

A MECHANICAL ANALYSIS OF E-GLASS/VINYL-ESTER IN HOT, HUMID ENVIRONMENTS

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Abstract

Moisture sorption of polymer composites immersed in deionized water at different temperatures has been investigated at length as a means for performing accelerated degradation. The ability to isolate thermal effects from moisture degradation is often limited by absence of complementary environmental conditions. This test program considers thirteen environments involving three temperatures and three relative humidities as well as immersion in deionized water at four Tension, short beam shear, and temperatures. DMTA testing was executed to investigate the degradation of the E-glass/vinyl-ester considered here. Gravimetric observations complemented all mechanical tests. Testing shows exposure to wet environments at elevated temperatures results in irreversible degradation while lower temperature wet exposures result in less severe reversible decreases in material properties.

1 Title of Section (e.g., Introduction)

The durability of composite materials has traditionally been investigated by exposing material to immersion in hot water environments [1-5]. It is not always clear, however, how these immersion tests relate to long term exposure to in-service humid environments [6-7]. Degradation of composites in immersion environments occurs in the fiber and matrix as well as the interphase. Glass fibers are known to chemically degrade when water attacks the Si-O bond [8]. Polymer composite matrices plasticize, swell, and chemically degrade via hydrolysis of the backbone. Water enters the composite via diffusion, a process which is accelerated with increasing temperature. However, temperature also accelerates the degradation processes and the relation between the effect of water and temperature is not always taken into

account. That is, the physio-chemical breakdown of the fiber, as shown in Fig. 1 is thermally accelerated while increases in material properties such as short beam shear strength are increased at the same temperature in low humidity.

This work investigates an E-glass/vinyl ester unidirectional pultruded composite system as it is exposed to 13 environments. Four environments are hot water immersion at 20°C, 40°C, 60°C, and 80°C. The other nine environments consider relative humidities of 18%RH, 50%RH, and 99%RH at 20°C, 40°C, and 60°C. All samples were tested Wet and "Dry," where "Wet" samples were tested immediately after exposure. "Dry" samples were removed from their environment at the same time as the "Wet" set but redried for six weeks at 40°C, 18%RH. The redrying of exposed samples removes any moisture effects so that the thermal effects in immersion environments may be compared to thermal effects at the same temperature in low humidities.

2 Experimental Program

2.1 Material System

The material system under investigation is a unidirectional pultruded E-glass/vinyl-ester composite composed of a bisphenol-epoxy vinylester resin matrix reinforced with unidirectional single-end E-glass fibers. The fiber volume fraction determined from burn-off experiments and corroborated by optical measurements is about 68% assuming void content is negligible. The material was received in the form of a 10cm wide and 1.36mm thick coil. The composite was cut with a diamond wet saw and finished by wet sanding all edges with 320 grit silicon carbide wet/dry polishing paper. Samples were labeled prior to environmental exposure.

2.2 Environmental Exposures

Thirteen environments were selected for investigation, with four temperatures of immersion in deionized water (20°C, 40°C, 60°C, 80°C) and three relative humidities (18%RH, 50%RH, 99%RH) at three temperatures (20°C, 40°C, 60°C). Humidities were selected in order to represent conditions which may realistically be encountered in the environment at ambient conditions.

Prior to exposure in these environments, all samples were dried for 6 weeks at 40°C, 18%RH in order to remove any moisture present while minimizing post-cure and embrittlement. Samples were tested after 12 weeks, 24 weeks, and 36 weeks of exposure. After each exposure period, a set was removed, half were tested immediately after exposure (referred to as "Wet"), and half were placed in the conditioned environment for redrying (referred to as "Dry") for 6 weeks at 40°C, 18%RH prior to testing.

An ambient set was added later in the test program. Composite material which was tested under ambient conditions was not conditioned and, so, can be considered raw. Ambient conditions were investigated in order to compare the results of exposure to aggressive environments to behavior which may be expected if the material sits at ambient conditions, documented as 20°C, 30%RH on average. Presented here are results through 12 weeks.



Fig. 1. Scanning electron micrograph of surface of composite exposed to immersion in 80°C water for 12wk.

2.3 Test Program

Gravimetric Measurements were performed by weighing 25.4mm x 25.4mm specimens at 0h, 1h, 2h, 4h, 6h, 9h, 1d, 2d, 3d, 1w, 2w, 4w, 6w, 8w, 10w, 12w, 15w, 18w, 24w, 36w. Samples were also weighed after redrying in order to reveal any weight loss due to material degradation or retained water. Measurements were taken on a balance with resolution to 0.00001g. Prior to weighing, all samples were allowed to equilibrate to room temperature and wet samples from high humidity and immersion environments were wiped dry.

Tensile testing was performed according to ASTM-D3039 on a single load cell testing machine with a crosshead speed of 2mm/min on specimens 25.4mm x 254mm in order to obtain longitudinal tensile modulus and strength.

Short beam shear testing was performed according to ASTM-D2344 with a span of 6.35mm in the longitudinal direction. Specimens were 5mm x 11mm.

Dynamic Mechanical Thermal Analysis (DMTA) was conducted in a three-point bending setup loading the transverse axis at a frequency of 1 Hz and a heating rate of 4°C/min. Specimens were 9mm x 35mm, tested over a span of 28mm.

3 Experimental Results

3.1 Gravimetric Measurements

Moisture uptake as a function of time, M_t , was calculated as follows, with the initial weight taken after conditioning prior to exposure.

$$M_t = \frac{\text{Exposed Weight - Conditioned Weight}}{\text{Conditioned Weight}}$$

The weight change in "Dry" material is calculated using the conditioned pre-exposed weight as the initial weight.

$$M_t = \frac{\text{Reconditioned Weight - Conditioned Weight}}{\text{Conditioned Weight}}$$

A negative "Dry" weight change indicates there was some net weight loss experienced beyond the removal of any sorbed water. That is, when the exposed material was redried, some degraded material was removed. The origin of this degraded material is unclear at this point. SEM images, such as Fig. 1, indicate that there is significant loss of surface resin and degradation of glass fiber at higher temperatures. Weight loss could also be a result of low weight molecular species leaching out during desorption in the reconditioning process.

Gravimetric results are presented in Fig. 2 and The spikes in moisture uptake for the Fig. 3. 18%RH and 50%RH, 20°C environments correlate to temporary rises in relative humidity to 30%RH and 65%RH, respectively. After 36 weeks, the only environments which have reached equilibrium are Low humidity environments those at 50%RH. appear to continue to approach some equilibrium moisture content. The high temperature dry environment at 60°C, 18%RH experiences a weight loss, as shown in Fig. 2. This desorption could be a result of the removal of residual moisture or uncured styrene in the hot, dry environment, though the mechanism responsible for this weight loss is unclear at this time.

At a low humidity level, there does not appear to follow a traditional Fickian sorption trend. That is, whatever rate of absorption or desorption exists is too slow for a sorption trend to be identified. It is clear, however, that temperature affects the moisture uptake of these specimens in low humidity. 60°C, 18%RH results in a net weight loss, 40°C, 18%RH produces a minor non-zero weight gain, and exposure to 20°C, 18%RH results in a minor weight gain larger than that at 40°C. While these trends tend to jump around, their differences are statistically significant.

At the 50%RH level, equilibrium was reached within 12 weeks at all temperatures. The 20°C environment was the slowest to approach the maximum moisture content. The 60°C, 50%RH environment quickly equilibrated after 8 weeks. However, the composite material in this environment has since begun to lose weight, as Fig. 2 indicates. Conversely, while it appears that the material in the 40°C environment has approached the maximum moisture content, the moisture uptake continues to increase after 36 weeks. This trend represents the relaxation model discussed in [9]. Additional long term data must be obtained in order to verify the maximum moisture content at 50%RH. Initial observations indicate that exposure to 60°C environments result in some sort of weight loss while 40°C environments result in a relaxation phenomenon.

The relaxation phenomenon can further be demonstrated by considering the high humidity and immersion environments. After 36 weeks, no composite in a saturated environment has reached a maximum moisture uptake level. While exposure to 80°C immersion in deionized water results in an apparent maximum moisture content of 1.0%, the "Dry" results must be considered in order to fully understand the subsequent weight loss after 12 weeks. Redrying of the specimens reveals that after just 12 weeks, specimens exposed to 80°C water have lost 0.13% of their initial weight. After only 36 weeks, there is a net weight loss of 0.93%. One can then recalculate the moisture uptake with the following relationship:

$$M_t (\text{adjust}) = M_t (\text{wet}) - M_t (\text{dry})$$
$$M_t = \frac{\text{Exposed Weight - Reconditioned Weight}}{\text{Conditioned Weight}}$$

Reconditioning of all samples indicates that 80°C water immersion is the only condition which results in statistically significant material loss. Fig. 4 provides the adjusted moisture uptake results for 80°C immersion. The composite appears to reach an equilibrium of 1.14% after 12 weeks. Further testing is required to verify these results.



Fig. 2. Gravimetric results for 18%RH and 50%RH.



Fig. 3. Gravimetric results for 99%RH and immersion.



Fig. 4. Adjusted moisture uptake for 80°C, immersion.

It is important to observe that there is little notable difference between the moisture uptake of the composite at higher temperatures in 99%RH and immersion in deionized water. The 20°C saturated environments do deviate from one another such that the difference between the two sorption trends is statistically significant.

It is unclear at this point what mechanism is responsible for moisture sorption. The 50%RH environments are initially linear with respect to the square root of time, indicating a concentration driven Fickian sorption trend. However, high humidity and immersion sorption curves do not demonstrate a clear linear trend when considering moisture uptake against the square root of time. The rate of moisture sorption decreases with respect to time and no saturated environment has reached an equilibrium. This non-Fickian trend indicates a relaxation of the polymer or some activity in the interphase region. Degradation of the interphase and glass fiber in these high temperature, high moisture environments results in the formation of voids where water may accumulate, leading to a wicking phenomenon. An extension of these moisture trends with time will allow for a more accurate assessment of the mechanisms responsible for moisture sorption at all humidity levels.

3.2 Tensile Degradation

Tension results are presented in Fig. 5 through Fig. 8. "Wet" and regained "Dry" material properties are provided together in each figure, superimposed. When considering the tensile modulus, it is clear that there is no statistically significant loss in longitudinal modulus for any environment. The changes in longitudinal tensile modulus of composites tend to be strongly based upon the fibers which do not change modulus significantly after exposure to harsh environments.

Fig. 7 indicates that for low and medium humidity environments, there is no significant change in strength. However, in the presence of water at elevated temperatures, there is clear permanent degradation. At the relatively low temperature of 20°C in high humidity and immersion environments, the glass composite loses over 10% of its initial strength.



Fig. 5. Tensile modulus for 18%RH and 50%RH.



Fig. 6. Tensile modulus for 99%RH and immersion.



Fig. 7. Tensile strength for 18%RH and 50%RH.



Fig. 8. Tensile strength for 99%RH and immersion.

Redrying the composite reveals the tensile strength is fully retained after exposure to 20°C saturated environments. Exposure to similar moist environments at higher temperatures (40°C, 60°C, 80°C) results in some permanent loss in strength. Higher temperatures resulted in more severe degradation of material strength. When comparing the strengths of material exposed to saturated elevated temperatures environments at after redrying, material exposed to high humidity environments experienced a more severe permanent That is, 40°C immersion loss in degradation. resulted in a permanent degradation 3%-8% greater than that experienced in 40°C, 99%RH. Similarly, at 60°C, the redried strengths after immersion is 4%-7% less than in 99%RH. While immersion results are generally lower than the 99%RH sets, the standard deviation of the tested sets can reach as high as 4%. Thus, even a 2% standard deviation of tension values for both 99%RH and immersion environment will result in a statistically insignificant At this time, there is no temporal difference. correlation with the magnitude of the difference between 99%RH and immersion results.

3.3 Short Beam Shear and Tg Results

Short beam shear testing follows a slightly different trend than tension. At 18%RH and 50%RH, most environments did not experience any change. However, the 60°C, 50%RH environment did result in an increase in short beam shear strength, and this increase became more evident after redrying, as seen in Fig. 9. This increase in short beam shear strength at high temperatures and relatively low humidities indicates a post cure is occurring at higher temperatures in the absence of water. Fig. 11 provides the glass transition temperatures for the same exposures, as collected from DMTA. The increase in glass transition temperature, T_g , at 60°C, 18%RH and 50%RH indicates a post cure which is also evident from the short beam shear results. At 40°C in low and medium humidities, there is no clear change in short beam shear strength or glass transition temperature. The static nature of these values with increased exposure may indicate that there is no change occurring during exposure to 40°C, humid environments. It is more likely, however, that any decrease in properties due to moisture sorption is being counteracted by the thermal effects at 40°C. These thermal effects are more significant at higher temperature. At 20°C, there is no noticeable thermal effect, so the slight depression in short beam shear strength and glass transition temperature indicates that there is some plasticization of the composite due to moisture sorption alone.

In the presence of water in saturated environments, there is clearly some permanent degradation at elevated temperatures. At 20°C in 99%RH and immersion, the depressed short beam shear strength is wholly regained without postcure.



Fig. 9. Short beam shear strength for 18%RH and 50%RH exposures.



Fig. 10. Short beam shear strength for 99%RH and immersion exposures.



Fig. 11. Glass transition temperature for 18%RH and 50%RH exposures.



Fig. 12. Glass transition temperature for 99%RH and immersion exposures.

When considering the short beam shear strength in Fig. 10, it may be theorized that there is a minor postcure experienced by the composite in 40°C saturated environments. However, DMTA results of "Wet" and "Dry" material, as presented in Fig. 12, indicates that there is likely no postcure. This increase in short beam shear strength could simply be a statistically insignificant change in value. After 12 weeks, it is clear that even in 99%RH and immersion, the 60°C thermal exposure imparts some post cure upon the composite, as "Dry" testing indicates in both short beam shear tests and DMTA. After 12 weeks, the glass transition temperature in these environments continues to increase steadily while the short beam shear strength drops This contrasting behavior indicates dramatically. that the polymer experiences a thermal postcure effect while the mechanical short beam shear strength permanently degrades from the thermal exposure. Similar results are seen with 80°C immersion, where the glass transition temperature

increases dramatically despite a dramatic irreversible degradation in short beam shear strength.

The increase in glass transition temperature may be an indication of postcure. This increase in T_g could also be indicative of leaching of low weight molecular species [10]. Regardless, there is some change in the polymer's network which counteracts the macroscopic material degradation experienced at these high temperatures. Thus it is proposed that there is some threshold temperature or a combination of temperature and time which results in a irreversible mechanical degradation of the composite.

The relation between short beam shear strength and glass transition temperature for all environments is provided in Fig. 13. This plot clearly demonstrates the correlation between the depression of glass transition temperature and a decrease in short beam shear strength. The outliers for "Wet" material correspond to times where there is a permanent loss of short beam shear strength complemented with an increase in glass transition temperature.



Fig. 13. Short beam shear strength as compared to glass transition temperature. ◆18%RH, ■50%RH, ▲99%RH,
● Immersion, Filled "Wet", Open "Dry", 20°C, 40°C, 60°C, 80°C.

4 Conclusion

This paper has addressed the need for complementing accelerated testing in immersed water at elevated temperatures with exposures to humid environments at the same temperatures. Such testing does not have to be executed at low humidities, though low humidities do produce results which do not deviate much from higher humidities such as 50%RH. 99%RH appears to produce similar though slightly less severe results. Tensile testing provides important results which provide a clear indication of when there is irreversible degradation. Short beam shear testing and DMTA complement tension and each other, revealing information about material changes which may not be evident from longitudinal tension results. Because composites are used primarily for their longitudinal tensile properties, it is recommended that tensile tests be executed in addition to any smaller scale mechanical tests which may provide greater insight as to the degradative experience of the composite material.

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