Durability Prediction of FRP composite materials under Hygrothermal Environment

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Abstract. This paper proposes a novel degradation model of mechanical properties of fiber-reinforced-polymer (FRP) composites under hygrothermal environment. The influence of moisture concentration, temperature and the long-term effects of hydrolysis are considered in the degradation model. The experimental data of E-glass/Vinylester under five hygrothermal environment conditions is used for the model validation and comparative study with traditional models. The results show that the prediction results correspond well with the experimental data. Comparative study shows that the proposed model has better accuracy in predicting the FRP durability for close-to-room temperature conditions, and the required number of fitting parameters is less.

1. Introduction
Fiber reinforced polymer (FRP) composites are commonly-used in engineering application including aerospace, ships, and civil structures because of their exceptional mechanical and chemical properties. During their service lives, FRP structures can be exposed to harsh hygrothermal environmental conditions in addition to mechanical loading, which can lead to a series of matrix-related changes, including matrix expansion, plasticization and hydrolysis, and degradation of fibers/matrix interfaces[1]. These matrix-related changes will cause a decrease in the mechanical properties of the composite material, which in turn will cause a decrease in the reliability of the structure. The Long-term hygrothermal exposure is bound to be a potential threat to structural safety.

The experiment evidences show that the strength characteristics decline is more significant than the modulus. N. Tual et al. [2] carries an experimental study on the sea water aging of carbon/epoxy composites. A decrease of 20% to 40% in failure strengths was measured, and no significant effects on the elastic moduli have been observed. A similar pattern is reported by Surathi P et al.[3], studying on the hygrothermal durability of glass fiber reinforced composites. While, a more serious strength drop has been observed in glass fiber reinforced composites, nearly 80% of the tensile strength is lost after 1440 days continuously-immersed in the 95℃ water. In addition, the bending strength and shear strength are seriously affected comparable to tensile strength.

Current researches generally assess the FRP durability by focusing on the remaining material performance [4-6]. Life prediction models are often used to predict performance hygrothermal degradation of FRP, e.g. Arrhenius model[7], Phani &Bose model[8] and Phillips model[3]. Surathi P et al.[3] compares above three models predicting the strength and modulus degradation. However, the comparative result shows that the predictive accuracy could be not ideal. Besides, a great number of fitting parameters are possibly required when the environmental conditions is varied, which can increase the experimental data. Considering the limitations above, this paper develops a novel degradation model of mechanical properties, for the hydrothermal degradation of FRP. The example
of E-glass/Vinylester is presented to prove the validation of the degradation model. The improvements of the proposed model is demonstrated by the comparison study with the traditional model.

2. Theory

2.1. FRP Degradation model

The remaining mechanical properties of FRP is represented by \( E(t) \), and \( E_0 \) stands for the ungraded properties. It is assumed that the degradation process obeys the law of exponential degradation, and affected by the current temperature and humidity status of the material:

\[
E = E_0 e^{-\alpha(T)\gamma(C)}
\]  

(1)

where \( \alpha(T) \) is a temperature-dependent ratio parameter, and \( \gamma(C) \) is a humidity-dependent ratio parameter. \( \alpha(T) \) is assumed to have a linear relationship with natural logarithm of temperature:

\[
\alpha(T) = k_a \ln(T) + b_a
\]  

(2)

\( k_a, b_a \) should be constants for the same material, and fitted by the experimental results at different temperatures. The non-linearity relationship between \( \gamma(C) \) and the relative moisture concentration is considered:

\[
\gamma(C) = \left( \frac{C}{C_{\text{max}}} \right)^\eta
\]  

(3)

where \( C \) is the moisture concentration, and \( C_{\text{max}} \) is the moisture concentration after the material reaches saturation. Organize the above formula to get:

\[
E(t) = E_0 e^{-\left(k_a \ln(T) + b_a + \gamma(C)\right)C_{\text{max}}^{\eta}}
\]  

(4)

Finally, the performance degradation caused by hydrolysis is considered. Degradation caused by hydrolysis is usually slow and uniform. Therefore, a hydrolysis item is introduced separately from the exponential function:

\[
E(t) = E_0 (1-\lambda t) e^{-\left(k_h \ln(T) + b_h + \gamma(C)\right)C_{\text{max}}^{\eta}}
\]  

(5)

where \( \lambda \) is the degradation rate caused by the hydrolysis. The complete form of the degradation model is shown in eq.(5). There are four parameters in total (\( k_a, b_a, \eta \) and \( \lambda \) ) to be experimentally fitted.

3. Examples

3.1. Experimental validation

The experimental data is provided by the study on performance degradation of E-glass/Vinylester composites with a fiber volume ratio of 50% to 55\%[3]. Test performance includes longitudinal tensile strength, modulus, and flexural strength. The least squares method is used to fit the parameters of the degradation model, and the fitting results are shown in Table 1.

| Table 1 Parameter fitting results of the proposed degradation model |
|-----------------|--------|------|-------|
|                 | \( \lambda \) | \( \eta \) | \( k_a \) | \( b_a \) |
| Tensile strength| 0.0002 | 0.5134 | 0.8567 | -2.7529 |
| Tensile modulus | 0.000048 | 1.4821 | 0.1383 | -0.4712 |
| Flexural strength| 0.00018 | 0.7982 | 0.9814 | -3.0341 |
Fig 1-3 present the predicted degradation curves of the residual tensile strength, tensile modulus and flexural strength respectively. The predictive degradation curves correspond well with the experimental results, which shows that the validity of model predictions. Besides, five temperature prediction results are predicted, provided that only four parameters are used. The small number of fitted parameters requires small number of experimental data, which could save the experiment cost for a variety of environmental conditions. The rate of degradation varies greatly at close-to-room temperature and the temperature over 60°C, which reveals that the temperature is a critical factor influencing on the hygrothermal durability.

![Figure 1](image1.png)

Figure 1  Comparison of the predicted and experimental residual tensile strength[3]

![Figure 2](image2.png)

Figure 2 Comparison of the predicted and experimental residual tensile module[3]
The result shows that different types of FRP mechanical properties, and properties at different temperatures can be well predicted. Only four parameters are needed to predict the FRP durability in the humid environment with varied temperature. Much less experimental data can be saved possibly when the proposed model is applied in engineering.

3.2. Comparative study
Table 1(Appendix) gives a detailed comparison of the accuracy of different models for predicting tensile strength degradation. The prediction accuracy of the proposed model are significantly better than the Arrhenius, Phani & Bose. At 23℃, the maximum absolute error of the Arrhenius and Phani & Bose models is 37%, 39%. While the proposed model predict with the error of only 4.8%. At 95℃, the maximum absolute errors of the Arrhenius and Phani & Bose models reach 48% and 65%, while the proposed model reaches 18%.

Compared with Phillips model, the proposed model has a higher accuracy in predicting degradation at low temperatures. At 23℃, the accuracy of the model in this paper is only 4.8%, and that of the Phillips model is 20%. The accuracy of the medium ambient temperature is competitive, and the prediction accuracy of Phillips model is better when the temperature is high.

The result shows that the proposed model has a competitive predicting accuracy, and stands out for the conditions with the temperature close to room temperature.

4. Conclusion
This paper proposes a novel degradation model of mechanical properties of FRP under hygrothermal environment. The validation of the degradation model is demonstrated. Different types of FRP mechanical properties, and properties at different temperatures can be well predicted. The prediction accuracy of the proposed model are significantly better than the Arrhenius, Phani & Bose, and more advantageous at low temperatures compared with Phillips model. Only four parameters for one performance are needed fitting using the proposed model, which reduce the number of parameters of other models when the temperatures are various.

The temperature is a critical factor influencing on the hygrothermal durability. The rate of degradation varies greatly at close-to-room temperature and the temperature over 60℃. The high temperature has adverse effects on the durability of FRP which is exposed to humid environment.
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### Appendix

Table 2 Comparison of the predictive accuracy of residual ratio of tensile strength using different degradation models

| T         | Time/days | Experiment [3] | proposed model | Arrhenius [3] | Phani & Bose [3] | Phillips |
|-----------|-----------|----------------|----------------|---------------|------------------|----------|
| 23℃       |           |                |                |               |                  |          |
|           | 0         | 1.00           | 1.00           | 1.00          | 1.00             | 1.00     |
|           | 90        | 1.00           | 1.02 (2.0%)    | 0.72 (-28%)   | 0.64 (-36%)      | 0.92 (-8.0%) |
|           | 180       | 0.99           | 1.00 (1.0%)    | 0.67 (-32%)   | 0.63 (-36%)      | 0.91 (-8.1%)  |
|           | 270       | 1.01           | 0.99 (2.0%)    | 0.64 (-37%)   | 0.62 (-39%)      | 0.91 (-10%)  |
|           | 360       | 0.94           | 0.97 (3.2%)    | 0.62 (-34%)   | 0.61 (-35%)      | 0.91 (-3.2%)  |
|           | 720       | 0.84           | 0.89 (4.8%)    | 0.57 (-32%)   | 0.57 (-32%)      | 0.90 (7.1%)  |
|           | 1440      | 0.75           | 0.74 (-1.3%)   | 0.52 (-30%)   | 0.50 (-33%)      | 0.90 (20%)   |
|           |           | Maximum absolute error | -             | 4.8%          | 37%              | 39%       |
|           |           | Average absolute error | -             | 2.0%          | 32%              | 35%       |
| 45℃       |           |                |                |               |                  |          |
|           | 0         | 1.00           | 1.00           | 1.00          | 1.00             | 1.00     |
|           | 90        | 0.78           | 0.69 (-12%)    | 0.65 (-17%)   | 0.63 (-19%)      | 0.54 (-31%)  |
|           | 180       | 0.75           | 0.66 (-12%)    | 0.59 (-21%)   | 0.62 (-17%)      | 0.51 (-32%)  |
|           | 270       | 0.77           | 0.63 (-18%)    | 0.56 (-27%)   | 0.60 (-22%)      | 0.50 (-35%)  |
|           | 360       | 0.68           | 0.61 (-10%)    | 0.53 (-22%)   | 0.58 (-15%)      | 0.49 (-28%)  |
|           | 720       | 0.53           | 0.56 (5.7%)    | 0.47 (-11%)   | 0.53 (0.0%)      | 0.46 (-13%)  |
|           | 1440      | 0.43           | 0.46 (7.0%)    | 0.41 (-4.7%)  | 0.44 (2.3%)      | 0.44 (2.3%)  |
|           |           | Maximum absolute error | -             | 18%           | 27%              | 22%       |
|           |           | Average absolute error | -             | 11%           | 17%              | 13%       |
| 60℃       |           |                |                |               |                  |          |
|           | 0         | 1.00           | 1.00           | 1.00          | 1.00             | 1.00     |
|           | 90        | 0.59           | 0.53 (-10%)    | 0.59 (0.0%)   | 0.62 (5.1%)      | 0.54 (-8.5%)  |
|           | 180       | 0.58           | 0.49 (-16%)    | 0.52 (-10%)   | 0.60 (3.5%)      | 0.51 (-12%)  |
|           | 270       | 0.48           | 0.47 (-2.1%)   | 0.47 (-2.1%)  | 0.54 (19%)       | 0.50 (4.2%)  |
|           | 360       | 0.45           | 0.45 (0.0%)    | 0.44 (-2.2%)  | 0.55 (22%)       | 0.49 (8.9%)  |
|           | 720       | 0.44           | 0.40 (-9.1%)   | 0.37 (-16%)   | 0.47 (6.8%)      | 0.46 (4.6%)  |
|           | 1440      | 0.38           | 0.33 (-13%)    | 0.30 (-21%)   | 0.37 (-2.6%)     | 0.44 (16%)   |
|           |           | Maximum absolute error | -             | 16%           | 21%              | 19%       |
|           |           | Average absolute error | -             | 8.3%          | 8.6%             | 9.8%      |
| 80℃       |           |                |                |               |                  |          |
|           | 0         | 1.00           | 1.00           | 1.00          | 1.00             | 1.00     |
|           | 90        | 0.40           | 0.42 (5.0%)    | 0.52 (30%)    | 0.57 (43%)       | 0.41 (2.5%)  |
|           | 180       | 0.38           | 0.39 (2.6%)    | 0.44 (16%)    | 0.51 (34%)       | 0.38 (0.0%)  |
|           | 270       | 0.37           | 0.35 (-5.4%)   | 0.39 (5.4%)   | 0.46 (24%)       | 0.37 (0.0%)  |
|           | 360       | 0.37           | 0.34 (-8.1%)   | 0.36 (-27%)   | 0.42 (14%)       | 0.35 (-5.4%)  |
|           | 720       | 0.34           | 0.30 (-12%)    | 0.28 (-18%)   | 0.33 (-2.9%)     | 0.32 (-5.9%)  |
|           | 1440      | 0.29           | 0.26 (-10%)    | 0.20 (-31%)   | 0.26 (-10%)      | 0.29 (0.0%)  |
|           |           | Maximum absolute error | -             | 12%           | 31%              | 43%       |
|           |           | Average absolute error | -             | 7.2%          | 17%              | 21%       |
| 95℃       |           |                |                |               |                  |          |
|           | 0         | 1.00           | 1.00           | 1.00          | 1.00             | 1.00     |
| 90  | 0.34 | 0.30 (-12%) | 0.49 (44%) | 0.56 (65%) | 0.37 (8.8%) |
|-----|------|-------------|------------|------------|-------------|
| 180 | 0.34 | 0.29 (-15%) | 0.40 (18%) | 0.49 (44%) | 0.34 (0.0%) |
| 270 | 0.34 | 0.28 (-18%) | 0.35 (2.9%)| 0.44 (29%) | 0.32 (-5.9%)|
| 360 | 0.31 | 0.26 (-16%) | 0.31 (0.0%)| 0.40 (29%) | 0.31 (0.0%) |
| 720 | 0.29 | 0.25 (-14%) | 0.22 (-24%)| 0.30 (3.5%)| 0.28 (-3.5%)|
| 1440| 0.25 | 0.22 (-12%) | 0.13 (-48%)| 0.26 (4.0%)| 0.24 (-4.0%)|

Maximum absolute error - 18% 48% 65% 8.8%
Average absolute error - 14% 23% 29% 3.7%

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