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SIMPLE RELAXATION MODEL OF THE REVERSIBLE PART OF THE StepScan® DSC RECORD OF GLASS TRANSITION

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The results of the StepScan® DSC obtained for $15Na_2O\cdot xMgO\cdot(10–x)CaO\cdot 75SiO_2$ glasses were described in the frame of the commonly accepted theory of the glass transition. A new simplified model of the reversible part of StepScan® DSC record was developed on the basis of the Tool Narayanaswamy Moynihan relaxation theory. Equivalence between the formal activation energy of enthalpy relaxation process on one side, and the viscous flow activation enthalpy on the other side, was found.

Keywords: *DSC, enthalpy relaxation, glass transition, silicate glasses, StepScan*

Introduction

The kinetic-relaxation nature of the glass transition is commonly accepted and well understood today [1, 2]. The kinetics of the glass transition and of the attendant relaxation phenomena describes plausibly the Tool-Narayanaswamy-Moynihan (TNM) theory [3–6] originating in the Tool concept of the fictive temperature, T_f [7, 8]. The older hypothesis of the second-order phase transition underlying the glass transition is merely of a textbook historical illustration value today, at least in the case of inorganic glasses [9]. The relaxation character of the glass transition implies straightforwardly the characteristic hysteresis of the cooling-heating temperature dependence of state functions like volume and enthalpy as well as the well-known shape of the temperature dependence of the temperature coefficients of these state functions, i.e. of the thermal expansion coefficient and heat capacity. At heating, the last ones typically exhibit a shape with one local maximum (the so called overshoot), that can be in some cases preceded with one local minimum (undershoot). The classical DSC method is broadly used for measuring the temperature dependence of heat capacity in the range of the glass transition. The glass transition temperature is commonly identified with the inflexion point preceding the local maximum. The heating and cooling rates used for the glass sample preparation affect, in principle, the shape and all the characteristic temperatures (i.e. those of minimum, maximum, and inflexion point) of the DSC heating curve.

New experimental techniques, i.e., the dynamic differential scanning calorimetry (DDSC) and StepScan® DSC [10–12], bring a new insight into study of the glass transition. Both methods enable to split the glass transition into two types of processes – the fast one (denoted as in-phase, thermodynamic or storage process) and the slow one (out-of-phase, kinetic or loss process). It was found experimentally that the so-called thermodynamic part of the glass transition is completely independent of the thermal history of glass, and thus this process depends only on the sample chemical composition [13, 14]. The exothermic change during the melt→glass transition and the endothermic change in the opposite direction is thus reflected exclusively in the so-called kinetic part of glass transition [13–16].

The thermodynamic part of StepScan® glass transition record has been the subject of a recent study [17, 18]. It was found that it could be formally regarded as a glass↔undercooled melt transition with a conversion degree α dependent (at isobaric conditions) on temperature only. This quasi-equilibrium can be plausibly described by the empirical equation proposed by Holubová *et al.* [17–19].

$$\alpha(T) = 1 - \exp[-(T/T_g)^n] \qquad (1)$$

where T is the thermodynamic temperature, n is an empirical positive constant and T_g is the glass transition temperature determined from the position of inflexion point of the reversible part of StepScan DSC record. The conversion α is calculated from the temperature dependence of the apparent reversible heat

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capacity $c_p(\mathrm{rev},T)$ obtained from the StepScan® DSC record:

$$\alpha(T)=\frac{c_\mathrm{p}(\mathrm{rev},T)-c_\mathrm{p}(\mathrm{rev,glass})}{c_\mathrm{p}(\mathrm{rev,melt})-c_\mathrm{p}(\mathrm{rev,glass})}=\frac{c_\mathrm{p}(\mathrm{rev},T)-c_\mathrm{pg}}{\Delta c_\mathrm{p}} \tag{2}$$

where $c_p(\mathrm{rev,melt})=c_{pm}/c_p(\mathrm{rev,glass})=c_{pg}$ is identified with the maximum/minimum value of the measured sigmoid $c_p(\mathrm{rev},T)$ curve and corresponds to the isobaric heat capacity of metastable melt/glass at particular temperature.

Recently, another type of semi-empirical description of the thermodynamic part of StepScan DSC record was proposed [20]. The reversible part of StepScan® DSC record of a glass in the region of the glass transition was formally interpreted as a measure of the conversion α of the A↔B type equilibrium reaction identified with a reversible part of the glass↔undercooled melt transition. In the case of the standard state of pure substance at the pressure and temperature of the system, the ratio of equilibrium mole fractions $x(\mathrm{A})$, $x(\mathrm{B})$ of A, B can be expressed by the corresponding equilibrium constant K:

$$K(T)=\frac{x(\mathrm{B})}{x(\mathrm{A})}=\frac{x(\mathrm{B})}{1-x(\mathrm{B})}=\frac{\alpha}{1-\alpha} \tag{3}$$

or

$$\alpha=\frac{K(T)}{1+K(T)} \tag{4}$$

where α is the conversion (transformation ratio). The temperature course of the conversion degree, $\alpha(T)$, was expressed in terms of the temperature dependence of the equilibrium constant based on the van't Hoff's equation [21]:

$$K(T) = K_0 \exp(-\Delta H/RT) \tag{5}$$

where R is the gas constant, ΔH is the temperature independent formal reaction enthalpy, and

$$K_0 = K_r \exp(\Delta H/RT_\mathrm{ref}) \tag{6}$$

where T_ref is an arbitrary reference temperature and $K_r=K(T_\mathrm{ref})$ holds. The glass transition temperature is identified with the inflexion point of the $\alpha(T)$ curve.

Recently, the model describing the StepScan® DSC record in the frame of Tool-Narayanaswamy-Moynihan's relaxation theory was proposed [22, 23]. The aim of the present study is to verify a simplified version of this model by its application on a set of sodium-magnesium-calcium silicate glasses.

Theory

Following Tool's concept of the fictive temperature [7, 8], the specific enthalpy, H, can be expressed as a function of temperature, T, and the fictive temperature, T_f:

$$H(T,T_f)=H(T_r,T_r)+\int_{T_r}^{T_f}c_\mathrm{pm}(T')\mathrm{d}T'+\int_{T_f}^{T}c_\mathrm{pg}(T')\mathrm{d}T' \tag{7}$$

where c_{pm} and c_{pg} are specific isobaric heat capacities of metastable melt and glass, respectively, and T_r is an arbitrary sufficiently high (to ensure instantaneous formation of metastable equilibrium) reference temperature. Supposing the temperature independence of the both specific heat capacities and realizing that both the fictive and thermodynamic temperatures are in principle time dependent, the following time dependence of specific enthalpy is obtained:

$$H(t) = H[T(t),T_f(t)] = H_0 + (c_{pm} - c_{pg})T_f + c_{pg}T = H_0 + \Delta c_p T_f + c_{pg}T \tag{8}$$

where

$$H_0 = H(T_r,T_r) - c_{pm}T_r \tag{9}$$

The heat flow can be obtained from the time derivative of enthalpy:

$$\frac{\mathrm{d}q}{\mathrm{d}t}=\dot{q}=\left(\frac{\partial H}{\partial T}\right)_{T_\mathrm{f}}\frac{\mathrm{d}T}{\mathrm{d}t}+\left(\frac{\partial H}{\partial T_\mathrm{f}}\right)_{\mathrm{T}}\frac{\mathrm{d}T_\mathrm{f}}{\mathrm{d}t} \tag{10}$$

The time dependence of the fictive temperature, T_f, is obtained within the frame of Tool-Narayanaswamy-Moynihan's model [3–6]:

$$T_\mathrm{f}(t)=T(t)-\int_0^t \mathrm{d}t'(\mathrm{d}T/\mathrm{d}t)M[\xi(t)-\xi(t')] \tag{11}$$

where M is the Kohlrausch-Williams-Watts (KWW) relaxation function:

$$M(\xi)=\exp(-\xi^b) \quad 0<b\leq 1 \tag{12}$$

where b is constant and ξ is the dimensionless relaxation time:

$$\xi(t)=\int_0^t \mathrm{d}t'/\tau(t') \tag{13}$$

where τ is the relaxation time given by the Moynihan approximation:

$$\tau(T,T_f) = \tau_0 \exp[x\Delta h/RT + (1-x)\Delta h/T_f] \tag{14}$$

Δh is the formal activation enthalpy, and x is a constant $(0<x\leq 1)$.

The StepScan® experiment proceeds via temperature steps $\Delta_{\mathrm{st}}T$ realized within the time $\Delta_{\mathrm{st}}t$ by the constant heating/cooling rate β ($\beta=\Delta_{\mathrm{st}}T/\Delta_{\mathrm{st}}t$). After each temperature step (n-th step dwells from $t_{\mathrm{sb,n}}$ to $t_{\mathrm{se,n}}$) an isothermal regime follows during which a stationary state is reached. The isothermal regime following the n-th temperature step starts at time $t_{\mathrm{it,n,0}}\equiv t_{\mathrm{se,n}}$ and dwells until the beginning of the next temperature step, i.e. until the time $t_{\mathrm{sb,n+1}}$. The end of the isothermal delay is given by fulfilling the following condition:

$$\dot{q}(t_{\mathrm{it,n,k}}) = \left|H(t_{\mathrm{it,n,k+1}}) - H(t_{\mathrm{it,n,k}})\right| / \Delta_{\mathrm{st}}\, t < \varepsilon \qquad (15)$$

where ε is a sufficiently small threshold, and $t_{\mathrm{it,n,k}}$ is the time of the end of the k-th time step of the n-th isothermal delay (Fig. 1). The above heat flux check is repeatedly performed for each $\Delta_{\mathrm{st}}t$ time interval during the isothermal regime. The reversible isobaric heat capacity is calculated from the enthalpy change taking place during the temperature step:

$$c_{\mathrm{p,rev}}\,(T_{\mathrm{it,n}} + \Delta_{\mathrm{st}}\,T/2) = [H(t_{\mathrm{se,n}}) - H(t_{\mathrm{sb,n}})]/\Delta_{\mathrm{st}}\,T \qquad (16)$$

while the kinetic part of enthalpy change is formally expressed by the 'kinetic heat capacity' calculated from the enthalpy change during the isothermal temperature delay

$$c_{\mathrm{p,kin}}(T_{\mathrm{it,n}}) = [H(t_{\mathrm{sb,n+1}}) - H(t_{\mathrm{se,n}})]/\Delta_{\mathrm{st}}T \qquad (17)$$

The abbreviation of particular times and temperatures for the n-th temperature step and succeeding isothermal delay is presented in Fig. 1.

To obtain an analytical form of the reversible StepScan® curve it is sufficient to analyze the cooling curve. At the beginning of the temperature step the stationary state is established which can be characterized by $T_{\mathrm{f}}=T$ in a prevailing part of the curve. Only for the low temperature part, where α approaches zero, the stationary state is characterized by a constant value of fictive temperature, i.e. $T<T_{\mathrm{f}}=\mathrm{const.}$ Therefore, it seems reasonable to simplify Eq. (14):

$$\tau(T)\approx\tau_0 \exp(\Delta h/RT) \qquad (18)$$

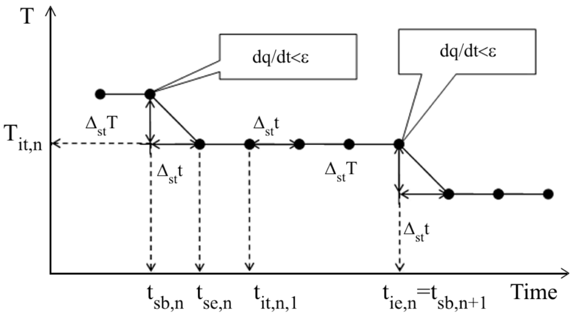

Fig. 1 Schematic drawing of the time-temperature schedule during the StepScan® DSC

For the change of dimensionless time Δξ taking part during the temperature step we then obtain:

$$\Delta\xi\approx(\Delta_{\mathrm{st}}t/\tau_0)\exp(-\Delta h/RT) \qquad (19)$$

It has been shown [13, 24] that if relaxation takes place near the metastable equilibrium, the KWW relaxation function can be approximated with by a single exponential function (i.e. b=1) with a sufficient accuracy. In this case, combining Eqs (16), (8), (11) and (19) we obtain an analytical expression describing the reversible part of the StepScan® DSC record:

$$\alpha = \frac{\Delta_{\mathrm{st}}T_{\mathrm{f}}}{\Delta_{\mathrm{st}}T} = 1-\exp\left[-\left(\frac{\Delta_{\mathrm{st}}\,t}{\tau_0}\right)\exp\left(-\frac{\Delta h}{RT}\right)\right] = \\ = 1-\exp\left[-A\exp\left(-\frac{\Delta h}{RT}\right)\right] \qquad (20)$$

where $A=\Delta_{\mathrm{st}}t/\tau_0$.

Experimental

Stepwise DSC technique, the StepScan® method (PerkinElmer) [10], was used. Samples (mass around 10 mg) were measured in sealed aluminium pans using Pyris 1 DSC (PerkinElmer). The temperature step $\Delta_{\mathrm{st}}T$=1 K was used and the heating or cooling rate during the temperature steps of ±10°C min^{-1} was applied. The isotherm duration was software controlled. The maximal heat flow difference during an isotherm was $\Delta(\mathrm{d}Q/\mathrm{d}t)=\pm0.0001$ mW per approximately 10 s before next step.

The low temperature viscosity of Na_2O–MgO–CaO–SiO_2 glasses was measured by the thermo-mechanical analysis (Netzsch, TMA402). The viscosity, η, was calculated from the isothermal axial deformation rate of a rhombic sample [25]. The viscous flow activation enthalpy, Δh_η was estimated by the regression analysis of experimental data based on the Arrhenius-like equation:

$$\ln[\eta(T)/\mathrm{dPas}] = C + \frac{\Delta h_\eta}{RT} \qquad (21)$$

where C is a constant.

The lead-silica glass NBS 711 is a commercial product [26]. The barium crystal glass RONA was taken from the industrial production of the glasswork RONA, Lednické Rovne (Slovak Republic). The $15Na_2O\cdot x MgO\cdot(10-x)CaO\cdot 75SiO_2$ (x=0, 10, 2, 4, and 6) glasses (Table 1) were prepared by mixing the appropriate quantities of high purity reagents Na_2CO_3, $MgCO_3$, $CaCO_3$, and SiO_2 to yield 200 g of glass. The powder reagents were dry-mixed and melted in a 10%-RhPt crucible in air in an electric furnace, and held for 2 h at the melting temperatures be-

Table 1 Chemical composition of studied Na_2O–MgO–CaO–SiO_2 glasses (mol%)

Glass	Na_2O	MgO	CaO	SiO_2
ALK1	15	0	10	75
ALK2	15	10	0	75
ALK3	15	2	8	75
ALK4	15	4	6	75
ALK5	15	6	4	75

tween 1400–1550°C. The glass melts were homogenized by hand-mixing. The melt was poured onto a stainless steel plate. The samples were subsequently annealed in a muffle furnace for 1 h at 520°C. After annealing, the glasses were slowly cooled down to the room temperature.

Results and discussion

The applicability of the proposed simplified relaxation model was first tested [23] on NBS viscosity standard glass (NBS 711), and on the commercial barium crystal glass (RONA). The results obtained are plotted in Figs 2 and 3 where a comparison of the relaxation model suggested in this paper with the models of Holubová and van't Hoff is presented. It can be concluded that the results of this simplified relaxation model are practically identical with those of Holubová, when only the quality of fit is considered. However, the present relaxation model enables the straightforward interpretation of the physical meaning of parameters. The quality of fit obtained by the van't Hoff model is also acceptable, but is not so good as in the case of the other two models.

The results of regression analysis of experimental reversible StepScan® data are summarized in Table 2 for five Na_2O–MgO–CaO–SiO_2 glasses. From the values of standard deviation it follows that the model presented here describes the experimental data with sufficient accuracy. The experimental data of not a very high quality were used in case of some glasses, mainly for the ALK2 glass. In the case of ALK5 glass, the experimental points from the temperature range 540–545°C are shifted to higher α values. And, finally, experimental data from the low temperature branch of the record between 520 and 540°C are missing for the ALK4 sample. These ill situations were not artificially corrected to retain the possibility of appreciating the sensitivity of the model to such wrong, but sometimes experimentally occurring, situations. From the results presented in Figs 4–8 it can be seen that the present model is significantly robust with respect to errors in experimental data.

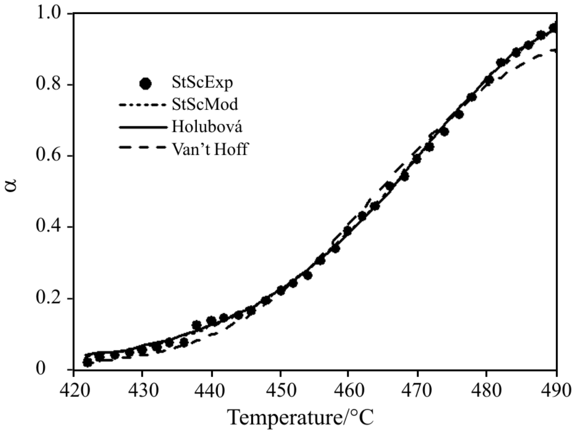

Fig. 2 Comparison of the experimental StepScan® record (points) of NBS711 glass with the empirical models (Holubová *et al.* – full line, Van't Hoff – dashed line) and with Tool-Naraynaswamy-Moynihan's relaxation theory (short dash line coinciding with the full line)

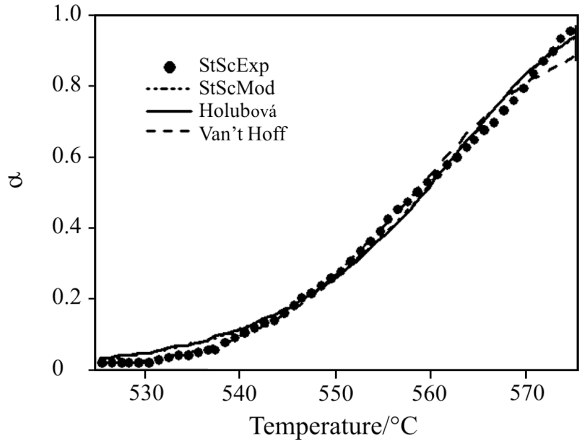

Fig. 3 Comparison of the experimental StepScan® record (points) of RONA glass with the empirical models (Holubová *et al.* – full line, Van't Hoff – dashed line) and with Tool-Naraynaswamy-Moynihan's relaxation theory (short dash line coinciding with the full line)

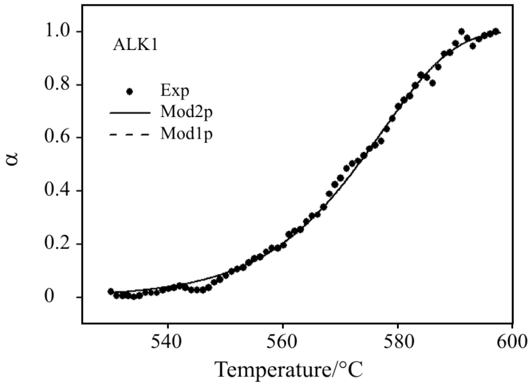

Fig. 4 Comparison of the experimental StepScan® record (points) of ALK1 glass with the two parameters (Mod2p) and single parameter (Mod1p) relaxation model

From Table 2 it can be deduced that the regression estimates of Δh are close to the viscous flow acti-

Table 2 Results of non-linear regression analysis of reversible part of StepScan® DSC record of Na_2O–MgO–CaO–SiO_2 glasses. Results of two parameters (Eq. (20)) model (A, Δh), and of single parameter (Eq. (22)) model (A) using the low-temperature viscous flow activation energy (Δh_η). The standard deviation of approximation, s_{apr} is reported for each model

Glass	log$A$	Δh/kJ mol^{-1}	s_{apr}	log$A$	Δh_η/kJ mol^{-1}	s_{apr}
ALK1	30.73	500.5	0.019	30.65	499.1	0.019
ALK2	21.48	347.1	0.071	24.67	398.3	0.074
ALK3	21.77	355.0	0.038	27.03	440.3	0.053
ALK4	25.01	401.9	0.046	27.49	441.6	0.048
ALK5	25.11	401.7	0.035	26.12	417.8	0.036

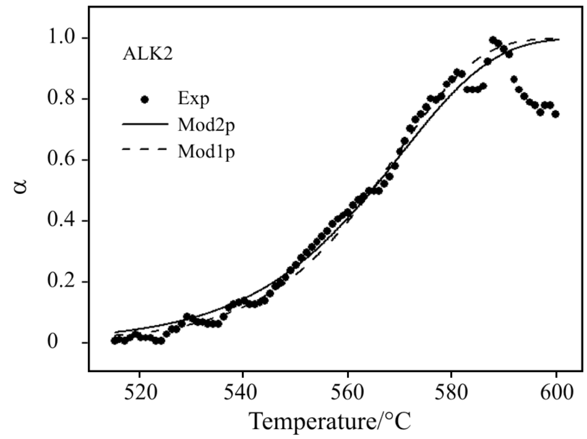

Fig. 5 Comparison of the experimental StepScan® record (points) of ALK2 glass with the two parameters (Mod2p) and single parameter (Mod1p) relaxation model

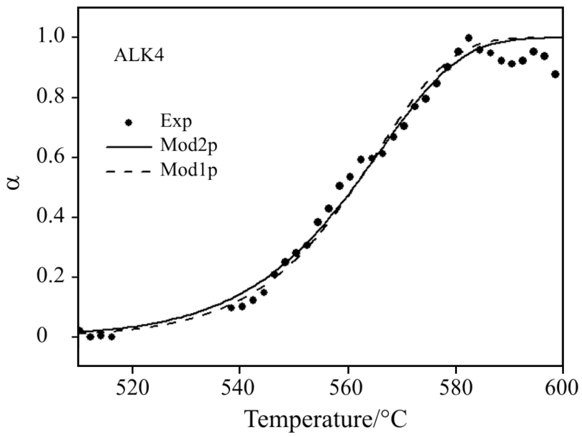

Fig. 7 Comparison of the experimental StepScan® record (points) of ALK4 glass with the two parameters (Mod2p) and single parameter (Mod1p) relaxation model

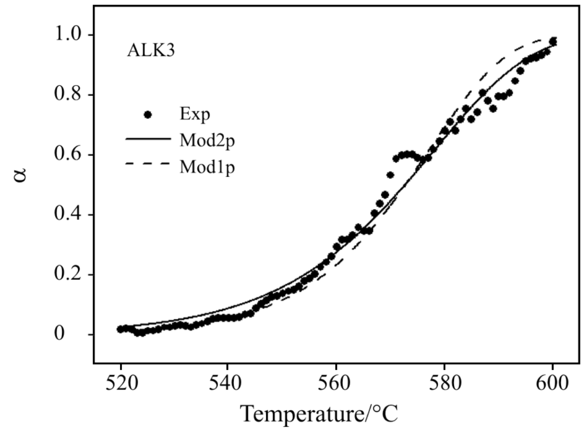

Fig. 6 Comparison of the experimental StepScan® record (points) of ALK3 glass with the two parameters (Mod2p) and single parameter (Mod1p) relaxation model

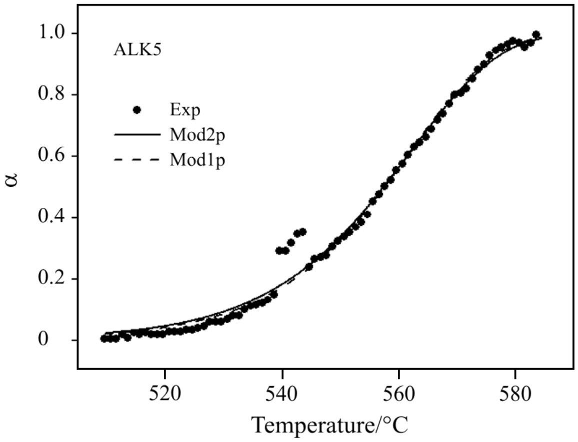

Fig. 8 Comparison of the experimental StepScan® record (points) of ALK5 glass with the two parameters (Mod2p) and single parameter (Mod1p) relaxation model

vation enthalpy values Δh_η, at least for the case of experimental data of a better quality. Therefore, an attempt was made to simplify the model by reducing the number of adjustable parameters to one parameter. When replacing Δh by the experimental value of Δh_η, then only the A estimate has to be obtained by regression analysis:

$$\alpha = \frac{\Delta_{st} T_f}{\Delta_{st} T} = 1 - \exp\left[-A\exp\left(-\frac{\Delta h_\eta}{RT}\right)\right] \qquad (22)$$

As shown from the values of standard deviations of approximation listed in Table 2, the fit for the single parameter model given by Eq. (22) is practically of the same quality as in the case of two parameters model given by Eq. (20). Moreover, from visual inspection of Figs 4–8 it can be deduced that both models coincide in the case of experimental data of a good quality (ALK1, ALK5).

Conclusions

The experimental results obtained by the StepScan® DSC method can be described alternatively by the empirical model of Holubová or by the present simplified relaxation model based on the Tool-Narayanaswamy-Moynihan's relaxation theory of the glass transition.

The viscous flow activation enthalpy is a good estimate of the activation enthalpy describing the temperature dependence of enthalpy relaxation times.

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