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Modeling of load responses and aging of high strength fibers considering UV-radiation

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ABSTRACT

Long-term illumination can damage the mechanical properties of high strength fiber composites, resulting in the material aging and loss of mechanical properties. To reveal the mechanism of ultraviolet- (UV-) induced damage, in this paper, a nonlinear constitutive model is developed to describe the elastic and inelastic deformation behavior of high strength fibers under UV-radiation and mechanical loadings. Two internal variables are employed to measure the effects of damage caused by UV-radiation and by mechanical loadings, respectively. The Helmholtz free energy function and the evolution equations of these two internal variables are investigated elaborately and given explicitly for high strength fibers. The proposed theoretical model is then applied to analyze the mechanical degradation of high-performance high strength fibers under uniaxial tension. The modulus and strength of the material predicted by the theoretical model match the aging experimental results rather well, which verifies the rationality and accuracy of the present model. This model is expected to predict the evolution of mechanical properties of high-strength fibers under UV-radiation, which can also provide a theoretical basis for the development of anti-UV technology of fiber reinforced composites.

1. Introduction

By virtue of their high strength and modulus, excellent fold characteristics, outstanding cut resistance, and high impact resistance, high strength fibers have been widely used in civilian and military fields [1,2], such as various apparels [3], sunshade textiles [4], airships [5], stratospheric balloons [1], and space capsules [6]. Due to their excellent mechanical properties, high strength fibers are used in various polymer composite as reinforcement component [7,8]. In these cases, high strength fibers are expected to bear most of load. In many practical environments, these high-performance fibers are inevitably exposed to sunlight (see Fig. 1). Hence, ultraviolet (UV) radiation is potentially dangerous to composite materials because it can accelerate fiber aging and lead to material degradation [9,10]. Especially, the composites tend to lose their modulus and strength significantly upon exposure to UV-radiation [10–12] and greatly limits their applications. Hence it is crucial to understand the mechanical responses of high strength fibers upon exposure to UV-radiation.

Experiments showed that micro surface cracks of high strength fibers were initiated by UV-radiation and extended inward as the exposure time continues [10]. According to scanning electron microscopy (SEM) observation, as the time of such ionizing radiation increases, the irradiation can cause voids among the fiber surface structures [13]. Previous studies found that this might associate with the break of intermolecular bonds between the fiber surface and the matrix induced by UV-radiation [14,15]. It has been reported that UV irradiation would cause the fracture of main molecular chains and cross-linking with covalent bonds of fibers [2,16], and the cracks would extend till the material fails when the stretch increases to the ultimate elongation during the tensile test [17]. Based on the experimental analysis, the influence of UV-radiation on the macroscopic properties of composites is reflected in the degradation of bending strength and elastic modulus [18]. In addition, most synthetic fiber products degrade in their working environment in two main ways: oxidation caused by UV irradiation and slow mechanical wear [13]. Therefore, the mechanical degradation of high strength fibers mainly arises from damages caused by UV-radiation and mechanical loading.

The aging process of high strength fiber composites was mostly investigated using experimental approach, which has high engineering

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significance for the application of materials. In order to study the response of high-strength fibers damaged by long-term UV exposure, the stiffness and damage of Kevlar® yarn under different radiation time were measured in the literature [11], and the results show that the fiber damage changes nonlinearly with time. Exposure to UV and water spraying accelerated the aging of fiber reinforced composites, and the photooxidation reaction resulted in a significant decrease of the tensile strength of the composites by 12% and the bending strength by 7% [19]. To date, a large number of experimental studies have been performed to evaluate the UV aging of high strength fibers and composites [11, 20–22], but there exist few reports on the modeling of this mechanical degradation process. To fill this gap, herein, a theoretical model describing the UV aging of high strength fibers is proposed based on non-equilibrium thermodynamics. Two internal variables are introduced to characterize the degradations induced respectively by UV-radiation and mechanical loadings. The elastic modulus and strength predicted by the theoretical model are basically consistent with the experimental values of high strength fiber under UV irradiation, which verifies the rationality and accuracy of the established model. The proposed model can be used to analyze the load responses of high strength fiber composites under UV radiation and evaluate the effective life of composites under long-term aging.

The paper is organized as follows. In Section 2 the general Helmholtz free energy function and the total energy dissipation inequality under small strain assumption are presented. In Section 3, the constitutive model and the damage evolution equations of two internal variables are specified to describe the mechanical behaviors of high strength fibers under UV-radiation and mechanical loadings, respectively. In Section 4, theoretical estimations for modulus and strength of high strength yarns, with Zylon® and Vectran® as examples, under UV-radiation are compared with relevant experiment results. In Section 5, we draw conclusions.

2. Thermodynamics

The model is established for a fiber or a bundle of fibers, such as a yarn consisting of many fibers. Under the assumption of neglecting the interfacial contact between fibers in a yarn, we consider the fibers as a long cylinder, illustrated in Fig. 1. Generally, the ultimate strain at peak load of high strength fibers decreases with increasing exposure time. In view of the fact that the ultimate strain at peak load without UV-radiation is ordinarily below 4% [1], small deformation assumption can be used in the development of the model for a single high strength yarn [23]. As shown in Fig. 1, the high strength yarn is initially assumed to be free to deform without initial stress when exposed to UV-radiation (initial state A). UV causes inelastic strain, resulting in cross section expansion (intermediate state B). In uniaxial tensile tests, axial displacement is controlled so that uniform strains can be attained (current state C).

In the literature [10], the fiber after deterioration was observed from SEM. It was found that microcracks generated on the surface of the fiber by UV irradiation and extended inward gradually [13]. The fiber volume would increase due to microcracking under the assumption that the fiber mass keeps unchanged. Since the yarn is configured in an elongated cylindrical shape, UV radiation is mainly concentrated on the side surface of the cylinder. Therefore, we can assume that the fiber expands uniformly in any direction with a strain e under UV irradiation so that $\frac{r}{R_0} = \frac{l}{L_0} = 1 + e$, where R_0 and r are respectively the radii of a yarn at state A and state B, L_0 and l are respectively the lengths of a yarn at state A and state B, as shown in Fig. 1. Hence, the volume ratio of configuration in state B to the initial state A can be expressed as

$$J = \left(\frac{r}{R_0}\right)^2 \frac{l}{L_0} = (1+e)^3 \tag{1}$$

Obviously, the uniform strain e is a function of the internal variable α_1 related to UV-radiation, namely, $e = e(\alpha_1)$.

Two internal variables α_1 and α_2, are introduced to describe the effects of damage induced by UV-radiation and by mechanical loadings respectively. Thus, the general form of the Helmholtz free energy can be assumed as

$$\psi = \psi(\varepsilon_i, \theta, \alpha_1, \alpha_2) \tag{2}$$

where $\varepsilon_i (i = 1, 2, 3)$ are three principal strains and θ is the absolute temperature.

Associated with three principal strain rates $\dot{\varepsilon}_i$, the power done by the mechanical stresses is $\sigma_i \dot{\varepsilon}_i$ and the thermal energy changes due to temperature changes. Thus, the Clausius-Duhem inequality can be written as:

$$\dot{\psi} - \sigma_i \dot{\varepsilon}_i + s\dot{\theta} \leq 0 \tag{3}$$

where s is the entropy and the time derivative is denoted by a superposed dot. Note that the Einstein summation convention is adopted in the above formula.

Since isothermal testing was used in specific experiments, the evo-

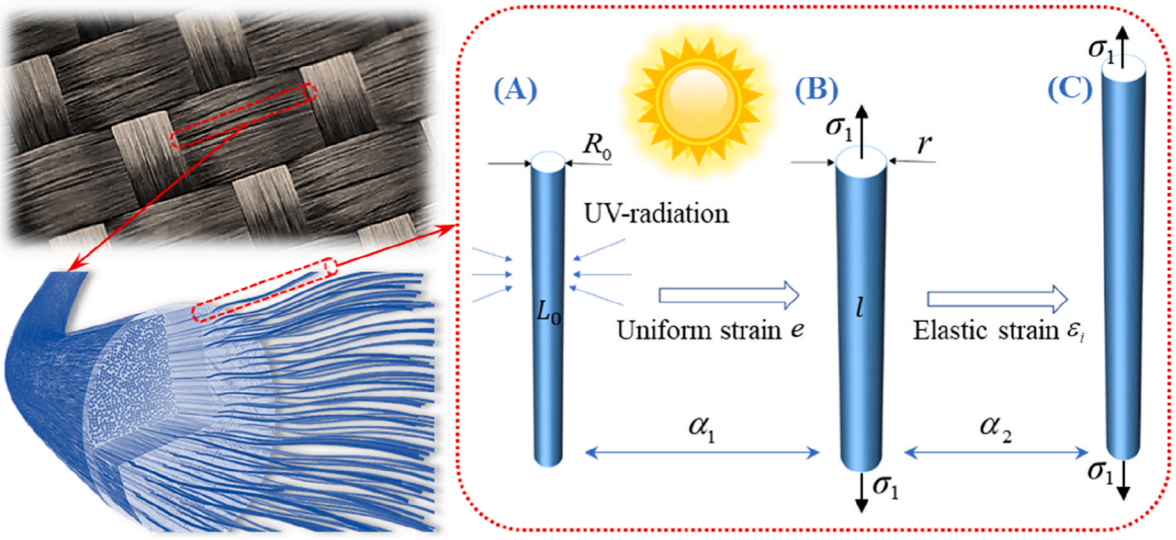

Fig. 1. The strain of a high strength fiber evolves induced by UV-radiation and mechanical loadings: (A) Initial state; (B) Intermediate state; (C) Current state.

lution of tensile modulus and ultimate strength of fibers under isothermal conditions is further considered [1,2,10,20]. Thus, the temperature term of the free energy in Eq. (3) can be neglected, and the Helmholtz free energy ψ can be further assumed to be composed of two parts: the elastic energy $\psi_e(\varepsilon_i, \alpha_1, \alpha_2)$ related to UV-radiation and mechanical deterioration, and volumetric expansion energy $\psi_r(e(\alpha_1))$ produced by UV-radiation, given as follows:

$$\psi(\varepsilon_i, \alpha_1, \alpha_2) = \psi_e(\varepsilon_i, \alpha_1, \alpha_2) + \psi_r(e(\alpha_1)) \tag{4}$$

Substituting Eq. (4) into Eq. (3) yields

$$\left(\frac{\partial \psi_e}{\partial \varepsilon_i} - \sigma_i\right)\dot{\varepsilon}_i + \frac{\partial \psi}{\partial \alpha_1}\dot{\alpha}_1 + \frac{\partial \psi_e}{\partial \alpha_2}\dot{\alpha}_2 \le 0 \tag{5}$$

the above inequality comprises three terms corresponding to different energy dissipation mechanisms. If the mechanical equilibrium is assumed to achieve instantaneously, the first term in Eq. (5) should vanish, which leads to

$$\sigma_i = \frac{\partial \psi_e}{\partial \varepsilon_i} \tag{6}$$

the second term and the third term can be equivalently expressed as:

$$\begin{cases} \dfrac{\partial \psi(\alpha_1, \alpha_2)}{\partial \alpha_1}\dot{\alpha}_1 \le 0 \\ \dfrac{\partial \psi_e(\alpha_1, \alpha_2)}{\partial \alpha_2}\dot{\alpha}_2 \le 0 \end{cases} \tag{7}$$

which describe the energy dissipation rates caused by the mechanical degradation due to fiber deterioration caused by UV-radiation and mechanical loading respectively. They can be denoted as

$$\begin{cases} \Xi_1(\alpha_1, \alpha_2, \dot{\alpha}_1) = -\dfrac{\partial \psi(\alpha_1, \alpha_2)}{\partial \alpha_1}\dot{\alpha}_1 \\ \Xi_2(\alpha_1, \alpha_2, \dot{\alpha}_2) = -\dfrac{\partial \psi_e(\alpha_1, \alpha_2)}{\partial \alpha_2}\dot{\alpha}_2 \end{cases} \tag{8}$$

where $-\partial\psi/\partial\alpha_1$ and $-\partial\psi_e/\partial\alpha_2$ are respectively the thermodynamic forces conjugate to the thermodynamic flow $\dot{\alpha}_1$ and $\dot{\alpha}_2$. Given the special forms of the dissipation rates Ξ_1 and Ξ_2, Eq. (8) gives the evolution of internal variables which can be solved analytically or numerically under specific initial conditions.

Based on non-equilibrium thermodynamics, this section constructs the irreversible energy dissipation form of high strength fiber material under UV-radiation. With the above form of Helmholtz free energy ψ, in what follows we further propose the damage evolution based on the analysis of damage mechanisms and derive the constitutive relation consequently.

3. Damage evolution and constitutive relation

UV-radiation can lead to breakage of covalent bonds of fibers [24], so this damage is an irreversible thermodynamic process with energy dissipation. In fact, studies have shown that steady light causes damage to the outer layers of the fibers first, while the inner layers retain their mechanical properties [11,25]. Therefore, the fiber damage caused by UV-radiation aging is an outside to inside process, depending on the thickness of the fiber layer (see Fig. 2). In order to better describe this process, we introduce an internal variable α_1 ($0 \le \alpha_1 \le 1$) and make the following assumptions:

(1) UV deterioration region expands along radius direction from outside to inside;
(2) In order to ensure the continuity of boundary deformation, the elastic shear moduli on the boundary between deteriorated and undeteriorated area are equal, and the elastic modulus in the deteriorated region varies linearly from G_0 to G_f ($G_0 < G_f$) along the radius from the outermost boundary (the boundary with air) to the inmost boundary (the boundary with undeteriorated region);
(3) The fiber keeps isotropic in both deteriorated and undeteriorated regions through the entire UV-radiation process.

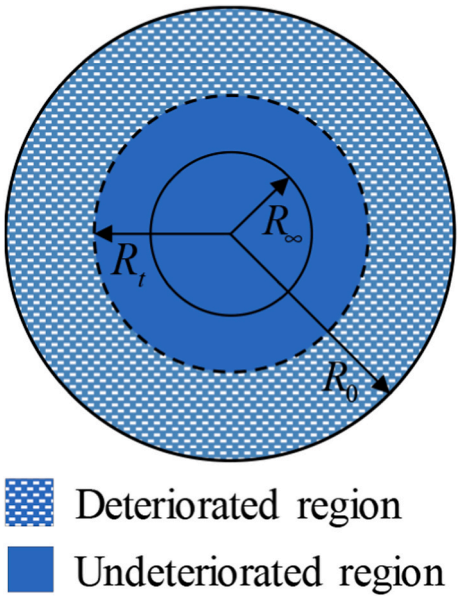

Fig. 2. The deteriorated and undeteriorated region of the fiber section.

As shown in Fig. 2, R_t , R_0, and R_∞ are the radii of the undeteriorated region of fiber section respectively at time t, initial and final instants. The internal variable α_1 can be expressed as a function of R_t, R_0 and R_∞ as

$$\alpha_1(t) = \frac{R_0 - R_t(t)}{R_0 - R_\infty} \tag{9}$$

Naturally, $\alpha_1(0) = 0$ and $\alpha_1(\infty) = 1$ corresponding to the initial state without degradation and the end state of the degradation process at the equilibrium state respectively.

As shown in Fig. 2, the shear elastic modulus of outermost boundary at degradation region G_0 should also decline over time. The relation between G_0 and the internal variable α_1 can be expressed as follows:

$$G_0 = G_f(1 - k\alpha_1) \tag{10}$$

where G_f is the shear modulus of the fiber material before UV-radiation and $k \in (0, 1]$ is the deterioration factor of shear modulus. The relation implies that at time $t = 0$, $\alpha_1 = 0$, G_0 achieves the maximum value G_f, and at time $t \to \infty$, G_0 takes the minimum value $G_f(1 - k)$.

Then, the energy density expressions of the undeteriorated region and the deteriorated region can be given respectively. In the case of linearly isotropic elasticity, the elastic energy density of undeteriorated region is written as:

$$\Psi_e^U = G_f\left[\frac{v_c}{1 - 2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] \tag{11}$$

where v_c is the Poisson's ratio of the fiber.

Since the UV-radiation would dramatically reduce the elastic modulus of the high strength fiber in the deteriorated region, a modification of the elastic energy density Ψ_e^D at radius R is given as

$$\Psi_e^D = G_R\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] \tag{12}$$

where G_R is the shear modulus at radius R in deteriorated region and has the following form:

$$G_R = G_f - \frac{G_f - G_0}{R_0 - R_t}(R - R_t) \quad (R_t \le R \le R_0) \tag{13}$$

where $G_0 \le G_R \le G_f$, because the degradation of the outside layer is much severer, or G_R takes its minimum G_0 at the outermost boundary ($R = R_0$) and its maximum at the innermost boundary ($R = R_t$). Next, by substituting Eq. (9) into (13) and (12), we obtain

$$\Psi_e^D = \left[G_0 + \frac{\beta}{\alpha_1}(R_0 - R)\right]\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] \tag{14}$$

where β is the linear shear modulus gradient along radius direction:

$$\beta = (G_f - G_0) / (R_0 - R_\infty) \tag{15}$$

Since the length of fiber is L_0, then the volume of the deteriorated region becomes $V_D = S_D \cdot L_0$ where S_D is the cross-sectional area of the deteriorated region (see Fig. 2). Thus, from the integral of Ψ_e^D, the elastic energy W_e^D in the deteriorated region is given by

$$W_e^D = \int_{S_D}\Psi_e^D L_0 dS_D = 2\pi\int_{R_t}^{R_0}\Psi_e^D L_0 R dR$$
$$= \left[\pi L_0\left(G_0 + \frac{\beta R_0}{\alpha_1}\right)(R_0^2 - R_t^2) - \frac{2\pi L_0\beta}{3\alpha_1}(R_0^3 - R_t^3)\right]\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] \tag{16}$$

and the elastic energy W_e^U in the undeteriorated region is given by

$$W_e^U = \int_{S_U}\psi_e^U L_0 dS_U = \pi L_0 R_0^2 G_f(1 - \alpha_1 + \alpha_1\gamma)^2\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] \tag{17}$$

where

$$\gamma = R_\infty / R_0 \in [0, 1) \tag{18}$$

is defined as the ratio of the final deterioration radius to the initial one and S_U is the cross-sectional area of undeteriorated region.

Furthermore, by using Eq. (9), we express the radius of undeteriorated area at time t in terms of the internal variable α_1 as follows:

$$R_t = R_0(1 - \alpha_1 + \alpha_1\gamma) \tag{19}$$

As a result, Eq. (16) can be rewritten in terms of the variable γ and the time dependent variable α_1:

$$W_e^D = \left\{\pi L_0 R_0^2\left(G_0 + \frac{\beta R_0}{\alpha_1}\right)\left[1 - (1 - \alpha_1 + \alpha_1\gamma)^2\right] - \frac{2\pi L_0\beta R_0^3}{3\alpha_1}\left[1 - (1 - \alpha_1 + \alpha_1\gamma)^3\right]\right\}$$
$$\times\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] \tag{20}$$

Subsequently, we can obtain the average free energy density of the fiber in the cross section through combining Eqs. (17) and (20):

$$\psi_e = \frac{1}{L_0\pi R_0^2}(W_e^U + W_e^D)$$
$$= \left[G_f\eta^2 + \left(G_0 + \frac{\beta R_0}{\alpha_1}\right)(1 - \eta^2) - \frac{2}{3}\frac{\beta R_0}{\alpha_1}(1 - \eta^3)\right]\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] \tag{21}$$

where η is introduced as the ratio of deterioration radius R_t at time t to the initial radius R_0, i.e., $\eta = R_t/R_0$. The expression of η can be obtained from Eq. (18) as:

$$\eta(\alpha_1) = 1 - \alpha_1 + \alpha_1\gamma \tag{22}$$

For a simpler expression, a new parameter G_t is further defined as the equivalent shear modulus at time t, which evolves with α_1 in the following form:

$$G_t(\alpha_1) = G_f\eta^2 + \left(G_0 + \frac{\beta R_0}{\alpha_1}\right)(1 - \eta^2) - \frac{2}{3}\frac{\beta R_0}{\alpha_1}(1 - \eta^3) \tag{23}$$

It is also noteworthy that through Eqs. (10) and (15), it can be found that both G_0 and β are determined by the internal variable α_1. Consequently, the linearly isotropic elastic energy density of the whole fiber region, without considering the damage from mechanical loadings, can be rewritten as the following simple form [23]:

$$\psi_e = G_t(\alpha_1)\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] \tag{24}$$

Then the Helmholtz free energy density can be obtained, from Eqs. (1) and (4), as

$$\psi = G_t(\alpha_1)(1 - \alpha_2)\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right] - G_f\ln\left[(1+e)^3\right] \tag{25}$$

where the first part is the modified elastic energy density in which $G_t(\alpha_1)(1-\alpha_2)$ describes both effects of damage respectively induced by UV-radiation and by mechanical loadings on the mechanical energy storing in the material, and the second part comes from the volumetric expansion induced by UV-radiation [26].

To quantify the energy dissipation in Eq. (8), we assume that the rate of dissipation is governed by the irreversible UV-radiation process, such that

$$\Xi_1(\alpha_1, \dot{\alpha}_1) = D\frac{\dot{\alpha}_1^{(m+1)/m}}{(1 - \alpha_1)^{1/n}} \tag{26}$$

where D is an evolution speed parameter related to material properties and mechanical physical stimuli, m and n represent the rate sensitivity indexes [27]. Since $0 \le \alpha_1 < 1$ and $\dot{\alpha}_1 \ge 0$, it is obvious that $\Xi_1(\alpha_1, \dot{\alpha}_1)$ in the above equality is non-negative, which is consistent with Eq. (7) and conforms to the inequality of energy dissipation. Such kind of energy has been successfully used in the analysis of thermo-oxidation [28], moisture absorption [23,29–32] and cavitation process [33]. It is further assumed that the strain e produced by UV-radiation (cf. Eq. (1)) varies linearly with the internal variable, namely,

$$e(\alpha_1) = K\,\alpha_1 \tag{27}$$

where K is the strain coefficient related to UV-radiation intensity and fiber properties. Moreover, there is no elastic strain when exposed to ultraviolet radiation, i.e.,

$$\varepsilon_i = 0 \tag{28}$$

Subsequently, by using the Helmholtz free energy (25) and Eqs. (26)-(28), the evolution of the UV-radiation process can be obtained as

$$D\frac{\dot{\alpha}_1^{1/m}}{(1 - \alpha_1)^{1/n}} = \frac{2G_f K}{1 + K\alpha_1} \tag{29}$$

Considering that the strain e induced by UV-radiation is sufficiently small, we can take $2G_f K/(1 + K\alpha_1) \approx 2G_f K$ so that Eq. (29) is reduced to

$$D_K\frac{\dot{\alpha}_1^{1/m}}{(1 - \alpha_1)^{1/n}} = 2G_f \tag{30}$$

where D_K represents the value of evolution speed parameter, defined by

$$D_K = D/K \tag{31}$$

Eq. (30) is a first-order ordinary differential equation for unknown $\alpha_1(t)$. Subjected to the initial condition $\alpha_1(0) = 0$, this initial-value problem can be solved. To get a analytical solution, we further set the rate sensitivity indexes in Eqs. (26) and (29) as $m = n = 1$. By doing so, the evolution equation of the internal variable α_1 can be obtained analytically, as follows:

$$\alpha_1 = 1 - \exp\left(-\frac{2G_f}{D_k}t\right) \tag{32}$$

As mentioned above, the damage of high strength fiber materials consists of two parts, UV-radiation aging and mechanical damage. Another damage variable α_2 is employed to measure the degree of degradation caused by mechanical loadings. The deformation promotes the development of existing micro-voids and micro-cracks in the high strength fibers. As the deformation continues to increase, the damage in the material would be exacerbated until the material finally fails.

Damage cracking of concrete was studied through loading experiments. Kaplan [17] found that strains at cracking and near ultimate failure are independent of the types of aggregate and water-cement ratio used, but related to strains. According to experimental results of Kaplan [17], Løland [34] believed that the damage degradation of materials was closely related to strain but independent of stress. Therefore, his study assumed the damage variable as a power law function of tensile strain, and established a continuous damage model through semi-empirical formula. Up to now, this model has been widely used in the load-response of concrete [35]. Based on the assumption of Løland [34], we extend the one-dimensional formulation of tensile strain to the three-dimensional deformation, so the strain energy term in Eq. (24) is given as

$$\alpha_2 = \frac{\chi}{1+\omega}\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right]^{\omega} \tag{33}$$

where χ is a material parameter and ω is the power law coefficient. Since the mechanical response of a high strength fibers is affected by the UV-radiation process, the material parameter χ is a function of the internal variable α_1. After the special form of the $\chi(\alpha_1)$ is determined which will be discussed in the next section, we have the evolution equation of the damage variable α_2.

By substituting Eq. (33) into (8), the energy dissipation rate Ξ_2 caused by the mechanical degradation from mechanical loadings, can be obtained:

$$\Xi_2(\alpha_2, \dot{\alpha}_2) = 2\omega\chi G_t\left[\frac{v_c}{1-2v_c}\left(\sum_{i=1}^{3}\varepsilon_i\right)^2 + \sum_{i=1}^{3}(\varepsilon_i)^2\right]^{\omega-1}\left\{\sum_{i=1}^{3}\dot{\varepsilon}_i\varepsilon_i + \frac{v_c}{1-2v_c}\sum_{j=1}^{3}\left[\dot{\varepsilon}_j\left(\sum_{i=1}^{3}\varepsilon_i\right)\right]\right\} \tag{34}$$

Since $\sum_{i=1}^{3}\varepsilon_i > 0$, $\sum_{i=1}^{3}\varepsilon_i\dot{\varepsilon}_i > 0$, and $\dot{\varepsilon}_j(\sum_{i=1}^{3}\varepsilon_i) > 0$ under mechanical loading of uniaxial tension, it is obvious that the above evolution function of internal variable α_2 is in line with the energy dissipation inequality Eq. (7).

Substituting Eqs. (25) and (33) into Eq. (6) gives the constitutive relation between mechanical stress and elastic strain:

$$\begin{cases} \sigma_1 = 2G_t(\alpha_1)(1-\alpha_2-\omega\alpha_2)\left(\varepsilon_1 + \dfrac{v_c}{1-2v_c}\displaystyle\sum_{i=1}^{3}\varepsilon_i\right) \\ \sigma_2 = 2G_t(\alpha_1)(1-\alpha_2-\omega\alpha_2)\left(\varepsilon_2 + \dfrac{v_c}{1-2v_c}\displaystyle\sum_{i=1}^{3}\varepsilon_i\right) \\ \sigma_3 = 2G_t(\alpha_1)(1-\alpha_2-\omega\alpha_2)\left(\varepsilon_3 + \dfrac{v_c}{1-2v_c}\displaystyle\sum_{i=1}^{3}\varepsilon_i\right) \end{cases} \tag{35}$$

4. Comparison with the experimental results

In this section, the constitutive model proposed in Section 2 and Section 3 is applied to predict the mechanical degradation induced by UV-radiation for high strength fiber materials. In order to validate the present model, the theoretically obtained tensile strengths and ultimate strains of Zylon® and Vectran® yarns are compared with available experimental results reported in the literature [1], in which four high strength fiber materials were exposed to UV rays using a Xenon lamp Weatherometer for 150 h, and tensile tests were made before and after ultraviolet radiation.

Firstly, for uniaxial tension in the fiber direction, the strains are given by

$$\begin{cases} \varepsilon_1 = \lambda_1 - 1 \\ \varepsilon_2 = \varepsilon_3 = -v_c(\lambda_1 - 1) \end{cases} \tag{36}$$

where λ_1 is the stretch along the fiber direction. Thus, by substituting Eq. (36) into Eq. (33), the internal variable α_2 can be expressed in terms of λ_1 as follows:

$$\alpha_2(\lambda_1) = \frac{\chi}{1+\omega}\left[(1+v_c)(\lambda_1-1)^2\right]^{\omega} \tag{37}$$

then the uniaxial stress can be obtained as

$$\sigma_1 = 2G_t(\alpha_1)\left\{1-\chi\left[(1+v_c)(\lambda_1-1)^2\right]^{\omega}\right\}\left[\lambda_1 - 1 + v_c(\lambda_1-1)\right] \tag{38}$$

Consequently, we can obtain the Young's modulus along the tensile direction as [36].

$$E = \left.\frac{d\sigma_1}{d\lambda_1}\right|_{\lambda_1=1} = 2(1+v_c)G_t(\alpha_1) \tag{39}$$

The following failure conditions should be satisfied for uniaxial tension of damaged fibers ($\alpha_1 \neq 0$) or undamaged fibers ($\alpha_1 = 0$) under UV-radiation [37]:

$$\sigma_1|_{\lambda_1=\lambda_c} = \sigma_c \tag{40}$$

$$\left.\frac{\partial\sigma_1}{\partial\lambda_1}\right|_{\lambda_1=\lambda_c} = 0 \tag{41}$$

where λ_c is the ultimate stretch along the tensile direction and σ_c is the uniaxial tensile strength. These two conditions lead to the following expressions for parameters χ and ω:

$$\chi = \left[1 - \frac{\sigma_c}{2G_t(\alpha_1)(\lambda_c-1)(1+v_c)}\right]\left[(1+v_c)(\lambda_c-1)^2\right]^{-\omega} \tag{42}$$

$$\omega = \frac{\sigma_c}{2[\sigma_c - 2G_t(\alpha_1)(\lambda_c - 1)(1 + \nu_c)]} \tag{43}$$

Recall that $G_t(\alpha_1)$ represents the deteriorated shear modulus related to the internal variable α_1 evolving with UV radiation time, whose expression is given by Eq. (23). From Eqs. (42) and (43), the parameters χ and ω can be determined by the uniaxial tensile strength σ_c and the ultimate stretch λ_c. Typically, the tensile strength can be expressed as

$$\sigma_c = 2G_t(\alpha_1)\left\{1 - \chi\left[(1 + \nu_c)(\lambda_c - 1)^2\right]^{\omega}\right\}[(1 + \nu_c)(\lambda_c - 1)] \tag{44}$$

When $\alpha_1 = 0$, σ_c reduces to the strength of the undamaged fiber. This means that the failure condition not only involves the damage but the strength of the undamaged fiber.

4.1. Elastic moduli

Now we study the evolution of elastic moduli of the testing samples during UV-radiation. The Young's moduli of yarns can be obtained from Eq. (23) as

$$E_t = 2(1 + \nu_c)\left\{G_f\eta^2 + \left(G_0 + \frac{\beta R_0}{\alpha_1}\right)(1 - \eta^2) - \frac{2}{3}\frac{\beta R_0}{\alpha_1}(1 - \eta^3)\right\} \tag{45}$$

Assuming that at the final deterioration stage (i.e., at time $t = 144h$), the deterioration evolution factor $\alpha_1 = 1$. In the present model, $k = 1$ are chosen for Eq. (10), namely,

$$G_0 = G_f(1 - \alpha_1) \tag{46}$$

$$\beta = \alpha_1 G_f \,/\, [R_0(1 - \gamma)] \tag{47}$$

Recalling Eqs. (15) and (22), and using Eqs. (46), (47) with $\alpha_1 = 0$ and $\alpha_1 = 1$, the Young's moduli at the initial configuration and at the final deterioration configuration, $E_1|_{t=0}$ and $E_1|_{t=\infty}$, can be respectively obtained as

$$\begin{cases} E_1|_{t=0} = E_1|_{\alpha_1=0} = 2(1 + \nu_c)G_f \\ E_1|_{t=\infty} = E_1|_{\alpha_1=1} = \dfrac{2}{3}(1 + \nu_c)G_f(1 + \gamma + \gamma^2) \end{cases} \tag{48}$$

Obviously, $E_1|_{t=\infty} = E_1|_{\alpha_1=0} < E_1|_{t=0} = E_1|_{\alpha_1=1}$ since $0 \le \gamma < 1$, which indicates longtime exposure to UV-radiation would degrade the elastic modulus. When $\gamma = 0$ or $R_\infty = 0$, the greatest modulus degradation is reached and we have $E_1|_{t=\infty}/E_1|_{t=0} = E_1|_{\alpha_1=0}/E_1|_{\alpha_1=1} = 1/3$ from Eq. (48). This means that the elastic modulus decreases to one third of the initial modulus due to UV-radiation.

Therefore, using the experimental results of the initial and final Young's moduli given in Table 1, and the commonly used Poisson's ratio $\nu_c = 0.3$ for high strength fibers [38], we can solve the equations from (48) for G_f and γ. Substituting Eq. (32) into Eq. (45), and then using it to determine the unknown parameter D_K through fitting the experimental data of tensile modulus versus time based on the least square method, as shown in Fig. 3 for Zylon® and Vectran® yarns respectively. The specific values of ν_c, G_f, γ and D_K for these two types of yarns are listed in Table 2.

From Fig. 3, we can see that both experimental and theoretical results decrease over UV-radiation time. With the increase of UV-radiation time, the theoretically predicted tensile modulus decreases rapidly at first and then slowly, which agrees well with the experimental data in the large trend, but deviates a little bit at some points, such as at $t = 72$h, 120h for Zylon® yarns and at $t = 24$h for Vectran® yarns. Part of the reason may be that the fibers have a certain degree of dispersion and our model does not take into account the interaction of individual fibers in the yarn. Moreover, the yarns are actually an irregular cross section shape but the model assumes a cylindrical shape.

Table 1
Radius, initial Young's modulus and final Young's modulus from experiment [1].

Yarn Type	R_0(cm)	$E\|_{t=0}$ (GPa)	$E\|_{t=\infty}$ (GPa)
Zylon®HM	0.475	125.094	85.922
Vectran®T-97	0.492	90.048	36.918

4.2. Tensile strength

In addition to elastic modulus, tensile strength is the most important mechanical property of high strength fibers. In order to determine the evolution equation of tensile strength given by (44), the specific forms of λ_c and χ should be given first. The ultimate stretch λ_c is assumed to take an exponential function which decreases with UV-radiation time, as follows:

$$\lambda_c = u_1 + u_2 \exp(-u_3 t) \tag{49}$$

where u_1, u_2, u_3 are three parameters which can be fitted via the least square method from the experimental results [1]. as shown in Fig. 4. The fitting values of u_1, u_2, u_3 are given in Table 4.

The degradation of mechanical properties of fibers is caused by both stress loading and UV-radiation, so the stress damage and UV radiation damage are dependent on each other. As shown in Eq. (33), the internal variable α_2 due to mechanical loading depends on the material parameter χ which is a function of the internal variable α_1 induced by UV-radiation. Hence, a most simple linear relationship between χ and α_1 is employed here:

$$\chi = \varphi_1 + \alpha_1\varphi_2 \tag{50}$$

where φ_1 and φ_2 are coefficients to be determined.

Substituting Eqs. (49) and (50) into (44), the tensile strength can be derived as

$$\sigma_c = 2G_t(\alpha_1)(1 - \xi_1 - \xi_2\alpha_1)(1 + \nu_c)(\lambda_c - 1) \tag{51}$$

with

$$\begin{aligned} \xi_1 &= \varphi_1\left[(1 + \nu_c)(\lambda_c - 1)^2\right]^{\omega} \\ \xi_2 &= \varphi_2\left[(1 + \nu_c)(\lambda_c - 1)^2\right]^{\omega} \end{aligned} \tag{52}$$

For yarns without UV-radiation ($\alpha_1 = 0$), Eq. (51) degenerates to the uniaxial tensile strength at the initial state:

$$\sigma_c|_{t=0} = 2(\nu_c + 1)G_f(1 - \xi_1)\left(\lambda_c|_{t=0} - 1\right) \tag{53}$$

For yarns in a UV-radiation equilibrium state ($\alpha_1 = 1$), Eq. (51) reduces to the uniaxial tensile strength at the finial state:

$$\sigma_c|_{t\to\infty} = \frac{2G_f}{3}(1 + \nu_c)\left(1 + \gamma + \gamma^2\right)(1 - \xi_1 - \xi_2)\left(\lambda_c|_{t\to\infty} - 1\right) \tag{54}$$

Considering $E|_{t=0} = 2(1 + \nu_c)G_f$, from Eqs. (49), (53) and (54), parameters ξ_1 and ξ_2 in Eq. (51) can be obtained as

$$\xi_1 = 1 - \frac{\sigma_c|_{t=0}}{E|_{t=0}(u_1 + u_2 - 1)} \tag{55}$$

$$\xi_2 = \frac{\sigma_c|_{t=0}}{E|_{t=0}(u_1 + u_2 - 1)} - \frac{3\sigma_c|_{t\to\infty}}{E|_{t=0}(1 + \gamma + \gamma^2)(u_1 - 1)} \tag{56}$$

With $\sigma_c|_{t=0}$, $\sigma_c|_{t\to\infty}$ given in Table 3 and $E|_{t=0}$ in Table 1, γ in Table 2, u_1, u_2, u_3 in Table 4, we can calculate ξ_1 and ξ_2 for Zylon® and Vectran® yarns respectively and list them in Table 4.

Fig. 4 shows the experimental and theoretical results of ultimate stretch of Zylon® and Vectran® yarns under different UV-radiation time. From Fig. 4, we can see that the ultimate stretch of these two yarns decreased with the increase of UV-radiation time, which indicates that the mechanical properties of yarns are damaged continuously with the increase of radiation time. However, the damage does not increase

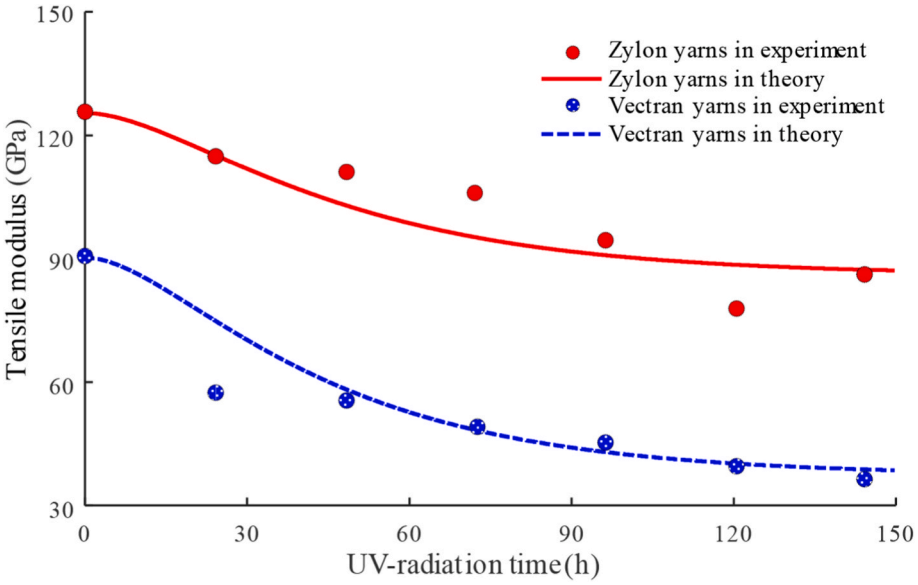

Fig. 3. The variation of tensile modulus of Zylon® and Vetcran® yarns with UV-radiation time.

Table 2
Parameters ν_c, G_f, γ and D_K from Eqs. (32), (45) and (48).

Yarn Type	ν_c	G_f (GPa)	γ	D_K (kN·h·mm^{-2})
Zylon®HM	0.300	48.113	0.645	3436.643
Vectran®T-97	0.300	34.634	0.261	2474.500

anymore when the radiation time exceeds 96 h, and the ultimate stretch gradually approaches a fixed value. After the radiation time exceeds 144 h (the damage was basically stable), Zylon® yarn decreased its ultimate stretch by 3% compared to its initial ultimate stretch (from 1.037 to 1.007), while Vectran® yarn decreased by only 2.2% (from 1.035 to 1.013). This indicates that the UV-radiation damage resistance of yarns is different, and the UV-radiation resistance of Zylon® yarn is lower than that of Vectran® yarn. It is worth noting that near 24 h of UV-radiation, the ultimate stretch of Vectran® yarn in the experimental data increased abnormally, far deviating from the varying trend of normal experimental results. Since the total energy of the material continues to dissipate, we believe that this abnormal point may be caused by the error and contingency of the experiment, which can be overlooked.

Substituting Eqs. (23) and (49) as well as ξ_1 and ξ_2 from Table 4 into

Table 3
Tensile strength $\sigma_c|_{t=0}$, $\sigma_c|_{t\to\infty}$ of yarns in experiment [1].

Yarn Type	$\sigma_c\|_{t=0}$ (GPa)	$\sigma_c\|_{t\to\infty}$ (GPa)
Zylon®HM	4.531	0.647
Vectran®T-97	3.133	0.423

Table 4
Parameters u_1, u_2, u_3 and ξ_1, ξ_2 of yarns in experiment [1].

Yarn Type	u_1	u_2	u_3	ξ_1	ξ_2
Zylon®HM	1.009	0.027	0.050	−0.006	0.170
Vectran®T-97	1.014	0.020	0.035	−0.023	0.266

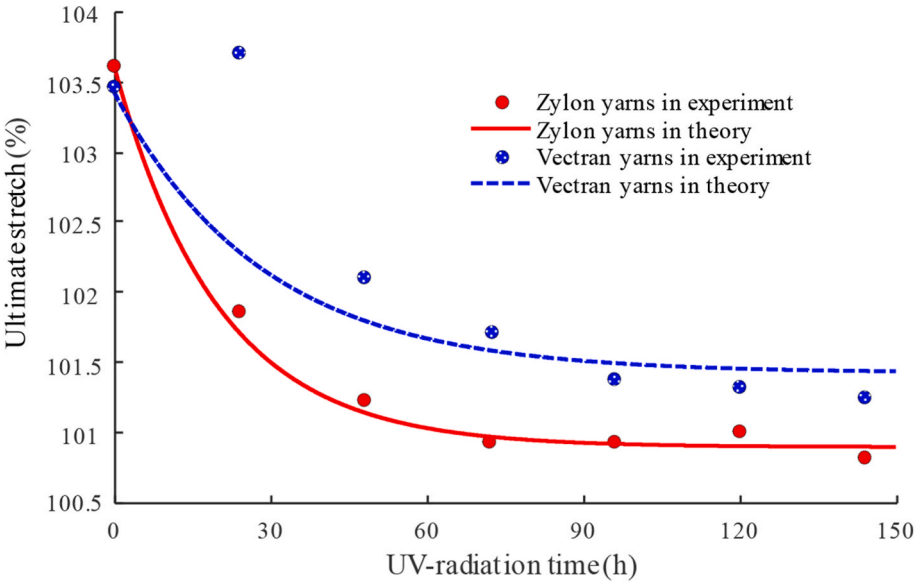

Fig. 4. Comparison of theoretical and experimental [1] of ultimate stretch.

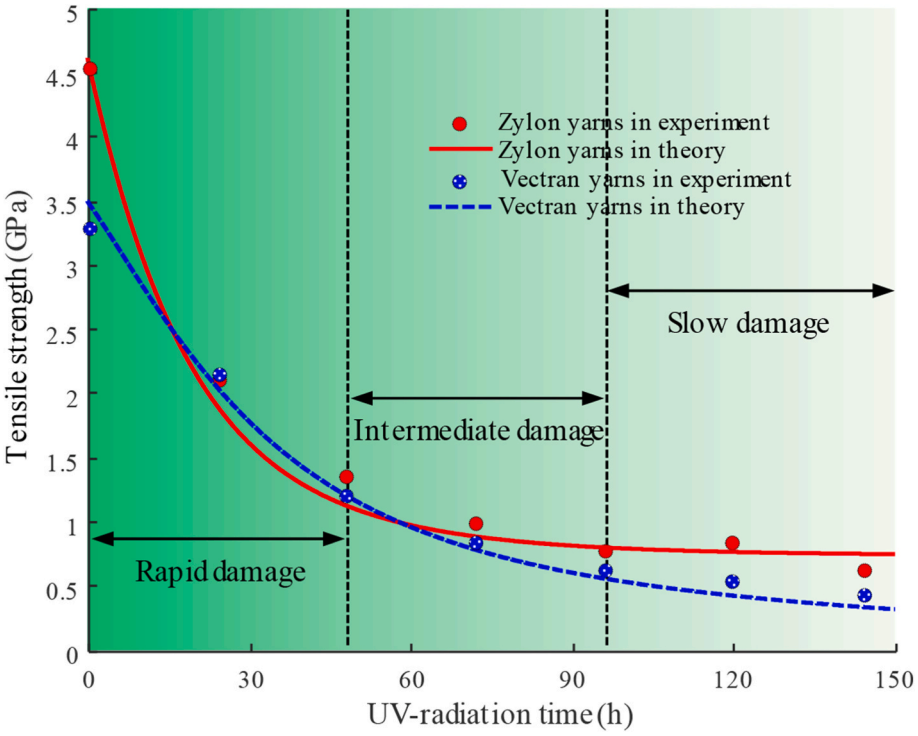

Fig. 5. Comparison of theoretical and experimental [1] uniaxial tensile strength.

Eq. (51), we can obtain the theoretical evolution laws of tensile strength for Zylon® and Vectran® yarns, as shown in Fig. 5. It can be seen that the theoretical results are in good agreements with the experiment data, which indicates that our model is rational and accurate. Both theoretical predictions and experimental observations reveal that the tensile strength of the yarns can be deteriorated in a radiation environment. With the increase of UV-radiation time, the tensile strength decreases gradually, the speed changes from fast to slow, and finally approaches a fixed value. Therefore, the curve can be roughly divided into three stages (see Fig. 5): rapid damage stage ($0 < t \leq 48$ h), intermediate damage stage ($48\text{h} < t \leq 96$ h) and slow damage stage ($96\text{h} < t < \infty$). The tensile strengths of these two materials decrease by more than half of the initial value at the rapid damage stage, and continue to decrease by nearly a quarter at the intermediate damage stage, and finally decline to a relatively stabilized value at the slow damage stage. The degradation in strength and modulus of high strength fibers is caused by microcracks or voids near the surface due to UV-radiation [13]. Therefore, in order to reduce such mechanical degradation and aging, the UV resistance of materials can be improved by surface coating process [39]. Although the present work focuses on high strength fiber materials, the proposed theoretical model can be applied to any fiber reinforced composites.

5. Conclusions

A constitutive model of high strength fibers is developed based on the thermodynamics considering the deterioration process included UV-radiation and mechanical loading during the tensile test. In the proposed model, the evolution equations of two internal variables are derived from the perspective of non-equilibrium thermodynamics, which can describe the thermodynamic dissipation process of fiber degradation under UV-radiation and mechanical loading. By comparing the theoretical model with the experimental results, it is proved that the present model is capable to effectively describe the evolution of elastic modulus and tensile strength of fibers under UV-radiation and mechanical loading. This model is expected to be used to analyze the load response of high strength fiber composites under UV radiation and to evaluate the effective life of the materials under long-term aging, providing theoretical basis for the engineering application of fiber reinforced composites.

Author contributions

All authors contributed to the study conception and design. **Haoran Song**: Conceptualization, Visualization, Software, Formal analysis, Writing-original draft. **Penghua Ying**: Conceptualization, Formal analysis, Methodology, Investigation, Writing-original draft. **Pingping Zhu**: Validation, Formal analysis, Funding acquisition, Writing-review & editing. **Yexin Zhou**: Methodology, Investigation, Writing-review & editing. **Zheng Zhong**: Conceptualization, Supervision, Validation, Funding acquisition, Writing-review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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