A deteriorating model for the prediction of elastic modulus of the aging fiber reinforced polymer under complex environmental effects

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Abstract
The fiber reinforced polymer is popularly applied for structural reinforcement and, however, usually suffers from long-term environmental effects, for example exposed to the ultraviolet radiation, alternating changes of moist-heat, and submerged in water chronically. As a result, the material aging and structural performance degradation are inevitable, which could eventually lead to the deterioration of mechanical behavior of fiber reinforced polymer, hence the attenuation or failure of repaired structures. It is very expensive and time consuming to use the experimental method to find out the aging patterns of fiber reinforced polymer. For fiber reinforced polymer with different volume fraction, the upper and lower limit of elastic modulus can be deduced by the energy principle. Combining this theory with tests, a semi-empirical deteriorating method can be used to analyze the change of fiber reinforced polymer mechanics behavior. And a series of empirical coefficients, determined by natural aging tests, are introduced. The coefficients are applied in the revised formula for the prediction of mechanics behaviors of fiber reinforced polymer. The elastic modulus of deteriorating fiber reinforced polymer is influenced by the fiber, the resin matrix, and the volume fraction of the fiber. For different fiber volume fraction, the experimental test is not the unique way to assess the durability of fiber reinforced polymer, as long as the laws of fiber aging, the laws of resin aging, and the fiber volume fraction are already known. The proposed model shows good agreement with the test results, hence can be used to predict the elastic modulus of aging fiber reinforced polymer, which can be utilized as references for engineering design and research in the future.

Keywords
Environmental effects, fiber reinforced polymer, durability, deteriorating model

Introduction
Fiber reinforced polymer (FRP) is a type of high-performance material composed of certain proportions of fiber and resin substrate material and is widely applied for the reinforcement of engineering structures. In actual reinforcement engineering cases, due to different environmental conditions, e.g. exposed to ultraviolet (UV) radiation, subjected to freeze–thaw cycling, and soaked in water for a long time, FRP material will inevitably suffer from aging and performance deteriorating problems. This will eventually lead to the decrease of the strength of FRP and change of material elastic constants, leading to performance deteriorating of the repaired structures and even structure failures.
The durability performances of FRP under the natural environment and durability design for FRP in structures always attract engineers’ attention. Luo et al. performed an experimental research to study the durability performance of different brands of FRP and resin substrate under climatic condition exposure in China; Cromwell et al. carried out a series of experimental program to investigate the behavior of three FRP systems subjected to nine different environmental conditioning protocols. The effect of environmental conditioning was assessed using four different standard test methods. Arun et al. carried out experiments on the glass/textile fabric reinforced hybrid composites under normal condition and sea water environments. Results show that the damage in hybrid composite under sea water environment is entirely different. The nature of fracture as a function of the reinforcement volume, loading, and environmental conditions has been analyzed with the aid of scanning electron microscopy.

Many factors, including fiber types, resin substrates, and the volume fraction of FRP, will affect the durability of FRP. It is expensive and very time-consuming to use test methods for the aging law of FRP. The best way to predict the aging performance of FRP is to combine both macro mechanics analytical method and experimental method.

In this study, a deterioration model for prediction of the elastic modulus of the aging FRP under complex environmental effects is proposed. The proposed method, a semi-empirical method, combines the energy theory and experimental test, which can be used to analyze the change of FRP mechanics behavior. The organization of this paper is summarized as follows: (1) Using energy principle to determine the upper and lower limit of elastic modulus of FRP. (2) Based on the theoretical analysis, using semi-empirical methods, a deteriorating model for the prediction of elastic modulus of the aging FRP under complex environmental effects is proposed, where the empirical coefficients are determined by natural aging test. (3) For different fiber volume fraction, the experimental test is not the unique way to assess the durability of FRP, as long as the laws of fiber aging, the laws of resin aging, and the fiber volume fraction are already known. (4) Conclusions are drawn to provide valuable information for the engineering design considering the deteriorating process of FRP.

**Determine the upper and lower limit of elastic modulus by energy principle**

FRP is a structure mixed with a polymer matrix reinforced with fibers. For fibers embedded in matrix, the strength and elastic performance have obvious directivity, which makes it anisotropic. From the perspective of macroscopic mechanics, considering the fact that the function of FRP is determined by average apparent performance, the material can be assumed uniformly distributed. Assumptions are listed as follows:

1. FRP is macro homogeneous, orthotropic linear elastic and none initial stress.
2. Constituent materials of FRP, both fibers and matrix are homogeneous, isotropic, and linear elastic.
3. FRP, fibers, and matrix are assumed to have small deformation.
4. The shape of fibers and its distribution in resin matrix are in regular forms.
5. Strain distribution at the fiber–matrix interface is continuous without relative slip.

Based on the above assumptions, a fraction of representative volume unit is chosen to study the deterioration of elastic modulus after natural aging. This fraction is small enough to reveal FRP microstructure composition, yet big enough to represent FRP performance. Figure 1 shows a single fiber of the representative volume unit. The fiber direction (x axis) is taken as the first direction, fiber spacing of the unit (y axis) as the second direction, while the thickness of fiber spacing (z axis) as the third direction. The cross section perpendicular to the x axis is assumed to always be plane. $E_1$ represents elastic modulus in the first direction $\sigma$. 

**Figure 1.** Representative volume unit.
As to the representative volume unit, \( V \) indicates total volume and \( A \) indicates the total cross-sectional area. Besides, the subscript \( f \) indicates the fiber and subscript \( m \) indicates the resin matrix. Then, the volume fraction of fiber and matrix can be expressed as follows

\[
v_f = \frac{V_f}{V} = \frac{A_f}{A}, \quad v_m = \frac{V_m}{V} = \frac{A_m}{A}
\]  

(1)

The volume of FRP is equal to sum of the volume of each fiber and matrix. Therefore

\[
v_f + v_m = 1
\]  

(2)

Define the fiber thickness \( t_f \) and the measured thickness of FRP \( t_{frp} \). Divide the fiber mass per unit area with the density of fiber, the fiber nominal thickness \( t_f \) is determined. Thus, fiber volume fraction \( v_f \) can be expressed with the ratio of \( t_f \) and \( t_{frp} \)

\[
v_f = \frac{t_f}{t_{frp}}
\]  

(3)

For linear elastic body, strain energy \( U_e \) can be expressed as follows

\[
U_e = \frac{1}{2} \int_\Omega (\sigma_x \varepsilon_x + \sigma_y \varepsilon_y + \sigma_z \varepsilon_z + \tau_{xy} \gamma_{xy} + \tau_{yz} \gamma_{yz} + \tau_{xz} \gamma_{xz}) \, dv
\]  

(4)

The relationship between stress and of the linear elastic body follows the generalized Hooke’s law. Therefore, equation (4) can be expressed as a function of the complementary energy \( U_\sigma \). The strain energy \( U_e \) is equal to the complementary energy \( U_\sigma \), thus

\[
U_e = U_\sigma = U
\]  

(5)

For the elastic body, the principle of minimum complementary energy indicates that, of the required equilibrium equation and the stress boundary condition, the complementary energy \( U_\sigma^0 \) of allowable stress field \( \sigma_0 \) is always equal to or greater than the complementary energy \( U_\sigma \) of the real stress field \( \sigma_i \)

\[
U_\sigma \leq U_\sigma^0
\]  

(6)

The principle of minimum potential energy indicates that, of the required displacement boundary condition, the strain energy \( U_e^0 \) of allowable strain field \( \varepsilon_i \) is always equal to or larger than the strain energy \( U_e \) of the real strain field \( \varepsilon_i \)

\[
U_e \leq U_e^0
\]  

(7)

The lower limit of elastic modulus \( E_1 \) be determined by the principle of minimum complementary energy. The allowable stress field, which satisfies the equilibrium conditions and the stress boundary condition, can be expressed as

\[
\sigma_1^0 = \sigma_1, \quad \sigma_2^0 = \sigma_3 = \tau_{12}^0 = \tau_{23}^0 = \tau_{31}^0 = 0
\]  

(8)

The complementary energy \( U_\sigma^0 \) of allowable stress field \( \sigma_0^0 \) is

\[
U_\sigma = \frac{1}{2} \int_\Omega \frac{(\sigma_0^0)^2}{E} \, dv = \frac{\sigma_1^0}{2} \int_\Omega \frac{d_1}{E}
\]  

(9)
where equation (9) is the whole volume integral of a representative volume unit, and could be decomposed into the integrals of fiber and resin matrix, respectively

$$U_0 = \frac{\sigma_i^2}{2} \left( \int \frac{d\nu}{E_f} + \int \frac{d\nu}{E_m} \right) = \frac{\sigma_i^2}{2} \left( \frac{\nu_f + \nu_m}{E_f + E_m} \right)$$

For a representative volume unit, the complementary energy $U_r$ of the real stress field $\sigma_i$

$$U_r = \frac{1}{2} \frac{\sigma_i^4}{E_1}$$

(10)

Equation (6) can be further written as follows

$$E_1 \geq \frac{E_f E_m}{E_f \nu_m + E_m \nu_f}$$

(11)

Therefore, the lower limit of the elastic modulus $E_1$ of deteriorated FRP is determined.

Determine the upper limit of elastic modulus $E_1$ by the principle of minimum potential energy. For the representative volume unit, using the average strain $\varepsilon_1$ and the apparent Poisson’s ratio $\nu$, the allowable strain field is expressed in equation (13)

$$\varepsilon_1^r, \varepsilon_2^r = -\nu \varepsilon_1, \gamma_{12}^r = \gamma_{23}^r = \gamma_{31}^r = 0$$

(12)

Apply the generalized Hooke’s law

$$\sigma_x = \frac{\nu E}{(1 + \nu)(1 - 2\nu)} (\varepsilon_x + \nu \varepsilon_y + \varepsilon_z) + \frac{E}{1 + \nu} \varepsilon_x$$

$$\tau_{xy} = \frac{E}{2(1 + \nu)} \gamma_{xy}$$

(13)

The fiber and resin substrate stress of allowable strain field can be obtained respectively

$$\begin{align*}
\sigma_{f1}^* &= \frac{1 - \nu_f - 2\nu_f \nu}{1 - \nu_f - 2\nu_f^2} E_f \varepsilon_1 \\
\sigma_{f2}^* &= \sigma_{f3}^* = \frac{\nu_f - \nu}{1 - \nu_f - 2\nu_f^2} E_f \varepsilon_1 \\
\tau_{f12}^* &= \tau_{f23}^* = \tau_{f31}^* = 0 \\
\sigma_{m1}^* &= \frac{1 - \nu_m - 2\nu_m \nu}{1 - \nu_m - 2\nu_m^2} E_m \varepsilon_1 \\
\sigma_{m2}^* &= \sigma_{m3}^* = \frac{\nu_m - \nu}{1 - \nu_m - 2\nu_m^2} E_m \varepsilon_1 \\
\tau_{m12}^* &= \tau_{m23}^* = \tau_{m31}^* = 0
\end{align*}$$

(14)

(15)

Substitute equation (13) and equation (15) into equation (4), and integrate in the fiber volume and resin substrate volume, respectively

$$U_+ = \frac{\varepsilon_1^2}{2} \left[ \frac{1 - \nu_f - 4\nu_f \nu + 2\nu^2}{1 - \nu_f - 2\nu_f^2} E_f \nu_f + \frac{1 - \nu_m - 4\nu_m \nu + 2\nu^2}{1 - \nu_m - 2\nu_m^2} E_m \nu_m \right] V$$

(16)
For a representative volume unit, the corresponding potential energy of the real strain field can be expressed as

\[ U_e = \frac{1}{2} E_i c_i^2 V \]  

(17)

Substitute equations (16) and (17) into equation (7)

\[ E_1 \leq \frac{1 - \nu_f - 4\nu_f\nu + 2\nu^2}{1 - \nu_f - 2\nu_f^2} E_f\nu_f + \frac{1 - \nu_m - 4\nu_m\nu + 2\nu^2}{1 - \nu_m - 2\nu_m^2} E_m\nu_m \]  

(18)

The apparent Poisson’s ratio \( \nu \) in equation (18) can be obtained by the minimum conditions of \( U_e \)

\[ \frac{\partial U_e}{\partial \nu} = 0 \quad \frac{\partial^2 U_e}{\partial \nu^2} > 0 \]

Take the derivative of equation (16) with respect to \( \nu \)

\[ \frac{\partial U_e}{\partial \nu} = \frac{c_i^2}{2} \left[ \frac{4\nu - 4\nu_f}{1 - \nu_f - 2\nu_f^2} E_f\nu_f + \frac{4\nu - 4\nu_m}{1 - \nu_m - 2\nu_m^2} E_m\nu_m \right] V \]  

(19)

Assume equation (19) be zero, and the solution can be obtained as follows

\[ \nu = \frac{\nu_f(1 - \nu_m - 2\nu_m^2) E_f\nu_f + \nu_m(1 - \nu_f - 2\nu_f^2) E_m\nu_m}{(1 - \nu_m - 2\nu_m^2) E_f\nu_f + (1 - \nu_f - 2\nu_f^2) E_m\nu_m} \]  

(20)

In addition, take the derivative of equation (19) with respect to \( \nu \) again

\[ \frac{\partial^2 U_e}{\partial \nu^2} = \frac{c_i^2}{2} \left[ \frac{4E_f\nu_f}{1 - \nu_f - 2\nu_f^2} + \frac{4E_m\nu_m}{1 - \nu_m - 2\nu_m^2} \right] V \]  

(21)

For the isotropic resin matrix and fiber, with Poisson’s ratio \( 0 < \nu_m < 0.5 \) and \( 0 < \nu_f < 0.5 \), \( \frac{\partial^2 U_e}{\partial \nu^2} \) is always positive in equation (21). Substitute equation (20) into equation (18), the upper limit of elastic modulus \( E_1 \) of the deteriorated FRP can be determined.

While \( \nu_f = \nu_m \), \( E_1 \) can be written in the form of equation (22)

\[ E_1 \leq E_f\nu_f + E_m\nu_m \]  

(22)

If the gap in deteriorating FRP is ignored, equation (22) can be expressed as

\[ E_1 \leq E_f\nu_f + E_m(1 - \nu_f) \]  

(23)

Therefore,

\[ \frac{E_fE_m}{E_f(1 - \nu_f) + E_m\nu_f} \leq E_1 \leq E_f\nu_f + E_m(1 - \nu_f) \]  

(24)

Equation (24) shows that elastic modulus \( E_1 \) of the deteriorated FRP meets the mixing law. When the value of fiber volume fraction \( \nu_f \) varies between 0 and 1, \( E_1 \) varies between elastic modulus of resin matrix \( E_m \) and elastic modulus of fiber \( E_f \).
Only resin substrate will remain in the natural aging FRP when \( v_m \) equals to 1 and \( v_f \) equals to 0. Using squeeze rule in mathematics, equation (24) becomes \( E = E_m \); while \( v_m = 0 \) and \( v_f = 1 \), there will only exist fiber in natural aging FRP and equation (24) becomes \( E = E_f \).

### Elastic modulus deteriorating model for FRP natural aging

Equation (24) is employed to predict the upper and lower limit of the elastic modulus of deteriorated FRP induced by natural aging with different volume fraction, where \( E_{ft} \) and \( E_{mt} \) stand for the elastic modulus of the deteriorated resin matrix and fiber after the aging time \( t \), respectively.

\[
\frac{E_{ft}E_{mt}}{E_{ft}(1 - v_f) + E_{mt}v_f} \leq E \leq E_{ft}v_f + E_{mt}(1 - v_f)
\]  

(25)

The upper and lower limits of elastic modulus are deduced from energy principle. Based on the theoretical analysis, the empirical coefficients are determined by the semi-empirical methods and natural aging test. The theoretical formula is revised to as simple as possible and is consistent with the test results. Since the degradation of fiber is generally slower and lighter than that of the resin matrix, the elastic modulus of deteriorated FRP is mainly determined by the elastic properties of the fiber, considering the influence of resin matrix. Coefficients \( K_1, K_2, K_3 \) are related to volume fraction of the fiber for different types of fiber. As parameter \( K_1 \) relates to the elastic properties of the deteriorated fiber; Parameter \( K_2 \) relates to the elastic properties of the deteriorated resin matrix, and \( K_3 \) relates to the collaborative work performance between deteriorated fiber and resin matrix, the deteriorating model for elastic modulus of aging FRP can be deduced as follows.

\[
E = K_1E_{ft}v_f + K_2E_{mt}(1 - v_f) + K_3\left[\frac{E_{ft}E_{mt}}{E_{ft}(1 - v_f) + E_{mt}v_f}\right]
\]  

(26)

### Table 1. Measured and predicted elasticity modulus of fiber reinforced polymer (FRP) after aging.

| Test specimens | Aging time | Measured elasticity modulus \( r/\text{MPa} \) | Predicted elasticity modulus \( r/\text{MPa} \) | Relative error % |
|---------------|------------|-------------------------------------|-------------------------------------|-----------------|
| AS-1 + RE-1   | 0.0        | 122.74                             | ——                                 | ——              |
|               | 0.5        | 119.35                             | ——                                 | ——              |
|               | 1.5        | 117.86                             | ——                                 | ——              |
|               | 3.0        | 114.37                             | 121.38                             | 6.13            |
|               | 4.5        | 112.13                             | 118.92                             | 6.06            |
|               | 6.5        | 105.44                             | 114.26                             | 8.36            |
| CS-1 + RE-1   | 0.0        | 230.0                              | ——                                 | ——              |
|               | 0.5        | 263.8                              | ——                                 | ——              |
|               | 1.5        | 253.4                              | ——                                 | ——              |
|               | 3.0        | 256.8                              | 223.5                              | -12.9           |
|               | 4.5        | 194.3                              | 209.7                              | 7.93            |
|               | 6.5        | 187.49                             | 201.1                              | 7.27            |
| CS-2 + RE-2   | 0.0        | 233.4                              | ——                                 | ——              |
|               | 0.5        | 234.4                              | ——                                 | ——              |
|               | 1.5        | 235.7                              | ——                                 | ——              |
|               | 3.0        | 245.0                              | 216.3                              | -11.70          |
|               | 4.5        | 210.5                              | 228.65                             | 8.62            |
|               | 6.5        | 195.7                              | 209.3                              | 6.95            |
| GS-1+RE-1     | 0.0        | 90.4                               | ——                                 | ——              |
|               | 0.5        | 84.23                              | ——                                 | ——              |
|               | 1.5        | 81.14                              | ——                                 | ——              |
|               | 3.0        | 82.25                              | 86.45                              | 5.11            |
|               | 4.5        | 70.34                              | 74.61                              | 6.07            |
|               | 6.5        | 62.58                              | 65.23                              | 4.23            |
An experimental research to study the durability performance of different brands of FRP and resin substrate under climatic condition in East China has been done for more than 6.5 years. There are three different kinds of test specimens, which are carbon fiber reinforced polymer (CFRP) CS-1+RE-1, CS-2+RE-2, aramid fiber reinforced polymer (AFRP) AS-1+RE-1, and glass fiber reinforced polymer (GFRP) GS-1+RE-1. According to the durability test data of elastic modulus for four different kinds of aging FRP under complex environmental effects after 0, 0.5, and 1.5 years, the coefficients in equations (26) is calculated as \( K_1 = 2.4, K_2 = -170.7, \) and \( K_3 = 83 \), which can be used for prediction the elastic modulus of AS-1+RE-1 aging after 3.0 years, 4.5 years, and 6.5 years. In addition to the measured values, the predicted elasticity modulus of CS-1+RE-1, CS-2+RE-2, and GS-1+RE-1 after 3.0 years, 4.5 years, and 6.5 years natural aging are calculated and tabulated in Table 1. The relative errors show that the predicted elasticity modulus values agree well with those obtained from the durability test.

Conclusions

The deteriorating model for the prediction of the elastic modulus of the aging FRP under complex environmental effects is proposed. The proposed model, based on a semi-empirical formula, is simple and convenient for engineering application. For different fiber volume fraction, the experimental test is not the unique way to assess the durability of FRP, as long as the laws of fiber aging, the laws of resin aging, and the fiber volume fraction (or fiber nominal thickness \( t_f \) and the measured thickness of FRP \( t_{frp} \)) are already known. Results show that the predicted elastic modulus for FRP natural aging is consistent with those obtained from the experimental tests. It is believed that the proposed deteriorating model for the prediction of elastic modulus of the aging FRP can provide reliable references for the engineering design considering the deteriorating process of FRP.

Declaration of conflicting interests

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