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Application of Time-Temperature-Stress Superposition Principle to Nonlinear Creep of Poly(methyl methacrylate)

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Abstract. The uniaxial tensile creep of a commercial grade Poly(methyl methacrylate) was measured for 4000 seconds under various temperatures and stress levels ranging from 14°C to 26°C and 6 MPa to 32 MPa. The resultant creep compliance curves depart from each other for stresses beyond a critical value which varies with temperature, indicating nonlinear viscoelastic behavior. The time-temperature-stress superposition principle (TTSSP) was used to construct a smooth master compliance curve with a much longer time-scale interval from the short-term tests at higher stresses and temperatures. It is shown that the master curve covers a period of over 290 days, which is nearly 3.9 decades longer than the test duration. Moreover, it is verified that the time-temperature shift factors are dependent on stresses at which the shifts are applied, and that the time-stress shift factors are dependent on reference temperatures.

Introduction

Since polymeric materials and polymer-matrix composites are widely used as load-bearing components in many structural applications, their time-dependent mechanical behavior and especially their long-term performances are crucial for structural designs. Linear viscoelastic theory has been well developed and has been used successfully to represent the mechanical behavior of polymers under low stress cases. For most polymers, however, their nonlinear viscoelastic behavior is significant in cases of intermediate and high stresses. Nonlinear single integral representations are widely accepted for modeling the nonlinear viscoelastic behavior of polymers; among them are the modified Boltzmann superposition model and the reduced time models [1-4]. The reduced time models use the concept of internal time, which differs from the laboratory time, to characterize the effects of stress or strain on the relaxation or retardation times of the materials. A stress or strain dependent shift factor is introduced to convert the experimental time into the internal time in a reference state of the material. The free volume theory is usually introduced to answer the possible underlying mechanism, assuming that free volume plays a fundamental role in the viscoelastic response of polymers, and a change in 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, physical aging, solvent concentration and mechanical pressure, strain or stress influence the free volume [2-6], thus changing the internal time of the materials. Among them, temperature and stress are the two most important factors for load-bearing polymeric components. Time temperature superposition principle (TTSP) has been extensively used to investigate the temperature dependence of viscoelastic properties of polymers. The individual effects stress on the internal time of polymeric materials has also received much attention, and consequently time stress superposition principle (TSSP) has been proposed and used to predict the long-term performance of polyethylene, polypropylene,

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polycarbonate and many other materials [6-8]. However, there are comparably few publications available that take into account the combined effects of both temperature and stress on the internal time of viscoelastic polymers. It has been found 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 time-temperature-stress superposition principle (TTSSP) is one of such accelerated characterization method. It has been used by Yen and Williamson [9] and Ma et al [10] to investigate the long-term creep response of continuous glass fiber reinforced unsaturated polyester and carbon fiber reinforced polyetheretherketone(PEEK) respectively. The objective of this study is to investigate the applicability of TTSSP to nonlinear creep of polymethyl methacrylate(PMMA) under various temperatures and stresses.

Nonlinear creep test

Isothermal uniaxial tensile creep tests with duration of 4000 seconds were performed by single-step loading PMMA strips and simultaneously recording the resulting axial strain as a function of time. The test temperatures vary from $14\,^{\circ}\mathrm{C}$ to $26\,^{\circ}\mathrm{C}$. In order to check the linearity of the creep behavior of the tested material, at each temperature level the tests were conducted at various stress levels, from 6 MPa to 32 MPa. The test conditions are summarized in Table 1.

Table 1. Test conditions applied in creep of PMMA

$T\,/\,^{\circ}\mathrm{C}$	σ / MPa													
	6	8	10	12	14	16	18	20	22	24	26	28	30	32
14			×		×			×	×	×	×	×		×
17					×		×		×	×	×	×		
22					×	×		×	×		×	×	×	
24				×	×	×	×		×		×	×		
26	×	×	×		×		×	×	×	×	×		×	×

Fig.1(a)-Fig.1(e) show the short-term creep compliance curves for various stresses at five specified temperatures. According to the theory of viscoelasticity, 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 stresses, doubling the stress more than doubles the amount of creep, resulting in discrepancies between compliance curves for different stress levels, and so the behavior is nonlinear. It can be seen from Fig.1 that there exist a critical stress beyond which the creep compliance curves depart from each other, indicating nonlinear viscoelastic behavior. This critical stress σ_c is found to linearly vary with test temperature within the temperature range indicated in this study, as shown in Table 2. Note that the data in parenthesis for $17\,^{\circ}\mathrm{C}$ is given by linear regression. It is also shown that an increase in temperature and/or stress results in an increase in both compliance and creep rate. Furthermore, according to TTSSP, the stress and temperature have equivalent effects on the creep behavior of viscoelastic materials. The compliance under some temperature T_1 and stress σ_1 should be equal to that under some other temperature T_2 and stress σ_2, this is true in two possible cases: (1) $T_1 > T_2$ and $\sigma_1 < \sigma_2$; and (2) $T_1 < T_2$ and $\sigma_1 > \sigma_2$. This equivalence is evidenced by the present test as shown in Fig.2.

Table 2. Temperature dependence of the critical stress σ_c

$T\,/\,^{\circ}\mathrm{C}$	14	17	22	24	26
σ_c / MPa	22	(19)	14	12	10

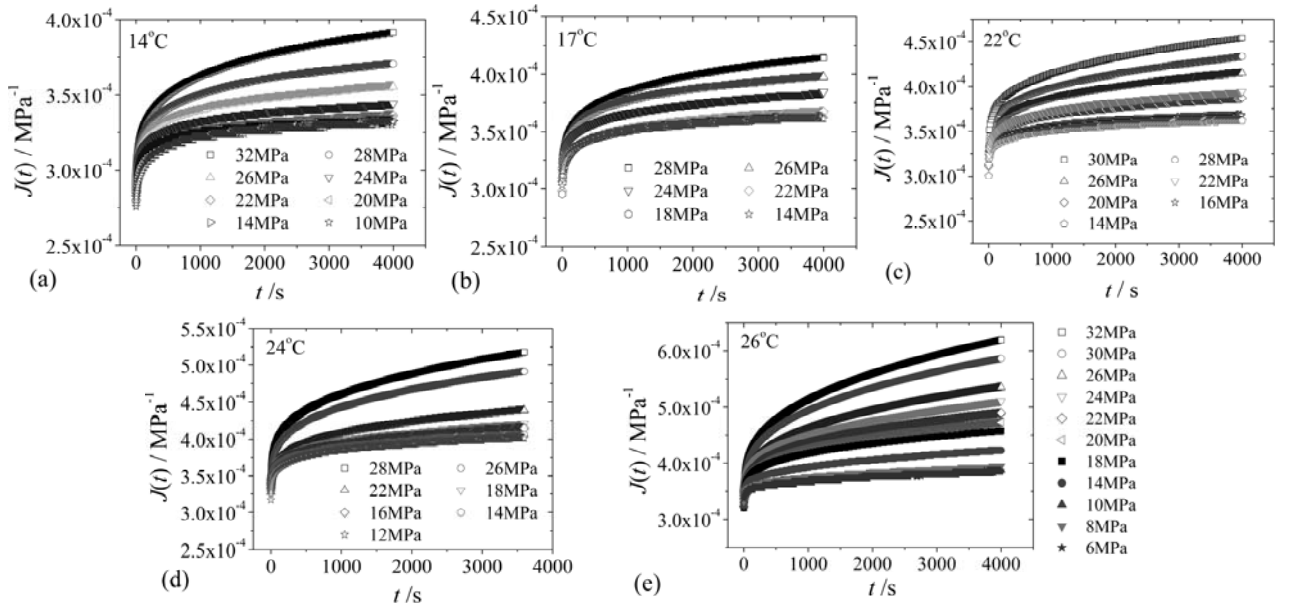

Fig.1 Short-term creep compliance curves of PMMA at five temperatures and various stresses

Long-term performance assessment

In order to predict the long-term behavior of viscoelastic materials, a time shift method based on TTSP has been extensively used to obtain the master curve at reference temperature. Another manner of producing a master curve is through the use of TSSP. Combining the effects of temperature and stress, TTSSP has been proposed and used as a more potential accelerated prediction procedure for long-term performance of viscoelastic materials. Based on the free volume theory, Luo et al[3] assumed that the free volume fraction of the viscoelastic materials linearly depends on the temperature change and stress change, and have derived the time-temperature shift factor at fixed stress ϕ_{Γ}^{σ}, the time-stress shift factor at fixed temperature ϕ_{σ}^{T} and the combined temperature- stress shift factor $\phi_{\Gamma\sigma}$. Using these shift factors, the creep compliances under different thermomechanical states will have an equal value but with different time scale.

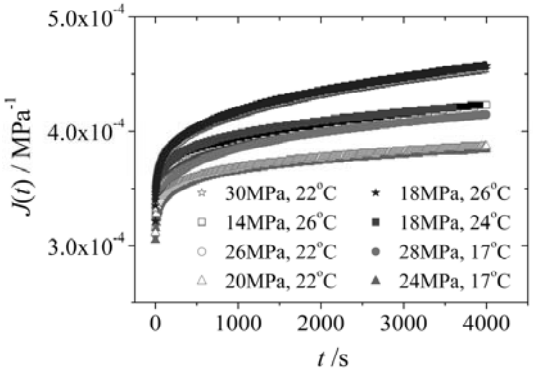

Fig.2 Equivalent compliances at different test conditions

$$J(T,\sigma,t) = J(T_0,\sigma,t/\phi_{\Gamma}^{\sigma}) = J(T,\sigma_0,t/\phi_{\sigma}^{T}) = J(T_0,\sigma_0,t/\phi_{T\sigma}) \tag{1}$$

These shift factors are interrelated via the following equation [3]

$$\phi_{T\sigma} = \phi_{\Gamma}^{\sigma_0}\phi_{\sigma}^{T} = \phi_{\sigma}^{T_0}\phi_{\Gamma}^{\sigma} \tag{2}$$

It is shown from Eqs.(1) and (2) 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 combined temperature-stress shift factor, $\phi_{T\sigma}$, or in two steps via a combination of the time-stress shift factor for fixed temperature, (ϕ_{σ}^{T} or $\phi_{\sigma}^{T_0}$), and the temperature shift factor for fixed stress level, ($\phi_{\Gamma}^{\sigma_0}$ or ϕ_{Γ}^{σ}). In the following two subsections,

the TSSP and TTSP will be applied to the prescribed creep test data respectively, it will be demonstrated that it is possible to construct master curves by time-stress shifting at each test temperature or time-temperature shifting at various specified stress levels, and finally an unified master curve will be presented by combining both the stress and temperature accelerating effects.

Master curves by time-stress shifting. According to the TSSP, if the isothermal creep compliance curves within the nonlinear range are plotted in a logarithmic timescale, then all the curves for various stress levels can be superposed to construct a master curve by a certain horizontal shift value, indicating that $J(\sigma,t)=J(\sigma_0,t/\phi_\sigma^{\mathrm{T}})$, and this horizontal shift value is described by the time-stress shift factor at fixed temperature, ϕ_σ^{T}. In the present study, the chosen reference state for the master curve was the test temperature and its corresponding critical stress as indicated in Table 2. 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 isothermal master compliance curves are shown in Figs. 3 (a)-3(e), the corresponding horizontal time-stress shift factors, ϕ_σ^{T} ,are listed in Table 3.

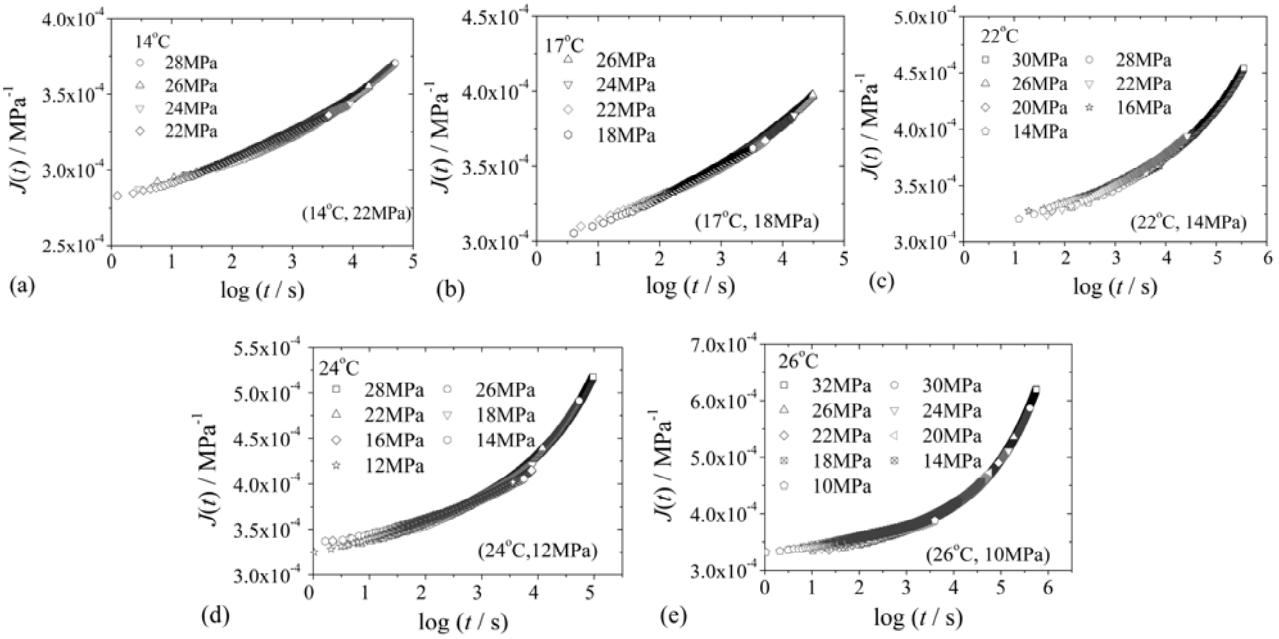

Fig.3 Master compliance curves for different reference state indicated in parentheses

Table 3. Time-stress shift factors $\log\phi_\sigma^{\mathrm{T}}$ at different test temperatures

σ / MPa	T / °C				
	14	17	22	24	26
10					Ref. State
12				Ref. State	
14			Ref. State	-0.1939	-0.5000
16			-0.2885	-0.3307	
18		Ref. State		-0.3403	-0.9944
20			-0.6517		-1.1499
22	Ref. State	-0.1156	-0.8238	-0.5230	-1.3466
24	-0.3579	-0.5874			-1.5590
26	-0.6634	-0.8867	-1.3088	-1.1717	-1.6711
28	-0.9035		-1.6416	-1.4219	
30			-1.9416		-2.0109
32					-2.3444

Master curves by time-temperature shifting. In an analogous manner to the TSSP, a TTSP approach, which indicating that $J(T,t)=J(T_0,t/\phi_T^\sigma)$ is used to construct the master curve from the tests conducted at various temperatures and a fixed stress level. A reference temperature of 14°C was selected for this study. Figs 4(a)-4(d) show the short-term test curves and their corresponding master curves at reference thermomechanical states. The master curves shown in these figures cover an expanded period of time reaching 10^6-10^7 seconds. The shift factors, ϕ_T^σ, were determined for each master curve. The data are plotted as $\log\phi_T^\sigma$ versus temperature in Fig.5 for four different applied stress levels, 22MPa, 24MPa, 26MPa and 28MPa. At the reference temperature, $\log\phi_T^\sigma$ is zero, that is the shift factor ϕ_T^σ=1. It is shown from Fig.5 that at a given stress level, $\log\phi_T^\sigma$ decreases with increase in temperature. Because $\log\phi_T^\sigma$ is negative for the temperatures beyond the reference one, it indicates increases in temperature cause the acceleration of creep deformation. Furthermore, the time-temperature shift factors for the same temperature depend on the stress level at which this shift applies.

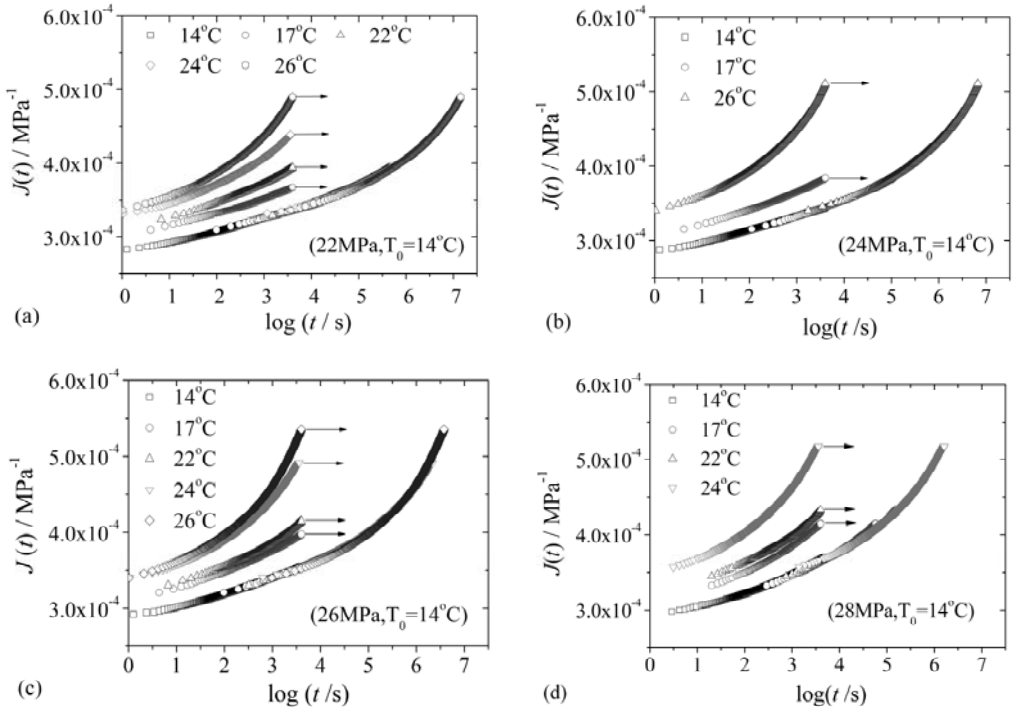

Fig.4 Master curves by time-tmeprature shifting at four given stresses

Unified master curve: application of TTSSP. As mentioned in the first section, there are two possible ways to get a unified master curve. Below we use the master curves given above from time-temperature shifting procedure to construct the unified master curve. This goal can be reached by a further horizontal shifting the sub-master curves for different applied stresses along the logarithmic time axis to overlap each other, based on the reference sub-master curve. In this study, the reference thermomechanical state of 14°C and 22MPa was chosen. The smooth unified master curve is shown in Fig. 6. The inset of this figure shows the sub-master curves for 14°C and various stresses. The corresponding shift factors, $\log\phi_\sigma^{(T=14^oC)}$, are -0.4133, -0.8218 and -1.2595 for 24MPa, 26MPa and 28MPa respectively. It is also seen from Fig.6 that the master curve covers a period of approximate $10^{7.5}$ seconds (namely 290 days), which is nearly 3.9 decades longer than the test duration. Thus TTSSP provides an accelerated characterization method of long-term performance of viscoelastic polymers. Usually, the unified master curve can be expressed by the Prony series, $J(t)=J_0+\sum_{i=1}^{n}J_i\left[1-\exp\left(-t/\tau_i\right)\right]$, as shown in the right part of Fig.6.

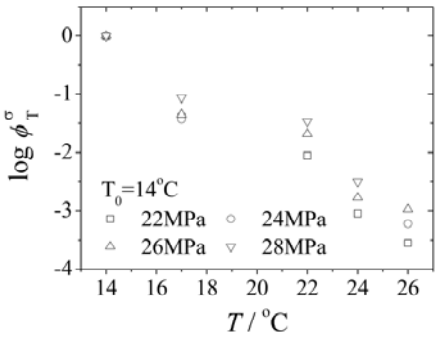

Fig.5 Time-temperature shift factors at various stress levels

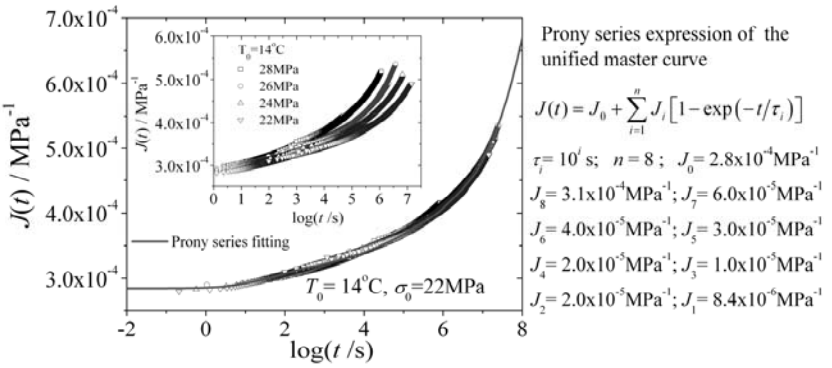

Fig.6 Unified master curve for reference state of 14°C and 22MPa

Conclusions

The effects of temperature and stress on short-term creep behavior of viscoelastic PMMA have been experimentally investigated in this study. Increasing temperature and/or stress will increases the free volume in materials to allow more active motion of polymer chains and their segments, resulting in shorter relaxation or retardation times. The creep compliance of PMMA was found to be a function of both stress and temperature, the TTSSP was used to construct the master creep compliance curves for a selected reference thermomechanical state based on the short-term tests in the region of nonlinear viscoelasticity. The critical stress, beyond which nonlinear viscoelastic behavior occurs, increases with decrease in temperature. The TTSP is applicable to construct master curves at given stresses and the time-temperature shift factor is dependent on the stress level at which the time shifting is used; similarly, TSSP is applicable to construct master curves at given temperatures and the time-stress shift factor varies with the selected reference temperature. It is also shown that a unified master curve for $\sigma_0 = 22$MPa and T_0=14°C has been constructed by the use of TTSSP, which extends test data by 3.9 decades.

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References

[1] R.A. Schapery: Polym. Eng. Sci. Vol.9(4)(1969), p.295

[2] G.U. Losi and W.G. Knauss: Polym. Eng. Sci. Vol.32(8) (1992), p.542

[3] W. Luo, T-Q. Yang, and Q. An: Acta Mechanica Solida Sinica, Vol.14(3) (2001), p.195

[4] W. Brostow: Mater. Res. Innov. Vol.3 (2000), p.347

[5] J. Kolark and A. Pegoretti: Polymer Vol.47 (2006), p.346

[6] J. Lai and A. Bakker: Polymer, Vol.36(1) (1995), p.93

[7] S. Jazouli, W. Luo, F.Bremand and T.Vu-Khanh: J. Mat. Sci., Vol.41(2006), p.531

[8] M. Hadid, S. Rechak and A. Tati: Mat. Sci. Eng. A , Vol.385(2004), p.54

[9] S.-C. Yen, and F.L. Williamson: Compos. Sci. Technol. Vol.38(1990), p.103

[10] C.C.M. Ma, N.H. Tai, and S.H. Wu et. al.: Composites Part B Vol.28B (1997) p.407