STRUCTURAL RELAXATION OF NBS711 GLASS - RELIABILITY OF THE REGRESSION ESTIMATES OF RELAXATION MODEL

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Thermomechanical experiments with different zigzag time temperature regimes and different applied axial loads were performed on viscosity standard glass NBS711. Experimental data were described by the Tool-Narayanaswamy-Moynihan's and Mazurin's model using the non-linear regression analysis. Both applied models described the experimental data with sufficient accuracy. It was found, that the statistically robust estimates of the regression model parameters can be obtained only if more TMA experiments with different zigzag time-temperature schedule are combined. The use of higher loads is preferable.

INTRODUCTION

The relaxation phenomena taking place in the glass transition temperature range are of great importance for both the glass science and glass technology [1,2]. The kinetics of the glass transition and of the related relaxation phenomena describes with reasonable accuracy the Tool-Narayanaswamy-Moynihan's theory (hereafter referred to as the TNM or Moynihan's model) [3-7] based on the Tool's concept of fictive temperature, T_f [8,9]. A frequently used alternative to the TNM is the Mazurin's model (M), [10,11] which can be used for description of experimental data with comparable accuracy. The Mazurin's model is also based on the Tool-Narayanaswamy's relaxation theory but uses different formula for the temperature-structure dependence of the mean relaxation time. Moreover, in the Mazurin's approach, the mean relaxation time is simply related to the value of viscosity.

It is worth noting that also other not so frequently used relaxation models were developed. Numerous studies have shown that a variety of available models for temperature-structure dependence of the relaxation time can adequately describe kinetics of relaxation (enthalpy as well as volume) [12,13]. The significant contribution of Avramov to the relaxation theories and to the theoretical concepts of the viscosity of glass forming melts has to be mentioned here [7, 14, 15].

The parameters of relaxation models are typically obtained by non-linear regression analysis of thermodilatometric (structural relaxation) or DSC (enthalpy relaxation) experimental data [16-18]. Due to strong linear bonds between regression parameters the obtained parameters' estimates are not independent, and the same experimental data can be described with comparable accuracy by different sets of parameters' estimates. The mathematical model was therefore proposed of thermodilatometric curve obtained from thermomechanical (TMA) experiment under the conditions when structural relaxation and viscous flow take place simultaneously [19]. 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 and Moynihan's approximation were alternatively used for description of dependences of the mean relaxation time on thermodynamic and fictive temperatures. The non-linear regression treatment of experimental data allowed the estimation of relaxation parameters together with the thermal expansion coefficients of glass and of metastable liquid. This model was typically used for evaluation of data from single TMA experiment. The aim of the present work is to verify the statistical robustness of regression estimates of relaxation parameters obtained from a set of TMA experiments with different time-temperature regimes and different axial loads. The viscosity standard glass NBS 711 [20] was used for this purpose.

METHOD

Let us consider, the sample length, l, as a function of thermodynamic temperature, T, and Tool's fictive temperature T_f:

$$\mathrm{d}l = \left(\frac{\partial l}{\partial T}\right)_{T_f} \mathrm{d}T + \left(\frac{\partial l}{\partial T_f}\right)_T \mathrm{d}T_f = l\left(\alpha_g \mathrm{d}T + \Delta\alpha\, \mathrm{d}T_f\right) \qquad (1)$$

$$\Delta\alpha = \alpha_m - \alpha_g \qquad (2)$$

where α_g and α_m is the thermal expansion coefficient of glass and of metastable equilibrium melt, respectively. The values of both thermal expansion coefficients are considered as temperature independent in the present work.

In the case when viscous flow takes place, an additional source of changes of the sample length has to be included:

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

where σ is axial stress, t is time, and η stands for viscosity. Let us suppose a change of the sample state from an initial state 1 to final state 2. The relative length change of the sample during the above transition, i.e. the sample strain, can be expressed as:

$$\varepsilon = \frac{l_2 - l_1}{l_1} \approx \int_{T_1}^{T_2} \alpha_g \, \mathrm{d}T + \int_{T_{f,1}}^{T_{f,2}} \Delta\alpha \, \mathrm{d}T_f - \left(1 + \int_{T_1}^{T_2} \alpha_g \, \mathrm{d}T + \int_{T_{f,1}}^{T_{f,2}} \Delta\alpha \, \mathrm{d}T_f\right) \int_{t_1}^{t_2} \frac{\sigma}{3\eta(T, T_f)} \mathrm{d}t \qquad (4)$$

The time course of fictive temperature T_f is obtained within the frame of the Tool – Narayanaswamy – Moynihan's/Mazurin's model [3-11] with the Kohlrausch – Williams – Watts's relaxation function [21]:

$$M(\xi) = \exp(-\xi^b) \qquad 0 < b \leq 1 \qquad (5)$$

where ξ is the dimensionless relaxation time:

$$\xi(t) = \int_0^t \frac{\mathrm{d}t'}{\tau(t')} = \int_0^t \frac{K}{\eta(t')} \mathrm{d}t' \qquad (6)$$

and η is the viscosity expressed alternatively by the Mazurin's approximation:

$$\log \eta(T, T_f) = \left(A + \frac{B}{T - T_0}\right)\frac{T_f}{T} + \log \eta_0 \left(1 - \frac{T_f}{T}\right) \qquad (7)$$

or by the Moynihan's approximation:

$$\log \eta(T, T_f) = A' + x\frac{\Delta h}{2.303RT} + (1-x)\frac{\Delta h}{2.303RT_f} + \log K \qquad (8)$$

where Δh is the formal activation enthalpy, R is the molar gas constant and the numerical factor 2.303 is included for convenience.

The modulus K relating the viscosity and relaxation time in the equation (6) is considered as characteristic constant dependent on the glass composition [22].

An arbitrary subset of the above model parameters, i.e. a subset chosen from $\{K, b, A, B, T_0, A', x, \Delta h, \eta_0, \sigma, \alpha_g$, and $\alpha_m\}$, can be estimated by means of the non-linear regression analysis.

EXPERIMENTAL

The thermal mechanical analyser (TMA) NETZSCH 402 was used for recording the sample length during the pre-defined zigzag time-temperature schedule under the constant axial load of (49, 491, 981) mN (table 1.). Prismatic samples of the lead-silicate viscosity standard glass NBS 711 supplied by NIST [20] with the dimensions of $(5.40 \times 5.90 \times 20.40)$ mm^3 were used for the measurement. After each experiment, the sample was heated with the rate of 5°C/min from 290 K to 800 K, and cooled down to 290 K at 5°C/min with zero applied load. The non-linear regression analysis of experimental data was performed by the in house developed FORTRAN computer code based on the simplex minimization of the sum of squares of deviations.

RESULTS AND DISCUSSION

Table 1 summarizes the conditions of TMA experiments. The upper temperature range around 773 K corresponds to sufficiently short relaxation time $\tau \approx 2$ s. Thus the sample is in the state of thermodynamic metastable equilibrium ($T = T_f$) at the beginning of the TMA experiment.

Figure 1 (2) compares the experimental strain values with the calculated values of the Mazurin's (Moynihan's) model obtained by the regression analysis of the experiment No.5. The subset of six parameters $\{K, b, B, \eta_0, \alpha_g\ \alpha_m\}$ was selected as the set of unknown parameters for the Mazurin's model, and the subset of seven parameters $\{K, b, A', \Delta h, x, \alpha_g, \alpha_m\}$ was chosen as the set of unknown parameters for the Moynihan's model. In case of the Mazurin's model the values of $\{A, T_0\}$ were taken from the NBS 711 viscosity certificate [20].

Regression estimates of individual parameters obtained for the Mazurin's and Moynihan's model are summarized in the table 2, and 3, respectively. Sufficiently low values of standard deviations of approximations, as well as relatively high values of Fisher's statistics indicate (table 2, 3) that in all cases the model describes the experimental data with sufficient accuracy. On the other hand, the values of individual parameters obtained for different experiments within each studied model differ significantly. In some particular cases the results are obviously erroneous, e.g. the value of parameter $x = 1$ in the experiment No.3 in Moynihan's model removes the structural dependence of relaxation time - see equation (8).

The same probably applies for extreme values, like $\log(K(\mathrm{dPa})) = 8.5$ in the experiment No.5 in the Mazurin's model. It is interesting, that the best results from the purely statistical point of view (i.e. the highest F value) were for both models observed in the experiment No.4. In this experiment the highest load of 981 mN was used, and the contribution of deformation by viscous flow is the most significant. Moreover, the values of estimated parameters obtained in the experiment No.4 are in good agreement with the data published for similar glasses previously [10,11]. On the other hand, the experiments No.1 and 4 use only two different heating/cooling rates and their time-temperature schedule is therefore simpler than in the other experiments. This is probably the reason for obtaining the lowest values of standard deviations of approximations in the experiment No.1. Also the regression estimates obtained in the experiment No.1 are close to those obtained for both relaxation models in the experiment No.4. Moreover, if

Table 1. The time-temperature regimes of five different TMA experiments*.

Experiment No.	Load (mN)	Heating/Cooling (K/min)	Temperature limits (K)
1	49	5	785 - 570 - 785 - 570 - 785
		10	785 - 570 - 785 - 570 - 785
2	491	20	785 - 570 - 785
		10	785 - 570 - 785
		5	785 - 570 - 785
		20	785 - 570
		5	570 - 780 - 570
		20	570 - 785
3	491	20	810 - 570 - 810 - 570
		10	570 - 795 - 570 - 795 - 570
		5	570 - 795 - 570 - 975
4	981	10	795 - 570 - 795
		5	795 - 570 - 795
5	491	20	810 - 470 - 810 - 470
		10	470 - 795 - 520 - 795 - 520
		5	520 - 790 - 570 - 790

* *For example, the time-temperature regime of the experiment No.1 starts with the temperature (in K) scans 785 - 570 - 785 - 570 - 785 carried out with the heating/cooling rate of 5 K/min followed immediately by the scans 785 - 570 - 785 - 570 - 785 with the heating/cooling rate of 10 K/min. In the course of the whole experiment the sample is under the constant load of 49 mN.*

Table 2. Results of non-linear regression analysis for Mazurin's model; F - Fisher's statistics, s_{apr} - standard deviation of approximation.

Parameter	Experiment No.					Average
	1	2	3	4	5	
log {K (dPa)}	10.03	10.29	9.98	10.08	8.54	9.78 ± 0.7
b	0.586	0.679	0.551	0.565	0.315	0.539 ± 0.115
log{η_o/dPa.s}	2.45	4.46	-1.87	2.03	-2.09	0.996 ± 2.87
B (K)	4149	4172	4169	4194	4162	4169 ± 17
$10^7.\alpha_g$ (K^{-1})	95	96	83	92	72	88 ± 10
$10^7.\alpha_m$ (K^{-1})	289	287	354	297	469	339 ± 78
F	15 065	2 192	1 679	42 446	7 259	
$10^6.s_{apr}$	19	56	143	31	73	

Table 3. Results of non-linear regression analysis for Moynihan's model, F - Fisher's statistics, s_{apr} - standard deviation of approximation.

Parameter	Experiment No.					Average
	1	2	3	4	5	
log {K (dPa)}	10.14	9.87	10.02	10.18	9.18	9.88 ± 0.41
$\acute{A}$	-30.64	-22.32	-22.24	-26.91	-25.27	-25.48 ± 3.51
b	0.609	0.716	0.518	0.661	0.335	0.568 ± 0.149
x	0.34	0.53	1	0.43	0.63	0.59 ± 0.26
$10^7.\alpha_g$ (K^{-1})	96	97	81	95	76	89 ± 10
$10^7.\alpha_m$ (K^{-1})	287	287	336	284	408	320 ± 54
Δh/kJ.mol^{-1}	456	339	334	403	391	382 ± 51
F	14 203	8 999	2 518	32 545	2 294	
$10^6.s_{apr}$	20	28	117	35	130	

the standard deviations of average values of individual parameters (the +/- values in the column "Average" in the tables 2 and 3) are taken into account, the results of both experiments can be considered as identical.

The obtained results suggest that too complex time-temperature schedules consisting of too many cooling-heating-cooling loops give incorrect results due to the accumulation of various experimental errors during a long lasting experiment (e.g. temperature instability, sample misalignment, and, last but not least, sample deformation). This was most likely the reason for the lowest values of F and the highest values of s_{apr} obtained from the most complex experiments with five loops (No.3 for Mazurin's model, and No.5 for Moynihan's model).

In case of the Mazurin's model an internal gauge can be defined when the regression estimate of the parameter B (see the equation (7)) is compared with the certified value of 4257.6 K [20]. From this point of view the best results were obtained from the experiments No.1 and 4.

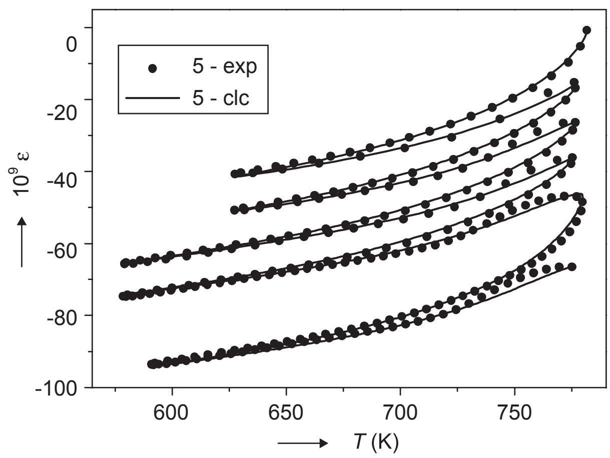

Figure 1. Calculated (line) and experimental (circles) strain values, Mazurin's model, experiment No.5.

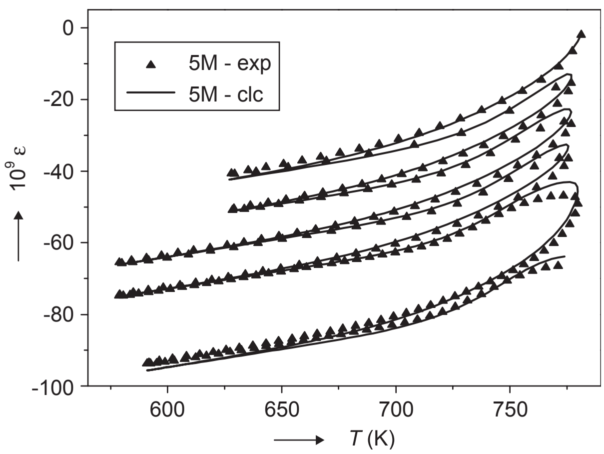

Figure 2. Calculated (line) and experimental (circles) strain values, Moynihan's model, experiment No.5.

The analogous role to the parameter B of the Mazurin's model plays the Moynihan's parameter Δh, both reflecting the activation enthalpy. While in case of the Mazurin's model the activation enthalpy is temperature dependent

$$\Delta h_\eta = 2.303RB\frac{T^2}{\left(T-T_0\right)^2} \tag{9}$$

and equals to the activation enthalpy of viscous flow, in case of the Moynihan's model the Δh value is temperature independent. The highest values of h were obtained for the best fitted experiments No.1 (456 kJ/mol) and 4 (403 kJ/mol). According to the certified viscosity equation [20], these values correspond to the Δh value at the temperature of 737 K and 773 K, respectively. For comparison, the dilatometric T_g value of NBS711 glass measured during the cooling (5 K/min) is equal to 701 K. This discrepancy can be perhaps explained by the fact that the viscosity equation is certified [20] only up to the viscosity value of 10^{12} dPas.

Due to the same origin of enthalpy and structural relaxation, the results of enthalpy relaxation study of NBS711 glass performed by Davis and Ihinger [23] can be compared with the present study of structural relaxation. The value of activation energy of the viscous flow (447 kJ/mol) reported by Napolitano et al. [24] was used, among others, by Davis and Ihinger for fitting the DSC data. This value corresponds well with the values obtained from the experiments No.1 and 4 in this work. For this activation enthalpy Davis and Ihinger found by regression analysis of the DSC data the value of $b = 0.629$. In this work the Mazurin's model yielded in almost all experiments in lower b values than the Moynihan's model. The only exception is the experiment No.3 that gives obviously physically erroneous result ($x = 1$). The Moynihan's estimates of the b value for the best fitted experiments No.1 (0.609) and 4 (0.661) are close to the value obtained by Davis and Ihinger.

Comparison of regression estimates of thermal expansion coefficients of both the metastable melt and of the glass revealed reasonable agreement of thermal expansion coefficient in all experiments, except of the experiments No.3 and 5, where outlying values were obtained.

CONCLUSION

The strain values calculated with the use of both proposed models agree well with the experimental data. Both applied models can be thus considered as equivalent, at least from the phenomenological point of view. On the other hand, the statistically robust estimates of the regression model parameters can be obtained only if more TMA experiments with different zigzag time-temperature schedule are combined and compared. The use of higher loads is preferable. The long lasting experiments comprising more than four cooling-heating-cooling loops have the tendency to give erroneous results due to the accumulation of experimental errors.

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ŠTRUKTÚRNA RELAXÁCIA SKLA NBS711 - SPOĽAHLIVOSŤ REGRESNÝCH ODHADOV RELAXAČNÉHO MODELU

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Na viskozitnom štandardnom skle NBS 711 sa uskutočnila séria piatich termomechanických experimentov s odlišným cyklickým časovo-teplotným režimom a s odlišným axiálnym zaťažením prizmatickej vzorky. Experimentálne dáta sa pomocou nelineárnej regresnej analýzy opísali Tool-Narayanaswamy-Moynihanovým a Mazurinovým modelom. Zistilo sa, že obidva modely opisujú experimentálne dáta s vyhovujúcou presnosťou. Ukázalo sa, že na získanie spoľahlivých odhadov parametrov oboch použitých modelov je potrebné vyhodnotiť väčší počet termomechanických experimentov s rozličným cyklickým časovo-teplotným režimom. Spoľahlivejšie výsledky sa pritom získali pri použití vyšších hodnôt axiálneho zaťaženia vzorky. Dlhodobé experimenty s viac ako štyrmi cyklami chladenie – ohrev – chladenie majú tendenciu poskytovať chybné výsledky vďaka akumulácii experimentálnych chýb.