Evaluation of Seawater Exposure on Mechanical Properties and Failure Behavior of E-Glass/BMI Composite for Marine Use

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ABSTRACT

Since composite material is playing an increasingly important role in the marine and offshore drilling industry, it is essential to have a good understanding on degradation of the material in the seawater environment. This study investigates the influence of seawater exposure on the mechanical and failure behavior of E-Glass/BMI composite. The water diffusion behavior in the composite has been studied through immersing the specimens in seawater under different conditions. The diffusion rate accelerates with increase of temperature, and the material shows irreversible damage due to seawater absorption at the temperature of 80°C. It is also found that external stress would significantly increase the water absorption. The water uptake in the specimen at 50°C showed a two stage behavior dominated by Fickian law and polymeric relaxation respectively, and saturation was not achieved in 8 months. After diffusion, the $\epsilon$ of the material is considerably lowered due to plasticization effect. However the effect was found to be reversible after drying the specimen. Based on the testing results of tensile, flexure and fatigue properties of the composites, it is concluded that seawater exposure especially at elevated temperature leads to significant degradation on mechanical properties of the composite. However, the flexural strength of BMI composite with seawater absorption becomes less susceptible to temperature change. It is also found that the seawater absorption doesn't show significant effect on the stiffness of the material.

Keywords: Bismaleimide, Environmental effect, Water diffusion, Hygrothermal behavior

1. INTRODUCTION

BMI composites have excellent physical property retention at elevated temperature which makes them suitable for applications requiring a wide range of service temperature such as risers and pipelines. However, researches have shown in literature that water absorption has great effect on mechanical properties of composite materials. For most fiber reinforced polymers, fibers are relatively insensitive to water absorption compared with their polymeric matrices. Therefore, the change of mechanical properties is mainly through matrix phase. This subject has become more and more important for ever-increasing applications of composites in offshore structures, submersibles and civil infrastructures. In addition, the uncertainty of long-term durability of the polymeric composites in natural environment has been a limiting factor to further use of these materials. Therefore, this study investigates the effects of seawater exposure on the mechanical properties of BMI composites at different temperatures.
2. EXPERIMENTAL

The material used in this study, denoted as GF/BMI, was fabricated by prepregs of bismaleimide resin system Hexply F655 premixed with plain woven fiber glass HexForce 1581. The laminate is laid with 8 plies of prepregs and cured in autoclave. The post cure process was carried out by 6 hours of heating at 243°C. All the laminates were cut into rectangular strips using water-jet cutting and smaller specimens using diamond cutter. The dimensions of the specimens are listed in Table 1. In diffusion test, the specimens were first desiccated in vacuum oven for 48 hours at 50°C before soaking in artificial seawater in plastic containers and kept in the oven maintaining at testing temperature. The artificial seawater, which contains 3.5% salinity, was prepared by dissolving sea salt into water. Five specimens with similar weights after desiccation were chosen to obtain the average value of the weight change in percentage. For re-dried samples, they were desiccated in vacuum oven again after the diffusion test until the difference was less than 0.1% compared to their original weight. Dynamic mechanical analysis was conducted in cantilever bending mode to study the viscoelastic behavior of the polymeric composite. Temperature sweep with fixed frequency mode determines the glass transition temperature while temperature step with frequency sweep mode, on the other hand, was used to generate master curves and shift factors for time temperature superposition method. A computer program based on least Chi-square method automates the procedure in this study. Tensile test and tension-tension fatigue tests was carried out on MTS 810 elastomer test system. Extensometer attached on the specimen test measures the strain in tensile test. In fatigue tests, constant amplitude loading pattern with force control were used and the testing frequency and waveform were set to be 5Hz and tapered sine curve respectively for all the tests. The flexural strengths of the material at temperatures ranging from 30°C to 260°C were measured by three-point bending on Instron 5569 with cross head speed of 0.5mm/min.

<table>
<thead>
<tr>
<th>Testing Methods</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic Mechanical Analysis</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>3-point bending test</td>
<td>80</td>
<td>15</td>
</tr>
<tr>
<td>Diffusion test/Tensile test/Fatigue test</td>
<td>230</td>
<td>15</td>
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</table>

3. RESULTS AND DISCUSSION

3.1 Water absorption behavior of woven GF/BMI laminate

Fig. 1 exhibit the diffusion characteristics of 8-ply GF/BMI laminates immersed in 30°C, 50°C and 80°C seawater environment, respectively. The averaged results of five specimens were used at each temperature level. The \( M(t) \) is the percentage change in weight of the specimen after immersing in seawater for time \( t \), and is given as

\[
M(t) = \frac{m(t) - m_{dry}}{m_{dry}} \times 100\% \tag{1}
\]

where \( m(t) \) is the weight of the specimen at time \( t \) after immersion and \( m_{dry} \) is the weight of dry specimen. As shown in Fig. 1, an increase in temperature accelerates the diffusion rate of seawater, indicating that the diffusion is a thermal activated process. However, in 80°C environment, a rapid rise in water content of the weight gain curve of 80°C suggests irreversible fluid-induced damage of the material. As described by Y.J. Weisman and M. Elahi [1], this kind of diffusion behavior is commonly associated with extensive interfacial fiber/matrix debondings. For all three experimental temperatures, GF/BMI specimens had not reached saturation in the entire period of diffusion tests.
It was reported in several studies [2, 3] that the widely used Fickian model is not sufficient in describing hygrothermal diffusion behavior in many fiber reinforced polymer composites. A two-stage diffusion behavior was found in the moisture uptake in those polymeric composites. The first stage diffusion is dominated by concentration gradient and the diffusion followed Fickian model. The second stage diffusion however is dominated by polymer relaxation as the rearrangement of polymer chains slowly took place, which increases the water absorption. In this two-stage diffusion, the diffusion rate at first stage is much higher than the second stage since polymer relaxation is a very slow process comparing to gradient concentration diffusion. Fig. 2 shows the diffusion characteristic of BMI composite immersed in 50°C seawater. Initially, the experimental data is in good agreement with Fickian law, which can be expressed as,

$$M(t) = M_\infty \left[ 1 - \frac{G}{k} \right]$$

where $t$ and $h$ are the time and specimen thickness respectively, and $M_\infty$ is the Fickian equilibrium of water absorption per unit weight. However, a second stage water absorption is observed where the absorption diverges from the Fickian equilibrium. This non-Fickian absorption behavior is the result of combined effect of concentration gradient controlled diffusion and polymer relaxation. Normally the concentration dominates the initial water absorption behavior since it is a more rapid process than relaxation of polymer. Berens and Hopfenberg [4] proposed a diffusion model as a linear superposition of Fickian diffusion and polymeric relaxation and the mathematical expression of this model is expressed as,

$$M(t) = M_\infty G + \sum_i M_{\infty,i} [1 - \exp(-k_i t)]$$

and

$$G = 1 - \frac{8}{\pi^2} \sum_{j=0}^\infty \left( \frac{1}{2j+1} \right)^2 \exp \left[ -\left(2j + 1\right)^2 \pi^2 \frac{Dt}{h^2} \right]$$

where $G$ is the absorption due to polymer relaxation.
where $M_{\infty,F}$ is the Fickian equilibrium. $M_{\infty,i}$ and $k_i$ are the equilibrium absorption and relaxation rate constant of $i^{th}$ relaxation mode respectively. It was found in this study that the model is sufficiently accurate with first three terms in Fickian law and single relaxation mode. The obtained $M_{\infty,F}$ and $M_{\infty,1}$ are 0.96% and 0.52% respectively. The diffusivity and relaxation rate constant were calculated as $M_{\infty,1} = 1.79 \times 10^{-3} \, mm^2 / hr$ and $k_1 = 1.14 \times 10^{-4} / hr$.

Figure 2: Modelling diffusion behavior of 8-ply woven GF/BMI laminate at 50°C

3.2 Long-term viscoelastic response GF/BMI composites in seawater environment

Dry, wet and re-dried specimens were tested for their viscoelastic responses. The wet specimen in the following sections denotes to the 8-ply specimen having the same water content as those specimens at the end of 50°C diffusion test. Water as a spacer in the matrix strongly enhances the molecular mobility in the vicinity of glass transition temperature and therefore shifted the $T_g$ of the materials to a lower value. The $T_g$ of GF/BMI dropped about 40°C after diffusion due to the plasticization effect. Fig. 3 shows the glass transition temperatures and onset temperatures of specimens under different conditions. Three wet samples were dried in vacuum oven again and tested as re-dried samples. The storage modulus curve of re-dried specimen returns to the similar shape of dry specimen with about 2.4% reduction, and the $T_g$ is back to the original value as well. This suggests that the effect of water absorption of BMI composite up to 50°C is reversible and no obvious chemical reaction has taken place. Similar conclusion was given by Li et al. [2] using FTIR analysis.

The viscoelastic response curves at different temperatures can be shifted along the logarithmic time axis to construct the superimposed master curve. This is the well-known time-temperature superposition principle of viscoelastic material, and it is the key idea of predicting long-term properties of composite material by short-term tests [5]. Fig. 4 demonstrates the construction of master curve of storage modulus log $E'$ verses reduced time $t'$ for dry specimen by shifting storage modulus curve at different temperatures along time axis in log scale. The obtained master curves for wet and re-dried specimens are also presented in Fig. 4 as solid and dash lines respectively. All the shifting procedures were successfully done using the computer program. The results show that storage modulus of GF/BMI composite at various temperatures superimposed perfectly, generated smooth master curves. The shift factors of the master curves are displayed in Fig. 5. At low temperatures, the shift factors of wet samples are almost identical to that of dry sample while the deviation starts when temperature rises close to glass transition temperature.
Figure 3: Onset temperatures and of specimen

Figure 4: Construction of master curves of storage modulus for GF/BMI specimens
3.3 Tensile and flexural behavior of GF/BMI composites with seawater exposure

Five GF/BMI specimens were tested with tensile stress loaded until failure at room temperature with cross head speed of 0.2mm/min for each condition (dry and wet). The averaged experimental results of basic mechanical properties obtained from tensile tests are presented in table 2. The water absorption effect on the Young's modulus of the GF/BMI composite was negligible, however the ultimate tensile strength of the material dropped slightly. In general, the GF/BMI composite seems to have a good retention of its tensile properties while working in wet environment, which is apparently an advantage for marine use. The experimental results of ultimate flexural strengths of dry and wet GF/BMI composites by three-point bending tests at different temperatures are shown in Fig. 6. The failure strength of dry specimen do not have much variation from room temperature up to 195°C, and even have a trend of increasing with elevated temperature. Nevertheless, the measured flexural strength reduced by 23.6% when temperature rose from 195°C to 260°C. The failure strength of wet specimen has been significantly reduced by 23% at temperature below 195°C due to the water absorption effect. However, it seems that the flexural strength of wet specimen is less susceptible with elevated temperature. A typical flexural failure process of GF/BMI composite was captured by high speed camera. The fracture appearances at the initial stage of matrix failure and crack propagation of the specimen are displayed in Fig. 7. The photo on the left shows that, at initial stage, a visible sign of failure occurred at the lower surface of the specimen on the tensile side where the stress is the highest. Then, with the deflection increased, the initiated cracks propagated from edge into the middle of the thickness accompanying with matrix failure, warp fiber buckling, pullout and breakage. An obvious delamination occurred in the middle plane as shown in the photo on the right and finally led to the failure of the specimen. The upper surface which suffered with highest compressive force remained almost intact throughout the entire failure process. The failure modes and processes were found similar in all three-point bending tests at various temperatures and strain rates. This indicates that all failures of flexural tests in this study were actually tensile failures with similar fracture process.
Table 2 Basic tensile properties of GF/BMI

<table>
<thead>
<tr>
<th>Condition</th>
<th>Young's modulus (Gpa)</th>
<th>Ultimate tensile strength (Mpa)</th>
<th>Poisson's ratio (v12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>26.42±0.36</td>
<td>315.5±15.48</td>
<td>0.133</td>
</tr>
<tr>
<td>Wet</td>
<td>26.56±0.52</td>
<td>285.24±14.23</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6: Flexural strength vs. Temperature for dry and wet GF/BMI specimens at 0.5mm/min

Figure 7: Sideviews of fracture appearances of GF/BMI composites at initial stage (left) and final stage (right)

3.4 Fatigue life of GF/BMI composite with seawater exposure

Fatigue tests were conducted to study the long term behavior and fatigue life of the material under cyclic loading. Tension-tension loading at various constant stress levels and ratios were performed and presented in terms of S-N curves. The testing results of dry and wet samples with stress ratio R=0.1, R=0.2 and R=0.5 are displayed in Fig. 8. This diagram demonstrates the relationship between the maximum tensile stresses applied on the specimens against its fatigue life in terms of failure cycles in log scale. Weibull distribution is commonly adopted in characterizing the probability of failure...
for composite materials. Here, the median failure cycles were obtained at each stress level through Weibull distribution and the semi-log linear relationship between applied cyclic stress and the number of cycles to failure is written as:

$$S = a \log(N) + b$$  \hspace{1cm} (2)$$

where $N$ and $S$ are fatigue life in terms of failure cycles and maximum tensile stress respectively. The parameters $a$ and $b$ are determined by curve fitting. Although the linear relation appears to be very accurate, it is not wise to blindly extend the prediction too much over the scale of the experiment results. Compared to dry samples at $R=0.1$, the samples with sea water absorption show significant reduction in fatigue life. For example, under 60% of ultimate tensile strength loading, the effect of water absorption results in a reduction of 36% of failure cycles for wet samples. However, the difference gets smaller with lower stress levels.

![Stress-life data](image)

**Figure 8:** Stress-life data for fatigue testing of stress ratios of $R=0.1$, $R=0.2$ and $R=0.5$

The normalized degradation curves of stiffness during fatigue tests are shown in Fig. 9. The curves exhibit a quick drop of stiffness within first 5% to 10% of life and then decrease linearly until failure occurs. Wet samples exhibit lower stiffness and faster degradation rate compared to dry samples especially within the linear region. Moreover, the degradation of stiffness is much more apparent for wet samples between higher and lower stress levels.
4. CONCLUSIONS

This study is concerned with the effect of seawater exposure on the mechanical properties and failure behavior of woven E-Glass/BMI composites. The diffusion rate increase with increase of temperature, and the material shows irreversible damage due to seawater absorption at the temperature above 80°C. At 50°C, the water diffusion showed a two stage behavior dominated by Fickian law and polymeric relaxation respectively. The saturations were not achieved for all temperatures. The glass transition temperature of the composite is considerably lowered due to plasticization effect of water. However, the effect was found to be reversible after drying the specimens at 50°C. The master curves constructed by storage modulus show that the degradation of the material has been accelerated due to seawater absorption and hence the life span is shortened as well. Based on the results of tensile, flexure and fatigue testing of the composites, it is concluded that seawater exposure especially at elevated temperature leads to significant degradation on many mechanical properties of the composite. However, the flexural strength of BMI composite with seawater absorption becomes less susceptible to temperature change. It is also found that the seawater absorption doesn't show significant effect on the elastic stiffness of the material.

ACKNOWLEDGEMENTS

This research was supported by Science and Engineering Research Council of Singapore under the program of Materials Innovation for Marine and Offshore applications (MIMO). The support is gratefully acknowledged.

REFERENCES