Guijun Xian*, Peng Yin, Innocent Kafodya, Hui Li and Wei-lun Wang

Durability study of ramie fiber fabric reinforced phenolic plates under humidity conditions

Abstract: A durability study of a ramie fiber fabric reinforced phenolic resin (RFRP) plate under 50%, 85%, and 98% relative humidity for 6 months at room temperature was performed. Water absorption and desorption, tensile and short beam shear strengths of the RFRP plates were investigated as a function of exposure time. RFRP samples show strong hydrophilic characteristics and the saturated water content varies from 0.73% to 4.5% with relative humidity ranging from 50% to 98%. After 6 months of exposure to 98% relative humidity, an abnormal extra amount of moisture was absorbed, which may have resulted from cracks in the resin matrix or from debonding between fiber and resin due to swelling of the fibers with high moisture content. It was found that the tensile modulus is more susceptible to moisture uptake, which is ascribed to the degradation of ramie fibers with the water ingress. An approximate linearity between the mechanical properties and the moisture content is observed if the abnormal extra water uptake is neglected. Both tensile and short beam shear strengths of the RFRP samples recovered remarkably when samples were fully dried at 60°C, indicating a low degree of permanent degradation occurred due to the exposure.

Keywords: desorption; humidity; mechanical properties; ramie fiber; water absorption.

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1 Introduction

There is a growing urgency to develop and commercialize plant fiber reinforced polymer composites in different applications, such as aerospace structures, automotive parts, building materials, and sporting tools [1]. The main advantages of these materials include competitive mechanical properties, low density, low cost, less equipment abrasion, less toxicity, good vibration damping properties, excellent recovery of energy, renewability, recyclability, etc. Natural fiber composites have been designed for different applications ranging from products of commodity to aerospace, examples including auto parts, building, and constructive materials [2]. The conventional fiber reinforced petroleum-based composites, such as aramid, carbon and glass fibers, can be replaced by natural fibers, such as hemp, jute, wood, ramie, and some other cellulose products that are environmental friendly [1, 3–8].

Ramie, also called China grass is a hardy perennial herbaceous plant of the Urticaceae family, which can be harvested up to six times a year in China. Ramie grows up to 1–2.5 m tall and the fiber is stripped from the bast layer surrounding its stem core. Ramie fiber is best used as fiber reinforcement, due to its long length, high strength, and good thermal conductivity. It is known especially for its ability to hold shape, reduce wrinkling, and provide a silky luster to the fabric appearance [9–11].

However, all plant fiber reinforced polymer composites absorb moisture when exposed to humid environments or immersed in water [12]. Several studies have reported the effects of moisture absorption on mechanical properties of fiber reinforced polymer. It has been found that moisture absorption leads to swelling of the fibers, formation of voids and micro-cracks at the fiber-matrix interface. These moisture induced defects inhibit stress transfer through the fiber-matrix interface and, in turn, causes reduction of composites’ mechanical properties [3, 12–17]. The principal components of the ramie fiber are cellulose, hemicelluloses, and lignin. Lignin is composed of large number of hydroxyl groups [9, 18–20]. The disadvantages of ramie fiber reinforced composite (RFRP) in engineering application include its susceptibility to
moisture absorption and poor physical, mechanical, and thermal properties under humid environment.

In the present study, ramie fiber reinforced phenolic resin plates were produced by preparing prepregs using hand layup method followed by a hot compression molding process. The phenolic resin was selected as matrix, mainly due to its excellent fire resistance. The prepared RFRP samples were exposed to various humid environments at room temperature. The water uptake and the mechanical properties were investigated over a given exposure period. In addition, the effects of drying RFRP samples after exposure were also studied. The study aimed to bring an understanding of the relationship between the water uptake and the moisture induced degradation in mechanical properties of RFRP composite.

2 Materials and methods

2.1 Raw material

Ramie fiber fabric was provided by the Beijing Institute of Aeronautical Material (Beijing, China). The warp/weft density was 64×66 and the areal density was 140 g/m². The phenolic resin with brand name F51 was purchased from Nantong Xingchen Synthetic Material Co. Ltd. (Nantong City, China). This resin is specially designed to facilitate the manufacture of fiber prepregs. The solid content of the resin system was 65%∼80%, with viscosity of ~300 cPs. The resin curing temperature and period were 130°C and 2 h, respectively. The final cured resin was a thermosetting.

2.2 RFRP sample fabrication

The ramie fiber fabric reinforced phenolic resin (RFRP) plate samples were prepared with ramie fiber fabric and liquid phenolic resin. Two steps were used to prepare RFRP plates, that is, preparation of ramie fiber prepregs and hot compression molding.

The preparation of prepregs was carried out using the following procedures. First, phenolic resin was diluted with acetone to 80% solid content. Ramie fabric was then impregnated with the diluted phenolic resin using brushes. The impregnated fabrics were finally kept in a dark and well-ventilated room for at least 2 days until acetone in the resin volatilized completely. The ramie prepregs with phenolic resin were then ready for the hot compression molding process.

Hot compression molding process was carried out by the following procedures. First, 12 pieces of prepregs (25×25 cm) were molded in a hot compression molding machine (XLB model, Dongya Nanxing Jixie Co., Qingdao, China) at 130°C with a pressure of 10 MPa for 2 h and then the mold was cooled at the constant pressure until the temperature dropped to room temperature. The cooling speed of mold was about 2°C/min. The prepared RFRP plate was 2.77 mm in thickness and the volume of ramie fabric was about 40.4% determined by the areal density of the plate.

2.3 Humid environments

The experimental humidity environments were prepared by saturated salt solution. The types of salt solution and their corresponding relative humidity are shown in Table 1.

2.4 Moisture absorption and desorption tests

Prior to exposure to various humid conditions, all samples (25×25×2.77 mm³) for water absorption and desorption tests were oven-dried for 48 h at 60°C in accordance with ASTM D5229/5229M standard procedure D. After drying, each sample was weighed, and the mass was designated as its initial mass, M₀. During exposure, samples were periodically weighed according to the test plan (i.e., 2 h, 4 h, 8 h, 1 day, 2 days, 4 days, 1 week, 2 weeks, 1 month, 3 months, and 6 months) and mass changes were recorded.

After exposure for 180 days, samples were taken out and dried at 60°C in an oven. The mass change of the samples was recorded as a function of drying time.

For each condition, ten samples were repeatedly tested; mean value and standard deviation were reported.

2.5 Mechanical properties test

Tensile test for RFRP samples was conducted according to ASTM D3039. The RFRP plates were cut into 250×15×2.77 mm³ test samples. The test was carried out at load speed of 5 mm/min with extensometer gage length of 50 mm.

<table>
<thead>
<tr>
<th>Salt solution type</th>
<th>Relative humidity</th>
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<tbody>
<tr>
<td>NaBr</td>
<td>50%</td>
</tr>
<tr>
<td>KCl</td>
<td>85%</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>98%</td>
</tr>
</tbody>
</table>
The short beam shear strength (SBS) of the RFRP samples was tested according to ASTM D2344/D2344M. The size of the samples was 16.6×5.5×2.77 mm³. The testing span was 11 mm and the test speed rate was 1 mm/min.

3 Results and discussion

3.1 Moisture absorption and desorption

The moisture uptake of RFRP samples exposed to three relative humidity environments at room temperature in 6 months are presented in Figure 1, by plots of weight gain as a function of square root of exposure time. Under 50% and 85% relative humidity, the moisture uptake increases linearly at the beginning of the exposure period, followed by levelling off with extended exposure time.

However, under 98% relative humidity (RH) environment, except for the last testing value, the moisture uptake curve clearly follows the trend of lower relative humidity conditions. The last testing value of the moisture uptake curve tends to increase with the exposure time, deviating from the saturated moisture content. The phenomenon may be attributed to cracks of resin or interfacial debonding between the fiber and resin matrix due to the fiber swelling with the high moisture content (~4.4% for saturated moisture content) of the RFRP samples. The mechanisms of crack formation due to fiber swelling with water uptake was also reported elsewhere [21].

According to the moisture absorption curves (Figure 1), the moisture diffusion process in the RFRP samples can be described by the classic Fick’s law for the case of the lower relative humidity (i.e., 50% and 85% RH) environments. For the case of 98% RH, the last testing value is believed to be due to the cracks of resin or interfacial debonding in the samples, therefore, Fick’s law is not applicable for the whole moisture absorption process.

To facilitate comparison of moisture absorption and diffusion parameters, Fick’s law was also applied to the 98% RH cases. The last abnormal moisture uptake point was not considered for curve fitting. The coefficient of diffusion was determined by curve fitting method using the simplified Fick law equation [22]:

\[ M(t) = M_\infty \{ 1 - \exp[-7.3(Dt/h^2)^{0.75}] \} \]

where \( M(t) \) is the moisture absorption after exposure time \( t \), \( M_\infty \) is the saturated moisture content, \( D \) is the water diffusion coefficient, and \( h \) is the average thickness of the samples (\( h = 2.77 \text{mm} \)).

The determined saturated moisture content \( (M_\infty) \) and the coefficient of diffusion \( (D) \) with curve fitting method are summarized in Table 2. It is indicated that the saturated water content increases remarkably with increase in relative humidity, while \( D \) decreases rapidly.

It is reported that the saturated moisture content \( (M_\infty) \) mainly depends on the relative humidity of the environment while \( D \) depend on the temperature. The variation of the saturated moisture content as a function of humidity \( (\Pi) \) can be described by the following equation [23]:

\[ M_\infty = a\Pi^b \]

where \( a \) and \( b \) are constants, depending on the type of materials.

The constants of \( a \) and \( b \) for the present studied RFRP samples determined with Equation 2 are 0.12 and 2.48, respectively. Note, for the carbon fiber reinforced FRP composites [24], \( a \) is around 0.01–0.02 and \( b \) is about 1. The much higher values of \( a \) and \( b \) of RFRP samples indicate that the RFRP possesses much higher hydrophilic characteristics compared to the synthetic fiber based FRPs.

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>( M_\infty ) (wt%)</th>
<th>( D ) (mm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.73</td>
<td>5.50×10⁻⁶</td>
</tr>
<tr>
<td>85</td>
<td>2.09</td>
<td>2.08×10⁻⁶</td>
</tr>
<tr>
<td>98</td>
<td>4.40</td>
<td>0.83×10⁻⁶</td>
</tr>
</tbody>
</table>

Figure 1 Moisture uptake curves of ramie fiber fabric reinforced phenolic resin under three kinds of humidity at room temperature. Note the solid lines represent the curve fitting results with Equation 1.
It is known that plant fiber is composed of groups of cellulose macromolecules and lignin, which possess a high portion of hydroxyl groups [18]. In addition, there are cell cavities in natural fibers, which offer extra spaces for absorbed water [25]. The high proportion of hydroxyl groups and the cell cavities endow the RFRP with the strong hydrophilic characteristics (as shown in Table 2).

After 6 months of exposure to the humid environments, RFRP samples were subsequently dried in an oven at 60°C and the weight change was recorded periodically. The percentage of the moisture desorption, \( W_t \), was determined using the following equation:

\[
W_t(\%) = \frac{(M_t - M_o)}{M_o} \times 100
\]

where \( M_t \) is the weight after drying time \( t \), \( M_o \) is the initial weight (before exposure to humid environment).

The moisture desorption results are presented by the plot of weight loss of the samples as a function of square root of drying time in different humid environments as shown in Figure 2.

It is indicated that the moisture desorption decreases rapidly in the initial stage, and slowly reaches a leveling-off stage. After being fully dried, the weight loss of the samples (indicated by negative \( W_t \) after drying) determined from Figure 2 is around 2.87%, 3.14%, and 3.10% for 50% RH, 85% RH, and 98% RH, respectively. The weight loss of the samples is attributed to the evaporation of the residual acetone (used for diluent during prepreg preparation) and/or small phenolic resin molecules, which were unreacted during the hot compression process.

3.2 Tensile and short beam shear properties

The tensile stress-strain curves of the un-aged and aged RFRP samples in humid environments for 6 months are presented in Figure 3. As shown, the tensile strain-stress curve of the un-aged RFRP plate is approximately linear. After exposure to relative humidity environments, the stress-strain curve departs from linearity, with increased elongation at break, and reduced fracture stress and modulus.

Figure 4 presents the variation of the tensile strength of RFRP samples as a function of exposure time under three humidity environments at room temperature. As indicated, under 50% RH condition, the tensile strength of the samples exhibits a slight decrease after the first 30-day exposure, and then recovers slowly with extension of the exposure time. After 180 days of exposure, the tensile strength of the RFRP samples under 50% RH is slightly higher than that of un-aged samples. The increase of the tensile strength is caused by the postcuring of the resin system.

Samples exposed to relatively higher RH conditions (i.e., 85% RH and 98% RH) exhibit remarkable degradation in the tensile strength (Figure 4). The effects of 85% RH and 98% RH on the tensile strength are very similar.
After 6 months of exposure to 85% RH and 98% RH environments, the tensile strength of the RFRP samples remains 80%–83% of the original value (81 MPa).

In comparison, the tensile modulus of RFRP samples are more susceptible to the humidity than tensile strength. As presented in Figure 5, after the initial 30 days of exposure, the tensile modulus of RFRP samples decreased by 43%, 56%, and 70% for 50% RH, 85% RH, and 98% RH, respectively. With further increase in the exposure time, the tensile modulus tends to increase slightly. After 6 months, the tensile modulus of the RFRP samples remains 78.4% of the initial value for 50% RH and ~50% for the rest RH conditions.

As shown in Figure 6, the elongation at break increases significantly with exposure to the humid environments and the maximum value is reached after 60 days of exposure. After 6 months of exposure, the elongation at break increases by 87%, 138%, and 177% under 50% RH, 85% RH, and 98% RH, respectively.

Natural fibers, such as ramie fibers, show strong hydrophilic characteristics. Thus, the water ingress into RFRP samples causes the fiber, resin matrix, and the fiber-matrix interfaces to degrade. The deterioration of the ramie fibers is believed to play a key role in the degradation of the tensile properties, especially the degradation of the tensile modulus. This trend is contrary to that of conventional fibers, that is, glass or carbon fiber reinforced polymer composites, whose tensile modulus is generally not affected by hygrothermal aging [26]. The difference in trend can be attributed to the synthetic fibers being insusceptible to moisture ingress, contrary to the natural fibers. The modulus of RFRP is mainly dependent on the modulus of the reinforcing fibers of a continuous fiber reinforced FRP composite.

Figure 7 shows the tensile fracture surfaces of aged and un-aged RFRP samples. Compared to the un-aged samples (Figure 7A and B), the surfaces of RFRP samples exposed to 98% RH for 6 months show remarkable fiber-resin matrix debonding (Figure 7C and D). No fibers and fiber bundles are covered by any resin matrix after fracture. On the contrary, the fibers, as well the fiber bundles, are attached to a thick layer of resins for the un-aged samples (Figure 7A and B). The scanning electron microscopy (SEM) pictures clearly indicate that water ingress dramatically reduces the bonding between the resin and...
the ramie fibers. As expected, the water ingress between the interfaces may destroy the hydrogen bonding between the resin and the fibers. In addition, the ramie fibers may swell with the absorbed water. Those effects of the water ingress are believed to be responsible for the degradation of the bonding properties between the fiber and resin system.

Variation of the short-beam shear strength of RFRP samples with the exposure time is shown in Figure 8 for three humidity conditions. As shown for 50% RH condition, the SBS strength is slightly enhanced. However, higher humidity cases indicate remarkable decrease of SBS strength after the first month of exposure, and SBS strength bounces back to some extent with extended exposure time. The ultimate loss of the strength after 6 months for samples under 85% RH and 98% RH was 9.48% and 21.77%, respectively.

Take note that the short beam shear strength can indirectly reflect the interlaminar bonding strength between fiber and resin matrix. The degradation of the SBS strength of RFRP subjected to high humidity is in accordance with the above SEM observation and analysis on the bonding between the fiber and resin matrix.

![Figure 7](image_url) Scanning electron microscope pictures of ramie fiber fabric reinforced phenolic resin (RFRP) fracture surfaces due to tension. (A, B) Un-aged RFRP sample. (C, D) Aged RFRP samples under 98% relative humidity for 6 months.

![Figure 8](image_url) Variation of the short-beam shear strength as a function of exposure time of ramie fiber fabric reinforced phenolic resin samples at room temperature.
In view of this, the final moisture content does not count, and the mechanical properties seem to decrease linearly with the moisture content. Therefore, the retention of each mechanical property as a function of water content (M) can be obtained by linear fit. The retention of the tensile strength ($\sigma_r$) is described as $\sigma_r = 1.033 - 0.065m$; the retention of the tensile modulus ($E_r$) is described as $E_r = 0.81 - 0.10m$; and the retention of SBS strength ($\sigma_{sr}$) is described as $\sigma_{sr} = 1.02 - 0.08m$. Clearly, the modulus is much more susceptible to the moisture content. The effect of the moisture content on the tensile strength and SBS strength shows a similar trend.

3.4 Mechanical properties of dried samples

To understand the effect of water ingress on the mechanical properties of RFRP samples, the RFRP samples exposed to various humidity environments for 6 months were tested immediately after exposure and after fully dried at 60°C. The variation of the mechanical parameters compared to those of un-aged RFRP samples are summarized in Table 3.

As shown, after drying, the tensile strength, modulus and SBS strength increase remarkably compared to the “wet” samples. The tensile strength of dried samples exposed to 50% and 85% RH conditions is even higher than that of un-aged samples. It is worth noting that the tensile modulus of dried samples remarkably recovers by 90–95% of its original values.

The remarkable recovery of the mechanical properties of the RFRP samples due to drying indicates that the degree of the permanent degradation of the fiber, resin, and the bonding between the fiber and resin matrix after exposure was limited. However, the permanent degradation in the tensile strength and modulus is much more serious under 98% RH compared to the other conditions.
4 Conclusions

In the present study, RFRP plates were subjected to three humidity environments at room temperatures for 6 months. The moisture uptake and the mechanical properties of RFRP plates were investigated. The following conclusions were drawn after the study.

RFRP samples show strong hydrophilic characteristics and the saturated water content varies from 0.73% to 4.4% under the environments from 50% to 98% RH. After 6 months of exposure to 98% RH, extra moisture absorbed by cracks or interphases between fiber and resin might be due to swelling of fibers with high moisture content.

RFRP samples show clear degradation in tensile strength, modulus, and short beam shear strength when exposed to humidity. Tensile modulus is much more susceptible to the moisture uptake, which is ascribed to the degradation of ramie fibers with water ingress.

The tensile strength, modulus and short beam shear strength are decreased with the moisture content. An approximate linearity between the mechanical property and the moisture content is observed if the abnormal moisture content is negligible.

After fully dried at 60°C, both the tensile and short beam shear properties of the RFRP samples recovered remarkably, indicating low degree of permanent degradation after exposure. However, the RFRP samples show more permanent degradation under higher humidity.

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