TIME-TEMPERATURE-STRESS EQUIVALENCE AND ITS APPLICATION TO NONLINEAR VISCOELASTIC MATERIALS^{*}

Luo Wenbo^{1,2} Yang Ting-Qing¹ An Qunli¹

(¹Department of Mechanics, Huazhong University of Science and Technology, Wuhan 430074, China) (² Institute of Fundamental Mechanics and Material Engineering, Xiangtan University, Xiangtan 411105, China)

ABSTRACT Stress-dependence of the intrinsic time of viscoelastic materials was investigated in this paper. The influence of stress level on the intrinsic time is considered to be similar to that of temperature, pressure, solvent concentration, damage and physical aging. The time-temperature-stress equivalence principle is proposed. Using which, the creep curves at different temperatures and stress levels can be shifted into a master curve at reference temperature and stress level. Thus the long-term creep behavior of viscoelastic materials at lower temperature and stress can be predicted from the short-term one at higher temperature and stress. As an example, the nonlinear creep behavior of high-density polyethylene (HDPE) at room temperature was studied using the presented time-temperature-stress equivalence principle

KEY WORDS creep, viscoelastic, time-temperature-stress equivalence principle

. INTRODUCTION

The importance of the viscoelastic properties of materials has been realized because of the rapid developments in rubber and plastics industry. Many advances in the studies of constitutive relations, failure theories and life prediction of viscoelastic materials and structures were reported and reviewed in the last two decades^[1-5]. Time dependence of mechanical behavior of viscoelastic materials reveals the existence of inner clock or intrinsic time, which can be influenced by many factors such as temperature^[6], physical aging^[7-9], damage^[10], pressure, solvent concentration^[11,12], strain and stress level ^[13-15] etc. The changes in intrinsic time of viscoelastic materials are usually studied in the framework of the free volume theory. In this paper, the dependence of intrinsic time of viscoelastic materials on the combination of applied stress level and temperature was considered. Based on the free volume theory, the time-temperature-stress shift factor was deduced and the time-temperature-

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stress equivalence principle was proposed. Using which, the nonlinear creep behavior of high-density polyethylene (HDPE) at room temperature was studied and the master curve at reference stress level was given. It is shown that the long-term creep behavior at lower temperatures and stress levels can be predicted from the short-term one at higher temperatures and stress levels, which is important and practically valuable for the studies of mechanical behavior and life prediction of viscoelastic materials and structures.

. TIME-TEMPERATURE-STRESS EQUIVALENCE PRINCIPLE

According to the free volume theory, the viscosity of materials, η , can be related to the free volume fraction, f, via Doolittle equation^[6] in the form as:

$$\eta = A \exp(B / f) \tag{1}$$

where A and B are material constants.

Eq.(1) is the basis of the time-temperature superposition principle^[6], which states that the mechanical behavior of viscoelastic materials at different time scales can be equivalent by changing their serving temperatures. A linear dependence of the free volume fraction on temperature change is widely used ^[2,6]:

$$f = f_0 + \alpha_T (T - T_0) \tag{2}$$

where α_T is the thermal expansion coefficient of the free volume fraction, f_0 is the free volume fraction at reference temperature. Define the time-temperature shift factor as $\phi_T = \tau / \tau_0 = \eta / \eta_0$, in which η_0 and τ_0 are material viscosity and relaxation time at reference temperature T_0 respectively, η and τ are material viscosity and relaxation time at temperature *T* respectively, then

$$\log \phi_T = \frac{B}{2.303} \left(\frac{1}{f} - \frac{1}{f_0} \right)$$
(3)

Substituting Eq.(2) into Eq.(3) yields the well-known Williams-Landel-Ferry(WLF) equation^[6]:

$$\log \phi_T = -\frac{B}{2.303f_0} \left(\frac{T - T_0}{f_0 / \alpha_T + T - T_0} \right) = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)}$$
(4)

in which $C_1 = B/(2.303f_0)$, $C_2 = f_0/\alpha_T$.

The concept of "stress clock" or time-stress superposition was first proposed by Bernstein and Shokooh^[14]. From which it is assumed that, like with temperature, the relaxation times of viscoelastic materials can be affected by the applied stress level via the stress-induced free volume changes. Considering both the temperature and stress dependence of the free volume fraction of viscoelastic materials, we suppose the free volume fraction can be expressed in a form similar to Eq.(2):

$$f = f_0 + \alpha_T (T - T_0) + \alpha_\sigma (\sigma - \sigma_0) \tag{5}$$

where α_{σ} refers to the stress-induced expansion coefficient of the free volume fraction.

Suppose there exists a combined temperature-stress shift factor $\phi_{T\sigma}$, which satisfies

$$\eta(T,\sigma) = \eta(T_0,\sigma_0)\phi_{T\sigma} \tag{6}$$

then from Eqs.(1) and (5) we have

$$\log \phi_{T\sigma} = -C_1 \left[\frac{C_3 (T - T_0) + C_2 (\sigma - \sigma_0)}{C_2 C_3 + C_3 (T - T_0) + C_2 (\sigma - \sigma_0)} \right]$$
(7)

where $C_3 = f_0 / \alpha_{\sigma}$. Eq.(7) reduces to Eq.(4) if there is no stress change.

Moreover, we define stress shift factor at constant temperature ϕ_{σ}^{T} and temperature shift factor at constant stress level ϕ_{τ}^{σ} in such forms that

$$\eta(T,\sigma) = \eta(T,\sigma_0)\phi_{\sigma}^{T} = \eta(T_0,\sigma_0)\phi_{\sigma}^{T_0}\phi_{\sigma}^{T}$$
$$= \eta(T_0,\sigma)\phi_{T}^{\sigma} = \eta(T_0,\sigma_0)\phi_{\sigma}^{T_0}\phi_{T}^{\sigma}$$
(8)

then

$$\log \phi_{\sigma}^{T} = -C_{1} \frac{C_{2}}{C_{2} + (T - T_{0})} \left[\frac{C_{2}(\sigma - \sigma_{0})}{C_{2}C_{3} + C_{3}(T - T_{0}) + C_{2}(\sigma - \sigma_{0})} \right]$$
(9)

$$\log \phi_T^{\sigma} = -C_1 \frac{C_3}{C_3 + (\sigma - \sigma_0)} \left[\frac{C_3 (T - T_0)}{C_2 C_3 + C_3 (T - T_0) + C_2 (\sigma - \sigma_0)} \right]$$
(10)

In addition, from Eqs.(5) and (7), we have

$$\phi_{T\sigma} = \phi_T^{\sigma_0} \phi_\sigma^T = \phi_\sigma^{T_0} \phi_T^{\sigma}$$
(11)

It is shown from Eq.(11) that the time-dependent mechanical properties of viscoelastic materials at different temperatures and stress levels for some convenient time scales can be shifted along the time scale to construct a master curve of a wider time scale at a given temperature T_0 and stress level σ_0 by one step via the combined temperature-stress shift factor $\phi_{T\sigma}$ or by two steps via the stress shift factor at constant temperature ϕ_{σ}^{T} and the temperature shift factor at constant stress level ϕ_{T}^{σ} .

. APPLICATION TO NONLINEAR CREEP ANALYSIS OF HDPE

Uniaxial tensile creep tests of high-density polyethylene (HDPE) at four different stress levels were performed under room temperature. The stress dependence of creep compliance was analyzed using the above proposed time-temperature-stress equivalence principle, where the creep compliance is defined as the ratio of strain to applied stress. The tensile load divided by the initial cross sectional area of the specimen is defined as the stress under which the creep tests were conducted. The strain here is referred to as engineering strain.

The test temperature is chosen as the reference temperature T_0 . Defining ϕ_{σ} as the stress shift factor at reference temperature , from Eq.(7), we have

$$\log \phi_{\sigma} = -\frac{B}{2.303f_0} \left(\frac{\sigma - \sigma_0}{f_0 / \alpha_{\sigma} + \sigma - \sigma_0} \right) = -\frac{C_1(\sigma - \sigma_0)}{C_3 + (\sigma - \sigma_0)}$$
(12)

The creep compliance curves at different stress levels can be related to each other by the reduced time ξ ($\xi = t / \phi_{\sigma}$) in the following form:

$$J(t,\sigma) = b_{\sigma}J(t/\phi_{\sigma},\sigma_0) = J(\xi,\sigma_0)$$
(13)

where $\tilde{J}(\xi, \sigma_0)$ is the master curve of creep compliance at reference stress σ_0 , b_{σ} is the vertical shift factor along the creep compliance axis, which can reflect the effects of stress-induced

microstructure changes on the mechanical properties of materials(e.g. creep compliance) and have the form similar to the stress shift factor:

$$\log b_{\sigma} = -\frac{D_1(\sigma - \sigma_0)}{D_2 + (\sigma - \sigma_0)} \tag{14}$$

in which D_1 and D_2 are material constants.

Fig.1 shows the experimental creep compliance curves at four different stress levels. The experimental curves indicate that HDPE exhibits a strong nonlinear behavior with the stress dependence and time dependence of creep compliance coupled. The creep rate increases with the stress level, which is similar with temperature.



Fig.1 Creep compliance curves at four different stress levels

Fig.2 Master curve of creep compliance for $\sigma_0 = 7.31 \text{ MPa}$

If the creep compliance is plotted versus time in a double logarithmic coordinate system, as shown in Fig.1, a consistent master curve can be constructed by applying horizontal and vertical shifts of creep compliance curves into a reference curve. Fig.2 shows the master curve of creep compliance at 7.31MPa. The corresponding horizontal and vertical shifts, i.e. $\log \phi_{\sigma}$ and $\log b_{\sigma}$, are shown in Fig.3 and Fig.4 respectively. By nonlinear fitting it is known that C_1 =8.694, C_3 =15.457, D_1 =2.174 and D_2 =33.346.



Using Eq.(13), the nonlinear creep strain $\varepsilon(t)$ under constant stress σ can be expressed as:

$$\varepsilon(t) = \sigma J(t,\sigma) = \sigma \widetilde{J}(\xi,\sigma_0)$$
(15)

where $\tilde{J}(\xi, \sigma_0)$ is the master curve of creep compliance for reference stress σ_0 , and can be represented by the Prony series as :

$$\widetilde{J}(t) = J_0 + \sum_{i=1}^n J_i \left[1 - \exp\left(-\frac{t}{\tau_i}\right) \right]$$
(16)

It is found that taking seven terms in the Prony series and choosing the intrinsic relaxation time τ_i as 10^i suffices to obtain a good fit of Eq.(16) to the data in Fig.2. J_0 and J_i are thus determined and listed in Fig.5.



Fig.5 Master curve of creep compliance (\cdot) and its representation of Prony series (-) for $\sigma_0 = 7.31$ MPa

In the case of uniaxial tensile creep, the hydrostatic pressure in tested materials can be expressed by $p = -\frac{1}{3}\sigma$. Substituting which into Eq.(12) leads to

$$\log \phi_{\sigma} = -\frac{B}{2.303f_0} \left(\frac{p_0 - p}{f_0 / \alpha_p + p_0 - p} \right)$$
(17)

in which $\alpha_p = 3\alpha_\sigma$, named isothermal compressibility of the free volume. The expression in the right hand side of Eq.(17) is the time-pressure shift factor, $\log a_p^{[11,12]}$, when pressure changes from p_0 to p. Therefore, the time-stress equivalence is consistent with the time-pressure equivalence in the case of uniaxial loading.

CONCLUSIONS

In the framework of the free volume theory, the effects of temperature and applied stress level on the intrinsic time of viscoelastic materials were synthetically considered. The time-temperature-stress equivalence principle was proposed. The expressions of the combined temperature-stress shift factor $\phi_{T\sigma}$, the stress shift factor at constant temperature ϕ_{σ}^{T} and the temperature shift factor at constant stress level ϕ_{T}^{σ} were derived. It is shown that the time-dependent mechanical properties of viscoelastic materials at different temperatures and stress levels for some convenient time scales can be shifted along the time scale to construct a master curve of a wider time scale at a given temperature

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and stress level by one step via the combined temperature-stress shift factor $\phi_{T\sigma}$ or by two steps via the stress shift factor at constant temperature ϕ_{σ}^{T} and the temperature shift factor at constant stress level ϕ_{T}^{σ} . The creep rate at higher stress level is great than that at lower stress level, which is similar to the effect of temperature on the creep behavior of materials. Therefore the long-term creep behavior of viscoelastic materials at lower temperature and stress can be predicted from the short-term one at higher temperature and stress, which is important and practically valuable for the studies of mechanical behavior and life prediction of viscoelastic materials and structures.

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