STRUCTURAL RELAXATION OF BARIUM CRYSTAL GLASS

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Structural relaxation of barium crystal glass contemporary produced by RONA glassworks was described by Tool-Narayanaswany-Mazurin (TNMa) model. The distribution of relaxation times was expressed by empirical Kohlrausch Williams Watts relaxation function with relaxation time directly proportional to dynamic viscosity. The parameters of relaxation model were obtained by the nonlinear regression analysis of thermo-mechanical experiments with different zigzag time temperature regimes. According to this method, the simultaneous obtaining of both thermal expansion coefficients is possible together with the determination of viscosity curve and of the parameters characterizing the structural relaxation process. It was found that the structural relaxation of studied glass is well described by the TNMa model and the parameters obtained can be used in modeling of the mechanical stress formation/relaxation during the glass forming/annealing.

INTRODUCTION

The knowledge of the structural relaxation of commercially produced glasses is the essential prerequisite for the correct numerical modeling of mechanical stress formation and release during the glass product formation and annealing [1-4]. The present paper deals with the structural relaxation of the barium crystal glass.

EXPERIMENTAL

The relaxation model of Tool - Narayanaswamy and Mazurin was used for the description of structural relaxation [5-7]. According to Narayanaswamy, the Tool's fictive temperature [8], T_f, can be calculated for an arbitrary temperature time schedule T(t):

$$T_f(t) = T(t) - \int_0^t \mathrm{d}t' \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{t'} M[\xi(t) - \xi(t')] \qquad (1)$$

where M is the Kohlrausch William Watts (KWW) relaxation function [9]:

$$M(\xi) = \exp(-\xi^b) \qquad (2)$$

where b is a constant ($0 < b \leq 1$) and ξ is the dimensionless relaxation time:

$$\xi(t) = \int_0^t \frac{\mathrm{d}t'}{\tau(t')} \qquad (3)$$

where $\tau(t')$ is the relaxation time at time t'. The value of relaxation time is a function of thermodynamic temperature T and the fictive temperature T_f. Moynihan [10] expressed this function in the form analogous to the Arrhenius equation by separating the activation enthalpy into two parts - one related to thermodynamic temperature and the other to fictive temperature. Thus viscosity is not explicitly included in the Tool-Narayanaswamy-Moynihan (TNMo) model. On the other hand, Mazurin [7] started with the viscosity dependence on temperature and fictive temperature $\eta(T, T_f)$. He described the equilibrium viscosity (i.e. $\eta(T, T_f = T)$) by the commonly used Vogel Fulcher Tammann Equation [1]:

$$\log \eta = A + B/(T - T_0) \qquad (4)$$

where A, B and T_0 are empirical parameters. For the temperature dependence of isostructural viscosity (i.e. $\eta(T, T_f = \text{const} \neq T)$) the Arrhenius like equation was used. Using the simple relationship between the modulus K and viscosity η:

$$\tau = \eta/K \qquad (5)$$

Mazurin obtained the equation describing the dependence of relaxation time on T and T_f:

$$\begin{aligned} \log\tau(T, T_f) &= \log\eta(T, T_f) - \log K = \\ &= \left(A + \frac{B}{T_f - T_0}\right)\frac{T_f}{T} + \left(1 - \frac{T_f}{T}\right)\log\eta_0 - \log K \end{aligned} \qquad (6)$$

where η_0 is an empirical parameter.

Axial viscous flow caused by the load σ is described by:

$$\dot{\varepsilon} = \frac{1}{l}\left(\frac{\partial l}{\partial t}\right)_{T,T_f} = \frac{\sigma}{3\eta} \qquad (7)$$

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The thermodilatometric experiment during which the viscous flow takes part is described [11] by:

$$\varepsilon = \frac{\Delta l}{l_0} \approx \int_{T_1}^{T_2} \alpha_g dT + \int_{T_{f,1}}^{T_{f,2}} \Delta\alpha \, dT_f - \\ - \left(1 + \int_{T_1}^{T_2} \alpha_g dT + \int_{T_{f,1}}^{T_{f,2}} \Delta\alpha \, dT_f\right) \int_{t_1}^{t_2} \frac{\sigma}{3\eta\left(T, T_f\right)} dt \tag{8}$$

where α_g and α_m are thermal expansion coefficients of glass and metastable melt and $\Delta\alpha = \alpha_m - \alpha_g$.

Prismatic samples with approximate dimensions of (5×5×20) mm^3 were prepared from the glass products supplied by RONA glassworks. The viscosity was obtained by measuring the axial strain rate of the sample under constant load at isothermal conditions (see the Equation (7)). Temperature dependence of viscosity was described by the VFT equation (Figure 1) using the nonlinear regression analysis. The relatively high values of standard deviations of parameters estimate are caused by the low statistical robustness implied by the almost linear course of the equilibrium viscosity temperature dependence in the measured viscosity range (10^8-10^{12} dPas). Thermal expansion coefficients were estimated by thermodilatometry (Thermal Instruments, TMA Q400 EM) from the slope of the cooling curve recorded with the cooling rate of 5°C/min. Obtained values of VFT equation parameters and thermal expansion coefficients are summarized in Table 1. Then the thermomechanical analysis was performed under the constant load of 5 g with the zigzag time temperature regime consisting of two cooling/heating loops: the first one with the rate of 5°C/min. was followed by the second one with the rate of 10°C/min.

RESULTS AND DISCUSSION

The nonlinear regression treatment of the thermodilatometric data was performed by the own software written in FORTRAN [11]. The values of log(K/dPa), b, B, α_g, α_m and log(η_0/dPas) were estimated. The results of regression treatment are summarized in Table 2 and in Figure 2. It can be seen (Figure 2) that the relaxation model well describes the experimental values. This is confirmed by the standard deviation of approximation ($s_{apr} = 4.6 \times 10^{-4}$) that is on the level of experimental error as well as by the relatively high value of Fisher's statistics (F = 7 894). Another check of the model appropriateness is represented by the values of regression estimates of parameters that were measured also by preliminary experiments, i.e. B, α_g, α_m. Only the α_g estimate seems to be shifted when compared with the preliminary experimental result. It can be therefore concluded that the obtained model of structural relaxation of the contemporary produced barium crystal glass is correct and can be used in subsequent modeling of the mechanical stress formation/release during the forming/annealing of the glass products.

Table 1. Measured characteristics of the RONA barium crystal glass.

Parameter	Value
A	-0.52 ± 0.06
B (K)	3 686 ± 483
T_0 (K)	528 ± 23
$10^7 \times \alpha_g$ (K^{-1})	114 ± 5
$10^7 \times \alpha_m$ (K^{-1})	327 ± 10
T_g (K)	799 ± 1

Table 2. Results of nonlinear regression analysis.

Parameter	Estimate
log(K/dPa)	8.98 ± 0.03
b	0.478 ± 0.008
B (K)	3 531 ± 1
$10^7 \times \alpha_g$ (K^{-1})	100 ± 1
$10^7 \times \alpha_m$ (K^{-1})	326 ± 1
log(η_0/dPa.s)	3.54 ± 0.32

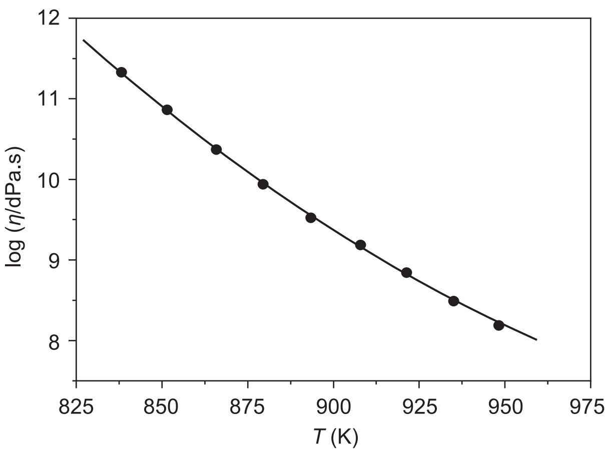

Figure 1. Temperature dependence of viscosity - experimental values (points) and VFT equation (line).

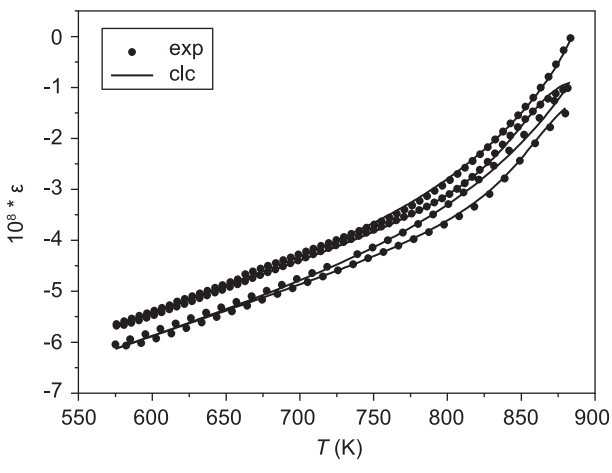

Figure 2. Comparison of experimental (points) and calculated (line) strain values.

CONCLUSIONS

The regression analysis of thermo-mechanical (TMA Q400 EM) experimental data was used for estimation of parameters of Tool – Narayanaswamy - Moynihan's models of structural relaxation of barium crystal glass contemporary produced by RONA. The relaxation model well describes the experimental values. This is confirmed by the standard deviation of approximation that is on the level of experimental error as well as by the relatively high value of Fisher's statistics. The parameters B, α_g, α_m were measured also by preliminary experiments, only one value of regression estimate of parameter for α_g was shifted when compared with the preliminary experimental result. Even though, TNM model can be used for obtaining the parameters needed as input values for mathematical modeling of stress relaxation in glass products [12].

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