



Short Communication

The unusual effect of temperature on stress relaxation and mechanical creep of polycarbonate at low strain and stress levels

M. Abu-Abdeen *

Physics Department, College of Science, King Faisal University, P.O.B. 400, Alhasa 31982, Saudi Arabia
 Physics Department, College of Science, Cairo University, Giza, Egypt

ARTICLE INFO

Article history:

Received 30 June 2011

Accepted 24 August 2011

Available online 1 September 2011

ABSTRACT

The effects of temperature, strain level during stress relaxation tests and stress level during mechanical creep tests on the viscoelastic characteristics of polycarbonate films were investigated. When the testing temperature increased the un-relaxed elastic modulus was found to increase during relaxation tests (at low strain levels <2.0%) and the initial strain was found to decrease during creep tests (at low stress levels <20 MPa), in an unusual behavior. A transition from poly-domain to a more coiled and more entangled chains poly-domain configuration took place at low strain and stress levels. At high strain and stress levels ($\geq 2.0\%$ and ≥ 20 MPa) a usual behavior of the un-relaxed stress and initial strain was observed and a transition from poly-domain to mono-domain configuration took place. The thermal energy required for the transition from poly-domain to another poly-domain and from poly-domain to the mono-domain during both relaxation and creep tests were calculated. Besides, both the relaxation and creep strengths were calculated and studied.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Polymers are widely used in many engineering applications so knowledge of their mechanical properties is important. Most polymers exhibit time-dependent mechanical behavior, usually referred to as viscoelasticity. Stress relaxation, creep and dynamic loading tests are the commonly used techniques to measure this viscoelastic behavior. The main idea of either stress relaxation or creep denotes the process of the establishment of static equilibrium in a physical or a physico-mechanical system. Its rate depends on the probability of the transition of the system from one stage of equilibrium to another [1]. The viscoelastic behavior of polymeric materials can be influenced by many factors such as temperature [2], physical aging [3,4], pressure [5], solvent concentration [6], strain [7] and stress level [8–10].

The ideal polymer behaves like a perfect Hookean spring. When it is under constant stress or strain, the resulting deformation remains constant as long as it is strained, and so it is time independent. When the stress or strain removed, the deformation returns to zero instantaneously, and the material recovers its original dimensions. Hence, no change in the deformation is observed during stress relaxation or creep experiments of an ideal polymer [11]. Similarly, for cases in which the applied stresses or strains are sufficiently small to have

a negligible effect on the material's properties, Boltzmann superposition principle can be used to predict the deformation of linear viscoelastic polymeric solids subjected to arbitrary time-dependent deformations [12].

However, at higher stresses or strains, most polymers exhibit nonlinear viscoelastic behavior due to the fact that stresses change the distribution of relaxation times to shorter times. A modification to the Boltzmann superposition principle has been proposed to account for the effects of elevated stresses and strains [12,13].

The present work reports the effect of temperature on the un-relaxed stress, relaxation strength, initial strain and creep strength at different strain and stress levels during stress relaxation and creep tests, respectively.

2. Experimental

2.1. Material and preparation

Polycarbonate resin (product by ACROS ORGANICS Company, New Jersey (USA), MW 64,000) was dissolved in dichloromethane and stirred at 30 °C using the magnetic stirrer for 2 h. This viscous solution was casted in a glass petri dish (dia. of 10 cm). The solvent was evaporated at room temperature for 24 h and placed inside oven at 40 °C for 2 h and a sheet of polycarbonate with thickness of 0.1 mm was formed.

* Address: Physics Department, College of Science, King Faisal University, P.O.B. 400, Alhasa 31982, Saudi Arabia. Tel.: +966 35800000x1885.

E-mail addresses: mmaabdeen@yahoo.com, maboabdeen@kfu.edu.sa

2.2. Stress relaxation tests

The stress relaxation tests were carried out on 0.1 mm thick, 5.0 mm width and 30 mm length samples. The measurements were done on a Dynamic Mechanical Analyzer DMA Q800 (TA Instruments LLC, Delaware, USA) instrument with tension film clamps. The strain level was adjusted at a 0.3% and the temperature was equilibrated at 298 K. Sample was then left isothermally at this temperature for 5 min. After that, sample was strained suddenly to the previously adjusted strain level and the variation of stress was recorded with time for 20 min. Then, the strain was removed and the temperature was equilibrated at another higher temperature of 308 K and the process was repeated at same strain level of 0.3%. The experiment was repeated at other high temperatures of 318, 328 and 328 K and same strain level 0.3%. The experiment was repeated using other samples and stress relaxation was tested at other strain levels of 0.5%, 1.0%, 2.0% and 4.0%. Note that the temperature was incrementally increased in steps for each strain level.

2.3. Creep tests

Creep tests were carried out on sample films with same dimensions mentioned in stress relaxation tests using same DMA Q800 instrument with same tension film clamps. Stress level was adjusted at 2.0 MPa and the temperature was equilibrated at 298 K. Sample was then left isothermally at this temperature for 5 min. After that, sample was suddenly loaded with the stress level previously adjusted and the variation of strain was recorded with time for 20 min. Then, stress was removed and the temperature was equilibrated at another higher temperature of 308 K and the process was repeated at same stress level of 2.0 MPa. The experiment was repeated at other high temperatures of 318, 328 and 328 K and same stress level 2.0 MPa. The experiment was repeated using other samples and creep tests were done at other stress levels of 10, 15, 20 and 25 MPa. Note that the temperature was incrementally increased in steps for each stress level.

3. Results and discussions

3.1. Stress relaxation

Figs. 1 and 2 present stress relaxation curves at different strain levels of 0.3%, 0.5%, 1.0%, 2.0% and 4% and at successive accumulated steps of temperature increments 10 °C followed by 20 min

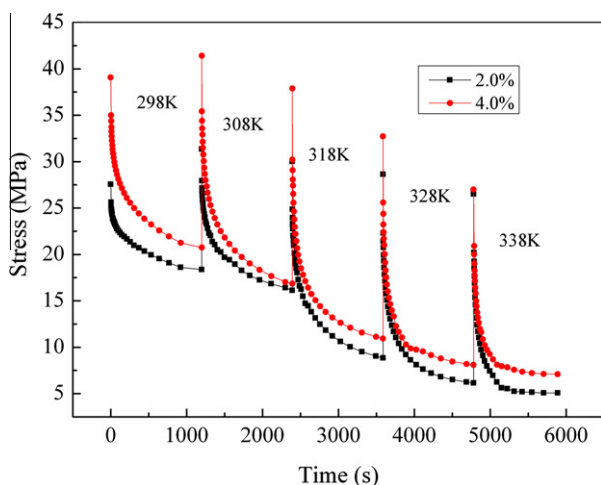


Fig. 1. Stress relaxation of polycarbonate at different high strain levels and at different temperatures.

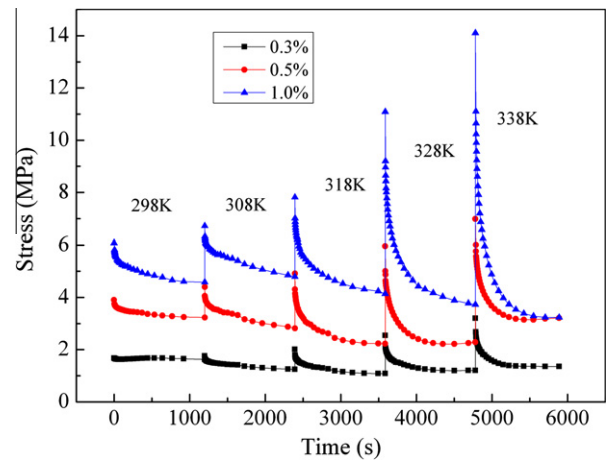


Fig. 2. Stress relaxation of polycarbonate at different low strain levels and at different temperatures.

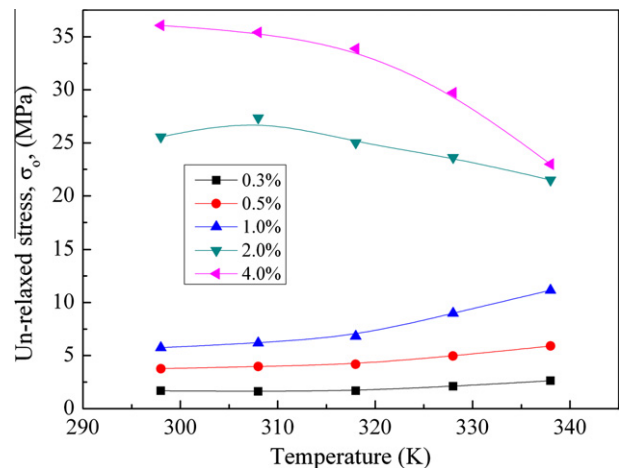


Fig. 3. Temperature dependence of the un-relaxed stress of polycarbonate at different strain levels.

stress relaxation. At high strain levels ($\geq 2.0\%$ Fig. 1) a usual and expected relaxation behavior is observed. It is found that the un-relaxed stress, σ_o , decreases by 13.07 and 4.06 MPa at strain levels of 4.0% and 2.0%, respectively when the temperature is changed from 298 to 338 K. This, consequently, corresponds to a decrease in the un-relaxed elastic modulus ($E_o = \sigma_o/\epsilon$, where ϵ is the strain level) by 326.75 and 203 MPa at the mentioned strain levels in same temperature range. Besides, σ_o increases from 25.71 to 36.1 MPa as the strain level increases from 2.0% to 4.0% at 298 K. The corresponding values of E_o are 1.286 and 0.903 GPa, respectively. The decrease in E_o with increasing strain level is due to yielding of the material and the presence of plastic deformation.

At strain levels less than 2.0% (0.3%, 0.5% and 1.0%) a transition from the usual to unusual behavior is detected for the dependence of the un-relaxed stress on temperature as shown in Fig. 2. The un-relaxed stress increases by 0.95, 2.13 and 5.44 MPa at strain levels of 0.3%, 0.5% and 1.0% as the temperature is changed from 298 up to 338 K. The changes in the un-relaxed modulus corresponding to these changes in σ_o are 316, 426 and 544 MPa, respectively. Fig. 3 shows the dependence of the un-relaxed stress on temperature at different strain levels. Opposite behaviors are clearly observed at strain levels $\leq 1.0\%$ and $\geq 2.0\%$.

Ortiz et al. [14] assumed that liquid crystal elastomers have a poly-domain configuration at low strains and make a transition to a mono-domain at high strains. The poly-domain configuration

is characterized by equilibrium randomly coiled and entangled polymer chains, while the mono-domain has the property of the rearranged, uncoiled and disentangled polymer chains. In the studied polycarbonate during stress relaxation tests at low strain levels and when the temperature is elevated, the material may undergoes a transition from one poly-domain configurations to another poly-domain one with the polymer chains are more coiled and entangled. When the test temperature increases under the effect of this low strain, also, thermal agitation may takes polymer chains to a new poly-domain configuration which results in an increase of the un-relaxed stress. Besides, thermal energy gives rise to the entropic forces which overcome the drag forces caused by applied stress [15]. These entropic forces may tend to produce more coiling of polymer chains. This needs more un-relaxed stress to maintain same strain level and hence increases the un-relaxed elastic modulus. During an isothermal relaxation process, as the sample left large time intervals to relax, more chains are coiled and entangled and the next isothermal step at higher temperature needs more stress to reach same strain level. On the other hand, at high strain levels and higher temperatures of relaxation, transition from poly-domain configuration to mono-domain takes place and produces uncoiling, disentangling and aligning of polymer chains which results as softening of the material. Moreover, during relaxation of polymers at high temperatures, competition between coiling due to entropic forces from heat and uncoiling due to drag forces from strain may exist at same time. At low strain levels, drag forces on polymer chains due to the applied strain are lower than the entropic forces and the poly-domain configuration exist. At high strain levels drag forces overcome the entropic ones and transition to mono-domain takes place. The effect of strain level and temperature on the relaxation behavior is described well in other works [16,17].

The data in Fig. 3 show straight lines as shown in Fig. 4 when re-plotted between $\ln\left(\frac{\ln\sigma_o}{\sigma'_o}\right)$ on the vertical axis and $\frac{1}{T}$ on the horizontal axis according to the equation:

$$\ln\left(\frac{\ln\sigma_o}{\sigma'_o}\right) = \pm \frac{w}{kT} \tag{1}$$

where σ'_o is a fitting parameter with values listed in Table 1 and depend on the strain level, k is the Boltzmann constant and w may be considered as the net activation energy of the polymer chains caused by the difference between drag and entropic forces. Thermal energy may increase the length of the chains at high strain levels (uncoiling) and w appears positive. On the other hand, at low strain levels, the chains shortened (coiling) and w appears negative. The calculated values of w are listed in Table 1.

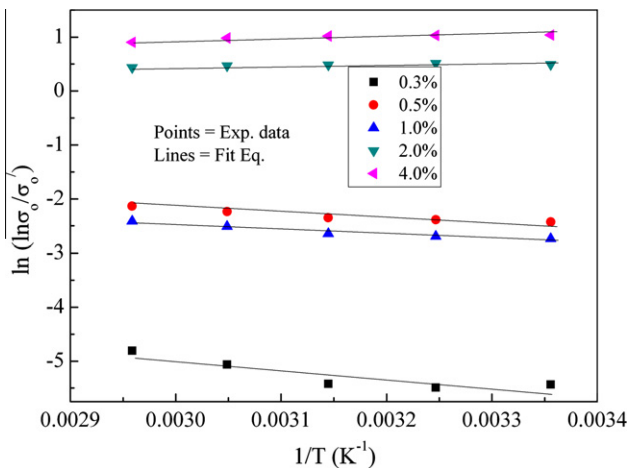


Fig. 4. Fitting of the temperature dependence of the un-relaxed stress of polycarbonate at different strain levels.

Table 1
The calculated values of σ'_o , w , Δ_o and w' .

Strain level (%)	Un-relaxed stress		Relaxation strength	
	σ'_o (MPa)	w (eV)	Δ_o	w' (eV)
0.3	117	-0.144	27.29	0.18
0.5	15	-0.072	24.87	0.30
1.0	27	-0.063	18.24	0.47
2.0	1.98	+0.013	11.70	0.63
4.0	1.27	+0.027	7.20	0.69

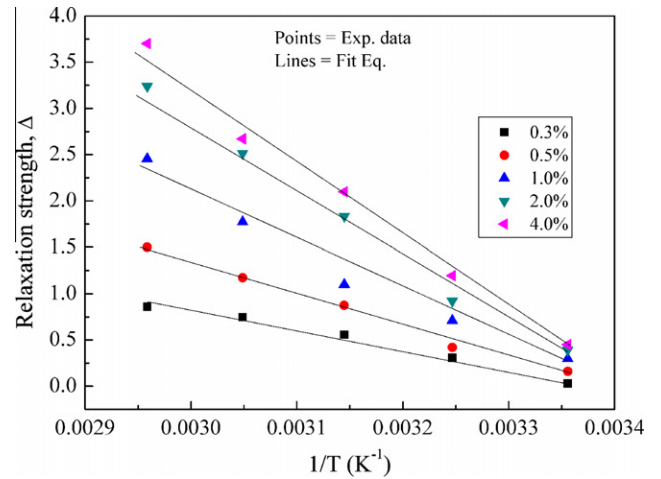


Fig. 5. Temperature dependence of the relaxation strength of polycarbonate at different strain levels.

3.2. Relaxation strength

Fig. 5 presents the dependence of the relaxation strength on the temperature at different strain levels. The relaxation strength is calculated from the expression $\Delta = (\sigma_o - \sigma_f) / \sigma_f$ [14], where σ_f is the final stress at the end of the relaxation process at constant temperature and strain level. The figure detects a group of straight lines and found to obey the equation:

$$\Delta = \Delta_o - \frac{w'}{kT} \tag{2}$$

where Δ_o is the relaxation strength at certain temperature T_o less than T and w' can be considered as the thermal energy acquired by polymer chains. The calculated values of both Δ_o and w' are listed in Table 1. As the strain level increases, w' increases too which means that more energy is needed to stretch chains to form a mono-domain configuration.

3.3. Mechanical creep

Figs. (6–8) present mechanical creep curves at different stress levels of 2.0, 10, 15, 20 and 25 MPa at successive accumulated steps of temperature increments of 10 °C followed by 20 min mechanical creep. Creep curves for stress levels of 20 and 25 MPa are plotted in separate figures because of the high change in strain, especially at high temperatures. Again, at high stress levels “(≥ 20 MPa Figs. 6 and 7)” a usual and expected creep behavior is observed. The initial strain is found to increase slightly with increasing temperature which is in consistent with the results obtained for high strain level stress relaxation data illustrated in Fig. 1. This can be ascribed as a transition from poly-domain to mono-domain configuration as discussed before. An unusual behavior for the initial strain is detected here, also, at low stress

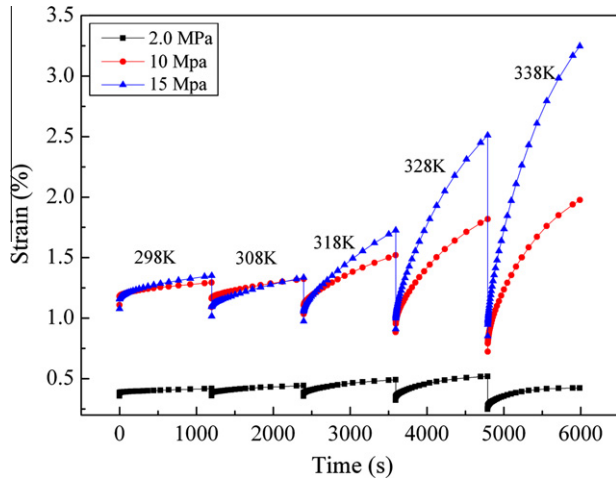


Fig. 6. Mechanical creep curves of polycarbonate at different low stress levels and at different temperatures.

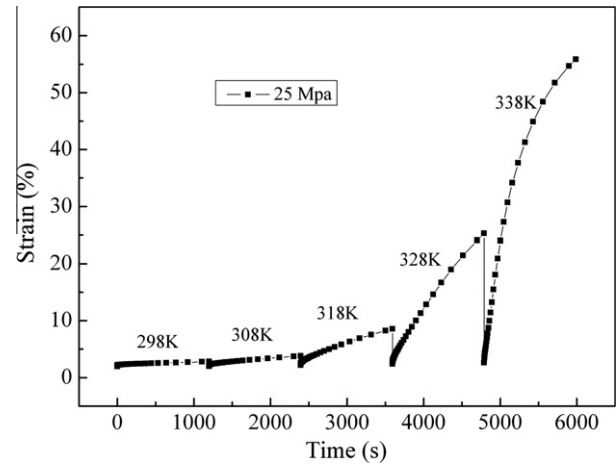


Fig. 8. Mechanical creep curve of polycarbonate at stress level of 25 MPa and at different temperatures.

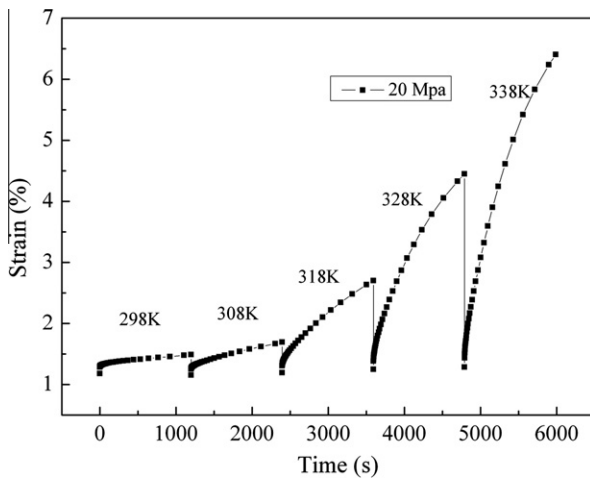


Fig. 7. Mechanical creep curve of polycarbonate at stress level of 20 MPa and at different temperatures.

levels (≤ 15 MPa) as shown in Fig. 8. This is due to the transition of polymer chains from poly-domain, coiled and entangled configuration to another poly-domain, more coiled and more entangled configuration. More discussions of this behavior are similar to the previously described in stress relaxation section. The creep behavior is described well before [18,19].

The dependence of the initial strain, ϵ_0 , on temperature at different stress levels is illustrated in Fig. 9. The data in this figure is found to obey an exponential equation of the form:

$$\epsilon_0(T) = \epsilon'_0 \exp\left(\pm \frac{w_c}{kT}\right) \quad (3)$$

where ϵ'_0 is a fitting parameter, and w_c resembles w in Eq. (1) but during creep tests. The positive sign is taken for high stress levels while the negative is taken for low stress levels as in the case of high and low strain levels in stress relaxation, respectively. The values of ϵ'_0 and w_c are illustrated in Table 2.

3.4. Creep strength

Fig. 10 presents the dependence of the creep strength on the temperature at different stress levels. The creep strength can be calculated, in same manner of relaxation strength, from the expres-

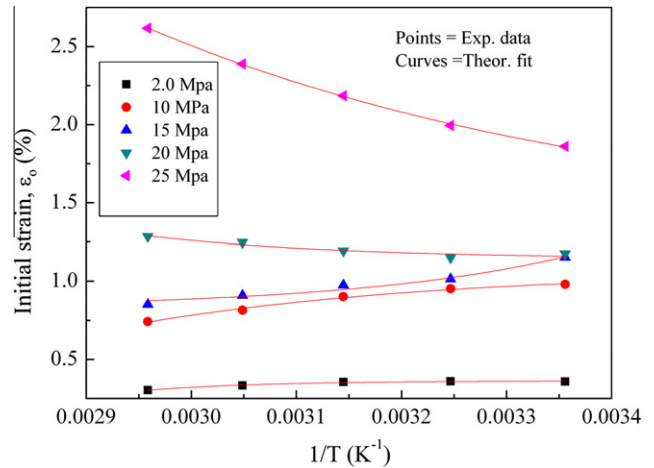


Fig. 9. Temperature dependence of the initial strain of polycarbonate at different stress levels.

Table 2

The calculated values of ϵ'_0 , w_c , Δ_{co} and w'_c .

Stress level (MPa)	Initial strain		Creep strength	
	ϵ'_0 (MPa)	w_c (eV)	Δ_{co}	w'_c (eV)
2	0.094	-0.035	2.3×10^{14}	0.34
10	0.092	-0.061	7.6×10^9	0.54
15	0.10	-0.062	7.2×10^8	0.57
20	2.69	+0.022	2.1×10^8	0.62
25	2.41	+0.075	7.7×10^4	0.88

sion $\Delta_c = (\epsilon_f - \epsilon_0) / \epsilon_0$, where ϵ_f is the final strain at the end of the creep process at constant temperature and stress level. The figure detects a group of curves and found to obey the equation:

$$\Delta_c = \Delta_{co} \exp\left(-\frac{w'_c}{kT}\right) \quad (4)$$

where Δ_{co} is the relaxation strength at certain temperature T_0 less than T and w'_c can be considered as the thermal energy acquired by polymer chains. The calculated values of both Δ_{co} and w'_c are listed in Table 2.

During stress relaxation tests the strain remains constant while the stress relaxes to a value at which polymer chains go to a

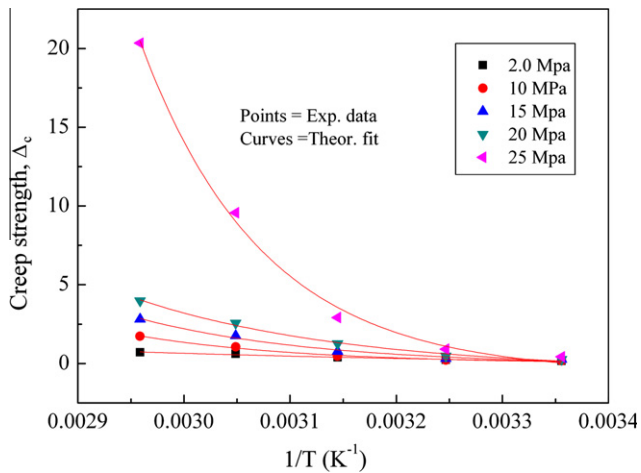


Fig. 10. Temperature dependence of the creep strength of polycarbonate at different stress levels.

configuration of minimum potential energy. Besides, the energy density ($=\frac{1}{2}\sigma\varepsilon$) supplied to the chains by the external applied stress decreases during the relaxation process. On the other hand, during creep tests, one can say that polymer chains make transitions to configurations of minimum mutual binding energy and at constant stress the strain increases and the energy density increases. This may be the reason behind the larger values of w'_c (in Table 2) over those of w' (in Table 1).

4. Conclusions

From stress relaxation and creep tests on polycarbonate at different strain levels, stress levels and temperatures one can conclude an increase of the un-relaxed elastic modulus with increasing strain level during relaxation tests. It also increases, in an unusual behavior, with increasing temperature at low strain levels ($<2.0\%$) while it decreases at high strain levels ($\geq 2.0\%$) with increasing temperature. During creep tests, the initial strain increases with increasing stress level. It decreases, in an unusual behavior, with increasing temperature at low stress level (<20 MPa) while it increases at high stress levels (≥ 20 MPa) with increasing temperature. The relaxation and creep strengths are

found to be activated with temperature with activation energy increases with increasing strain and stress levels. The activation energy of creep strength is found to be greater than that of relaxation strength.

References

- [1] Tager A. Physical chemistry of polymers, Mir Moscow; 1987.
- [2] Aklonis JJ, MacKnight WJ. Introduction to polymer viscoelasticity. 2nd ed. New York: Wiley-Interscience; 1983.
- [3] Struik LCE. Physical aging in amorphous polymers and other materials. Amsterdam: Elsevier; 1978.
- [4] Bradshaw RD, Brinson LC. A continuous test data method to determine a reference curve and shift rate for isothermal physical aging. *Polym Eng Sci* 1999;39(2):211–35.
- [5] Knauss WG, Emri I. Volume change and nonlinearly thermo-viscoelasticity constitution of polymers. *Polym Eng Sci* 1987;27(1):86–100.
- [6] Losi GU, Knauss WG. Free volume theory and nonlinear thermoviscoelasticity. *Polym Eng Sci* 1992;32(8):542–57.
- [7] O'Connell PA, McKenna GB. Large deformation response of polycarbonate: time-temperature, time-aging time, and time-strain superposition. *Polym Eng Sci* 1997;37(9):1485–95.
- [8] Bernstein B, Shokoh A. The stress clock function in viscoelasticity. *J Rheol* 1980;24:189–98.
- [9] Lai J, Bakker A. Analysis of the non-linear creep of high density polyethylene. *Polymer* 1995;36(1):93–9.
- [10] Luo W, Yang T, An Q. Time-temperature-stress equivalence and its application to nonlinear viscoelastic materials. *Acta Mechanica Solida Sinica* 2001;14(3):195–9.
- [11] Abu-Abdeen M. Single and double-step stress relaxation and constitutive modeling of viscoelastic behavior of swelled and un-swelled natural rubber loaded with carbon black. *Mater Des* 2010;31:2078–84.
- [12] Jazouli Said, Luob Wenbo, Bremandc Fabrice, Vu-Khanh Toan. Application of time-stress equivalence to nonlinear creep of polycarbonate. *Polym Test* 2005;24:463–7.
- [13] Findley WN, Lai JSY. A modified superposition principle applied to creep of nonlinear viscoelastic material under abrupt change in state of combined stress. *Trans Soc Rheol* 1967;11(3):361–80.
- [14] Ortiz C, Ober CK, Kramer EJ. Stress relaxation of main-chain, smectic, polydomain liquid crystalline elastomers. *Polymer* 1998;39(16):3713–8.
- [15] Douglas ES, Hazen PB, Steven C. Single polymer dynamics in steady shear flow. *Science* 1999;283:1724–7.
- [16] Sullivan PL, Dykeman D, Shao Q. Mechanical relaxations in heat-aged polycarbonate. Part I: comparison between two molecular weights. *Polym Eng Sci* 2003;43(2):369–82.
- [17] Kapnistos M, Lang M, Vlassopoulos D, Pyckhout-Hintzen W, Richter D, Cho D, et al. Unexpected power-law stress relaxation of entangled ring polymers. *Nat Mater* 2008;7:997–1002.
- [18] Qaiser AA, Price J. Estimation of long-term creep behavior of polycarbonate by stress-time superposition and effects of physical aging. *Mech Time-Depend Mater* 2011;15:41–50.
- [19] Sakai T, Somiya S. Effect of thermal history on the creep behavior of polycarbonate. *J Solid Mech Mater Eng* 2009;3(11):1193–201.