J MATER SCI **41** (2006) 531–536

Nonlinear creep behavior of viscoelastic polycarbonate

SAID JAZOULI[*]
Department of Mechanical Engineering, École de technologie supérieure, 1100, Notre-Dame Street West, Montreal (Quebec), H3C 1K3 Canada
E-mail: said.jazouli@etsmtl.ca

WENBO LUO
College of Civil Engineering and Mechanics, Xiangtan University, Xiangtan 411105, People's Republic of China

FABRICE BRÉMAND
Laboratoire de Mécanique des Solides, Université de Poitiers, SP2MI - Téléport 2 - BP 179 - 86960, FUTUROSCOPE CEDEX, France

TOAN VU-KHANH
Department of Mechanical Engineering, École de technologie supérieure, 1100, Notre-Dame Street West, Montreal (Quebec), H3C 1K3 Canada

A study of the tension behavior of polycarbonate (PC) under room temperature and various sustained loads is presented. Time-dependent axial elongations and transverse contractions of the specimen were simultaneously measured at nine different stress levels, from 15.89 to 59.4 MPa, and modeled according to a time-stress superposition principle. The test duration was only one hour. It was shown that creep compliance vs. log time curves at different stresses can be horizontally shifted to form a smooth master curve for one year at a reference stress of 30.97 MPa. Moreover, the stress shift factors for axial extension creep curves and transverse contraction creep curves are found to be identical for the stress levels considered, and this is verified using the Poisson's ratio measurements.

1. Introduction

Since polymeric materials and polymer-matrix composites are being used as load-carrying components in many structural applications, there is a very good case for adequate constitutive equations being developed to characterize their mechanical behaviour, especially their long-term performance. In some cases, it may be enough to use elastic relations but, in general, their behavior is viscoelastic and often nonlinear. Linear viscoelastic behavior is usually described using the well-known Boltzmann single integral representation or the differential form with a mechanical analogy in terms of springs and dashpots. As for nonlinear viscoelastic behavior, which is present at intermediate and high stresses, multiple and single integral representations are widely used. Multiple hereditary integral representations are essentially extensions of the Boltzmann single integral representation using higher order stress or strain terms to account for nonlinear behavior [1]. The major drawback of this approach is the large number of kernel functions that need to be experimentally determined, and with limited success. For the sake of application simplicity, the nonlinear single integral representations are easily accepted for use in modeling the nonlinear viscoelastic behavior of polymers, among them, the modified Boltzmann superposition model [2] and the reduced time models [2–8]. This paper will discuss the nonlinear creep behavior of polycarbonate, and so we will next be giving a brief review of these two types of nonlinear representations.

The modified Boltzmann superposition model is in the form of linear viscoelasticity convolution integrals, with the nonlinearities appearing only in stress measurements

---

[*] Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-2276-1

[2]:

$$\varepsilon(t)=\int_{0^-}^{t} J\,(t-\tau)\frac{df[\sigma(\tau)]}{d\tau}d\tau \tag{1}$$

where f is a nonlinear function of stress, σ. Let $\varepsilon_c(t,\sigma_0)$ denote the strain response in a creep test defined by the loading $\sigma(\tau)=\sigma_0 H(\tau)$, where $H(\tau)$ is the Heaviside step function, and then we have

$$\varepsilon_c(t,\sigma_0)=J(t)\cdot f(\sigma_0). \tag{2}$$

It is shown that the creep response has a separable form. If the creep curves are plotted in a log strain vs. log time graph, then different curves at different stress levels can be superposed by a purely vertical shifting. The shift factor is, of course, stress-dependent.

There are several reduced time models for description of the nonlinear viscoelasticity of polymeric materials [2–8]. The first simple reduced time representation for modeling nonlinear viscoelasticity was first proposed by Schapery based on the concept of time-stress equivalence [3], even though the phenomenon was in fact experimentally recognized by O'Shaughnessy [9] early in 1948. This nonlinear single integral representation is in the following form:

$$\varepsilon(t)=\int_{0^-}^{t} J(\psi-\psi')\frac{d\sigma(\tau)}{d\tau}d\tau \tag{3}$$

where $\psi=\int_{0^-}^{t}\frac{dt'}{a_\sigma}$ and $\psi'=\psi(\tau)=\int_{0^-}^{\tau}\frac{dt'}{a_\sigma}$ are stress-reduced times, and a_σ is a stress-dependent shift factor, which is usually known as the stress-reduced factor. The creep strain by the load history $\sigma(\tau)=\sigma_0 H(\tau)$ reads:

$$\varepsilon_c(t,\sigma_0)=J\left(\frac{t}{a_\sigma}\right)\cdot\sigma_0 \tag{4}$$

Thus, if the creep compliance readings are plotted in double logarithmic scale, the curves at different stresses can be horizontally shifted to form a master curve.

Soon afterwards, Schapery [4] proposed another nonlinear single integral representation for isothermal conditions by using irreversible thermodynamics; a representation combining the features of both previous representations:

$$\varepsilon(t)=g_0 J_0\sigma(t)+g_1\int_{0^-}^{t}\Delta J(\psi-\psi')\frac{dg_2\sigma(\tau)}{d\tau}d\tau \tag{5}$$

where g_0, g_1 and g_2 are stress-dependent, g_0 reflects the nonlinearity of the instantaneous response, g_1 serves as a multiplier of the heredity integral, and the parameter g_2 accounts for the effect of the load rate on the creep response. J_0 is the instantaneous uniaxial elastic compliance and ΔJ is the uniaxial transient compliance. For a constant temperature creep test at constant stress σ_0, we obtain the creep compliance function as follows

$$J(t)\equiv\frac{\varepsilon_c(t,\sigma_0)}{\sigma_0}=g_0 J_0+g_1 g_2\Delta J\left(\frac{t}{a_\sigma}\right) \tag{6}$$

From the above, the measured transient compliance may be superimposed by a combination of horizontal and vertical shifting on the log-log representation. The magnitude of the vertical shift will be $\log(g_1 g_2)$, and the magnitude of horizontal shift will be $\log(a_\sigma)$. Thus the Schapery model is one of the reduced time models, the time-scale is stretched or shrunk by a stress-dependent factor of a_σ.

Besides the Schapery model, another generally accepted physical model for the nonlinear behavior of glassy polymers at small strains is the Knauss and Emri approach [5, 6], which is based on the free volume concept and also can be considered as a reduced time model. The underlying assumption with this is that free volume plays a fundamental role in the viscoelastic response of polymers, and a change in the free volume directly influences the mobility of the material and changes the inherent time scale. The larger the free volume, the greater the mobility of the molecular response to external loading. It has been shown that temperature, solvent concentration [10], physical aging [11] and mechanical pressure [12] influence the free volume, thus changing the time scale of the materials. So the free volume approach is essentially one of the reduced time models. In recent decades, the accelerated assessment of long-term performance, especially of the long-term creep response, of materials has received much research attention. Different accelerated characterization procedures have been developed to predict the long-term creep behavior of viscoelastic materials and composites. The Time-Temperature-Stress-Superposition Principle (TTSSP) is one such procedure. It is based on the fact that higher temperatures and higher stress levels cause an acceleration of creep deformation. Therefore, long-term creep deformation can be predicted based on short-term creep data at higher temperatures and stress levels, by a time-shifting method. The TTSSP can be derived from the free volume theory [13, 14] and has been used to predict the long-term performance of low-density polyethylene [15], high-density polyethylene [13, 16], polypropylene [14], and many other composite materials [17, 18]. Under isothermal conditions, the TTSSP reduces to the Time-Stress Superposition Principle (TSSP).

Plenty of papers, using different models, have been reported to fit the nonlinear viscoelastic behavior of polymeric materials in current literature; and what we are intent on in this paper is not to contribute more at this aspect. The objective of this paper is the application of TSSP to the nonlinear creep analysis of polycarbonate (PC), including the axial extension and transverse contraction as well. As a result, smooth master compliance curves spanning much longer time periods, for axial extensions and transverse contractions will be created.

2. Experimental procedure

The material used for tests in this study is the Tuffak® polycarbonate (PC). Dog-bone-shaped specimens with a cross-section of 12.15 × 2.15 mm are cut from a very regular transparent PC sheet with polished surfaces. All the tests were completed under isothermal axial tensile creep conditions.

Most classical methods used in strain measurement are inappropriate for polymers because they require the preparation of the surface. It is important to make sure 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 that reason, in this study we adopted a dot-tracking technique [19, 20], according to which 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 biaxial testing machine developed by LMS (University of Poitiers), a data acquisition unit and an imaging processing device [19, 21]. The maximal loading is limited to 5000 N, and we impose 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. This requires a central symmetry in the geometry of the testing machine. Furthermore, we also chose to separate the center for each direction in order to apply independent loading. Practically, we chose four stepper motors controlled by a microcomputer. Each of them introduces a maximal displacement of 50 mm on each axis; some mechanical and photoelectric sensors were introduced to give the two extreme positions and the middle position. The command allows the control of displacement and effort in order to allow any type of loading to be applied [19]. One of the loading programs consists in applying an imposed uniaxial tension. The geometrical transformations of the dots during loading exactly reflect the specimen's surface strains. Thus, determining the strain field means following the dots' geometrical transformation (displacement). Then, through the process giving the Cartesian coordinates of dots coupled with the procedure of strains kinetics, we can determine the amplitude of the principal strains by comparing the undeformed and the deformed states. The dots are recorded in quasi-real time by a CCD video camera (512 × 512 pixels), and digitally analyzed to calculate the axial strain and lateral 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 [22].

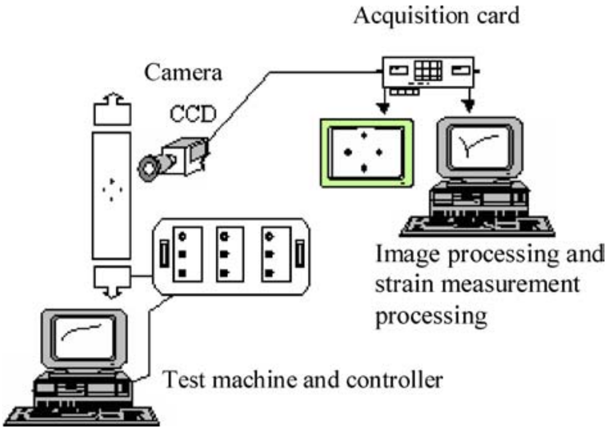

Figure 1 Schematic of the test device system.

Uniaxial tensile creep tests were performed by single-step loading PC strips and simultaneously recording the resulting axial strain and lateral 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.

3. Time-temperature-stress superposition principle

According to the free volume theory, the viscosity of the material, η, can be related to the free volume fraction, f, via the Doolittle equation in the form [23]:

$$\eta = A \exp\left[B\left(\frac{1}{f} - 1\right)\right] \tag{7}$$

where A and B are material constants.

Luo *et al.* assumed 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, and that the free volume fraction can be expressed as [13, 14]:

$$f = f_0 + \alpha_T(T - T_0) + \alpha_\sigma(\sigma - \sigma_0) \tag{8}$$

where α_T is the thermal expansion coefficient of the free volume fraction, α_σ 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 combined temperature-stress shift factor $\phi_{T\sigma}$, which satisfies

$$\eta\,(T,\sigma) = \eta\,(T_0,\sigma_0)\,a_{T\sigma} \tag{9}$$

then from Equations 8 and 9 we have [13, 14]

$$\log a_{T\sigma} = -C_1\left[\frac{C_3\,(T-T_0)+C_2(\sigma-\sigma_0)}{C_2C_3+C_3\,(T-T_0)+C_2(\sigma+\sigma_0)}\right] \tag{10}$$

where $C_1 = B/(2.303 f_0)$, $C_2 = f_0/\alpha_T$, $C_3 = f_0/\alpha_\sigma$. It can easily be shown that Equation 10 reduces to the well-known WLF equation if there is no stress difference.

Moreover, we define the stress shift factor at a constant temperature a_σ^T and the temperature shift factor at a constant stress level a_T^σ as follows:

$$\begin{aligned}\eta\,(T,\sigma) &= \eta(T,\sigma_0)a_\sigma^T = \eta(T_0,\sigma_0)a_T^{\sigma_0}a_\sigma^T\\ &= \eta(T_0,\sigma)a_T^\sigma = \eta(T_0,\sigma_0)a_\sigma^{T_0}a_T^\sigma\end{aligned} \tag{11}$$

then we have

$$\phi_{T\sigma} = a_T^{\sigma_0}a_\sigma^T = a_\sigma^{T_0}a_T^\sigma \tag{12}$$

It is shown from Equation 12 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 σ_0 in one step, via the temperature-stress shift factor $a_{T\sigma}$ or in two steps via the combination of the stress shift factor at a constant temperature a_σ^T and the temperature shift factor at a constant stress level a_T^σ.

Under isothermal conditions, the TTSSP reduces to TSSP. In such cases, Equation 10 reduces to

$$\begin{aligned}\log a_\sigma &= -\frac{B}{2.303 f_0}\left(\frac{\sigma-\sigma_0}{f_0/\alpha_\sigma+\sigma-\sigma_0}\right)\\ &= -\frac{C_1(\sigma-\sigma_0)}{C_3+(\sigma-\sigma_0)}\end{aligned} \tag{13}$$

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

$$J(\sigma,t) = J(\sigma_0, t/a_\sigma) \tag{14}$$

4. Results and discussions

Fig. 2 shows the axial stain and lateral contraction strain curves of PC at nine different stress levels. During creep at a constant force, the strain magnitude increases with time. Moreover, the higher the applied 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, σ_0, we get the axial extension creep compliance curves and transverse contraction creep compliance curves, as shown in Figs 3 and 4 respectively. It can be seen from these that 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 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 time scale: at higher stress levels, the material will creep faster.

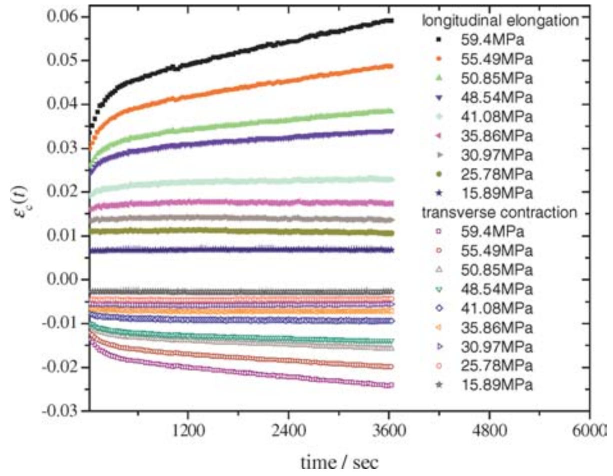

Figure 2 Creep strain of polycarbonate at room temperature and indicated stress levels.

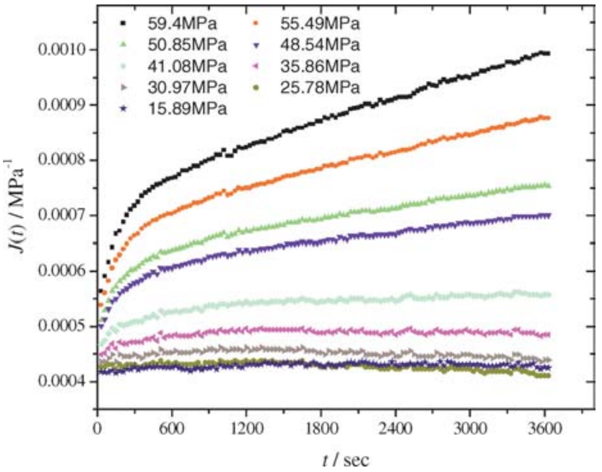

Figure 3 Axial extension creep compliance vs. time curves for indicated stress levels.

According to the prescribed TSSP, if the creep compliance curves are plotted on graphs on which the abscissa is defined as log-time, then the individual compliance curves

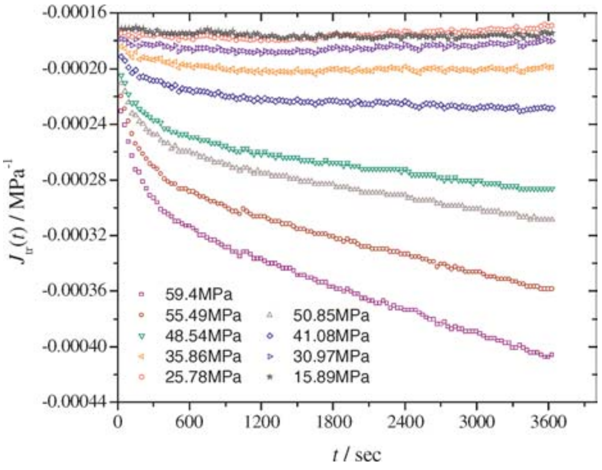

Figure 4 Transverse contraction creep compliance vs. time curves for indicated stress levels.

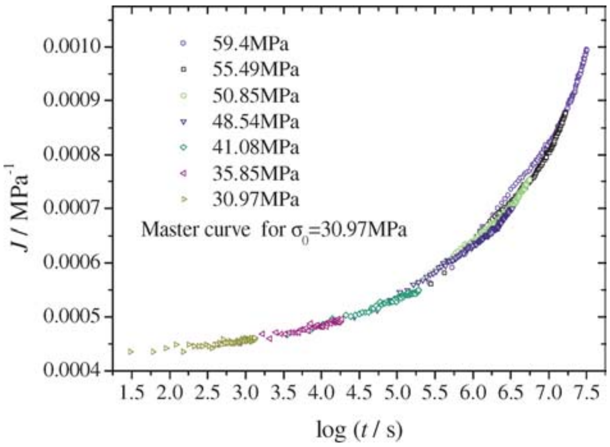

Figure 5 Master curve of the data in Fig. 3, for a reference stress of 30.97 MPa.

at different stress levels can be superposed by a horizontal shift. To obtain the master 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 master compliance curves constructed are shown in Figs 5 and 6. The corresponding horizontal stress shift factors, $\log a_\sigma$, are shown in Fig. 7 and in Table I.

Fitting the data in Fig. 7 with Equation 13, we can determine the corresponding values of C_1 and C_3, which are also shown in Fig. 7. The solid circles and open squares are the calculated stress shift factors for axial extension creep and transverse contraction creep at different stress levels, respectively, while the solid line represents the equation fit.

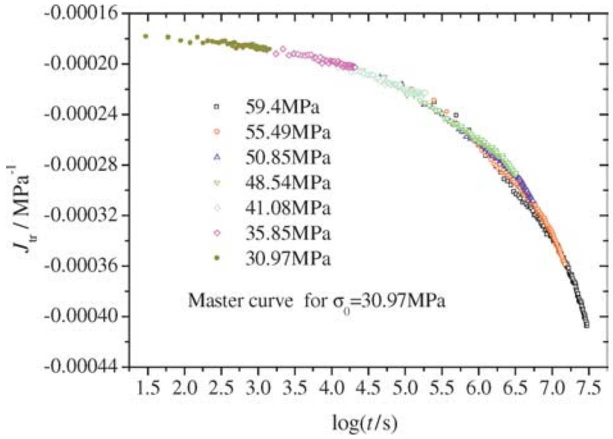

Figure 6 Master curve of the data in Fig. 4, for a reference stress of 30.97 MPa.

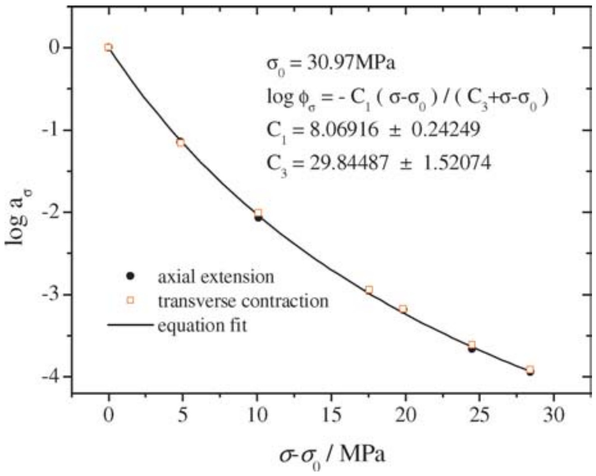

Figure 7 Relationships between the shift factor and stress.

It should be pointed out that the master curves in Figs 5 and 6 indicate an accelerated creep characterization of approximate 4 decades beyond the test duration. In other words, to predict the creep behavior in a one-year (7.5 decades) duration at room temperature and 30.97 MPa, we only need to perform several creep tests at stresses of up to 59.4 MPa with one-hour (3.5 decades) durations. However, it should also be noted that these constructed master curves are 'virtual' curves for long-term prediction, because the actual one-year creep may be affected by physical aging during the life of the creep, and moreover, at relatively higher stress levels, creep damage

TABLE I Values of $\log a_\sigma$ obtained from the construction of the master curves in Figs 5 and 6

σ/MPa	30.97	35.86	41.08	48.54	50.85	55.49	59.40
$\log a_\sigma$							
Longitudinal extension	0	−1.14749	−2.06806	−2.95909	−3.18782	−3.66789	−3.94765
Transverse contraction	0	−1.16376	−2.01157	−2.94544	−3.17968	−3.61602	−3.91843
Relative difference	0	1.418%	−2.732%	−0.461%	−0.255%	−1.414%	−0.740%

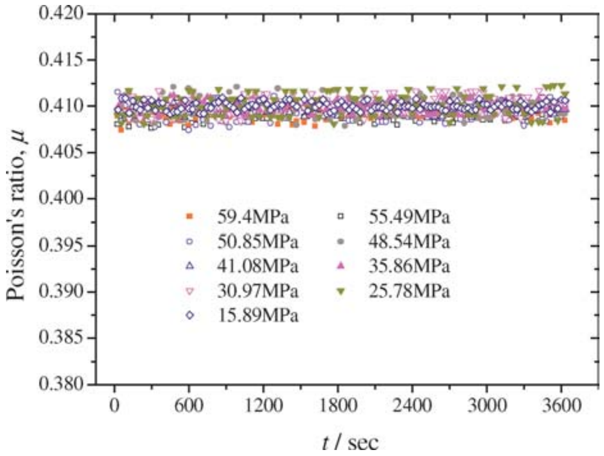

Figure 8 Poisson's ratio vs. time.

in the form of shear bands and/or crazing may occur during the creep. To get an accurate long-term prediction, these two effects must be taken into account.

It can be seen from Fig. 7 and from Table I that the relative difference between the shift factors for axial extension creep and the shift factors for transverse contraction creep is less than 3%. It can be concluded that the stress shift factors for axial extension creep curves and transverse contraction creep curves are identical for the stress levels considered. To verify this result, we investigated the Poisson's ratio, which is defined as the ratio of the negative lateral contraction strain, $-\varepsilon_c(t,\sigma_0)|_{\text{trans}}$, to the axial extension strain, $\varepsilon_c(t,\sigma_0)|_{\text{axial}}$, during the creep tests. The calculated results from simultaneous measurements of axial extension strains and lateral contraction strains are shown in Fig. 8. It is shown that the Poisson's ratio is time-independent and holds a constant value of about 0.41. Let $J_{\text{tr}}(t)$ denote the transverse contraction creep compliance, and we will have

$$J_{\text{tr}}(t) = \frac{\varepsilon_c(t,\sigma_0)|_{\text{trans}}}{\sigma_0} = -\mu\frac{\varepsilon_c(t,\sigma_0)|_{\text{axial}}}{\sigma_0} = -\mu J(t) \tag{15}$$

Therefore, in the nonlinear region, the transverse contraction creep compliance at σ, $J_{\text{tr}}(t,\sigma)$, can be expressed by $J_{\text{tr}}(t,\sigma) = J_{\text{tr}}(t/a_\sigma,\sigma_0)$ with the same a_σ as that for the axial extension creep compliance.

5. Conclusion

This paper has investigated the change in the stress-induced time scale for PC. The time-dependent axial elongations and transverse contractions of the specimen were simultaneously measured at nine different stress levels, from 15.89 to 59.4 MPa, and modeled according to a time-stress superposition principle. It is found that the creep compliances above 26 MPa are stress-dependent and that the material is nonlinear viscoelastic in nature. The master curves with axial extension and transverse contraction creeps with a one-year duration are constructed from the one-hour tests, and the shift factors for axial extension creep and transverse contraction creep are found to be identical due to the time-independent Poisson's ratio.

Acknowledgments

One of the authors (W. Luo) wishes to express special thanks to the China Scholarship Council. Experiments were completed at the Laboratory of Solid Mechanics, University of Poitiers, France.

References

1. W. N. FINDLEY, J. S. LAI and K. ONARAN, in "Creep and Relaxation of Nonlinear Viscoelastic Materials" (Dover Publications, New York, 1976).
2. H. LEADERMAN, in "Elastic and Creep Properties of Filamentous Materials and Other High Polymers" (Textile foundation, Washington, 1943).
3. R. A. SCHAPERY, *Int. J. Sol. Struct.* **2** (1966) 407.
4. *Idem.*, *Polym. Eng. Sci.* **9** (1969) 295.
5. W. G. KNAUSS and I. EMRI, *Comp. Struct.* **13** (1981) 123.
6. *Idem.*, *Polym. Eng. Sci.* **27**(1) (1987) 86.
7. G. U. LOSI and W. G. KNAUSS, *ibid.* **32**(8) (1992) 542.
8. W. BROSTOW, *Mat. Res. Innovat.* **3** (2000) 347.
9. M. T. O'SHAUGHNESSY, *Text. Res. J.* **18** (1948) 263.
10. W. G. KNAUSS and V. H. KENNER, *J. Appl. Phys.* **51**(10) (1980) 5131.
11. L. C. E. STRUIK, in "Physical Aging in Amorphous Polymers and Other Materials" (Elsevier Scientific Publishing Co., Amsterdam, 1978).
12. R. W. FILLERS and N. W. TSCHOEGL, *Trans. Soc. Rheol.* **21** (1977) 51.
13. W.-B. LUO, T.-Q. YANG and Q.-L. AN, *Acta Mechanica Solida Sinica* **14**(3) (2001) 195.
14. W.-B. LUO, "Studies on deformation-induced heat effect, nonlinear viscoelastic behavior and crazing in polymers," Doctoral dissertation (Huazhong University of Science and Technology, 2001).
15. C. H. POPELAR, V. H. KENNER and J. P. WOOSTER, *Polym. Eng. Sci.* **37**(12) (1991) 1693.
16. J. LAI and A. BAKKER, *Polymer* **36**(1) (1995) 93.
17. S. C. YEN and F. L. WILLIAMSON, *Compos. Sci. Technol.* **38** (1990) 103.
18. D. W. SCOTT, J. S. LAI and A. H. ZUREICK, *J. Reinfor. Plast. Compos.* **14** (1995) 588.
19. S. JAZOULI, "Identification expérimental et numérique des lois de comportement viscoélastiques et photoviscoélastiques non linéaire du Polycarbonate," Thèse de Doctorat (Université de Poitiers, 1999).
20. J. C. DUPRÉ, "Traitement et analyse d'image pour la mesure de grandeurs cinématique, déplacements et déformations à partir de la granularité laser et de réseau croisés, et pour l'étude de couplage thermomécanique," Thèse de Doctorat (Université de Poitiers, 1992).
21. S. JAZOULI, P. DUVAL and F. BRÉMAND, in Proceedings of the 11th International Conference on Experimental Mechanics (Oxford, UK, August 1998).
22. F. BRÉMAND, J. C. DUPRÉ and A. LAGARD, *Eur. J. Mech., A/Solids* **11**(3) (1996) 349.
23. J. J. AKLONIS and W. J. MACKNIGHT, "Introduction to Polymer Viscoelasticity" (Wiley-Interscience Publication, New York, 1983).

Received 10 September 2004
and accepted 16 May 2005