Durability Assessment of Combined Environmental Exposure and Bending

by C. Helbling and V.M. Karbhari

Synopsis: Although fiber reinforced polymer (FRP) composites are increasingly being used in civil infrastructure applications, there is still a lack of well documented data and understanding regarding their long-term performance especially under combined exposure to environmental conditions and sustained load. This paper presents the results of an investigation into synergistic effects of hygrothermal exposure and sustained strain on pultruded E-glass/vinylester composites. It is seen that effects of increasing strain levels can be significant and can lead to changes in damage mechanisms, especially in conjunction with moisture uptake. High strains in combination with moderate to elevated temperatures resulted in substantially more catastrophic failure than elevated temperatures in combination with lower strains. These effects were noted in tension and short-beam-shear modes, and overall deterioration was corroborated by moisture uptake, Dynamic Mechanical Thermal Analysis (DMTA) and Fourier Transform Infrared Spectroscopy (FTIR) investigations.

Keywords: durability; e-glass; hygrothermal; sustained strain; vinylester; water

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INTRODUCTION

While fiber reinforced polymer (FRP) composites are increasingly being used in civil infrastructure, an obstacle still hindering the full acceptance of FRPs in civil engineering applications by owners and design engineers is the lack of awareness and knowledge of their properties in real service-life conditions. Although glass fiber reinforced polymer (GFRP) composites have been shown to have good durability in some applications through the use of high factors of safety and use of gel coats, it is well known that thermoset resins and glass fibers are susceptible to degradation by corrosive elements such as moisture and alkaline solution, elevated temperature, ultra-violet rays, and sustained levels of load. In fact, significant losses in their mechanical properties (Apicella et al, 1983; Bradley and Grant, 1995; Shridharan et al, 1998; Phifer et al, 2000) and integrity (Ghorbel and Valentin, 1993; Prian and Barkatt, 1999; Chin et al, 2001) have been reported when subjected to aggressive conditions even for relatively short durations. Harsh environmental conditions can realistically be expected in the course of their expected service-lives of the order of 50 to 75 years in civil infrastructure components exposed to the vagaries of nature. However, research studies pertaining to the long-term behavior under such environmental exposures are scarce. Hence, the success of GFRP composites in adaptation to various civil structural components will greatly depend on the ability to evaluate and comprehend the overall behavior of a composite structure, which is a function of each of its constituents, so as to predict its performance over prolonged periods of time in a given environment.

The aim of the present research is to study the environmental durability of pultruded unidirectional E-glass/vinyl-ester composites subjected to synergistic hygrothermal exposure and sustained bending load. The objectives are threefold. First, the influence of moisture and temperature will be investigated via full immersion of the composites in deionized water over a range of temperatures, while the influence of sustained load will be evaluated through the application of range of bending strains. The second objective is to reach a fundamental understanding of individual and synergistic environmental effects on each of the composite constituents as well as on the overall FRP composite. Changes in the mechanical, physical and chemical characteristics of the composites will be recorded as a function of environmental conditioning and exposure time, in addition to being correlated to each other in order to comprehensively characterize and analyze property degradation.

MATERIALS AND TEST METHODS

The material under investigation is a unidirectional pultruded E-glass/vinyl-ester composed of a bisphenol-epoxy vinyl-ester resin (Reichhold, DION VER 9102) reinforced with unidirectional single-end E-glass fibers (PPG 113Y). The speed of the pultrusion line was 910 mm per minute, the die temperature was in the range of 250ºF and no post-cure was performed as part of the fabrication process. The fiber volume fraction determined from burn-off experiments and corroborated by optical measurements is about 68%.

All FRP coupons were initially placed in an environmental chamber for 6 weeks at 40ºC and 18% relative humidity (R.H.) in order to obtain a stabilized weight baseline for further gravimetric measurements. For purposes of the current investigation the moderately elevated temperature of 40ºC was selected to accelerate the drying step, while providing some additional degree of post-cure to the vinyl-ester resin at the same time as preventing any damage by being well below the glass transition temperature of the polymer (T_g = 120.5ºC). Each 254 x 254 x 1.41 mm coupon was then subjected to one of 12 different environmental exposures. In order to characterize the effects of hygrothermal exposure, specimens were immersed in deionized water (DW) at 3 different temperatures (22, 40 and 60ºC), with a separate set of specimens being kept in controlled ambient conditions (22ºC and 60% R.H.) as a reference. The synergistic effects of imposed strain, moisture and temperature were additionally investigated through the use of a specially designed bending fixture, that enabled the application of sustained levels of 0, 30 and 45% bending strain to the composites in each of the 4 environments mentioned above. The percent bending strain (also denoted $\%\varepsilon_{BENDING}$ or ε_B) refers to the strain at mid-span on the tensile surface of the composite normalized to the ultimate longitudinal tensile strain at failure of the composite under ambient conditions, which is equal to 1.81%. Gravimetric measurements were performed at selected intervals of time in each environmental exposure in order to calculate the moisture-induced weight gain and study the moisture sorption behavior. Quasi-static tests were conducted in tension (pursuant to ASTM D3039) to evaluate changes in the ultimate tensile strength, elastic modulus and strain at failure of the conditioned specimens as a function of exposure time. Tension, rather than flexure, tests were used so as to accurately assess effects at both the fiber and interface levels. The motivation was to assess global rather than relatively local, specimen dominated, effects which would be emphasized by the flexure test, and which could provide erroneous results associated with scale effects. In addition, short beam shear (SBS) tests (pursuant to ASTM D2344 with fibers spanning the length of the specimen) were carried out to determine the interlaminar shear strength. Dynamic Mechanical Thermal Analysis (DMTA) was also performed in order to measure the glass transition temperature and dynamic moduli of the composites. These parameters were used to characterize physical and chemical changes occurring within the polymer matrix. The DMTA testing was complemented by Fourier Transform Infra-Red (FTIR) spectroscopy experiments in order to investigate resin degradation through hydrolysis. Finally, Scanning Electron Microscopy (SEM) was used to assess composite surface damage, interfacial degradation and stress corrosion of the fibers, while optical microscopy was used to examine fiber/matrix debonding. In addition to the above mentioned composite coupons that were conditioned to be tested directly after removal from their respective environments, additional coupons that were placed along with them during initial conditioning, were taken out at selected exposure times to be placed directly afterwards in a humidity chamber at 40ºC and 18%R.H. for 6 weeks (i.e. same parameters as used for pre-conditioning) in order to enable the desorption of water. These post-conditioned or redried specimens were then similarly tested in tension and by DMTA to provide an assessment of performance recovery.

RESULTS AND DISCUSSION

Moisture Sorption

The moisture uptake characteristics of the specimens in the various environments are shown in Figure 1 with the apparent moisture content being plotted against square root of time. Figures 2-4 similarly represent the change in moisture content as a function of square root of time under each bending strain level. After 1005 days of immersion in deionized water, the apparent moisture content reaches 0.45%, 0.74% and 0.84% at 22ºC, 40ºC and 60ºC, respectively. The moisture plots do not exhibit the typical Fickian-type behavior, i.e. a sharp initial linear increase followed by a plateau, but rather a progressive and continuous increase. At 22 and 40ºC, the moisture gain is still very strong even after the 3-year conditioning period signifying that saturation has not been yet attained, while it apparently reaches a plateau at 60ºC. The small decrease in apparent moisture content observed at 60ºC after about 505 days of immersion suggests the occurrence of chemical ageing processes causing an apparent reduction in weight gain. The final plateau may, therefore, either suggest moisture saturation of the vinyl-ester, or, most likely, a short-term equilibrium between weight gain due to moisture sorption and weight loss due to resin degradation. In addition, bending strains appear to have an indirect effect on moisture gain through the formation of significant damage to the composite. Previous research has shown that tensile stresses enhance diffusion processes by increasing the rate of moisture uptake and moisture saturation content (Neumann and Marom, 1987), the latter finding suggests that the tensile and compressive stresses across the composite centerline (due to bending) have opposing effects on diffusion that compensate each other, as observed previously in (Kasturiarachchi and Pritchard, 1983).

Results using Fick's diffusion model and the Langmuir diffusion model are listed in Tables 1 and 2, respectively. Only results predicted by the Langmuir-type diffusion model will be considered next, as only they accurately fit experimental data. In addition, the values of diffusivity were found to be consistent with those reported by Marshall et al. (1982) and Harper and Naeem (1989) on glass/vinyl-ester laminate systems, also suggesting the greater accuracy of that model to describe the composite sorption behavior. This finding is also corroborated by previous research (Mensitieri et al, 1995) showing that part of the water molecules freely diffuse through the polymer resin, while the rest is adsorbed in some ways to special groups located on the polymer chains or to excess free-volume. As seen in Figure 5, there is no clear influence of exposure temperature on the moisture saturation content. According to Reifsnider (1991), the moisture saturation level, if such exists, depends mostly on the relative humidity, and to a lesser extent on temperature, therefore, the present result is not unexpected. However,

Figure 6 shows that bending strains combined with moderate to elevated immersion temperatures apparently cause a progressive decrease in the moisture saturation content.

The departure of various moisture uptake profiles from the unstrained behavior is attributed to the occurrence of significant damage in the form of material leaching-out, chemical breakdown, interfacial debonding, and central delamination primarily. This comes from the fact that bending strains in combination with elevated immersion temperatures accelerate degradation mechanisms. In addition, the apparent weight loss observed after 18 and 12 months of exposure at 60ºC and 60ºC & 30%$\varepsilon_{\text{BENDING}}$, respectively, is associated with leaching-out of material, as shown on Figure 7. On the other hand, the final sudden weight increase experienced at 40ºC & 45%$\varepsilon_{\text{BENDING}}$ is correlated with interfacial degradation, which creates new routes for water penetration, along with the occurrence of delamination.

Tensile Characterization

Overall results on the change in the ultimate tensile strength of composites as a function of exposure time are presented in Figure 8 for all environmental conditions. The amount of scatter is very small, and on average on the order of ±24 MPa under no strain and ±30 MPa under sustained bending strains. As expected, a clear decrease in composite strength with increasing immersion time and temperature is seen. It is observed, for instance, that exposure to deionized water for 336 days under unstrained conditions results in strength retention levels equal to 87.5%, 66% and 49% at 22°C, 40°C and 60°C, respectively, while exposure for 1005 days yields strength retention levels of 78%, 56% and 40% at 22°C, 40°C and 60°C, respectively. The reduction in tensile strength is comparatively slow, but continuous in the 22°C immersion case, whereas it is initially more pronounced in the 40°C and 60°C immersion cases prior to leveling off. After about 841 days of exposure, the tensile strength appears to be reaching a plateau irrespective of the immersion temperature. This plateau is most likely to be temporary, since it is anticipated that the composite tensile strength will suddenly drop drastically once severe interfacial degradation and fiber stress corrosion take place causing catastrophic failure. The effect of bending strains is not, on the other hand, as significant. There is no perceptible influence of bending strains over the completed exposure duration on the tensile response of composite specimens immersed in deionized water at 22ºC. However, effects are visible at higher temperatures. Specimens immersed at 40ºC under 45%$\varepsilon_{\text{BENDING}}$ and at 60ºC under both 30% and 45%$\varepsilon_{\text{BENDING}}$ exhibit a pronounced decrease in tensile strength as compared to their unstrained counterparts. The departure from the unstrained response occurs after a period of 73 days at 60ºC & 45%$\varepsilon_{\text{BENDING}}$, 139 days at 40ºC & 45%$\varepsilon_{\text{BENDING}}$, and 332 days at 60ºC & 30%$\varepsilon_{\text{BENDING}}$ at various strength thresholds in each case. For instance, immersion at 40ºC under 0%, 30% and 45%$\varepsilon_{\text{BENDING}}$ yields strength retention levels of 84.5%, 87.5% and 86.5%, respectively, after 71-73 days, 79.6%, 78.0% and 73.0%, respectively, after 116-139 days, and 65.9%, 64.6% and 44.2%, respectively, after 332-336 days. In addition, failure is found to be less dramatic, as the decrease in tensile strength prior to failure became less sharp, and takes place at increasingly longer exposure times going from 60ºC & 45%$\varepsilon_{\text{BENDING}}$ to 40ºC & 45%$\varepsilon_{\text{BENDING}}$ and 60ºC & 30%$\varepsilon_{\text{BENDING}}$. The earlier deviation from unstrained behavior, shorter time to failure and more sudden failure at 60ºC & 45%$\varepsilon_{\text{BENDING}}$ as compared to

40ºC & 45%$\varepsilon_{BENDING}$ and 60ºC & 30%$\varepsilon_{BENDING}$ indicate that high bending strains in combination with moderate to elevated temperatures result in substantially more catastrophic failure than elevated temperatures in combination with lower bending strains. These observations suggest that a higher bending strain has greater detrimental effects on the composite tensile strength than those resulting from elevated immersion temperature. This expected strain-dependency comes from the fact that the level of stresses applied to specimens subjected to higher bending strains is obviously greater, and that once the composite tensile strength approaches that critical stress level, catastrophic failure should ensue. It is evident that the actual strength retention of specimens immersed at 60ºC & 45%$\varepsilon_{BENDING}$, 40ºC & 45%$\varepsilon_{BENDING}$, and 60ºC & 30%$\varepsilon_{BENDING}$ is comprised on average between 20 and 40%.

Considering that composite specimens were tested immediately after conditioning (referred to as wet state), and after both conditioning and post-conditioning (referred to as dry state), it is of interest to assess and compare percentage retention in tensile strength as a function of exposure condition and time in both cases. However, for purposes of true assessment within each case (wet and dry), baselines have to be considered differently. In the wet case, the baseline, $\sigma_{wet,0}$, relates to specimens tested immediately after the period of pre-conditioning, whereas in the dry case, the baseline, $\sigma_{dry,0}$, relates to specimens subjected to the full period of both pre-conditioning and post-conditioning, such that

$$\%\ \text{Strength Retention (Wet)} = \frac{\sigma_{wet,\,t}}{\sigma_{wet,\,o}} \cdot 100$$

$$\%\ \text{Strength Retention (Dry)} = \frac{\sigma_{dry,\,t}}{\sigma_{dry,\,o}} \cdot 100$$

$$\%\ \text{Relative Increase in Strength Retention} = \frac{\sigma_{dry,t} - \sigma_{wet,t}}{\sigma_{wet,t}} \cdot 100$$

where $\sigma_{wet,t}$ is the tensile strength of composites following environmental exposure for a time period t, and $\sigma_{dry,t}$ is the tensile strength of composites following both environmental exposure for a time period t and subsequent post-conditioning. As with most vinylester-based composites, the use of elevated temperatures results in post-cure. In fact, post-conditioning in an environmental chamber at 40ºC causes an increase in the average value of the tensile strength baseline from 1011.5 MPa (representing $\sigma_{wet,0}$) to 1070 MPa (representing $\sigma_{dry,0}$). Figures 9, 10 and 11 show comparative plots of tensile strength retention in the wet and dry (represented by the notation –R) states as a function of exposure time for conditioning under 0%, 30% and 45% bending strain, respectively. Overall, the level of strength retention in the dry state decreases with an increase in exposure time, temperature of immersion and amount of imposed bending strain, similarly to that in the wet state. Indeed, with the exception of the 22ºC immersion case initially, trends in both wet and dry states are very similar. The relative increase in strength retention going from the wet to dry state can be attributed to changes in the matrix properties due to water desorption (“reverse” plasticization) and increased cross-link density (additional post-cure) occurring during the post-conditioning step. It is observed that substantial regain in strength retention is obtained upon redrying for an immersion at 22ºC, irrespective of the bending strain level, for time periods up to 1 year long (336-340 days). Under 0% and 30%$\varepsilon_{BENDING}$, recovery is practically complete, i.e. retention tensile strength is back up to almost 100% after redrying, while it is slightly inferior under 45%$\varepsilon_{BENDING}$. For longer exposure times, recovery is only partial and dramatically reduced with increasing immersion periods. For instance, an exposure at 22ºC under 0%, 30% and 45%$\varepsilon_{BENDING}$ yields, overall, in the dry state, strength retention levels of 95.5-98.5%, 86-91% and 80.5-81.5% after approximately a 1-year (336-340 days), 2-year (672-678 days) and 3-year (970-1005 days) immersion period, respectively. Therefore, up to about a year of exposure, losses in retention tensile strength are found to be largely reversible upon redrying and associated with matrix effects, while afterwards, they become substantially irreversible. As noted previously, effects are more severe at higher immersion temperatures, and only little recovery is seen. For instance, an exposure under unstrained conditions at 40ºC yields, in the dry state, strength retention levels of 68%, 59.5% and 53.5% after approximately a 1-year (336 days), 2-year (672 days) and 3-year (1005 days) immersion period, respectively, while an exposure at 60ºC yields strength retention levels of 51%, 47% and 40.5%, respectively. Although the drop in tensile strength is not fully recovered upon redrying, even initially, in the 40°C and 60°C immersion cases, the relative percent increase in strength retention following post-conditioning is almost identical at 22°C, 40°C and 60°C up to about 168 days of immersion, as shown in Figure 12. However, for longer immersion periods, the percentage recovery is significantly less at temperatures above 22°C. In addition, the effect of imposed bending strain, within the limits investigated in this study, is relatively minor on the relative percent increase in strength retention following post-conditioning, as shown in Figure 13. Overall, the percentage recovery for immersions at all three temperatures under both 30% and 45%$\varepsilon_{BENDING}$ initially increases from 6 up to 14% on average, reaching the maximum after about a year of exposure, and then subsequently decreases down to about 8%.

Overall results on the retention of the longitudinal tensile modulus of composites as a function of exposure time are presented in Figure 14 for all exposure conditions. Despite the substantial amount of scatter, it appears that up to a 2½ -year period of conditioning, with the exception of the initial few months of immersion and of failed specimens, changes from the initial values are minor. In accordance with most previously published research, there is an almost negligible effect of exposure time and condition on the tensile modulus within the time durations investigated. However, it should still be noted that all specimens initially experienced about a 10% increase in modulus over the first 2-3 months of immersion with values returning to their original levels (~55-60 GPa) after about 6 months of immersion. The increase is attributed to effects of post-cure progression and plasticization of the resin. In addition, there is a significant final decrease in tensile modulus following 3 years of exposure in all environments. Finally, specimens immersed in deionized water at 60ºC under 30%$\varepsilon_{BENDING}$ exhibited a reduction of about 24% in modulus in the test period prior to failure. In most cases, a small increase in tensile modulus is observed following post-conditioning, as expected, primarily due to reverse plasticization effects and increased cross-linking density. Effects, therefore, are minor since they are related to physical changes occurring within the polymer matrix.

Since up to a moisture content of approximately 0.25%, which is attained over a period of time ranging from 4 to 282 days depending on the exposure temperature and level of bending strain, there is no discernible degradation at the fiber and interface level, as evidenced by the absence of fiber pitting, change in tensile failure mode and superficial damage, and there is substantial-to-full recovery in the level of strength retention upon reconditioning, the degrading effects due to immersion in deionized water are primarily attributed to matrix plasticization within that range. Consequently, the tensile strength was plotted against sorbed moisture content to a limit of $M_m = 0.25\%$, as shown in Figure 15, in order to verify that assumption and investigate the influence of temperature and bending strain on the composite tensile strength. As can be seen in Table 3, linear relationships with a high degree of correlation were obtained both for individual temperature-strain combinations and for the entire set collectively, demonstrating the significant and likely dominating effect of sorbed moisture till this juncture on the decrease in tensile strength. Taking all data together, it can be determined that due to an immersion in deionized water, on average, the longitudinal tensile strength decreases by 604 MPa per percent sorbed moisture content in the range considered, independently of the environment, although there is an apparent slightly greater strength loss per percent moisture content as temperature increases. Finally, this strength loss is associated with matrix plasticization almost exclusively.

A progressive change in tensile failure mode from a brush-like failure characterized by longitudinal splitting (for unaged to somewhat damaged material) to central fiber rupture (for severely damaged material) was observed as a function of increasing immersion time and increasingly severe environment. This change in tensile failure mode was used to try to qualitatively assess interfacial properties. Indeed, analysis of the various failure modes showed that the progressive transition from a brush-like failure to central fiber rupture can be attributed, in part, to a loss of adhesion between the fiber and matrix as indicated by greater fiber pull-out and smoother fiber surfaces at the microscopic level, and, to weakening of the glass fibers through the growth of existing flaws as well as formation of new ones, resulting in a more planar fracture surface at the macroscopic level. This, although approximate, was, therefore, proven to be rather informative of possible changes in the strength of the fiber/matrix bond as well as that of fibers. Up to about $M = 0.25\text{-}0.3\%$, the tensile failure mode is unaffected by moisture content, however, above that critical level, the tensile failure mode becomes increasingly brittle as the moisture content increases exhibiting a progressive and linear trend.

Short-Beam Shear

Overall results for short beam shear strength as a function of exposure time are presented in Figure 16 for all exposure conditions. Similar to the ultimate tensile strength, the short beam shear strength decreases with increasing exposure time at all test temperatures. However, this decrease is not as significantly affected by temperature as the tensile strength is. In addition, it appears that lower immersion temperatures lead to greater losses in interlaminar properties, with however, no clear influence of bending strains. During a 3-year exposure period, the short beam shear strength is reduced by a maximum of 16% corresponding to an immersion in water at 22ºC for 224 days, which is significant considering the ±2% scatter at that temperature. The surprising result is, therefore, that higher exposure temperatures seem to result in lesser shear strength loss, which is in contradiction with observations made by Chin et al. (2001) for instance. In the literature, a decrease in interlaminar shear strength has been attributed to resin hydrolysis, fiber/matrix debonding and fiber degradation (Liao et al, 1999), as well as matrix plasticization, swelling stress and water entering at the fiber/matrix interface (Nguyen et al, 1998**).**

Dynamic Mechanical Thermal Analysis

The glass transition temperature of the samples is reported in Figure 17 as a function of exposure time for all conditions. The amount of scatter is generally on the order of ±1.2ºC, even though, in some cases, it reached up to ±3ºC. As can be seen, the T_g of specimens exposed to ambient conditions is relatively constant and comprised roughly between 120 and 121.5ºC. This result suggests that the amount of ambient post-cure is minor to inexistent, which is also corroborated by the fact that the tensile strength of specimens exposed to ambient conditions is rather constant throughout the 3-year conditioning period. However, when immersed in deionized water, composite specimens exhibit 2 very distinct behaviors depending on the exposure temperature; an immersion at 22ºC and 40ºC is found to cause a decrease in T_g below its original value, while an immersion at 60ºC leads to a continuous increase in T_g. The initial sharp decrease in T_g with increasing exposure time, which is observed at 22ºC and 40ºC, has been widely attributed to plasticization effects in the literature (Ghorbel and Valentin, 1993). It is known that sorbed water molecules interact with the polymer matrix in multiple ways that primarily include the formation of an ordinary solution (phenomenon of simple dilution into the polymer network), sorption onto the surface of excess free volume holes within the polymer, hydrogen bonding to hydrophilic groups on the polymer chains (Apicella et al, 1985) , as well as formation of clusters (Kawagoe et al, 1999). However, as water molecules diffuse through the polymer matrix, it is the position that they occupy in-between polymer chains that is responsible for the increased molecular mobility, and therefore, flexibility of the polymer network. This, in turn, causes a general softening of the polymer, which is a phenomenon referred to as plasticization. In the present case, T_g reaches a minimum of 107.3ºC and 108.2ºC after 168 days of immersion at 22ºC and 40ºC, respectively. The subsequent increase in T_g following 336 days of immersion, which is greater at 40ºC than at 22ºC, may, on the other hand, be related primarily to the loss of low molecular-weight elements (LMWE) from the vinyl-ester resin. It has indeed been reported in the literature that the dissolution of LMWE results in an embrittlement of the matrix, and thus, in an increase in T_g (Apicella et al, 1983; Chin et al, 2001). Similarly, the continuous increase in T_g observed at 60ºC can be associated with predominant matrix embrittlement effects through the loss of LMWE, and possibly, post-cure, overcoming matrix softening effects through plasticization, and most likely, hydrolysis. A study by Chin et al. (2001) showed, for instance, that the immersion of vinyl-ester composites in water at room temperature and up to 60ºC resulted in a rather strong initial increase in T_g that was correspondingly correlated with the dissolution of low molecular-weight elements. Hygrothermal ageing in water at elevated temperatures can, in addition, favor "post-curing" reactions if there is sufficient macromolecular mobility for a slow diffusion-controlled cross-linking process to take place, resulting in an increase in T_g as well. For vinyl-ester composite systems, the post-cure process involves the continuation of polymerization reactions previously inhibited by the presence of oxygen in air, i.e. consumption of free residual styrene and disappearance of prepolymer chains through the formation of polystyrene and further polymerization of the vinyl-ester resin (Mensitieri et al, 1995; Lietard et al, 2000). Consequently, it is postulated that the main factors responsible for the overall increase in glass transition temperature with increasing exposure time at 60ºC include the loss of LMWE and a moisture-assisted post-cure process. However, plasticization is also, undoubtedly, taking place, most expectedly along with hydrolysis reactions, causing an relative decrease in T_g. In fact, studies on glass/vinyl-ester composite systems have shown that resin hydrolysis tends to govern hygrothermal ageing at long exposure times, overcoming plasticization effects (Ghorbel and Valentin, 1993). This chemical phenomenon consists of an attack on the terminal ester groups of the vinyl-ester resin with subsequent formation of carboxyl and hydroxyl groups (Apicella et al, 1983; Chin et al, 2001), which weakens the polymer network. The expected greater role that resin hydrolysis plays as exposure time increases could explain the leveling off in T_g around 130ºC after approximately 672 days of immersion at 60ºC. Thus, bending strains do not show any real or consistent trend on the glass transition temperature. Under ambient conditions, bending strains do not appear to have any significant effect on T_g, although they do seem to result in a slight reduction in T_g. At 22ºC and 40ºC, bending strains do not have any clear influence on T_g, with the exception of the 22ºC & 30%$\varepsilon_{BENDING}$ immersion case where T_g is inexplicably low. Finally, at 60ºC, bending strains seem to cause a substantial increase in T_g.

SUMMARY

The synergistic effects of water immersion, temperature, and bending strain on the sorption behavior and mechanical response of a unidirectional pultruded E-glass/vinyl-ester composite were investigated over a period of about 3 years. While this period is short compared to the expected service life of a structure, the results must be viewed in the context of an accelerated test approach. The environments are fairly severe and further work is ongoing to relate these results to expected field effects of time varying humidity and temperature regimes, which are expected to cause slower rates of deterioration and materials transformation. Composite specimens were found to follow a Langmuir-type diffusion behavior in all environments, with departure from that behavior attributed either to material leaching-out, chemical breakdown, interfacial debonding, or central delamination. The composite tensile strength decreased with increasing immersion time and temperature, with high bending strain levels having a more detrimental effect at elevated temperatures. The initial strength loss was associated with matrix plasticization, while later reductions were caused by the occurrence of mechanisms of fiber degradation via stress-corrosion and interfacial debonding. Changes in tensile strength were largely reversible for an immersion at 22ºC up to 1 year of exposure, but the level of regain decreased substantially for longer immersion periods and at higher immersion temperatures. The elastic modulus was relatively unaffected by environmental exposure, while the strain at rupture exhibited a trend very similar to that of the ultimate tensile strength. The composite short beam shear strength also decreased with increasing immersion time, however, lower exposure temperatures resulted in greater strength losses. Glass transition temperature results showed that irreversible physical/chemical changes occurred within the polymer matrix following an immersion at 22 and 40ºC after several months of exposure, while they occurred almost instantly following an immersion at 60ºC. The significant increase in T_g subsequent to the redrying step showed that plasticization was an important mechanism associated with an immersion in deionized water irrespective of the exposure temperature. FTIR analysis demonstrated the occurrence of ester hydrolysis reactions primarily for an immersion at 60ºC. Finally, exposure to the 3 most severe environments caused composite failure by delamination and central fiber fracture within the bending fixture itself. The more sudden failure experienced at 60ºC & 45%$\varepsilon_{BENDING}$ as compared to 40ºC & 45%$\varepsilon_{BENDING}$ and 60ºC & 30%$\varepsilon_{BENDING}$ indicated that high bending strains in combination with moderate to elevated temperatures resulted in substantially more catastrophic failure than elevated temperatures in combination with lower bending strains.

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Table 1 - Diffusion, moisture saturation and linear correlation coefficients obtained using the long-term approximation of the Fickian diffusion model.

Environment	D [mm^2/s]	M_∞ [%]	R
DW, 22°C	9.69 10^{-9}	0.39	0.964
DW, 22°C, 30%ε_B	8.94 10^{-9}	0.39	0.968
DW, 22°C, 45%ε_B	9.28 10^{-9}	0.39	0.966
DW, 40°C	1.10 10^{-8}	0.64	0.965
DW, 40°C, 30%ε_B	1.15 10^{-8}	0.61	0.968
DW, 40°C, 45%ε_B	4.11 10^{-8}	0.40	0.964
DW, 60°C	4.64 10^{-8}	0.65	0.966
DW, 60°C, 30%ε_B	1.37 10^{-7}	0.50	0.964
DW, 60°C, 45%ε_B	4.53 10^{-7}	0.35	0.961

Table 2 - Diffusion parameters and linear correlation coefficients obtained using the long-term approximation of the Langmuir diffusion model.

Environment	α (x10^5)	β (x10^5)	D [mm^2/s]	M_∞ [%]	R
DW, 22°C	18.70	6.35	1.48 10^{-7}	0.52	0.998
DW, 22°C, 30%ε_B	19.98	6.32	1.41 10^{-7}	0.515	0.999
DW, 22°C, 45%ε_B	19.96	6.51	1.51 10^{-7}	0.52	0.998
DW, 40°C	30.39	10.26	2.06 10^{-7}	0.76	0.998
DW, 40°C, 30%ε_B	44.18	12.93	4.29 10^{-7}	0.70	0.998
DW, 40°C, 45%ε_B	58.34	21.44	5.30 10^{-7}	0.57	0.996
DW, 60°C	104.93	39.28	8.08 10^{-7}	0.785	0.997
DW, 60°C, 30%ε_B	156.55	88.57	1.16 10^{-6}	0.58	0.995
DW, 60°C, 45%ε_B	1328.7	551.24	1.12 10^{-6}	0.39	0.991

Table 3 - Slope (α) and linear correlation coefficients obtained for the plots of ultimate tensile strength as a function of moisture content.

Environment	α [MPa/wt.%]	R
DW, 22°C	479	0.971
DW, 22°C, 30%ε_B	514	0.934
DW, 22°C, 45%ε_B	472	0.966
DW, 40°C	630	0.993
DW, 40°C, 30%ε_B	678.5	0.983
DW, 40°C, 45%ε_B	647	0.923
DW, 60°C	722.5	0.989
DW, 60°C, 30%ε_B	711	0.940
DW, 60°C, 45%ε_B	583	0.967

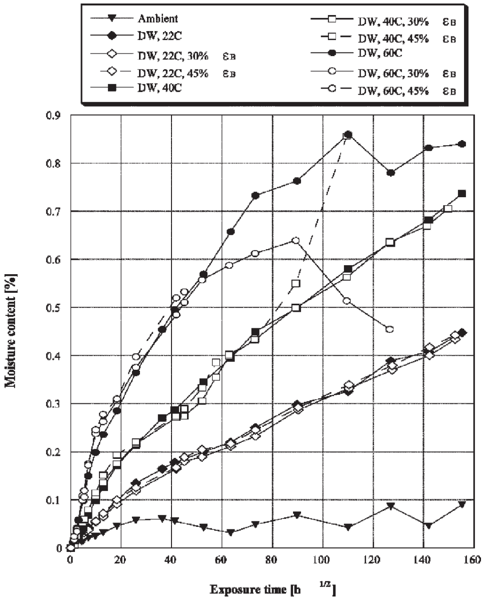

Figure 1 - Apparent moisture content of composites under environmental exposure as a function of square root of time.

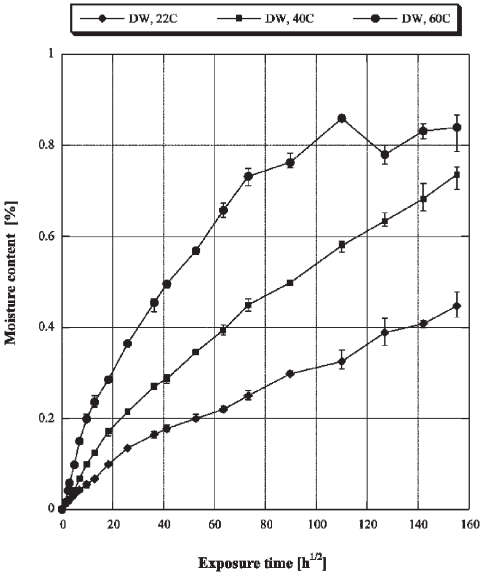

Figure 2 - Apparent moisture content of composites immersed in deionized water under unstrained conditions as a function of square root of time.

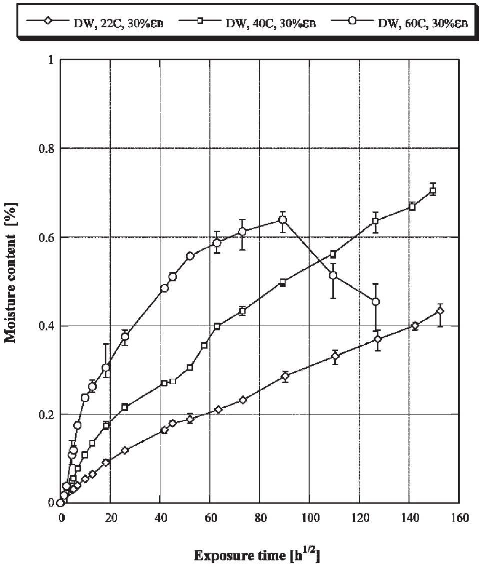

Figure 3 - Apparent moisture content of composites immersed in deionized water under 30% bending strain as a function of square root of time.

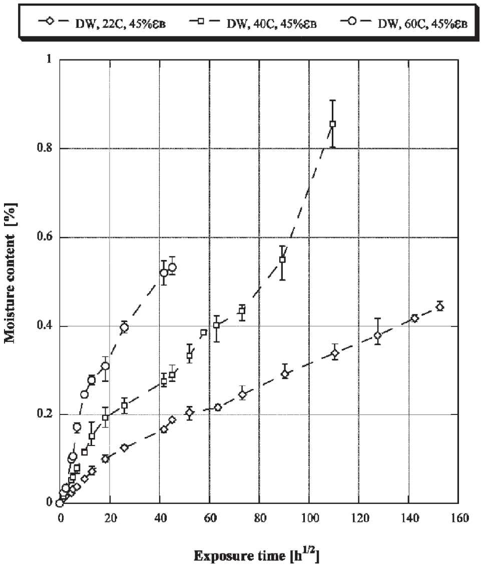

Figure 4 - Apparent moisture content of composites immersed in deionized water under 45% bending strain as a function of square root of time.

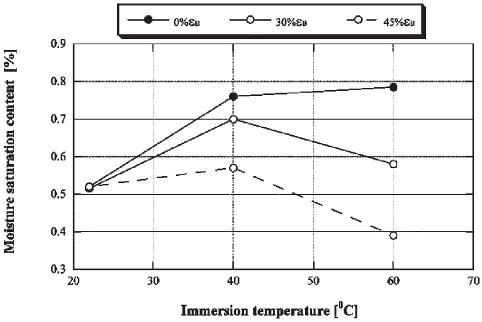

Figure 5 - Moisture saturation content (using Langmuir model) as a function of immersion temperature at each level of applied bending strain.

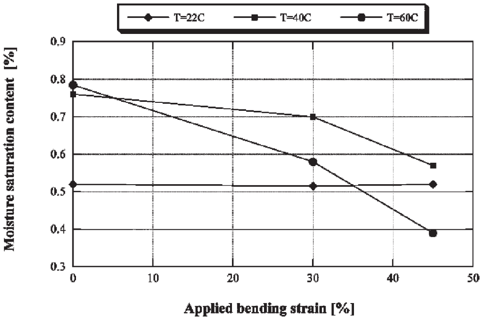

Figure 6 - Moisture saturation content (using Langmuir model) as a function of applied bending strain at each immersion temperature.

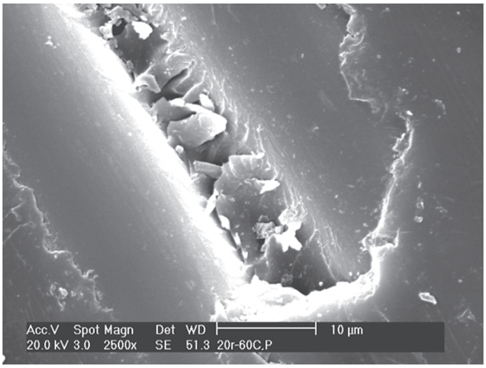

Figure 7 - Superficial resin dissolution.

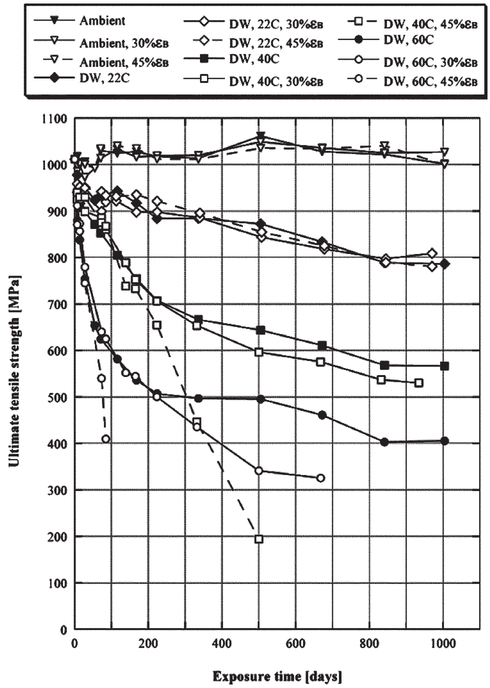

Figure 8 - Longitudinal ultimate tensile strength of composites under environmental exposure as a function of time.

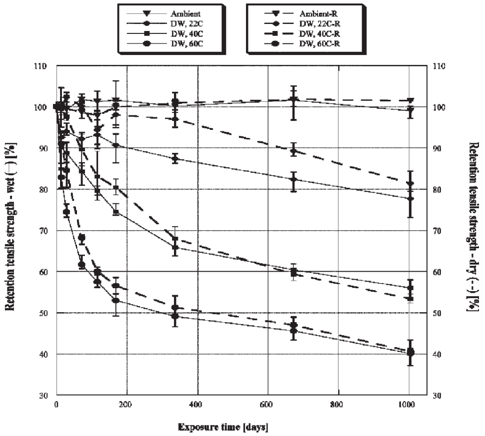

Figure 9 - Normalized longitudinal ultimate tensile strength after conditioning (wet) and post-conditioning (dry) of composites immersed in deionized water under unstrained conditions as a function of time.

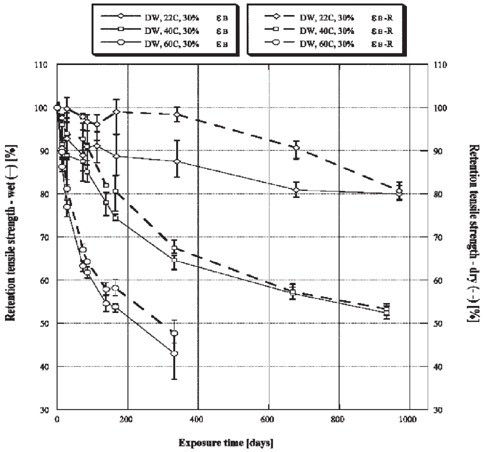

Figure 10 - Normalized longitudinal ultimate tensile strength after conditioning (wet) and post-conditioning (dry) of composites immersed in deionized water under 30% bending strain.

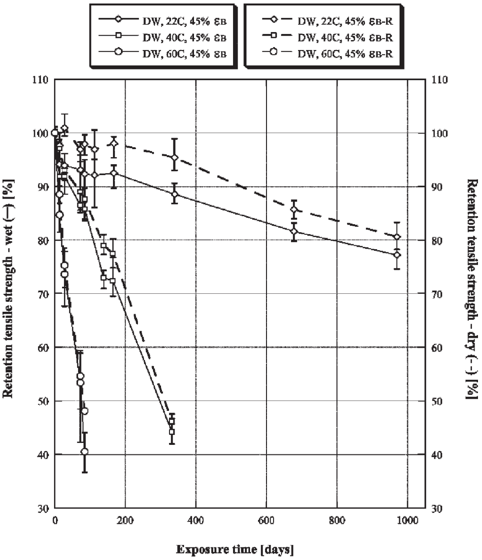

Figure 11 - Normalized longitudinal ultimate tensile strength after conditioning (wet) and post-conditioning (dry) of composites immersed in deionized water under 45% bending strain as a function of time.

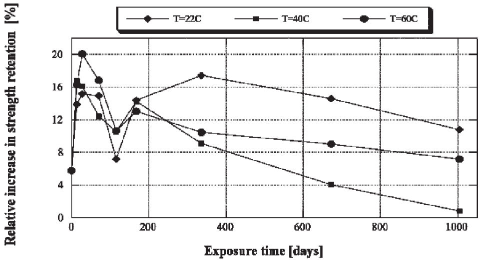

Figure 12 - Relative increase in strength retention following post-conditioning for immersion under unstrained conditions as a function of time.

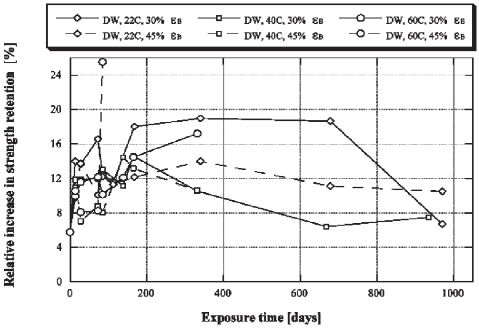

Figure 13 - Relative increase in strength retention following post-conditioning for immersion under strained conditions as a function of time.

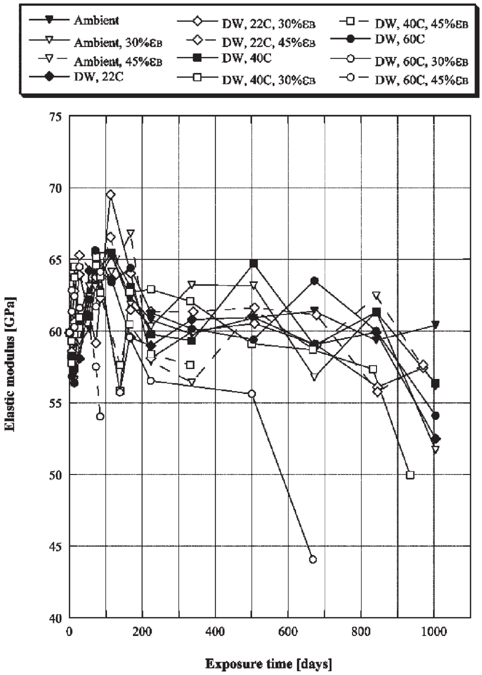

Figure 14 - Longitudinal elastic modulus of composites under environmental exposure as a function of time.

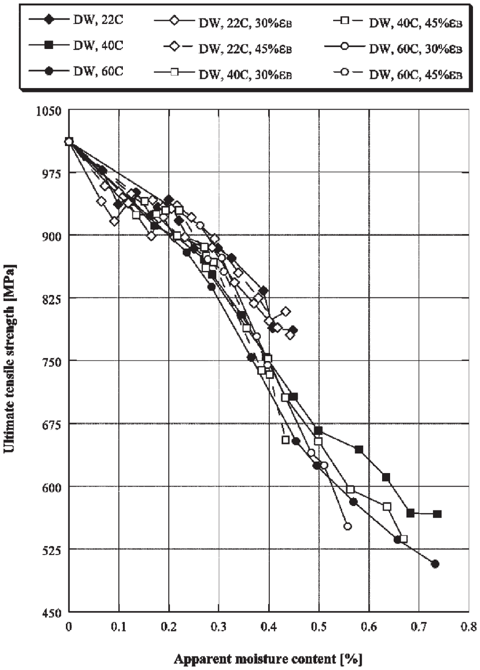

Figure 15 - Change in longitudinal ultimate tensile strength as a function of apparent moisture content for composites immersed in deionized water.

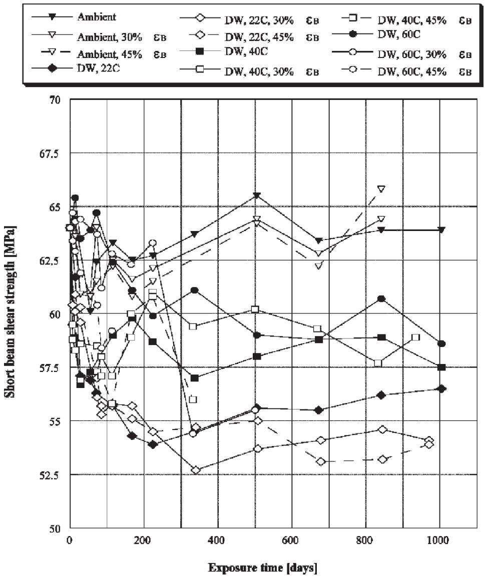

Figure 16 - Short beam shear strength of composites under environmental exposure as a function of time.

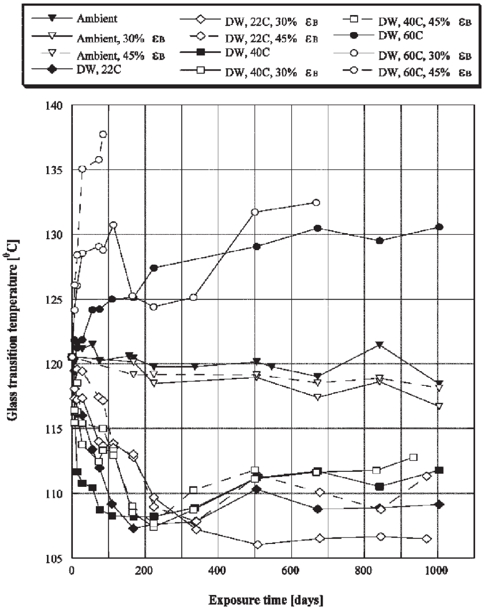

Figure 17 - Glass transition temperature of composites under environmental exposure as a function of time.