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SIMULTANEOUS VOLUME AND ENTHALPY RELAXATION
The effect of experimental conditions

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The ratio between the relaxed enthalpy and volume (so-called aging modulus, K_a) was expressed in frame of the Tool–Narayanaswamy–Moynihan theory. The common case where various experimental arrangements are used for measuring these quantities was analyzed. It was found that relatively small differences between the conditions of enthalpy and volume relaxation experiments may cause a significant shift of observed K_a value. The sensitivity of K_a modulus to the difference between the enthalpy and volume relaxation conditions is significantly higher in the case of organic polymeric glasses in comparison with silicate and chalcogenide glasses. The reason for such grouping resides in higher values of glass transition temperature and lower values of activation enthalpy of inorganic glasses.

Keywords: *aging modulus, DSC, glass, relaxation, thermodilatometry*

Introduction

The volume and the enthalpy relaxations of glasses are well understood and described on a semi-empirical level in frame of the Tool–Narayanaswamy–Moynihan (TNM) theory [1–5]. It is commonly accepted, that the time course of both these relaxation processes is very similar [3–7], i.e. the same value of the non-exponentiality parameter *b* of the Kohlrausch–Williams–Watts equation can be used for enthalpy and volume relaxation. The relaxation times of these processes can be considered to be almost identical since the origin of both is the structural relaxation. The assumptions mentioned above lead straightforwardly to the expected constant ratio between relaxed enthalpy and volume, when comparing these quantities during the same event of structural relaxation. On the other hand, some unsolved questions still exist regarding the correlation between the enthalpy and volume relaxation, which seems to proceed in a similar, but not identical way. In some cases, significant differences were observed; e.g., times required for equilibration are considerably longer for enthalpy relaxation than for relaxation of volume [8–11]. However, the simultaneous determination of relaxed enthalpy and relaxed volume within the same experiment is extraordinarily complex, and has been performed only rarely [7]. More frequently, DSC is used to study the enthalpy relaxation, and the volume relaxation is measured by thermodilatometry, under approximately the same conditions. In recent works [11–17], mainly by Slobodian *et al.*, such experiments were performed for various polymer blends and inorganic glasses. It was found that the ratio between the values of relaxed enthalpy and relaxed volume is approximately constant throughout the time of relaxation experiment, but the obtained value of this parameter differs significantly from the one expected on the basis of TNM relaxation model. The authors suggest an explanation of this phenomenon based on the irreversible thermodynamics theory of Nieuwenhuizen [18, 19]. However, the physical meaning of the parameters included in the above theoretical model is still not clear. Moreover, there is a possibility to explain the experimental results analyzing the difference between experimental conditions of the enthalpy relaxation experiment on one side and the volume relaxation on the other. The aim of the present work is the quantitative analysis of the consequences of different experimental conditions in relaxation experiments together with the estimation of the influence of possible differences in characteristic relaxation times of enthalpy and volume relaxation on the value of the relaxed enthalpy to relaxed volume ratio.

Method

For an arbitrary temperature-time schedule, $T(t)$, the Tool-Narayanaswamy-Moynihan (TNM) relaxation model [1–4] gives the following time dependence of the volume and enthalpy fictive temperature, respectively:

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$$T_{\mathrm{f,V}}(t)=T(t)-\int_0^t \mathrm{d}t'\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{t'} M_{\mathrm{V}}[\xi_{\mathrm{V}}(t)-\xi_{\mathrm{V}}(t')] \qquad (1)$$

$$T_{\mathrm{f,H}}(t)=T(t)-\int_0^t \mathrm{d}t'\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{t'} M_{\mathrm{H}}[\xi_{\mathrm{H}}(t)-\xi_{\mathrm{H}}(t')] \qquad (2)$$

For the case of isothermal relaxation at temperatures $T_{\mathrm{a,V}}$, and $T_{\mathrm{a,H}}$ starting at time t=0 with the values of fictive temperatures, $T_{\mathrm{g,V}}$ and $T_{\mathrm{g,H}}$, given by the time-temperature schedule used during the glass preparation (Fig. 1), Eqs (1) and (2) can be rewritten in a more simple form:

$$T_{\mathrm{f,V}}(t)=T_{\mathrm{a,V}}-(T_{\mathrm{a,V}}-T_{\mathrm{g,V}})M_{\mathrm{V}}[\xi_{\mathrm{V}}(t)] \qquad (3)$$

$$T_{\mathrm{f,H}}(t)=T_{\mathrm{a,H}}-(T_{\mathrm{a,H}}-T_{\mathrm{g,H}})M_{\mathrm{H}}[\xi_{\mathrm{H}}(t)] \qquad (4)$$

where M is the Kohlrausch-William-Watts (KWW) relaxation function [4, 20]:

$$M_{\mathrm{V}}(\xi_{\mathrm{V}})=exp(-\xi_{\mathrm{v}}^{\mathrm{b}}) \qquad (5)$$

$$M_{\mathrm{H}}(\xi_{\mathrm{H}})=exp(-\xi_{\mathrm{H}}^{\mathrm{b}}) \qquad (6)$$

where $b=b_{\mathrm{V}}=b_{\mathrm{H}}$ is the non-exponentiality parameter ($0<b\leq1$, and the same value is supposed for both the volume and the enthalpy relaxation) and ξ is the dimensionless relaxation time [2–4]:

$$\xi_{\mathrm{V}}(t)=\int_0^t \frac{\mathrm{d}t'}{\tau_{\mathrm{V}}(t')} \qquad (7)$$

$$\xi_{\mathrm{H}}(t)=\int_0^t \frac{dt'}{\tau_{\mathrm{H}}(t')} \qquad (8)$$

where the time dependent relaxation time τ can be expressed according to Moynihan [3, 4, 21]:

$$\tau_{\mathrm{V}}=\tau_{0,\mathrm{V}}\exp\left[\frac{x\Delta h^*}{RT}+\frac{(1-x)\Delta h^*}{RT_{\mathrm{f,V}}}\right] \qquad (9)$$

$$\tau_{\mathrm{H}}=\tau_{0\mathrm{H}}\exp\left[\frac{x\Delta h^*}{RT}+\frac{(1-x)\Delta h^*}{RT_{\mathrm{f,H}}}\right] \qquad (10)$$

where x, Δh^*, $\tau_{0\mathrm{V}}$, and $\tau_{0\mathrm{H}}$ are constants and R is the universal gas constant. The same values of x and Δh^* are supposed for enthalpy and volume relaxation process in the present semi-quantitative model. Due to the strong inter-correlations between x, Δh^*, and τ_0 the above simplification can be accepted as plausible and sufficiently general. In other words, the possible differences between x, and Δh^* values for volume and enthalpy relaxation can be compensated by corresponding difference between $\tau_{0\mathrm{V}}$, and $\tau_{0\mathrm{H}}$ values.

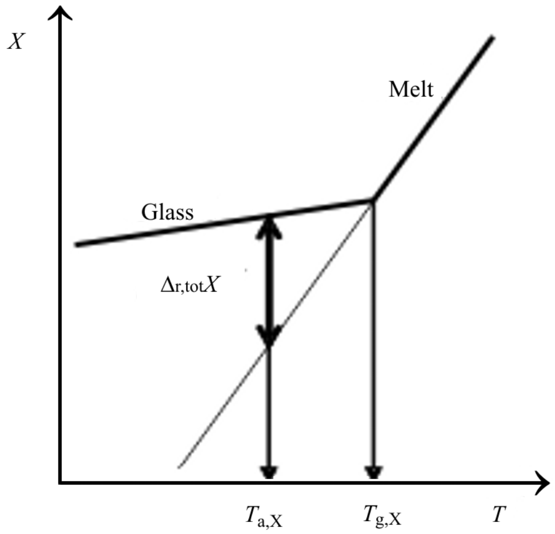

Fig. 1 The simplified scheme of volume ($X\equiv V$) and enthalpy ($X\equiv H$) relaxation

Results and discussion

Supposing the temperature independent values of specific isobaric heat capacity and volume thermal expansion coefficient of glass ($c_{\mathrm{p,g}}$, α_{g}) and meta-stable equilibrium melt ($c_{\mathrm{p,m}}$, α_{m}), the time course of relaxation volume and enthalpy can be expressed (Fig. 1):

$$\Delta_{\mathrm{r}}V(t)=\Delta_{\mathrm{r,tot}}V\{1-M_{\mathrm{V}}[\xi_{\mathrm{V}}(t)]\} \qquad (11)$$

$$\Delta_{\mathrm{r}}H(t)=\Delta_{\mathrm{r,tot}}H\{1-M_{\mathrm{H}}[\xi_{\mathrm{H}}(t)]\} \qquad (12)$$

where

$$\Delta_{\mathrm{r,tot}}V=V(\alpha_{\mathrm{m}}-\alpha_{\mathrm{g}})(T_{\mathrm{g,V}}-T_{\mathrm{a,V}})=V\Delta\alpha\Delta T_{\mathrm{V}} \qquad (13)$$

$$\Delta_{\mathrm{r,tot}}H=m(c_{\mathrm{p,m}}-c_{\mathrm{p,g}})(T_{\mathrm{g,H}}-T_{\mathrm{a,H}})=m\Delta c_{\mathrm{p}}\Delta T_{\mathrm{H}} \qquad (14)$$

where m and V are the mass and initial volume of the sample, respectively. From Eqs (11) and (12) the time dependence of the apparent modulus can be obtained:

$$K_{\mathrm{a}}=\frac{\Delta_{\mathrm{r}}H(t)}{\Delta_{\mathrm{r}}V(t)}=\frac{m\Delta c_{\mathrm{p}}\Delta T_{\mathrm{H}}}{V\Delta\alpha\Delta T_{\mathrm{V}}}\left\{\frac{1-M_{\mathrm{H}}[\xi_{\mathrm{H}}(t)]}{1-M_{\mathrm{V}}[\xi_{\mathrm{V}}(t)]}\right\} \qquad (15)$$

Now the limiting value of the apparent aging modulus can be obtained taking the limit of meta-stable equilibrium:

$$\lim_{t\to\infty}K_{\mathrm{a}}=K_{\mathrm{a,eq}}=\rho\frac{\Delta c_{\mathrm{p}}\Delta T_{\mathrm{H}}}{\Delta\alpha\Delta T_{\mathrm{V}}} \qquad (16)$$

where ρ stands for the sample density. In the case of volume and enthalpy experiments carried out under exactly the same conditions, the Eq. (16) simplifies to the form:

$$K_{\mathrm{iso,eq}}=\rho\frac{\Delta c_{\mathrm{p}}}{\Delta\alpha} \qquad (17)$$

Some insight into the time course of K_{a} can be obtained from a more simplified model. Replacing the time dependent volume fictive temperature $T_{\mathrm{f,V}}=T_{\mathrm{f,V}}(t)$ by an average value defined as the arithmetic mean between the starting value $T_{f,V}(0)= T_{g,V}$ and the limiting equilibrium value

$$\lim_{t\to\infty} T_{f,V}(t) = T_{a,V} \tag{18}$$

i.e.

$$T_{f,V,ave} = (T_{g,V} + T_{a,V})/2 \tag{19}$$

we can estimate the average volume relaxation time

$$\tau_{V,ave} = \tau_{0,V} \exp\left[\frac{x\Delta h^*}{RT_{a,V}} + \frac{2(1-x)\Delta h^*}{R(T_{g,V} + T_{a,v}}\right] \tag{20}$$

Now the dimensionless relaxation time can be simply expressed as

$$\xi_V(t) = \int_0^t \frac{dt'}{\tau_V(t')} = \frac{t}{\tau_{V,ave}} \tag{21}$$

The same procedure may be repeated for the enthalpy relaxation, yielding:

$$\tau_{H,ave} = \tau_{0H} \exp\left[\frac{x\Delta h^*}{RT_{a,H}} + \frac{2(1-x)\Delta h^*}{R(T_{g,H} + T_{a,H})}\right] \tag{22}$$

and

$$\xi_H(t) = \int_0^t \frac{dt'}{\tau_H(t')} = \frac{t}{\tau_{H,ave}} \tag{23}$$

For small values of dimensionless relaxation time, we can approximate the exponential function by a linear relationship

$$M_V(\xi_V)=\exp(-\xi_V^b)\cong 1-\xi_V^b \cong 1-(t/\tau_{V,ave})^b \tag{24}$$

$$M_H(\xi_H)=\exp(-\xi_H^b)\cong 1-\xi_H^b \cong 1-(t/\tau_{H,ave})^b \tag{25}$$

Substituting the above simplified relationships into the Eq. (15), one obtains:

$$K_a = \frac{\Delta_r H(t)}{\Delta_r V(t)} = \rho \frac{\Delta c_p \Delta T_H}{\Delta\alpha \Delta T_V}\left(\frac{\tau_{V,ave}}{\tau_{H,ave}}\right)^b = \\ = K_{a,eq}\left(\frac{\tau_{V,ave}}{\tau_{H,ave}}\right)^b \tag{26}$$

Thus, as a consequence of the assumption of the same non-exponentiality b for enthalpy and volume relaxation, the time independent result was obtained in the Eq. (26). However, this result is not contradictory to the limiting equilibrium value $K_{a,eq}$ obtained in the Eq. (17) because the approximation introduced in Eqs (24) and (25) is valid only for small values of ξ, i.e. for small values of t. Moreover, in the case of close values of $\tau_{V,ave}$ and $\tau_{H,ave}$ one obtains a K_a value close to the $K_{a,eq}$ value. In a case of different b values, say b_V and b_H, one obtains the time dependent value of K_a:

$$K_a = K_{a,eq}\left(\frac{\tau_{V,ave}}{t}\right)^{b_V}\left(\frac{t}{\tau_{H,ave}}\right)^{b_H} = \\ = K_{iso,eq}\frac{\Delta T_H}{\Delta T_V}(\tau_{V,ave})^{b_V}(\tau_{H,ave})^{-b_H}\, t^{b_H-b_V} \tag{27}$$

In the next simplification step we will assume, that the relaxation takes place in the vicinity of meta-stable equilibrium state. As shown by thorough experimental and numerical analysis performed by Černošek *et al.* [22–23], the non-exponentiality factor b approaches unity at these conditions. Thus, under the conditions near equilibrium the Eq. (26) further simplifies as follows:

$$K_a = K_{a,eq}\frac{\tau_{V0}}{\tau_{H0}}\exp\left[\left(\frac{x\Delta h^{\neq}}{R}\right)\left(\frac{1}{T_{a,V}} - \frac{1}{T_{a,H}}\right)\right]\exp \\ \left[\left(\frac{2(1-x)\Delta h^{\neq}}{R}\right)\left(\frac{1}{T_{g,V}+T_{a,V}} - \frac{1}{T_{g,H}+T_{a,H}}\right)\right] \tag{28}$$

The principal influence of the different conditions of enthalpy and volume relaxation experiments on the observed modulus value K_a resides in the difference between the $K_{a,eq}$ value on one side and the $K_{iso,eq}$ on the other (Eqs (16), (17)). The conversion factor ($\Delta T_H/\Delta T_V$) compares the differences between the glass transition temperature and the aging temperature (analogous to under-cooling) in the case of enthalpy and volume relaxation, respectively. The individual values of glass transition temperature and aging temperature are not important in this context. On the other hand, these values can be found in the Eq. (28). To estimate separately the influence of differences in glass transition temperature and aging temperature, we express these values for volume relaxation experiment in relation to those of enthalpy relaxation, i.e.

$$T_{g,V} = T_{g,H} + \Delta T_g \tag{29}$$

$$T_{a,V} = T_{a,H} + \Delta T_a \tag{30}$$

Then we can treat the K_a as a function of these quantities

$$K_a = K_a(\Delta T_g, \Delta T_a) \tag{31}$$

i. e.

$$K_a = K_{a,eq}\frac{\tau_{V0}}{\tau_{H0}}\exp\left[\left(\frac{x\Delta h^{\neq}}{R}\right)\left(\frac{1}{T_{a,H}+\Delta T_a} - \frac{1}{T_{a,H}}\right)\right]\exp \\ \left[\left(\frac{2(1-x)\Delta h^{\neq}}{R}\right)\left(\frac{1}{T_{g,H}+T_{a,H}+\Delta T_g+\Delta T_a} - \frac{1}{T_{g,V}+T_{a,V}}\right)\right] \tag{32}$$

and expand the exponential terms retaining only the linear contributions in the vicinity around the $K_a(0,0)$ point:

$$K_a = K_{\mathrm{iso,eq}} \frac{\Delta T_H \tau_{V0}}{\Delta T_V \tau_{H0}} \left\{ 1 - \frac{\Delta h^{\neq}}{R} \left[\frac{x}{T_{a,H}^2} \Delta T_a + \frac{2(1-x)}{(T_{g,H} + T_{a,H})^2} (\Delta T_g + \Delta T_a) \right] \right\} \tag{33}$$

according to Eqs (29) and (30):

$$\Delta T_V = \Delta T_H + (\Delta T_g - \Delta T_a) \tag{34}$$

and the Eq. (32) can be finally rewritten

$$K_a = K_{\mathrm{iso,eq}} \frac{1}{1 + (\Delta T_g + \Delta T_a)/\Delta T_H} \frac{\tau_{V0}}{\tau_{H0}} \left\{ 1 - \frac{\Delta h^{\neq}}{R} \left[\frac{x}{T_{a,H}^2} \Delta T_a + \frac{2(1-x)}{(T_{g,H} + T_{a,H})^2} (\Delta T_g + \Delta T_a) \right] \right\} \tag{35}$$

$$Q = \frac{1}{1 + (\Delta T_g + \Delta T_a)/\Delta T_H} \left\{ 1 - \frac{\Delta h^{\neq}}{R} \left[\frac{x}{T_{a,H}^2} \Delta T_a + \frac{2(1-x)}{(T_{g,H} + T_{a,H})^2} (\Delta T_g + \Delta T_a) \right] \right\} \cong \cong \frac{K_a}{K_{a,\mathrm{iso}}} \frac{\tau_{H0}}{\tau_{V0}} \tag{36}$$

From the Eq. (35) the sensitivity of K_a value to the x and Δh^* values can be straightforwardly deduced. Increase of the Δh^* value makes the K_a value more sensitive to both ΔT_g and ΔT_a values, hence increasing the x value enhances the sensitivity to ΔT_a value and decreases the influence of the ΔT_g value. Moreover, the decreasing sensitivity of K_a with increasing T_g can be deduced from the Eq. (35). However the validity of the Eq. (35) is confined to small values of ΔT_a and ΔT_g. This is illustrated in Table 1, where the values of quotient Q defined as Eq. (36), are listed for As_2Se_3, polyvinylchloride (PVC), polystyrene (PS), poly(vinyl-acetate) (PVA), and for the $15Na_2O \cdot 10CaO \cdot 75SiO_2$ glass (NCS). The sufficiently precise control of aging temperature T_a was supposed in both relaxation experiments, i.e. $\Delta T_a=0$. The Eq. (36) simplifies in this case to Eq. (37).

$$Q = \frac{\Delta T_H}{\Delta T_V} \left\{ 1 - \frac{\Delta h^{\neq}}{R} \frac{2(1-x)}{(T_{g,H} + T_{a,H})^2} \Delta T_g \right\} \tag{37}$$

The parameters of TNM model were taken from [24] for NCS glass, and from the summarised data found in the work of Málek [25] (for As_2Se_3, PVC, PS, and PVA). To fulfil the condition of near-equilibrium relaxation the value of ΔT_H=15 K was chosen. In the case of PVC, PS and PA, a negative value of Q resulted for ΔT_g=5 K, thus the value of ΔT_g=1 K was chosen. It can be seen from Table 1, that even for ΔT_g=1 K the value of Q is still on the level of those obtained for inorganic materials at ΔT_g=5 K condition. Thus, the substantially greater sensitivity of K_a value to the different conditions of enthalpy and volume relaxation experiments was found for organic polymers. This fact is in agreement with the experimental results of Slobodian [12].

To avoid the errors of linear approximation of exponential terms of Eq. (32) the exact value of quotient Q^{exact} defined as:

$$Q^{\mathrm{exact}} = \frac{K_a}{K_{a,\mathrm{iso}}} \frac{\tau_{0H}}{\tau_{0V}} \tag{38}$$

are plotted in Fig. 2 for considered materials with the exception of PVC. It can be seen, that the groups of inorganic and polymer glasses are clearly separated in the picture.

Table 1 The values of quotient Q calculated according to Eq. (37) for ΔT_H = 15 K and for various values of ΔT_g

Substance	As_2Se_3	PVC	PS	PVA	NCS
ΔT_g/K	5	1	1	1	5
Δh/kJ mol^{-1}	340	1871	915	732	568
x	0.49	0.10	0.41	0.27	0.59
$T_{g,H}$ / K	464	353	373	310	819
$T_{a,H}$ / K	449	338	358	295	804
ΔT_V / K	20	16	16	16	20
$\Delta T_H/\Delta T_V$	0.750	0.938	0.938	0.938	0.750
Q	0.562	0.142	0.710	0.608	0.670

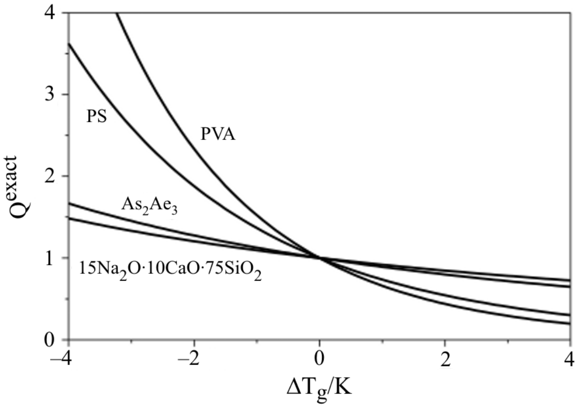

Fig. 2 The dependence of Q^{exact} modulus (Eq. 38) on ΔT_g

Conclusions

The time independent values of apparent modulus K_a can be obtained in the common case when the KWW exponent b reaches similar values for both enthalpy and volume relaxation.

Relatively small differences between the conditions of enthalpy and volume relaxation experiments may cause a significant shift of the observed K_a value.

The sensitivity of K_a modulus to the difference between the enthalpy and volume relaxation conditions is significantly higher in the case of organic polymeric glasses in comparison with silicate and chalcogenide glasses. The reason for such grouping resides in higher values of glass transition temperature and lower values of activation enthalpy of inorganic glasses. The last conclusion is based only on the set of substances studied in the present work and future investigation is needed to confirm its validity.

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