

STRUCTURAL RELAXATION WITH VISCOUS FLOW FOLLOWED BY THERMODILATOMETRY

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The mathematical model of the thermodilatometric curve obtained in conditions when the structural relaxation and the viscous flow take place simultaneously is presented. The structural relaxation part of the model is based on the stretched exponential relaxation function, and the relaxation times are expressed as proportional to instantaneous viscosity. Mazurin's approximation is used for the viscosity dependence on the thermodynamic and fictive temperatures. The non-linear regression treatment of experimental data enabling the estimation of relaxation parameters together with the thermal expansion coefficients of glass and metastable liquid is proposed. The method and the computer program are verified on the optical glass commonly used as a secondary viscosity standard.

INTRODUCTION

Thermodilatometry is one of the simplest experimental methods enabling the efficient study of oxide glass structural relaxation. A lot of work done in the field of analysis of the shape of dilatometric hysteresis curve has led to regression estimates of relaxation function parameters [1-6]. The presumption of zero or negligible viscous sample deformation included in the regression treatments resulted in a development of special constructions of dilatometers enabling measurements at near zero load [2]. More over, the oblique sample arrangement has resulted as an optimum compromise between the vertical and horizontal ones [1]. In the case of the vertical sample orientation the sample weight causes self-deformation at elevated temperatures. The sample frictional resistance is the main disadvantage of the horizontal sample arrangement. But even in the best oblique dilatometers, the sample deformation takes place at higher temperatures because of the viscous flow caused by the sample weight. To minimize this unwanted effect the upper working temperature limit must not be very much higher than the T_g range. This constraint leads to serious ambiguity in determination of thermal expansion coefficient of metastable liquid α_m . Sometimes the too low upper temperature limit may cause that the full relaxation (i.e. metastable equilibrium), that is a prerequisite of the regression models mentioned above, is not fully satisfied at the upper temperature end of the dilatometric curve.

Therefore it seems to be useful to include the viscous flow in the regression model of the dilatometric curve and thereby remove both the upper temperature limit constraint and the near zero load demand. Moreover the possibility to use various loads will improve the statistical characteristics of the regression estimates .

The development and experimental verification of such model is the subject of this paper.

THEORETICAL PART

In the case of zero viscous flow, the Tool [7] and Narayanaswamy's [8] model of structural relaxation describes the hysteresis of thermodilatometric curves [1]. The length $l(T, T_{f,l})$ of the sample characterized by thermodynamic temperature T and fictive (structural) temperature $T_{f,l}$ is given by

$$l(T, T_{f,l}) = l(T_r, T_r) [1 + \alpha_g (T - T_{f,l}) + \alpha_m (T_r - T_{f,l})] \quad (1)$$

where α_g and α_m are the thermal expansion coefficients of the glass and metastable glass-melt, respectively. The T_r is arbitrary, but a sufficiently high reference temperature, i.e. the temperature at which the relaxation rate is so high that the fictive temperature may be considered identical with the temperature T . For a given time-temperature schedule $T(t)$ the time dependence of fictive temperature $T_{f,l}(t)$ may be obtained from the integral equation

$$T_{f,l}(t) = T(t) - \int_0^t \left(\frac{dT}{dt} \right)_c M_l [\xi(t) - \xi(t')] \quad (2)$$

where M_l is the relaxation function of dimensionless time ξ that is defined as an time integral of inverse relaxation time τ_l

$$\xi(t) = \int_0^t \frac{dt'}{\tau_l(t')} = \int_0^t \frac{K_l}{\eta(t')} dt' \quad (3)$$

On the right hand side of equation (3) the relaxation time is expressed as proportional to the dynamic viscosity η

$$\tau_l = \frac{\eta}{K_l} \quad (4)$$

where the subscript l (length) reflects the dependence of the constant of proportionality K on the particular property studied. The property-dependent character of both the fictive temperature and dimensionless time follows directly from this fact. The validity of the relation (4) for oxide glasses has been proved experimentally [8,9].

Empirically, the relaxation function may be expressed either as a linear combination of single exponential terms with distinct relaxation times or by the stretched exponential function (known also as Kohlrausch-Williams-Watts function - KWW) [10]

$$M_l(\xi) = \exp(-\xi^b) \quad (5)$$

where the exponent b has a value between 0 and 1. The KWW function corresponds to continuous relaxation times distribution - a smaller value of b corresponds to a broader distribution of relaxation times. The systems (like oxide glasses) with temperature independent b value are said to be "thermorheologically simple" [1].

The last question to be solved in the case of zero plastic deformation is the viscosity dependence on both the fictive and thermodynamic temperatures $\eta = \eta(T, T_{f,l})$. In metastable equilibrium where $T_{f,l} = T$, the temperature dependence of the viscosity of glass forming liquids is well represented by the empirical Vogel-Fulcher-Tamman (VFT) equation

$$\log \{ \eta(T, T_{f,l} = T) \} = A + \frac{B}{T - T_0} \quad (6)$$

where A , B and T_0 are empirical constants and composed brackets denote the numerical value of viscosity. The simple Arrhenius-like equation

$$\log \{ \eta(T, T_{f,l} = T) \} = A' + \frac{B'}{T} \quad (7)$$

can be used only in limited temperature range. In the case of nonequilibrium glassy state where $T_{f,l}$ is constant, the isostructural viscosity temperature dependence is well described by equation (7) with the coefficients dependent on the particular value of the fictive temperature, i.e. $A' = A'(T_{f,l})$ and $B' = B'(T_{f,l})$. Mazurin [1,3,11] proposed the simplified model of this dependence assuming that all the isostructural viscosity lines have one common point with coordinates $\{1/T = 0, \log \eta = \log \eta_0\}$ in $\log \eta$ vs $1/T$ plot. Combining equation (6) with Mazurin's approximation the following formula for non-equilibrium viscosity temperature can be obtained

$$\log \{ \eta(T, T_{f,l}) \} = \log \{ \eta(T_{f,l}, T_{f,l}) \} \frac{T_{f,l}}{T} - \log \{ \eta_0 \} \left(\frac{T_{f,l}}{T} - 1 \right) \quad (8)$$

The time course of the sample length may now be calculated from equations (1) - (8) for arbitrary time-temperature schedule $T(t)$. In computer calculations $T(t)$ is approximated by a series of sufficiently small temperature jumps ΔT_k at times t_k , where $k = 1, 2, \dots, N$, $t_0 = 0$ and $T(0) = T_r$.

For the new stepwise temperature schedule we can write

$$T_a(t) = T_r + \sum_{i=1}^k \Delta T_i \quad \text{for } t_k \leq t \leq t_{k+1} \quad (9)$$

and the integrals in equations (2) and (3) can then be replaced with corresponding sums. It is worth noting that the sample length calculated according to equation (1) does not explicitly depend on time.

The velocity of the viscous sample deformation under axial load σ is described by

$$\frac{d\varepsilon}{dt} = \frac{1}{dt} \left(\frac{dl}{l} \right) = \frac{\sigma}{3\eta} \quad (10)$$

Thus introducing the viscous flow we obtain the sample length explicitly dependent on time, i.e. $l = l(t, T, T_{f,l})$. The dimensionless quantity (sample deformation)

$$\varepsilon = \frac{\Delta l}{l} = \frac{l[t, T(t), T_{f,l}(t)] - l(0, T_r, T_r)}{l(0, T_r, T_r)} \quad (11)$$

is plotted versus temperature in thermodilatometry. The decrease of the reference sample length caused by the viscous flow may be obtained from equation (10) by integration

$$l(t, T_r, T_r) = l(0, T_r, T_r) \left(1 - \int_0^t d\varepsilon \right) \quad (12)$$

where

$$\int_0^t d\varepsilon = \frac{\sigma}{3K_1} \xi(t) \quad (13)$$

The length changes connected with the sample thermal expansion are related to instantaneous reference length. It is the length, which the sample would reach if it is heated to the reference temperature T_r in a negligibly short time, what means that the viscous flow would not arise. The reference temperature must be chosen sufficiently high, so that the structural relaxation time is negligible at T_r , and the fictive temperature of the sample $T_{f,l}$ is equal to its thermodynamic temperature T_r . equation (1) then becomes

$$l(t, T, T_{f,l}) = l(t, T_r, T_r) [1 + \alpha_g(T - T_{f,l}) + \alpha_m(T_r - T_{f,l})] \quad (14)$$

Now equation (11) may be written in the final form

$$\varepsilon = \frac{\Delta l}{l} = \alpha_g(T - T_{f,l}) + \alpha_m(T_{f,l} - T_0) - \frac{\sigma}{3K_1} \xi(t) [1 + \alpha_g(T - T_{f,l}) + \alpha_m(T_{f,l} - T_r)] \quad (15)$$

Combining equations (15), (2), (5) and (3) the $\varepsilon^{\text{clc}}(t)$ values may be calculated for a given time-temperature schedule as a function of α_g , α_m , K_1 , η_0 , and b .

Let us suppose that the A , B , and T_0 parameters of the VFT viscosity equation are known for a given glass sample and that the thermodilatometric curve $\varepsilon^{\text{exp}}(t)$ was recorded under the known constant load σ for given time-temperature schedule $T(t)$. Then the unknown parameters of the proposed regression model may be estimated using the standard non-linear least squares method, i.e. minimizing the target function

$$F(\alpha_g, \alpha_1, K_1, \eta_0, b) = \int_0^{t_{\text{max}}} [(\varepsilon^{\text{clc}}(t) - \varepsilon^{\text{exp}}(t))^2] dt \quad (16)$$

where t_{max} is the time at completion of the dilatometric experiment.

EXPERIMENTAL PART

The proposed method was verified on optical glass "brylovina" commonly used as a secondary viscosity standard in our country. The glass composition determined by ICP spectral emission analysis is (wt.%): 70.45 % SiO₂, 11.75 % Na₂O, 4.03 % K₂O, 9.75 % CaO,

2.45 % BaO, 1.15 % Al₂O₃ and 0.42 % Sb₂O₃. The viscosity curve is described by the VFT equation with $A = -1.712$, $B = 4127.0$ and $T_0 = 260.0$ °C.

The thermodilatometric curve was recorded on the vertical TMA-402 thermomechanical analyser (Netzsch) with a constant load of 15.007 kPa (including the half sample weight contribution). The sample with a rectangular cross-section of 5.85 mm × 5.70 mm and with the length of 19.4 mm was used.

The data were collected by means of the SPECTRA-XB (Intercole) measuring station which was connected to a desktop PC 386 computer.

The time temperature schedule was controlled by a CHINOTHERM (Chinoin) temperature controller. The zigzag time-temperature schedule (figure 1) was combined from two heating and two cooling speeds (± 5 °C min⁻¹ and ± 10 °C min⁻¹).

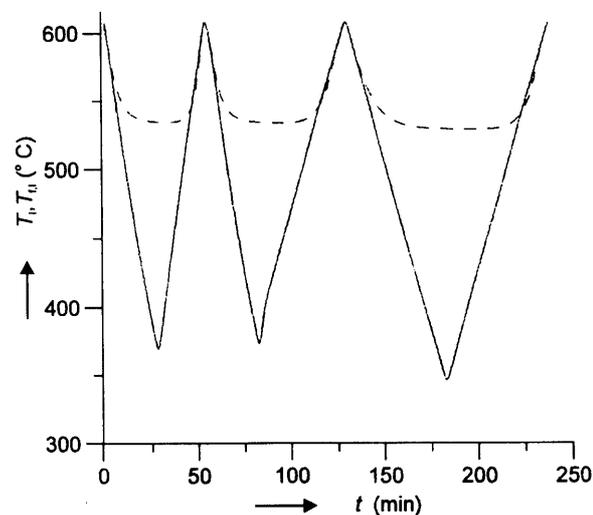


Figure 1. The time temperature schedule of thermodilatometric experiment (full line), and the course of fictive temperature obtained for optimal estimates of regression parameters (dashed line).

RESULTS AND DISCUSSION

The FORTRAN program NEMOR95 using the SIMPLEX minimization method [12,13] was written for a PC-486 desktop computer. All the integrals of the mathematical model were converted to sums using the stepwise computing time-temperature rectangular pattern (T_k, t_k) which replaces an arbitrary experimental $T(t)$ course (see equation (9)). The t_k values are not equidistant because all the experimental $T(t)$ points must be placed at the knots of the computational pattern to avoid an interpolation during the calculation of the residual sum of squares of deviations. The maximum values of the time ($\Delta_{\text{max}} t_k$) and temperature ($\Delta_{\text{max}} T_k$) jumps

in the computing pattern are limited by the program user. Thus the number of knots of the computing pattern is greater than or equal to the number of experimental points. In the present work the values of $\Delta_{\max} t_k = 30$ s and $\Delta_{\max} T_k = 2$ °C were satisfactory for the numerical stability of the computational scheme. Using these limiting values we have obtained 1179 knots of the computing pattern for 942 experimental points.

The experimental and computed dilatometric curves are compared in figure 2. Only every tenth experimental

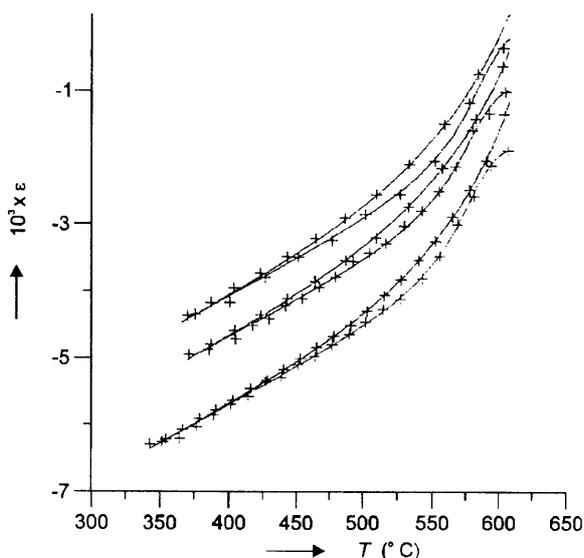


Figure 2. The comparison of calculated (full line) and experimental (+) dilatometric curves. Only every tenth experimental point is plotted.

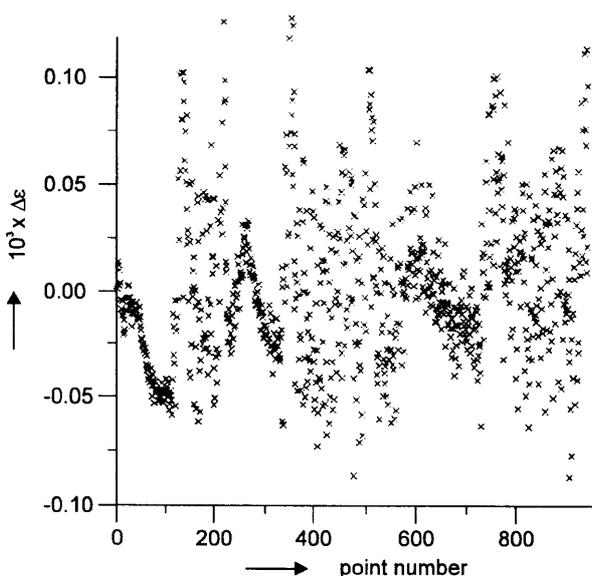


Figure 3. The deviations between calculated and experimental ϵ values plotted for all the experimental points.

point was plotted only for the sake of simplicity. Despite the complex shape of the experimental curve, the model describes it very well. This is confirmed in figure 3, where the deviations between the calculated and experimental points are visualized for all the data points. The residual standard deviation of 3.7×10^{-5} is equivalent to the Δl standard deviation of 0.7×10^{-6} m, which is close to the experimental error of Δl measurement.

The following estimates of the unknown parameters were obtained:

$$\alpha_g = (113.2 \pm 0.6) \times 10^7 / ^\circ\text{C}, \alpha_m = (345 \pm 1) \times 10^7 / ^\circ\text{C},$$

$$\log(K_1 / \text{dPa}) = 10.14 \pm 0.2, \log(\eta_0 / \text{dPa}\cdot\text{s}) = 2.05 \pm 0.26,$$

$$\text{and } b = 0.523 \pm 0.007.$$

Comparing the values of the parameters with their standard deviations it may be concluded that all the estimates are statistically significant (in the sense of Student's t-statistics), and, with the exception of the η_0 case, the standard deviations are very small.

Depending on the cooling rate, the glasses with the fictive temperatures of 526°C and 531°C were obtained (figure 1). The glass thermal expansion coefficient represents a mean value between this temperature and the lowest temperature of the thermodilatometric curve (i.e. 340°C). This fact was verified by direct investigation of the low temperature slope of the dilatometric curve.

The other parameter values are, from the physical point of view, fully acceptable and close to those obtained for other silicate glasses [1].

The structural relaxation is usually visualized through the hysteresis in thermodilatometric curves. Such results may be obtained if the values of estimated parameters are used for $\epsilon^{\text{clc}}[T(t)]$ evaluation and the zero

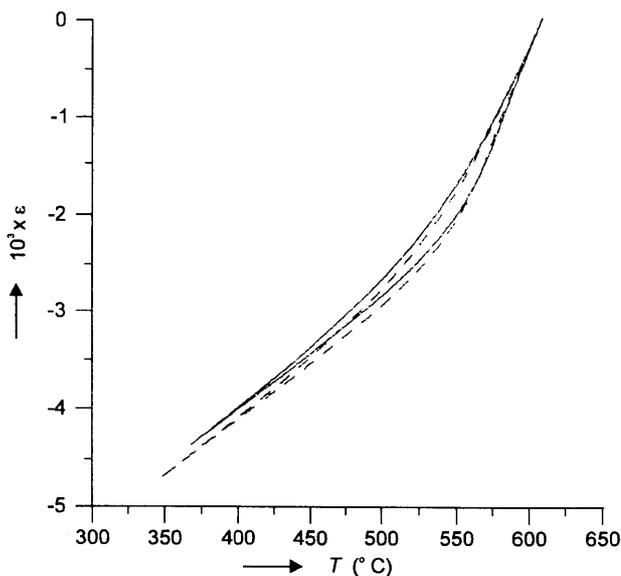


Figure 4. The dilatometric curves calculated for the case of zero viscous flow (full line - 10 °C min⁻¹; dashed line - 5 °C min⁻¹).

load value $\sigma = 0$ is inserted in equation (15). Such "pure" structural relaxation curves are illustrated in figure 4.

The typical problem of nonlinear multiparametric regression analysis represent the strong bonds between parameters which sometimes disables statistically significant and unambiguous determination of the individual parameter values [13]. Therefore we have calculated the matrix of correlation coefficients between estimated parameters. The strongest correlation was found between the $\log K_1$ and α_m values. However the value of correlation coefficient of -0.823 is not so high as to prevent statistically significant estimation of the individual parameter values. The other correlation coefficients were much lower.

CONCLUSION

The inclusion of viscous flow in the regression model of structural relaxation enables the efficient estimation of structural relaxation parameters together with the thermal expansion coefficients of glass and metastable liquid. Using this method, the problems connected with sample deformation in dilatometers with non zero load on one side, and the gravitational sample selfdeformation on the other, may be simply solved. The non linear regression method proposed seems to be sufficiently robust without significant bonds between the examined set parameters.

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TERMODILATOMETRICKÉ SKÚMANIE ŠTRUKTÚRNEJ RELAXÁCIE V PRÍTOMNOSTI VISKÓZNEHO TOKU

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Navrhol sa matematický model termodilatometrickej krivky opisujúci simultánny priebeh štruktúrnej relaxácie a viskózneho toku. V časti opisujúcej štruktúrnu relaxáciu sa použila Kohlrauschova-Williamsova-Wattsova relaxačná funkcia s relaxačným časom priamo úmerným momentálnej viskozite vzorky. Závislosť viskozity od termodynamickej a fiktívnej (štruktúrnej) teploty sa vyjadrila podľa Mazurina [1]. Navrhla a algoritmovala sa metóda nelineárnej regresnej analýzy na súčasný výpočet relaxačných parametrov a koeficientov teplotnej rozťažnosti založený na minimalizácii sumy štvorcov odchýlok medzi nameranou a vypočítanou termodilatometrickou krivkou. Metóda sa overila na termodilatometrickej krivke optického skla (brýlovina) používaného ako sekundárny viskozitný štandard.