intensities for isopolyester are shown in *Table 3*. Decreases in the intensities of O–H stretching, ester *C=O* stretching and ester C–O stretching peaks are observed for all exposure conditions and become more prominent with increased exposure temperature.

As with the vinyl ester specimens exposed to **90°C** water, the decrease in ester functionality paired with the appearance of carboxylate ion are consistent with

ester hydrolysis, which yields carboxylic acid and hydroxyl by-products. In ionic solution, the carboxylic acid is then converted to the carboxylate salt. Nguyen and Byrd observed the formation of a carboxylate doublet for stearic acid in ionic solution **(17)**.Spectral changes similar to those observed above for isopolyester and vinyl ester were also observed by Ghorbel and Valentin for isopolyester and vinyl ester materials following exposure to *60°C* water **(18)**.

Energy Dispersive X-ray Analysis (EDX)

Appreciable amounts of sodium, potassium or calcium were found only in the interior of the isopolyester specimen exposed to 60°C pore solution for 60 days. No evidence for the ingress of ions was **found** for any of the other specimens, which showed concentrations

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Table 3. FTIR Peak Height Ratios for Isopolyester Following Exposure to Water, Salt Solution and Pore Solution, Referenced to Aromatic C–H Stretch at 3027 cm^{-1}.

	$3439\ cm^{-1}$ O–H stretch	$1728\ cm{-1}$ C=O stretch	$1298\ cm^{-1}$ C–O stretch	$1233\ cm^{-1}$ C–O stretch	$1156\ cm^{-1}$ C–O stretch
Polyester Control	.88	5.9	2.6	4.3	4.3
Water/RT/52 weeks	.23	3.0	1.8	2.5	1.9
Water/60°C/20 weeks	.23	3.5	2.0	2.9	2.2
Water/90°C/10 weeks	.18	3.1	1.8	2.5	2.0
Salt solution/RT/52 weeks	.19	4.2	2.2	3.3	2.3
Salt solution/60°C/20 weeks	.19	3.5	2.0	2.9	2.2
Salt solution/90°C/10 weeks	.31	3.1	1.8	2.5	1.9
Pore soln./RT/52 weeks	.25	5.6	2.5	4.1	2.7
Pore soln./60°C/20 weeks	.17	2.7	1.5	2.2	1.7
Pore soln./90°C/10 weeks	.24	1.9	1.0	1.3	1.2

of sodium. potassium and calcium comparable to those of the unexposed control specimens. The presence of sodium, potassium and calcium in the isopolyester specimen exposed to *60°C* pore solution may be attributed to the visible degradation of this particular specimen and the subsequent ingress of ions via surface microcracks. It was shown by Katsuki and Uomoto (19)using electron probe analysis that significant penetration of sodium ions into fiber-reinforced vinyl ester rods occurred after 120 days in 2 mol/L NaOH. In another study, using atomic absorption spectrometry, Soulier reported that no transport of sodium or chloride ions occurred into fiber-reinforced epoxy composites following immersion in salt solutions (20).It should be noted, however, the transport of ions into fiber-reinforced materials will be mechanistically different because of the availability of additional pathways for ingress.

SUMMARY

Unreinforced free films of vinyl ester and isophthalic polyester were characterized with DMTA, DSC, TGA, FTIR and tensile testing following exposure to water, alkaline and saline environments at ambient and elevated temperatures for extended times. Increases in the T_g following exposure were observed for both vinyl ester and polyester, which were attributed to hydrolysis and subsequent dissolution of low molecular segments. Decreases in the tensile strengths of exposed specimens were appreciable, particularly in the isophthalic polyester exposed to elevated temperature concrete pore solution. Arrhenius plots generated by plotting log (time to reach 70% of the original tensile strength) vs. 1/T were fitted with lines having correlation coefficients of at least 0.95 for water and salt solution. This implies that accelerated aging methods utilizing temperature as the accelerating factor are valid for water and salt solution environments, but not for pore solution exposures in which severe resin degradation was observed. Spectroscopic analysis of the resins following exposure revealed varying degrees

of ester hydrolysis. Examination of the polymers with EDX following immersion in salt solution and simulated concrete pore solution showed essentially no ionic penetration into the bulk, except when specimens were visibly degraded.

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