

Test Method

# Application of time–stress equivalence to nonlinear creep of polycarbonate

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## Abstract

Stress induced changes in intrinsic timescale were investigated by nonlinear creep tests on polycarbonate at room temperature. The creep compliance vs. time curves at nine different stress levels were determined and shifted along the logarithmic time axis to get a master compliance curve at a given reference stress level according to the concept of time–stress equivalence. It is shown that the time–stress superposition principle provides an accelerated test technique for evaluating the material's long-term mechanical properties.

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## 1. Introduction

Since polymers are widely used in many engineering applications, a thorough knowledge of their mechanical properties is crucial. Most polymers exhibit time-dependent mechanical behavior, usually referred to as viscoelasticity. There are two time-scales in the study of viscoelasticity. The first is the observation time measured by the ordinary watch. The second is the material's intrinsic time that is revealed by viscoelastic relaxation or retardation time. This material intrinsic time can be influenced by many factors such as temperature [1], physical aging [2,3], damage [4], pressure, solvent concentration [5,6], strain [7], stress level [8–10], etc. With regard to the temperature effect on this intrinsic time, the well-known time–temperature superposition principle states that the mechanical behavior of viscoelastic materials at different time scales can be made equivalent by changing their service temperatures.

If the material is linear viscoelastic, the Boltzmann superposition principle can be used to predict the

deformation of polymeric solids subjected to arbitrary time-dependent loads. This is generally true for cases in which the applied stresses are sufficiently small to have a negligible effect on the material's properties. However, at higher stresses, most polymers exhibit nonlinear viscoelastic behavior due to the fact that stresses change the distribution of relaxation times to shorter times; that is stresses change the material's intrinsic timescale. A modification to the Boltzmann superposition principle has been proposed to account for the effects of elevated stresses [11].

Based on the fact that higher stresses quicken creep or relaxation of viscoelastic materials, which is similar to the effect of higher temperatures, several time–temperature–stress superposition principles (TTSSP) have been proposed [10,12–14]. According to TTSSP, the time-dependent mechanical properties of viscoelastic materials at different temperatures and stress levels can be shifted along the time scale to construct a master curve at a reference temperature and stress level. The objective of this research is to investigate the stress effect on the creep behavior of polycarbonate (PC), and to get the master compliance curve using a TTSSP.

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## 2. Time–temperature–stress superposition principle

Below, the TTSSP proposed by one of the authors [10] is briefly deduced within the framework of free volume theory. Free volume is the void space that is available for segmental motions in polymers. A change in free volume influences the mobility of the material and directly impacts upon its time-dependent mechanical properties. The larger the free volume, the greater the mobility of the molecular response to external loading.

According to the free volume theory, the viscosity of the material,  $\eta$ , which reflects the material's intrinsic time, can be related to the free volume fraction,  $f$ , via the Doolittle equation [1] in the form

$$\eta = A \exp \left[ B \left( \frac{1}{f} - 1 \right) \right] \quad (1)$$

where  $A$  and  $B$  are material constants.

We assume that the stress-induced change in the free volume fraction is linearly dependent on the stress change, much like the effect of temperature on the change in free volume. Considering both the temperature and stress dependence of the free volume fraction of viscoelastic materials, the free volume fraction can be expressed as [10]

$$f = f_0 + \alpha_T(T - T_0) + \alpha_\sigma(\sigma - \sigma_0) \quad (2)$$

where  $\alpha_T$  is the thermal expansion coefficient of the free volume fraction,  $\alpha_\sigma$  refers to the stress-induced expansion coefficient of the free volume fraction, and  $f_0$  is the free volume fraction at the reference state.

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

$$\eta(T, \sigma) = \eta(T_0, \sigma_0) \phi_{T\sigma} \quad (3)$$

then from Eqs. (1) and (2) we have

$$\log \phi_{T\sigma} = -C_1 \left[ \frac{C_3(T - T_0) + C_2(\sigma - \sigma_0)}{C_2 C_3 + C_3(T - T_0) + C_2(\sigma - \sigma_0)} \right] \quad (4)$$

where  $C_3 = f_0/\alpha_\sigma$ . Eq. (4) reduces to the WLF equation if there is no stress difference.

Moreover, we define the stress shift factor at a constant temperature,  $\phi_\sigma^T$ , and the temperature shift factor at a constant stress level,  $\phi_T^\sigma$ , in such a way that

$$\begin{aligned} \eta(T, \sigma) &= \eta(T, \sigma_0) \phi_\sigma^T = \eta(T_0, \sigma_0) \phi_T^\sigma \phi_\sigma^T = \eta(T_0, \sigma) \phi_T^\sigma \\ &= \eta(T_0, \sigma_0) \phi_T^\sigma \phi_\sigma^T \end{aligned} \quad (5)$$

then we have

$$\phi_{T\sigma} = \phi_T^\sigma \phi_\sigma^T = \phi_\sigma^{T_0} \phi_T^\sigma \quad (6)$$

It is shown from Eq. (6) 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 reference

temperature,  $T_0$ , and reference stress level,  $\sigma_0$ , in one step via the temperature–stress shift factor,  $\phi_{T\sigma}$ , or in two steps via a combination of the stress shift factor at a constant temperature,  $\phi_\sigma^T$ , and the temperature shift factor at a constant stress level,  $\phi_T^\sigma$ .

Where the service temperature is chosen as the reference temperature,  $T_0$ , Eq. (4) reduces to

$$\begin{aligned} \log \phi_\sigma &= -\frac{B}{2.303 f_0} \left( \frac{\sigma - \sigma_0}{f_0/\alpha_\sigma + \sigma - \sigma_0} \right) \\ &= -\frac{C_1(\sigma - \sigma_0)}{C_3 + (\sigma - \sigma_0)} \end{aligned} \quad (7)$$

where  $\phi_\sigma$  denotes the stress shift factor. With this shift factor, the nonlinear creep behavior can be described via the stress-induced reduced time,  $t/\phi_\sigma$ :

$$J(\sigma, t) = J(\sigma_0, t/\phi_\sigma) \quad (8)$$

## 3. Experiments

The material used for tests in this study was Tuffak<sup>®</sup> polycarbonate (PC). Dumb-bell shaped specimens, with a cross-section of 12.15 mm × 2.15 mm, were cut from a very regular transparent PC sheet with polished surfaces. All the tests were completed under isothermal axial tensile creep conditions.

Most of the conventional methods used in strain measurement are inappropriate for polymers because they require surface preparation. It is important to ensure that the method used does not actually influence measurement results, and so measurements must be carried out with non-contact and non-disturbing evaluations. Furthermore, the method must perform a two-dimension analysis. For this study, we therefore adopted a mark-tracing technique [15,16], whereby the gauge section of the specimen is directly marked with four tiny ink dots, which are used to detect surface strains during loading. The strain tensor measurement was carried out by calculating the geometrical state (density and orientation) of four dots with respect to the reference state (undistorted state) according to the process of large strain kinetics.

Fig. 1 shows the diagram of the test device system, including a testing machine developed by LMS (University of Poitiers), a data acquisition unit and an imaging processing device [16,17]. The maximal loading was limited to 5000 N, and we imposed a requirement that the center of the specimen stay in the same position during the test: this is in fact imposed by the strain measurement method. The command allows for the control of displacement and effort for any type of loading to be applied [15]. One of the loading programs consists of applying an imposed uniaxial tension creep test. The geometrical transformations of the dots during loading exactly

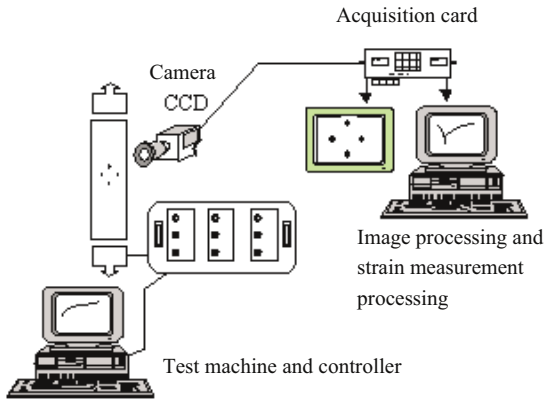


Fig. 1. Schematic of the test device system.

reflect the specimen's surface strains. Thus, determining the strain field means following the dots geometrical transformation (displacement). Then, through the process of giving the Cartesian coordinates of dots coupled with the procedure of strain kinetics, the amplitude of the principal strains can be determined by comparing the undeformed and the deformed states. The dots are recorded in quasi-real time by a CCD video camera ( $512 \times 512$  pixels), and digitally analyzed to calculate the axial strain, using a personal-computer-based image processing system after each deformation increment. The precise position of the center of each dot is found by using a centroid algorithm, which is well documented in the work of one of the authors [18].

Uniaxial tensile creep tests were performed at room temperature for 1 h by single-step loading PC strips and we record the resulting axial strain as a function of time. For each test, the creep compliance was determined as the ratio of the time-dependent strain to the constant applied stress. In order to check the linearity of the creep behavior of the tested material, the tests were conducted at nine different stress levels, from 15.89 to 59.4 MPa. If the creep strain is directly proportional to the applied stress at any given time, that is the creep compliance is independent of the imposed stress, the material is linear for the stress and strain levels encountered. This is generally true for small stresses, but in the case of higher stress levels, doubling the stress more than doubles the amount of creep, resulting in different compliances at different stress levels, and so the behavior is nonlinear.

#### 4. Results and discussion

Fig. 2 shows the creep behavior of PC at nine different stress levels. During creep at a constant force, the strain increases with time. Moreover, the higher the applied

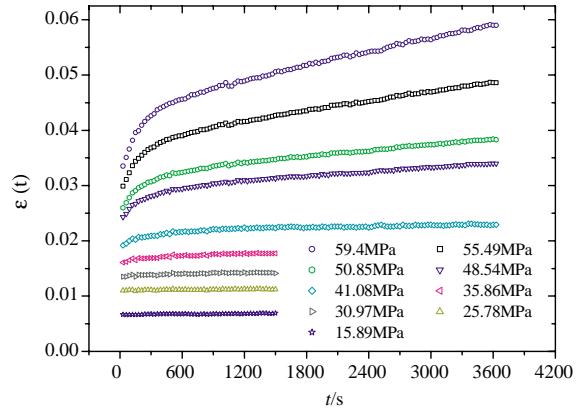


Fig. 2. Creep strain vs. time at different stress levels.

stress, the higher the strain rate at any given time. When we define the creep compliance  $J(t)$  as the ratio of measured time-dependent strain,  $\varepsilon(t)$ , to the applied constant stress,  $\sigma_0$ , we get the compliance curves as shown in Fig. 3, in which the compliance curves for the stresses of 15.89 and 25.78 MPa nearly coincide with each other. This implies that below approximately 26 MPa, the measured strain is usually proportional to the applied constant stress, and the creep behavior at stresses below 26 MPa can be characterized by a single  $J(t)$  curve, which indicates that the creep behavior is linear. However, at stresses higher than 26 MPa, the corresponding  $J(t)$  increases with the applied stress, which marks the onset of nonlinear creep behavior. This nonlinear effect results from the change of timescale: at higher stress levels, the material will creep faster.

According to the prescribed TTSP, if the creep compliance curves are plotted in a logarithmic timescale, then different curves at different stress levels can be superposed by a horizontal shift. To obtain the master

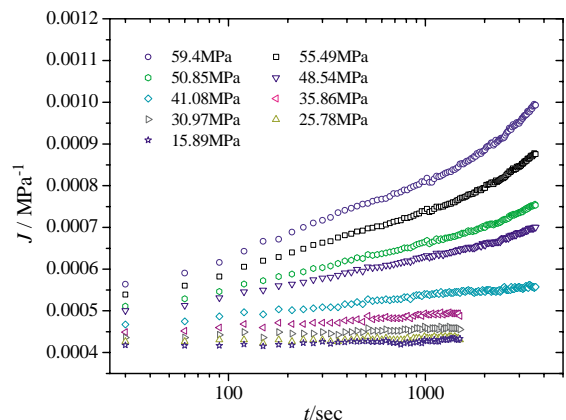


Fig. 3. Creep compliance curves of PC at various stress levels.

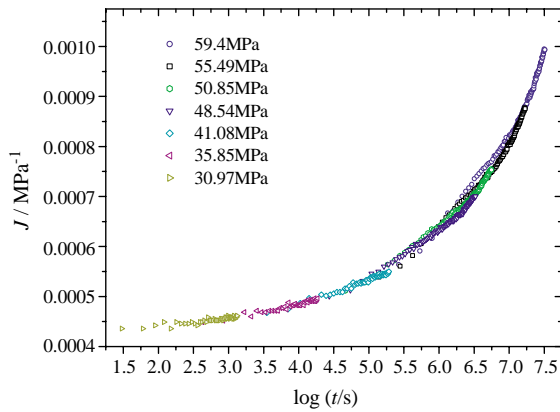


Fig. 4. The master curve for the creep compliance at 30.97 MPa and test temperature.

compliance curve, the reference condition chosen for this study was 30.97 MPa and the test temperature. A MathCAD procedure was programmed to calculate the horizontal shift factors with the least deviation between the reference compliance curve and the shifted one. The constructed master compliance curve and the corresponding horizontal stress shift factors,  $\phi_\sigma$ , are shown in Figs. 4 and 5, respectively.

Fitting the data in Fig. 5 with Eq. (7), we can determine the corresponding values of  $C_1$  and  $C_3$  as shown in Fig. 5. The open circles are the calculated stress shift factors for different stress levels, while the solid line represents the equation fit.

It should be pointed out that the results shown in Figs. 4 and 5 indicate an accelerated creep characterization of approximately 4 decades beyond the test duration. In other words, to predict the creep behavior in a 1-year

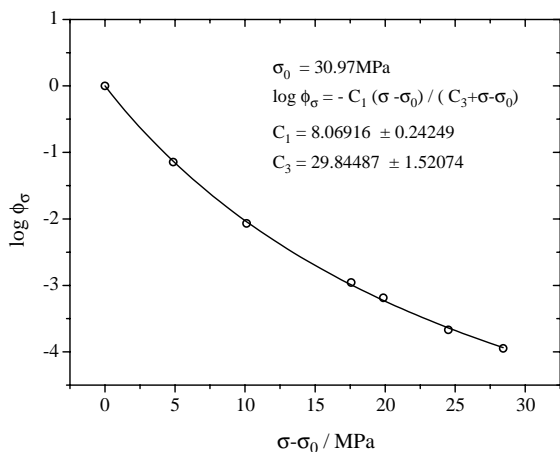


Fig. 5. Variation of stress shift factor with stress difference for  $\sigma_0 = 30.97$  MPa and room temperature.

(7.5 decades) duration at room temperature and 30.97 MPa, one needs only to perform several creep tests at stresses up to 59.4 MPa with 1-h (3.5 decades) duration.

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