Elevated Temperature Aging of Glass Fiber Reinforced Vinyl Ester and Isophthalic Polyester Composites in Water, Salt Water and Concrete Pore Solution

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ABSTRACT

In recent years, the use of fiber-reinforced vinyl ester and isophthalic polyester (isopolyester) composites in civil infrastructure has greatly increased, due to an optimum combination of desirable properties, processability, and ease of installation associated with these materials. One obstacle hindering greater acceptance of polymer composites in civil infrastructure applications is the susceptibility of the polymer matrices to degradation initiated by moisture, temperature and corrosive chemical environments.

The objective of this study was to characterize chemical and physical changes in glass-fiber reinforced vinyl ester and isopolyester materials following exposure to water, salt water and an artificial concrete pore solution. Exposures were carried out at room temperature, 40 °C, 60 °C and 80 °C; glass transition temperature and interlaminar shear strength were monitored as a function of aging time and temperature. In general, more rapid degradation in properties was observed in concrete pore solution than either water or salt solution for both polymers. A modified Arrhenius analysis was carried out on the data to determine whether any observed acceleration in degradation was valid over such a wide temperature range. Arrhenius plots for isopolyester generated by plotting ln [time to reach 70 % of original strength] vs. [temperature]$^{-1}$ could be fitted with straight lines for water and salt solution, but not for concrete pore solution. Arrhenius analyses carried out on the vinyl ester data resulted in approximately straight line fits for all three environments.

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INTRODUCTION

Deterioration of the world's infrastructure is motivating the use of advanced materials, such as fiber-reinforced polymer (FRP) composites, in civil engineering applications. Due 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 bars are also utilized in as internal reinforcements for concrete.

Questions pertaining to the durability of polymer composites in the applications described present 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.

The primary objective of this study was to 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. Furthermore, 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 APPROACH

Materials

Pultruded glass fiber-reinforced vinyl ester and isophthalic polyester (isopolyester) composites were obtained from Strongwell, Inc.[*] The composites were constructed from unidirectional roving and chopped strand mat. Fiber mass fraction was approximately 0.46 for the isopolyester composites, and approximately 0.44 for the vinyl ester composites. Laminate thicknesses ranged from 3.0 mm to 3.3 mm.

Exposure Environments

[*] Note: Certain commercial equipment, instruments or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose.

12 mm x 52 mm specimens for dynamic mechanical thermal analysis (DMTA), 25 mm x 25 mm specimens for thermogravimetric analysis (TGA) and infrared spectroscopic analysis, and 7 mm x 23 mm specimens for interlaminar shear testing 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). Specimens and their respective exposure solutions were contained in non-reactive Qorpak glass jars fitted with rubber stoppers. Ambient temperature exposures were carried out between 22 °C to 24 °C; elevated temperature exposures were carried out by burying the jars in sand baths calibrated to 40 °C, 60 °C and 80 °C. The variation in the temperature of the solutions was measured to be less than 6 ^{o}C in a 10 h period.

The composition of the salt solution was 0.58 mol/L NaCl in distilled water. Concrete pore solution was formulated according to the composition described by Christensen et al. [1] and consists of 0.32 mol/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. Specimens were removed at 2208 h (92 d), 4416 h (184 d), 6576 h (274 d) and 10,248 h (427 d) of exposure and were dried for one week under vacuum at 35 °C prior to thermal, spectroscopic and interlaminar shear measurements.

Dynamic Mechanical Thermal Analysis (DMTA)

12 mm x 52 mm bars were cut from the laminates and tested in 3-point bending mode in a Rheometrics Solids Analyzer (RSA) II at a frequency of 10 Hz and a dynamic strain of 0.02%. Specimens were cut so that the unidirectional fibers were parallel to the 52 mm dimension. Analysis was carried out from 30 °C to 180 °C, with data recorded in 2.0 °C increments. Throughout the test, a small static force (1 N) was applied to the specimen to prevent loss of contact with the test fixture. Three replicates were analyzed for each exposure condition. The glass transition temperature was taken as the peak of the loss modulus (E") curve, in accordance with ASTM D4092 [2].

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 recorded from 25 °C to 400 °C. Typical sample size was 10 mg and three replicates were run for each 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 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}.

Interlaminar Shear Testing

Interlaminar shear testing was carried out on 7 mm x 23 mm bars according to the methodology described in ASTM D 2344[3]. Specimens were cut so that the fibers were parallel to the 23 mm dimension. Six replicates were tested in 3-point bending on an Instron 1125 testing machine at a crosshead speed of 1.3 mm/min. The distance between the support points on 3-point fixture was adjusted to yield a span-to-depth ratio of 5.

RESULTS AND DISCUSSION

Dynamic Mechanical Thermal Analysis (DMTA)

Figures 1 and 2 show the glass transition temperatures (T_g) obtained by DMTA of the dried vinyl ester and isopolyester composites as a function of immersion time and environment. The standard deviation of the data was estimated to be approximately 2 °C.

Figure 1 shows the increases in the T_g for the vinyl ester composite - as much as 18 ^oC in some cases - that occurred following exposure to water, salt solution and pore solution at 60 ^oC and 80 ^oC. This trend was even more pronounced in the isopolyester composites, where increases in T_g of over 60 °C were observed at higher temperatures, as seen as in Figure 2. In a number of the exposures, the T_g would initially increase, then decrease. The observed initial increase in T_g is consistent with hydrolytic degradation and subsequent dissolution of hydrolyzed segments. It is postulated that the loss of the hydrolyzed, low molecular weight segments, which served to flexibilize the resin matrix, leads to embrittlement and hence an increase in T_g [4]. As degradation proceeds further, it is postulated that chain scission then occurs in the main network chains, hence leading to a decrease in T_g. Similar trends in the T_g were documented for neat (unreinforced) vinyl ester and isopolyester materials exposed to water, salt water and simulated concrete pore solution [3].

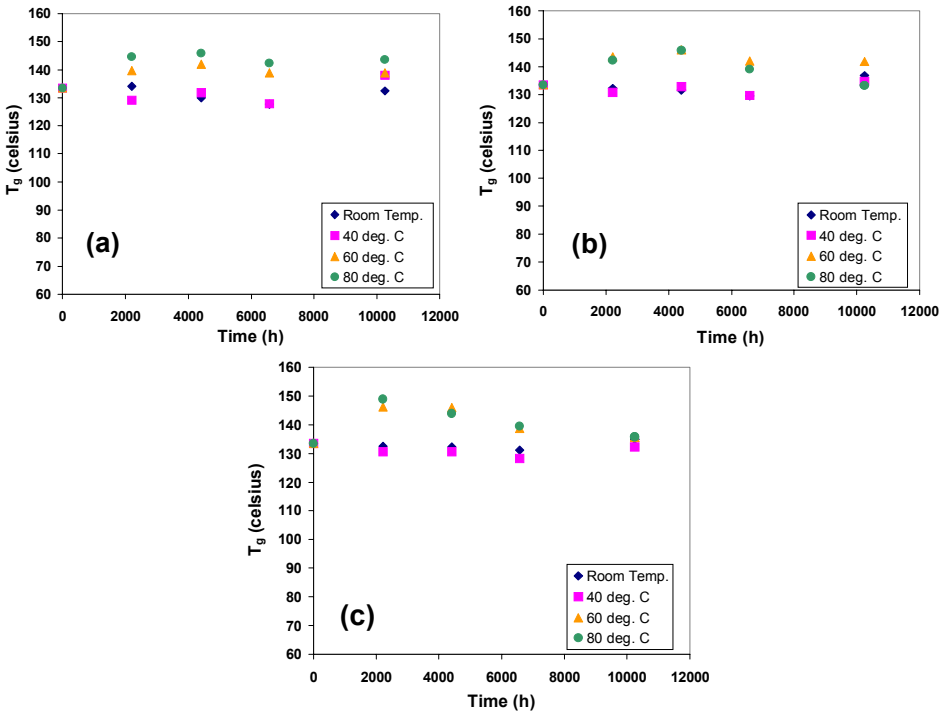

Figure 1: T_gs of vinyl ester specimens following exposure to (a) water, (b) salt solution, and (c) concrete pore solution. Standard deviation of the data is approximately 2 ^{o}C.

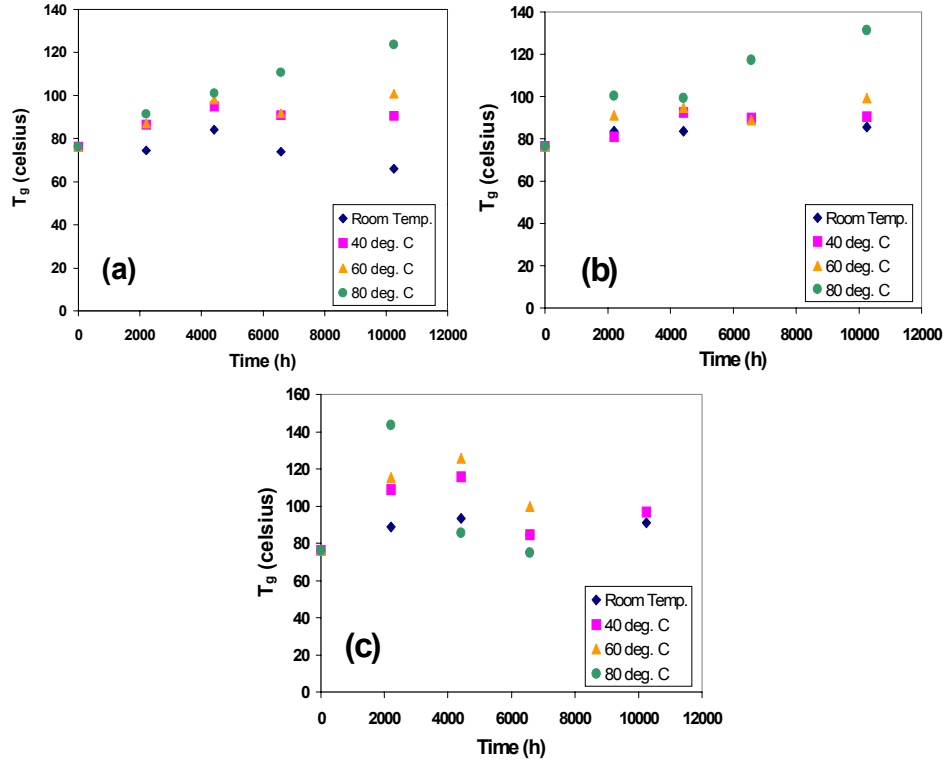

Figure 2: T_gs of isopolyester specimens following exposure to (a) water, (b) salt solution, and (c) concrete pore solution. Standard deviation of the data is approximately 2 ^{o}C.

Thermogravimetric Analysis (TGA)

Comparison of TGA decomposition profiles is useful in assessing the relative thermo-oxidative stability of polymeric materials [5]. 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 occur following exposure to severe conditions [6]. Above 300 °C, mass loss is rapid and severe for almost all organic materials, and is no longer sensitive to previous environmental history.

Average total mass loss (expressed in mass fractions) up to 300 °C for the vinyl ester composite following exposure in water, salt solution and concrete pore solution ranged from 0.018 to 0.025, compared to a mass loss of 0.025 for the unexposed controls. Similar data were recorded for the isopolyester composites with several exceptions: specimens exposed to salt solution at 80 °C and pore solution at 60 °C and 80 °C exhibited mass losses of 0.031, 0.034, and 0.032 respectively, relative to a mass loss observed in the unexposed control of 0.027. These observations are consistent with the changes in glass transition temperature.

Fourier Transform Infrared (FTIR) Spectroscopy

Some difficulty was encountered in interpreting the infrared spectra because the composite materials used in this study are commercial materials, and hence a number of components used in their manufacture are not known. However**,** a number of spectral changes were observed in the infrared spectra of specimens exposed to water, salt solution and pore solution, relative to the controls.

In the vinyl ester spectra, the ester carbonyl peak at 1730 cm^{-1} was observed to diminish with both time and temperature in all environments. An especially pronounced decrease in the 1730 cm^{-1} peak was noted for the specimens immersed in 80 ^{o}C pore solution. For specimens in salt solution and pore solution, increases in the height and width of the C-O stretching peaks at 1108 cm^{-1} and 1245 cm^{-1} were also observed.

Significant spectral changes were also observed in isopolyester specimens. Decreases in the height of the ester carbonyl peak at 1730 cm^{-1} were observed, with a substantial decrease observed for specimens immersed in 80 ^{o}C pore solution. These specimens also exhibited decreases in height of the C-O stretching peak at 1240 cm^{-1}.

These spectral changes observed in both the vinyl ester and isopolyester are consistent with ester hydrolysis, in which ester carbonyl functionality is converted to carboxylic acid and hydroxyl functional groups, which would account for the decrease in the carbonyl peak and subsequent increases in the C-O stretching peaks. Spectral changes similar to those observed above were also observed by Ghorbel and Valentin for isopolyester and vinyl ester materials following exposure to 60 °C water [7].

Interlaminar Shear Testing

Changes in normalized interlaminar shear strengths (ILSS) of vinyl ester and isopolyester specimens, reported as percentage of strength retained relative to the control, are shown in Figures 3 and 4. The coefficient of variation of the data is approximately 0.17. As shown in Figure 3, significant degradation (20% or greater loss in ILSS) in vinyl ester interlaminar shear strength was observed in water and salt water at 60 °C and above, whereas interlaminar shear strength degradation was observed in pore solution at all temperatures. A decrease in interlaminar shear strength with exposure time was observed for the isopolyester composites in all environments and at all temperatures, as seen in Figure 4. Isopolyester specimens exposed to elevated temperature pore solution exhibited the most rapid and severe strength loss.

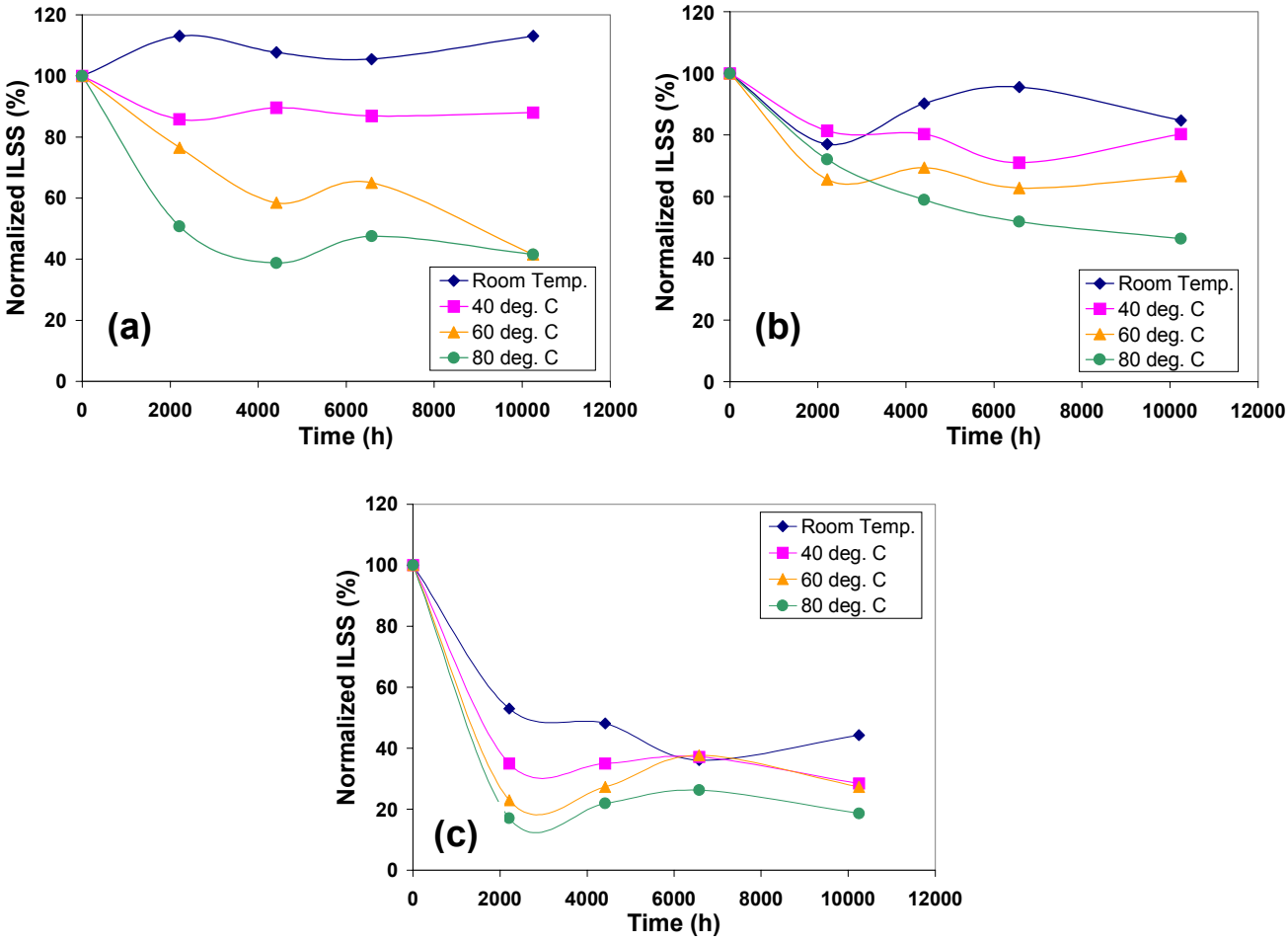

Figure 3: Interlaminar shear strengths of vinyl ester specimens following exposure to (a) water, (b) salt solution, and (c) concrete pore solution. Coefficient of variation of the data is approximately 0.17.

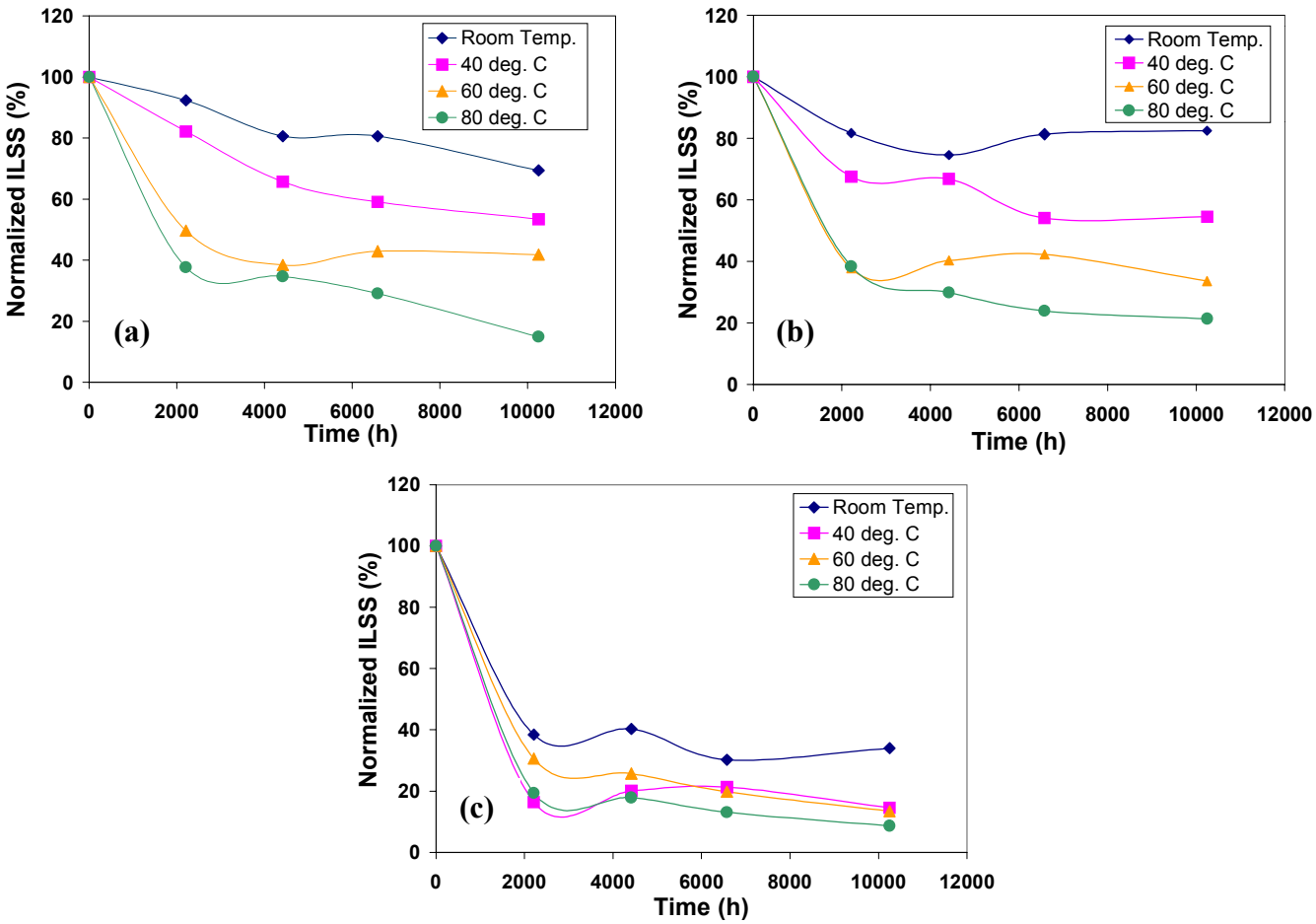

Figure 4: Interlaminar shear strengths of isopolyester specimens following exposure to (a) water, (b) salt solution, and (c) concrete pore solution. Coefficient of variation of the data is approximately 0.17.

Decreases in strength can be attributed to hydrolysis of the matrix, disruption of the matrix/fiber interface, and/or degradation of the fibers themselves by the various environments [8]. In terms of chemical degradation, isopolyester is more susceptible to hydrolysis than vinyl ester, because ester groups in vinyl ester are terminal and shielded by methyl groups, whereas in isopolyester they are distributed along the main chain, and hence more accessible for reaction [9]. Degradation in strengths of isopolyester and vinyl ester composites exposed to alkaline environments was also documented by Altizer et al.[10] and Sonawala and Spontak [11].

Arrhenius Analysis

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

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

where A is the pre-exponential factor, E_a 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 [12], 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 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. [13], Figure 5 shows Arrhenius plots generated by plotting the natural log of the time to reach a normalized interlaminar shear strength of 0.7 vs. 1/T. Straight lines were fitted to the data, assuming that the mechanism(s) responsible for interlaminar shear strength degradation has a constant activation energy. The correlation coefficient **r** for the fitted lines for each of the composites and exposure conditions is reported in Table I.

Reasonably good straight line fits were obtained for each exposure environment. Data obtained for vinyl ester in water, salt solution and concrete pore solution could be fitted with lines having correlation coefficients of at least 0.95. Similarly for isopolyester in water and salt water, straight lines could be fitted to the Arrhenius plots, with correlation coefficients of 0.99 and 0.94, respectively. However, data obtained for isopolyester in pore solution had a coefficient correlation of only 0.82, implying that accelerated aging methods utilizing temperature as the accelerating factor may be valid for water and salt solution environments, but may not work as well for the harsher pore solution environment in which severe degradation was often observed. In the study by Chin et al. [**Error! Bookmark not defined.**], it was also reported that the Arrhenius model was a good fit to vinyl ester and isopolyester in water and salt water, but not to the pore solution data.

It is also pointed out that the slopes of the lines are not equivalent, revealing that the activation energies for degradation of interlaminar shear strength in the various environments are different and hence different degradation mechanisms could potentially exist.

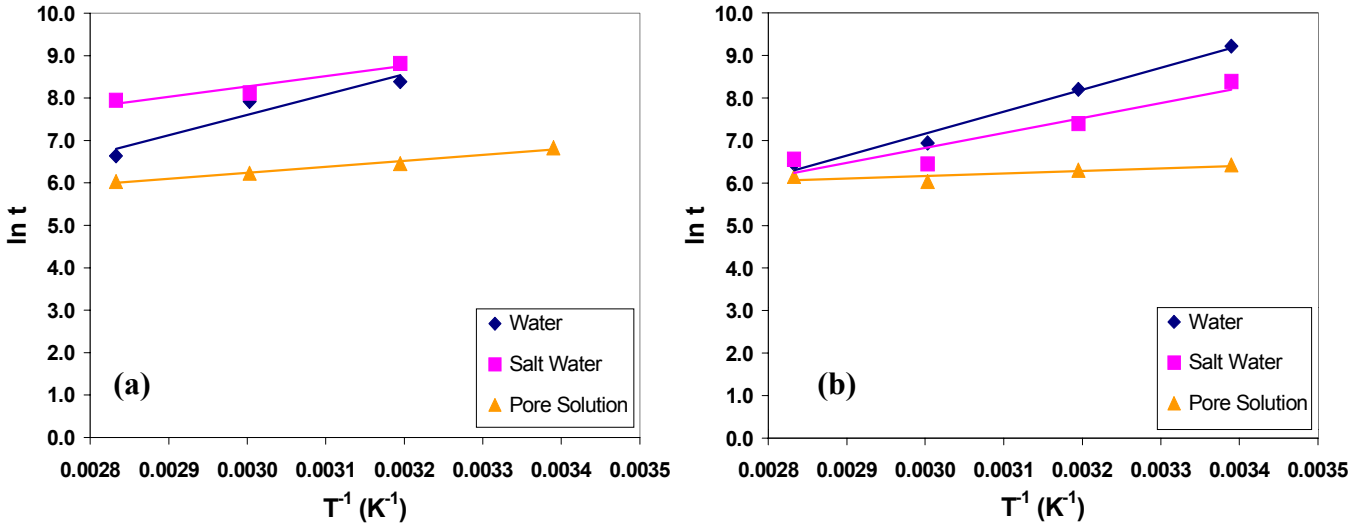

Figure 5: Arrhenius plots of interlaminar shear strength degradation for (a) vinyl ester and (b) isopolyester composites

Table I: Correlation Coefficients (r) for Arrhenius Plots

	Vinyl Ester	**Isopolyester**
Water	0.95	0.99
Salt Solution	0.95	0.94
Pore Solution	0.99	0.82

SUMMARY

Vinyl ester and isophthalic polyester were characterized with DMTA, TGA, FTIR and interlaminar shear testing following exposure to water, saline and alkaline environments at ambient and elevated temperatures for up to 427 days. Increases in the T_g following exposure were observed for both vinyl ester and isopolyester, which were attributed to hydrolysis and subsequent dissolution of low molecular segments. Spectroscopic analysis of the resins following exposure revealed varying degrees of ester hydrolysis. Interlaminar shear strength degradation following elevated temperature exposure was appreciable for both vinyl ester and isopolyester,

particularly in the elevated temperature concrete pore solution. In general, the vinyl ester composites were observed to be less susceptible than then the isopolyester materials to degradation by water and salt solutions, a characteristic attributed to the terminal position of the ester groups in vinyl ester.

Arrhenius plots for vinyl ester generated by plotting ln [time to reach 70 % of the original interlaminar shear strength] vs. $[temperature]^{-1}$ were fitted with lines having correlation coefficients of at least 0.95 for water, salt solution and concrete pore solution; isopolyester in water and salt solution also exhibited good straight line fits to the Arrhenius data. However, Arrhenius data for isopolyester in pore solution were not as linear. This implies that accelerated aging methods utilizing temperature as the accelerating factor are not valid not for exposures in which severe resin degradation was observed, as was the case for isopolyester in pore solution.

ACKNOWLEDGMENTS

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