PHYSICAL AND MECHANICAL CHARACTERIZATIONS OF GLASS/VINYL ESTER COMPOSITE UNDER ENVIRONMENTAL CYCLING

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SUMMARY: Hygrothermal freeze/thaw cycling exposures were performed on glass/vinyl ester composites to simulate the harsh temperature and moisture conditions the composites might encounter during their lifetime in services. Moisture absorption of the composite during the exposures and hygrothermal effects on the glass transition, thermal stability, and mechanical properties of the composite were investigated. It was found that moisture absorption of the composite showed a cyclic increasing, within the freeze duration, and decreasing in the thaw period, while glass transition temperature of the composite exhibited a steady increase with an increase in hygrothermal cycling duration and leveled off beyond 1000 hours of the exposure. Thermal stability of the composite was only slightly influenced by the hygrothermal exposures at 80°C. By comparison, it was also found that the degradation in compression property of the composite was less significant for the composite experienced the cyclic exposures than that with simply isothermal holding at the same temperature and with the same exposure duration. Upon compression tests, microstructural observations revealed that the matrix resin at fractured surface region showed a more fragmented feature for both the cyclic exposed and isothermal held samples.

KEYWORDS: Vinyl ester composite, hygrothermal aging, environmental durability.

INTRODUCTION

Composites based on vinyl ester are being increasingly used as various structural components due to their fast fabrication cycles and some desirable performance behaviors. These structural components might be exposed to various environmental conditions during their lifetime in services. Some of the most common environmental conditions encountered are various weathers, such as rain, snow, hot and cold climate. It is known that vinyl esters contain a large number of hydroxyl groups along their molecules, which makes vinyl ester based composites prone to absorb moisture from environments. Such moisture absorption could cause volumetric expansion of the matrix and debonding at the fiber/matrix interface [1-4]. It could also accelerate thermal decomposition of the matrix resin at elevated temperatures [5-6]. These effects will deteriorate the service performance and long-term durability of the materials [1, 7] and may result in a premature failure of whole structure.
Therefore, it is important to study the moisture absorption behaviors as well as environmental effects on the properties of the composites.

In this study, cycling exposures of hot/wet and cold/dry environments were applied to glass/vinyl ester composite samples. The use of this environmental cycling was to simulate the harsh temperature and moisture conditions the composites might encounter. Moisture absorption characteristics of the composite during the environmental exposures and hygrothermal effects on the glass transition, thermal decomposition behaviors, and mechanical properties of the composite were investigated.

**EXPERIMENTAL**

(1) Materials and Processing

Composite panels made of S2-glass fabric (2 x 2 twill weave) and vinyl ester 411-350 were used for the study. The panels were fabricated by vacuum aided resin infusion (VARI) with room temperature curing.

(2) Environmental Conditioning

The S2/411-350 composite samples were alternatively held in a container saturated with steam at elevated temperature and then a freezer to simulate hygrothermal freeze/thaw cycling. The cycling conditions were 80°C/saturated steam/48 hours ↔ -17.8°C/dry/24 hours.

The dimensions of the specimens were 64 x 36 x 22 mm, 25 x 25 x 22 mm, or 25 x 8 x 3 mm for moisture absorption measurements, compression testing, and dynamic mechanical analysis (DMA), respectively.

(3) Measurements and Testing

**Moisture Absorption Measurement** Specimens were weighed in certain time intervals during the hygrothermal exposures. The average weight change of three specimens was used to characterize the moisture absorption of the composite.

**Compression Testing** Compression tests were performed using MTS testing machine. A compressive load was applied along the direction of the thickness of the specimen, as shown in Fig. 1, and the crosshead speed used was 0.05 in/min.

![Fig.1 Schematic diagram of the fixture used for compression tests.](image-url)
**Dynamic Mechanical Analysis** Single-cantilever clamping was used for the DMA tests using TA Instruments DMA2980. The frequency used was 1 Hz and the heating ramp 5°C/min.

**Thermogravimetry Analysis** Thermal stability of the composite was determined using TGA2050 of TA Instruments with a heating rate of 5°C/min. The samples were in powders drilled from the specimens.

**Microstructural Observation** Fracture surfaces of the composites after compression tests were examined using an Amray 1610 scanning electronic microscope (SEM).

**RESULTS AND DISCUSSIONS**

(1) Moisture Absorption

The characteristics of moisture absorption of the glass/vinyl ester composite during the hygrothermal freeze/thaw cycles were shown in Fig. 2. It can be seen that the net moisture absorption amount increased with an increase in exposure time. The absorption rate was quite high at the early stage, followed by a moderate rate period, and reached to a saturate status after about 700 hours with a maximum of 0.24% weight gain. In addition, it was noticed that the moisture absorption amount also experienced cyclic increase and decrease during each freezing and thawing period, respectively.

![Fig. 2 Percentage weight gain of the specimens versus exposure duration for the glass/vinyl ester composite.](image-url)
The total permanent weight gain of the composite after the exposures was measured by removing the specimens from the hygrothermal environment and drying in a vacuum oven. It was about 0.15% after 33 cycles of the hygrothermal exposures.

(2) Physical and Mechanical Properties

It was observed that the color of the composites changed from initial light green, as-received, to yellow, and to light brown during the environmental exposures, which indicated that oxidation of the vinyl ester occurred.

Compression tests were performed to investigate the cycling effects on the mechanical properties of the composite. The retention ratios of compression strength as a function of cycling number and duration are shown in Fig. 3. There was only a minor drop in the compressive strength after 33 cycles, corresponding to a total duration of 1584 hours, at 80°C. The compression fracture of the composite was found to be caused by sliding between layers perpendicular to the load direction, as shown in Fig. 4.

In addition, these retention ratios of compression strength of the specimens experienced the freeze/thaw cycling were compared with those of the specimens experienced simply isothermal holding at the same temperature and moisture conditions, also shown in Fig. 3. It can be seen that the degradation of the compression property was less significant for the former than for the latter at the same temperature of 80°C and with the same exposure duration.
(3) Thermal Properties

Glass transition temperature and thermal decomposition onset temperature of the composite, both before and after the environmental conditioning, are listed in Table 1. It was found that the glass transition temperature, $T_g$, initially increased with hygrothermal cycling duration and then leveled off after 33 cycles, a total of 1584 hours exposures, at 80°C. It was believed that the increase in $T_g$ was due to the increase of crosslinking degree resulted from postcure and oxidation of vinyl ester.

Thermal decomposition onset temperature showed only a slight change with an increased hygrothermal duration, which indicated that thermal stability of the composite was not sensitive to hygrothermal exposure at 80°C.

Table 1 Glass transition temperature and thermal decomposition onset temperature of the glass/vinyl ester composite before and after the environmental conditioning.

<table>
<thead>
<tr>
<th>Cycling exposure duration at 80°C (hour)</th>
<th>Glass transition temperature $^1$ (°C)</th>
<th>Thermal decomposition onset temperature $^2$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>124.1</td>
<td>300.1</td>
</tr>
<tr>
<td>288</td>
<td>129.1</td>
<td>301.2</td>
</tr>
<tr>
<td>720</td>
<td>131.8</td>
<td>303.0</td>
</tr>
<tr>
<td>1200</td>
<td>135.4</td>
<td>302.7</td>
</tr>
<tr>
<td>1584</td>
<td>134.4</td>
<td>302.1</td>
</tr>
</tbody>
</table>

1. Defined as the peak temperature of tan δ in DMA spectra.
2. Defined as the temperature at 95% weight loss in TGA tests.

(4) Microstructures

Fracture surfaces of the composites after compression testing were examined by scanning electronic microscopy (SEM) to evaluate environmental cycling effects on the microstructures and failure modes. It was found that the matrix resin of the composites experienced the environmental cycling or isothermal exposure became more fragmented and showed deteriorated adhesion with fibers (Fig. 5a), as compared with that of the composite without conditioning (Fig. 5b).
CONCLUSIONS

From this study, the following conclusions can be drawn.

(1) Moisture absorption of the composite showed increasing and then decreasing cycles during each freeze and thaw period.
(2) Glass transition temperature of the composite increased with hygrothermal cycling duration and leveled off beyond 1000 hours in the hygrothermal exposures.

(3) Thermal stability of the composite was only slightly influenced by the hygrothermal exposure at 80°C.

(4) The degradation in compression property was less significant for the composite experienced hygrothermal cyclic exposures than that undergone simply isothermal holding at the same temperature and with the same duration.

(5) Microstructural observation revealed that, for the composite exposed to either hygrothermal cycling or simply isothermal holding, the matrix resin in fractured surface region showed a more fragmented microfeature, as compared with that without any environmental conditioning.

REFERENCES


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