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Rate-determining factors for structural relaxation in non-crystalline materials II. Normalized volume and enthalpy relaxation rate

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Abstract

The rate-determining factors for isothermal structural relaxation in non-crystalline materials are discussed. The normalized volume and enthalpy relaxation rate R_F is defined and analyzed for the Tool–Narayanaswamy–Moynihan phenomenological model. It is shown that the temperature dependent R_F is controlled mainly by the parameter $(1-x)\theta$, where x is the non-linearity parameter and $\theta = \Delta h^*/RT_g^2$. Materials with higher values of parameter $(1-x)\theta$ (e.g. vinylic polymers) exhibit low relaxation rate. In contrast, high relaxation rate is expected for materials with low values of $(1-x)\theta$ (inorganic glasses). The applicability of this approach for the analysis of isothermal volume and enthalpy relaxation data is shown for arsenic sulfide glass, polystyrene, poly(vinyl acetate), poly(methyl methacrylate) and poly(vinyl chloride). The normalized enthalpy and volume relaxation rates for these materials agree well within the limits of experimental errors. © 1998 Elsevier Science B.V.

Keywords: Structural relaxation; Volume; Enthalpy; Rate; Polymers; Glasses

1. Introduction

It is well established that non-crystalline materials below their glass transition temperature (T_g) can be considered as non-equilibrium systems. These systems are unstable and they undergo a *structural relaxation* process which attempts to reduce excess thermodynamic quantities (volume, enthalpy etc.) towards equilibrium. Volume changes associated with structural relaxation process can be monitored directly in isothermal conditions by dilatometry. On the other hand, corresponding enthalpy change is usually obtained by the integration of the DSC curve measured after isothermal annealing at temperature T. The advantages and shortcomings of both these techniques are discussed, for example, in Ref.[1].

Fig. 1 shows the typical volume relaxation isotherm (plotted on log time scale) of an non-crystalline material suddenly cooled (i.e. temperature jump experiment) from equilibrium at temperature T_0 (usually near T_g) to temperature T. The relative volume departure from equilibrium, δ, is defined as the excess specific volume normalized with respect to the equilibrium volume V_∞:

$$\delta = \frac{V(t) - V_\infty}{V_\infty} \quad (1)$$

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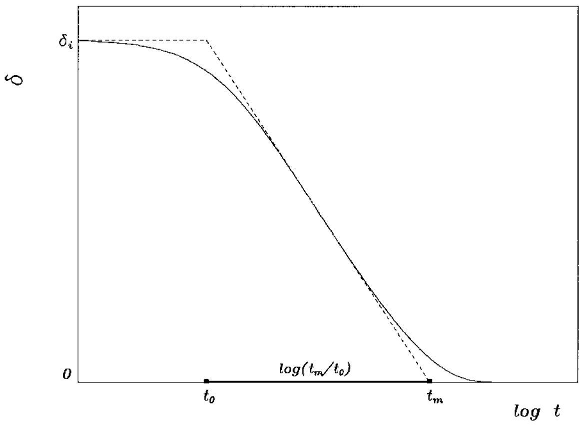

Fig. 1. Isothemal volume relaxation curve of a stabilized non-crystalline material subjected to a temperature jump ΔT. The stabilization period $\log(t_m/t_0)$ is defined as a reciprocal slope of the inflectional tangent (broken line).

The volume relaxation process can be characterized by the volume relaxation rate β_V defined as the inflectional slope of this relaxation isotherm:

$$\beta_V = -\left(\frac{\mathrm{d}\delta}{\mathrm{d}\log t}\right)_{\mathrm{inf}} \cong -\frac{1}{V_0}\cdot\left(\frac{\mathrm{d}\Delta V}{\mathrm{d}\log t}\right)_{\mathrm{inf}} \tag{2}$$

This parameter characterizing the relaxation process was introduced by Kovacs [2,3] and it is often used to compare the relaxation kinetics in various non-crystalline systems [2,4–7].

A similar relaxation rate can be defined also for isothermal enthalpy relaxation process [1]:

$$\beta_H = -\left(\frac{\mathrm{d}\delta_H}{\mathrm{d}\log t}\right)_{\mathrm{inf}} \tag{3}$$

The excess enthalpy with respect to the equilibrium δ_H is defined as:

$$\delta_H = \Delta H_\infty - \Delta H(t) \tag{4}$$

where ΔH is the relaxation enthalpy corresponding to the net area under the DSC peak of the annealed sample in comparison to the enthalpy change of the quenched sample taken as the reference.

Enthalpy relaxation rate is frequently used to characterize the relaxation kinetics in various materials [8–11]. There was also made an attempt to compare both volume and enthalpy relaxation rates as defined by Eqs. (2) and (3) for various polymer systems [1]. Nevertheless, no definitive study has yet been made to compare volumetric and enthalpic relaxation rates for the same systems and under the same conditions. The main objective of this paper is to analyze quantitatively the problem of relaxation rate for Tool–Narayanaswamy–Moynihan phenomenological model [12–14]. In the light of this analysis we examine previously reported isothermal volume relaxation data and enthalpy relaxation data for poly(vinyl acetate), (PVA); polystyrene (PS); poly (vinyl chloride), (PVC); poly-(methyl methacrylate), (PMMA) and arsenic sulfide glass (As_2S_3).

2. Theory

2.1. Phenomenological model

One of the most remarkable feature of structural relaxation is its universality. The same behavior is seen in a wide variety of glassy systems such as polymers and inorganic glasses. This suggests that the structural relaxation process is not linked purely with specific details of chemical structure of particular non-crystalline material, being inherent to the non-equilibrium glassy state and reflecting great similarity in the molecular processes controlling configurational rearrangements. This allows application of the same phenomenological model for such chemically dissimilar materials such as organic polymers and inorganic non-crystalline materials [15]. There are several phenomenological models that have been proposed for the description of the relaxation process. Any successful model must account for *non-linear* and *non-exponential* behavior characteristic of structural relaxation. The concept of non-linearity is based on the assumption that the relaxation time τ depends, not only on the temperature T but also upon the instantaneous structure of glass. This structure changes continuously during the relaxation process and it is characterized by means of fictive temperature T_{f} defined as the temperature at which the specimen volume (or enthalpy) would be equal to that of the equilibrium [12,13].

An expression of this dual dependence of τ upon temperature and the structure is often referred to as

Tool–Narayanaswamy–Moynihan (TNM) equation [12–14]:

$$\tau = A \cdot \exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_f}\right] \tag{5}$$

Eq. (5), which is one of the possible phenomenological expressions [15], introduces three constant parameters: the non-linearity parameter $x(0<x\leq 1)$, the effective activation energy Δh^* and the pre-exponential factor A. According to Narayanaswamy [13] linearity can be restored using reduced time defined by

$$\xi = \int_0^t \frac{\mathrm{d}t}{\tau(T,t))} \tag{6}$$

If a glass is equilibrated at temperature T_0 and then subjected to temperature jump $\Delta T = T_0 - T$, the fictive temperature is expressed as

$$T_f(t) = T_0 - \left[1 - \frac{\delta(\xi)}{\delta_\mathrm{i}}\right] \cdot \Delta T \tag{7}$$

where δ_i is an initial departure from equilibrium after the temperature jump. According to Eq. (7), the fictive temperature is equal to T_0 immediately after the temperature jump and during the isothermal relaxation it gradually changes towards T.

The non-exponentiality may be introduced into Eq. (7), e.g. by means of a stretched exponential function [14,15]:

$$\delta(\xi) = \delta_\mathrm{i}\exp(-\xi^\beta) \tag{8}$$

where the parameter β is inversely proportional to the width of a corresponding continuous distribution of relaxation times $(0<\beta\leq 1)$. It is assumed that the distribution of relaxation times exhibits thermorheological simplicity, i.e. the shape of the distribution is independent of temperature.

Eqs. (5)–(8) can be used for a quantitative description of the volume or enthalpy relaxation response of any non-crystalline material subjected to a simple temperature jump or to more complex thermal histories [15]. The parameters lnA, Δh^*, x and β can be evaluated from experimental data by a numerical curve fitting technique or by other methods (see e.g. [15] and the references quoted in it).

2.2. *Normalized volume and enthalpy relaxation rate R_F*

The volume relaxation rate can be expressed as the inflectional slope of a typical isothermal volume relaxation curve shown in Fig. 1

$$\beta_V = -\left(\frac{\mathrm{d}\delta}{\mathrm{dlog}t}\right)_\mathrm{inf} = \frac{\delta}{\log(t_m/t_0)} \tag{9}$$

where $\log(t_\mathrm{m}/t_0)$ is the stabilization period of the relaxation process. The initial departure from equilibrium immediately after the temperature jump is related to the magnitude of temperature jump ΔT and defined as [3]:

$$\delta_\mathrm{i} = \Delta\alpha \cdot \Delta T \tag{10}$$

where $\Delta\alpha$ is the difference between the volume thermal expansion coefficient of equilibrium undercooled liquid and asymptotic volume thermal expansion coefficient of glass. Therefore, it is evident that the volume relaxation rate depends on the value of $\Delta\alpha$ which is a characteristic constant for particular non-crystalline material. It is convenient to define the *normalized volume relaxation* rate in the following way:

$$R_F = \frac{\beta_V}{\Delta\alpha} = \frac{\Delta T}{\log(t_m/t_0)} \tag{11}$$

and similarly we can write for *normalized enthalpy relaxation rate* the following expression:

$$R_F = \frac{\beta_H}{\Delta C_p} = \frac{\Delta T}{\log(t_m/t_0)} \tag{12}$$

where ΔC_p is the difference between the heat capacity of equilibrium undercooled liquid and the heat capacity of glass. It is assumed that ΔC_p is temperature-independent and, therefore, the initial excess enthalpy δ_{Hi} (i.e. without any annealing at T) can be expressed as:

$$\delta_{Hi} = \Delta H_\infty \approx \Delta C_p \cdot \Delta T \tag{13}$$

In this case, the temperature difference ΔT corresponds to the temperature departure from T_g. Normalized volume and enthalpy relaxation rates as defined by Eqs. (11) and (12) are comparable quantities having the meaning of change of fictive temperature per decade of time. This parameter, therefore, defines the structural contribution of the relaxation time. It should be pointed out that the similar approach of normalization of enthalpy relaxation rate β_H with respect to ΔC_p was already used by Bauwens [8]. He found that for enthalpy relaxation of polycarbonate the following relation is fulfilled: $\beta_H/\Delta C_p \cong 3\,\mathrm{K}$.

For any practical application of the concept of normalized relaxation rate described above three essential comments should be made:

(i) It is important to be sure that experimentally determined volume (β_V) or enthalpy (β_H) relaxation rates defined by Eqs. (2) and (3) correspond to a truly inflectional tangent of the relaxation curve. There is always an initial curvature observed on the isothermal relaxation curves (see Fig. 1) which may be extended to several decades of time, particularly at lower temperatures. Consequently, if an insufficiently long experimental time scale is used the values of β_V or β_H (and also R_F values) can easily be underestimated [1,4].

(ii) At lower temperatures ($T<T_g-10$), volumetric and enthalpic equilibrium is extremely difficult to achieve within a reasonable experimental time scale. In this case it becomes necessary to make an extrapolation of the equilibrium line in order to get δ or δ_H values. Linear extrapolation as expressed by Eq. (10) will give acceptable values of δ for dilatometric measurements because $\Delta\alpha$ is approximately constant for many non-crystalline materials. Such extrapolation, however, is more problematic for calorimetric isothermal data since ΔC_p may change with temperature and therefore a linear relationship as expressed by Eq. (13) can be used only as a first approximation. It is not so easy to assess error limits of such linear approximation and this problem is further complicated by the fact that experimental errors are generally higher in the measurements of δ_H than δ. Therefore, it is reasonable to expect that the uncertainty in R_F data is generally higher for calorimetric than for dilatometric isothermal experiments.

(iii) Experimental errors for dilatometric temperature jump experiments increase considerably if the initial part of isothermal relaxation curve is truncated and $\delta_i \ll \Delta\alpha\cdot\Delta T$. This occurs particularly if the temperature T_0 is too high ($T_0 \gg T_g$) [16]. In this case it becomes quite difficult to construct a truly inflectional slope correctly and therefore the R_F values can seriously be in error. Such problems may also be important for the calorimetric experiments if the fast temperature jump ('quench') is replaced by a slower cooling rate.

The estimation of experimental errors in R_F data due to the factors mentioned in (i)–(iii) is rather difficult. Comparing available dilatometric data reported by several authors [3–6] the experimental error in R_F for dilatometric data is estimated to be about ±0.2 K. For normalized relaxation rate obtained from calorimetric data one can expect even higher limits of experimental errors.

2.3. The temperature dependence of R_F

Recently it was found [16] that for the TNM model the stabilization period of the relaxation process can be expressed as:

$$\log(t_m/t_0) = \frac{1.18}{\beta} + \frac{(1-x)\theta}{2.303}\cdot\Delta T \tag{14}$$

where $\theta = \Delta h^*/RT_g^2$ is a reduced effective activation energy first introduced in the KAHR model [40]. The value of θ is a characteristic constant for a particular non-crystalline material [15], generally being close to 1 for polymeric materials and 0.1–0.3 for inorganic glasses.

Combining Eqs. (11) and (12) and Eq. (14) a simple expression for normalized relaxation rate as a function of ΔT is found:

$$R_F(\Delta T) = \left(\frac{1.18}{\beta\cdot\Delta T} + \frac{(1-x)\theta}{2.303}\right)^{-1} \tag{15}$$

This equation predicts increasing normalized relaxation rate with ΔT. For dilatometric experiments ΔT corresponds to T_0-T under the assumption that the temperature jump is instantaneous. In fact, it is rather difficult to change the temperature so quickly (particularly for polymer samples) and there is always finite initial time t_i needed to reach thermal equilibrium of a real sample [3,4,16]. If T_0 is too high ($T_0 \gg T_g$) then the dilatometric relaxation response will be very fast immediately after the temperature jump and consequently the fictive temperature of the sample changes. For these reasons it seems to be more correct to define ΔT as the temperature departure from the fictive temperature after t_i has elapsed, i.e. $\Delta T = T_f(t_i) - T$. The $T_f(t_i)$ can be calculated using Eq. (7) for a given set of parameters $\ln A$, Δh^*, x and β [16]. In order to simplify this problem, it is assumed here that $T_f(t_i)$ is essentially close to T_g provided that $T_0 \geq T_g$. On the other hand, fictive temperature will not change considerably immediately after the temperature jump if $T_0 < T_g$. Thus the temperature departure is defined as follows:

$$\begin{array}{lcll} \Delta T & = & T_g - T & \text{for} \quad T_0 \geq T_g \\ \Delta T & = & T_0 - T & \text{for} \quad T_0 < T_g \end{array}$$

Dilatometric T_g is then defined (for temperature jump experiments where $T_0 \cong T_g$) as the temperature where the stabilization period apparently corresponds to the exponential volume relaxation response, i.e. $\log(t_m/t_0) = 1.18$ (see Eq. (14) for $\beta = 1$).

For calorimetric experiments ΔT corresponds to $T_g - T$. The glass transition temperature T_g should be obtained from the cooling DSC scan using the integration procedure described by Richardson and Savill [17] and Moynihan et al. [14]. Nevertheless, it is quite common in the literature that the T_g value is obtained from heating the DSC scan. Such a definition is rather problematic since T_g is affected by the previous thermal history of a non-crystalline material. It should also be pointed out that calorimetric and dilatometric T_g need not have necessarily the same value. These facts should also be taken into consideration when normalized volume and enthalpy relaxation rates are compared.

According to Eq. (15) the value of normalized relaxation rate R_F at given ΔT is controlled by two parameters: β and $(1-x)\theta$. The influence of these parameters is illustrated in Fig. 2. It is seen (Fig. 2(a)) that R_F decreases with increasing $(1-x)\theta$ and that for $(1-x)\theta \geq 0.7$ it does not change considerably for higher ΔT. The change of $R_F(\Delta T)$ function is more gradual for lower values of the parameter of non-exponentiality β. The influence of this parameter rapidly decreases for $(1-x)\theta > 0.7$ as shown in Fig. 2(b) for $\Delta T = 10$ K. For materials with parameter $(1-x)\theta$ higher than 0.7 (such as PMMA and PVC) a very slow relaxation can be expected with extremely low values of normalized relaxation rate $R_F(10) < 2$. The effect of the non-exponentiality parameter cannot then be distinguished from the $R_F(\Delta T)$ plot within the limits of experimental errors expected for dilatometric R_F data (i.e. ±0.2 K). Nevertheless, it was observed [15] that these materials usually exhibit higher non-exponentiality ($\beta < 0.4$). On the other hand, a relatively fast relaxation is expected for materials with parameter $(1-x)\theta$ lower than 0.3 (silicates, chalcogenides, B_2O_3 etc.) and normalized relaxation rate is then $R_F(10) > 3$. These materials usually exhibit lower non-exponentiality ($\beta > 0.6$) [15]. In this case it is possible to measure a reliable relaxation rate even for higher values of ΔT and consequently the effect of the non-exponentiality parameter β can clearly be elucidated from the $R_F(\Delta T)$ plot.

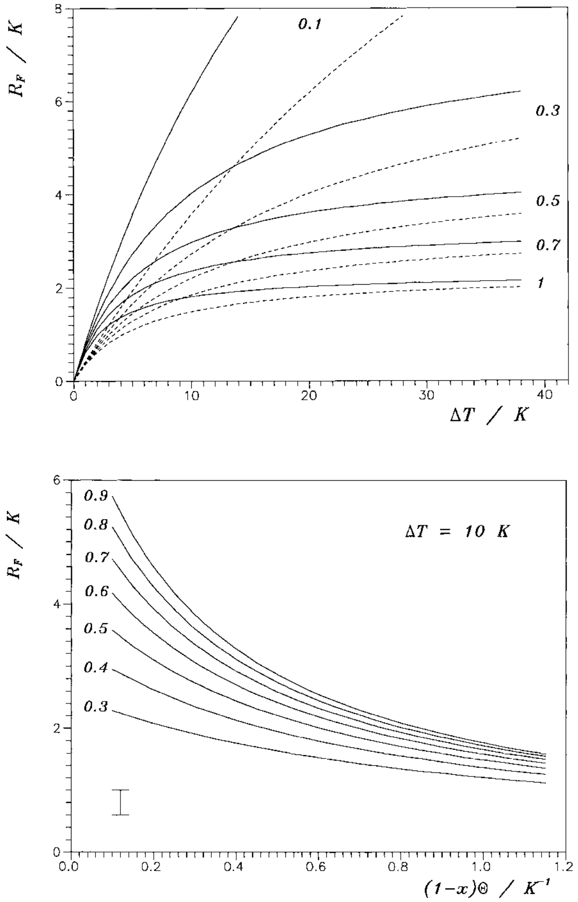

Fig. 2. (a) The temperature dependence of normalized relaxation rate calculated using Eq. (15) for $\beta = 1$ (full lines) and $\beta = 0.5$ (broken lines). The values of parameter $(1-x)\theta$ are marked by numbers. (b) The normalized relaxation rate for $\Delta T = 10$ K as a function of parameter $(1-x)\theta$ for different values of parameter β (marked by numbers). The bar represents a typical error limit for normalized volume relaxation rate.

It is important to stress that for a particular non-crystalline material the normalized volume and enthalpy relaxation rates should be the same provided that parameters β and $(1-x)\theta$ are identical for volume and enthalpy relaxation response. This prediction is examined and discussed in the following section.

3. Results and discussion

Table 1 summarizes three sets of volume relaxation data for PVA reported by Kovacs [3,18] for T=30°C ($32.5\leq T_0\leq 60$°C), T=35°C ($35.63\leq T_0\leq 40$°C) and for T_0=40°C ($25\leq T\leq 37.5$°C). The normalized relaxation rate R_F can be calculated from inflectional slopes of $\delta(\log t)$ plots using Eq. (11) for $\Delta\alpha=4.5\times10^{-4}$ K^{-1} [3]. Corresponding values of ΔT were determined as T_g-T for $T_0\geq T_g$ and T_0-T for $T_0<T_g$ (see Table 1). Dilatometric T_g of 38.9°C was determined by the extrapolation of $\log(t_m/t_0)$ vs. T plot to $\log(t_m/t_0)=$ 1.18 (for T_0=40°C data set). The temperature dependence of normalized volume relaxation rate for PVA is shown in Fig. 3 (points: □, Δ, ○). This figure also includes another $R_F(\Delta T)$ value calculated (using the same value of T_g and $\Delta\alpha$) from volume relaxation data for PVA reported by Delin et al. [19] (points: +). Normalized enthalpy relaxation rates were calculated from inflectional slopes of $\delta_H(\log t)$ plots using Eq. (12) for ΔC_p=0.46 J/gK [19] from data reported by Bair et al. [20], Cowie et al. [21], Wang and Filisko [22]. The temperature departure is defined as $\Delta T=T_g-T$. Calorimetric T_g for dry PVA were found to be 43.5°C [20] and 40°C [21]. In contrast, PVA containing water has considerably lower T_g (30°C for a sample with 1.8% water [20]). Nevertheless, the value of ΔC_p as well as the enthalpy relaxation rate is identical for a constant ΔT [20]. These values of R_F are shown in Fig. 3 (points: ■, ▲, ●). It is seen that R_F data for dilatometric and calorimetric experiments are very close within experimental errors. A full line was calculated using Eq. (15) for TNM previously reported by Hodge [23] (obtained by the curve fitting technique of calorimetric data, see Table 2). Eq. (15) gives relatively

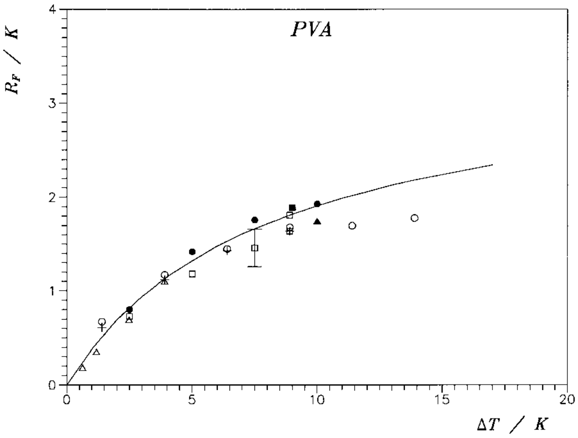

Fig. 3. The normalized relaxation rate as a function of ΔT for poly(vinyl acetate). Points correspond to dilatometric data: (□) T=30°C; (Δ) T=35°C; (○) T_0=40°C Kovacs [3,18]; (+) Delin et al. [19] and calorimetric data: (■) Bair et al. [20]; (▲) Cowie et al. [21]; (●) Wang and Filisko [22]. A full line was calculated using Eq. (15) for TNM parameters shown in Table 2.

Table 1
The volume relaxation rate for temperature jump experiments of poly(vinyl acetate), T=30°C ($32.5\leq T_0\leq 60$°C), T_0=40°C ($25\leq T\leq 37.5$°C) [3] and T=35°C ($35.63\leq T_0\leq 40$°C) [18].

T_0/°C	T/°C	ΔT/°C	$-10^4\beta_V$/K^{-1}
40	37.5	1.4	3.00
40	35	3.9	5.28
40	32.5	6.4	6.53
40	30	8.9	7.56
40	27.5	11.4	7.66
40	25	13.9	8.02
60	30	8.9	8.16
40	30	8.9	7.40
37.5	30	7.5	6.56
35	30	5.0	5.29
32.5	30	2.5	3.28
35.63	35	0.63	0.81
36.18	35	1.18	1.58
37.48	35	2.48	3.13
40	35	3.9	5.16

Table 2
The TNM parameters for structural relaxation of arsenic sulfide glass, polystyrene, poly(vinyl acetate), poly(methyl metacrylate) and poly(vinyl chloride).

Material	θ/K^{-1}	x	β	Refs.
As_2S_3	0.16	0.31	0.82	[36]
PS	0.79	0.41	0.47	[29]
PVA	0.92	0.27	0.51	[23]
PMMA	0.98	0.19	0.35	[23]
PVC	1.74	0.10	0.23	[23]

good prediction for R_F values for temperature departure ΔT up to 10°C but at lower temperatures it predicts higher values of R_F than observed experimentally. As the stabilization response rapidly increases for higher ΔT it is possible that true inflectional tangent is not reached yet for ΔT>10°C and consequently experimentally determined R_F values can easily be underestimated (see Section 2.2(i)). Another possible explanation, which should be taken into account, is that the idea of thermorheological simplicity is not expected to be strictly true for larger temperature departures from T_g.

Fig. 4 shows the temperature dependence of normalized volume relaxation rate for PS data reported by Greiner and Schwarzl [4] and Kovacs [2]. The $R_F(\Delta T)$ values (points: □, Δ) were calculated from inflectional slopes of reported δ(log t) data using Eq. (11) for $\Delta\alpha=3.3\times10^{-4}\ \mathrm{K}^{-1}$ [3,4] and T_g=99.5°C. This values of dilatometric T_g was found by extrapolation of log(t_m/t_0) vs. T plot for data of Greiner and Schwarzl [4]. Volume relaxation rates of PS reported by Struik [5,6] are practically identical if a lower value of T_g=91°C is taken (points: x). Normalized enthalpy relaxation rates were calculated from slopes of δ_H(log t) plots reported by Petrie [24], Marshall and Petrie (Koppers sample) [25], Roe and Millman [26] using Eq. (12) for T_g=104°C (points: ■, ▲, ●) and for the data reported by Chang and Li [27] for T_g=100°C (point: ◒). The value of ΔC_p used for these calculations is 0.31 J/gK [24]. Both volumetric and calorimetric relaxation data give comparable values of R_F within experimental errors. Similar results can also be found for dilatometric data of PS reported by Hutchinson [1]. On the other hand, calorimetric β_H data of Chen and Wang [28] gives extremely low values of R_F. In this case, however, $\Delta H(t)\leq0.2\cdot\Delta C_p\cdot\Delta T$ and therefore it seems that a truly inflectional slope was not reached which may cause an underestimation of R_F. The full line in Fig. 4 was calculated using Eq. (15) for TNM parameters previously reported by Privalko [29] (obtained by the curve fitting technique of calorimetric data, see Table 2). Similarly, as in the case of PVA also here Eq. (15) gives a relatively good prediction for lower ΔT but there is a systematic deviation for ΔT>15°C.

Fig. 5 shows the temperature dependence of normalized volume relaxation rate for PMMA data reported by Greiner and Schwarzl [4], and Hutchinson and Bucknall [30]. The $R_F(\Delta T)$ values (points: □, Δ) were calculated from reported β_V data and from inflectional slopes of Δ(log t) plots using Eq. (11) for $\Delta\alpha=3.0\times10^{-4}\ \mathrm{K}^{-1}$ [3] and T_g=112°C. This value of dilatometric T_g was found by extrapolation of

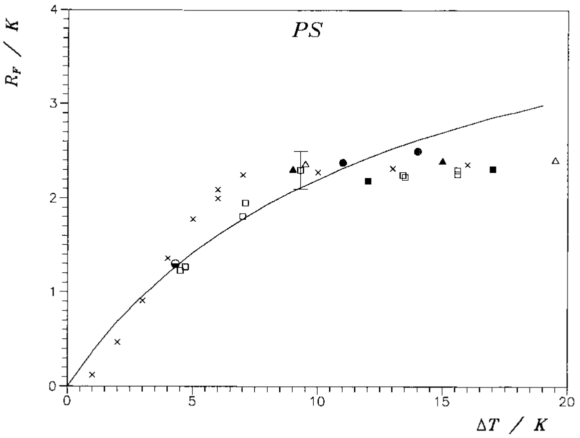

Fig. 4. The normalized relaxation rate as a function of ΔT for polystyrene. Points correspond to dilatometric data: (□) Greiner and Schwarzl [4]; (Δ) Kovacs [2]; (×) Struik [5,6] and calorimetric data: (■) Petrie [24]; (▲) Marshall and Petrie [25]; (●) Roe and Millman [26]; (◒) Chang and Li [27]. The full line was calculated using Eq. (15) for TNM parameters shown in Table 2.

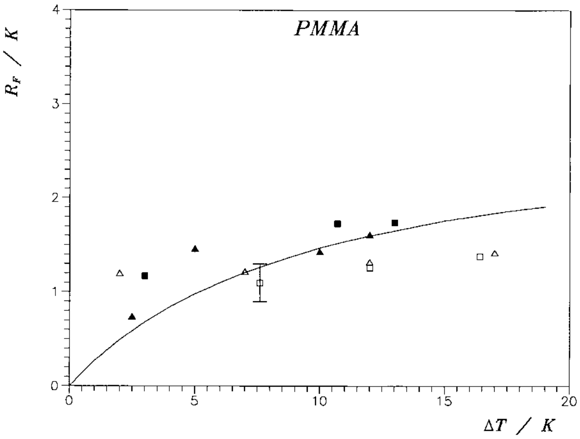

Fig. 5. The normalized relaxation rate as a function of ΔT for poly(methylmethacrylate). Points correspond to dilatometric data: (□) Greiner and Schwarzl [4]; (Δ) Hutchinson and Bucknall [30] and calorimetric data: (■) Cowie and Ferguson [31]; (▲) Perez and Cavaille [10]. The full line was calculated using Eq. (15) for TNM parameters shown in Table 2.

$\log(t_m/t_0)$ vs. T plot for data of Hutchinson and Bucknall [30]. Normalized enthalpy relaxation rates were calculated from slopes of $\delta_H(\log t)$ plots reported by Perez and Cavaille [10], and Cowie and Ferguson [31] using Eq. (12) for ΔC_p=0.27 J/gK [10] and T_g= 115°C (points: ■, ▲). In this case there is a relatively higher scatter of data than observed for PVA and PS but it is still within the limit of experimental error taking into account that the thermal history is not the same for all samples of PMMA compared in Fig. 5. The full line in Fig. 5 was calculated using Eq. (15) for TNM parameters previously reported by Hodge [23] (obtained by the curve fitting technique of calorimetric data, see Table 2). Values of β_H for PMMA can also be found from the data reported by Ott [32], but they are about two times larger than those given above. The reason for these discrepancies is not clear but it should be pointed out that for Ott's data: $\delta_{Hi} > \Delta C_p \cdot \Delta T$ which is a somewhat unexpected finding.

Fig. 6 shows the temperature dependence of normalized volume relaxation rate for PVC data reported by Greiner and Schwarzl [4] and Struik [6]. The $R_F(\Delta T)$ values (points: □, Δ) were calculated from β_V data using Eq. (11) for $\Delta\alpha=4.3\times10^{-4}$ K^{-1} [4] and T_g=76°C. The values of $R_F(\Delta T)$ calculated from the slope of $\delta(\log t)$ plots reported by Lee and McGarry [33] are very close if a different value of T_g=85°C is taken. Normalized enthalpy relaxation rates were calculated from slopes of $\delta_H(\log t)$ plots using Eq. (12) for data reported by Pappin et al. [34] (ΔC_p=0.34 J/gK [33], T_g=80°C) and for data reported by Gomez Ribelles et al. [35] (ΔC_p= 0.30 J/gK [34], T_g=81°C) and they are plotted in Fig. 6 (points: ■, ▲). Both dilatometric and calorimetric relaxation data give comparable values of R_F within experimental errors. The full line in Fig. 6 was calculated using Eq. (15) for TNM parameters reported by Hodge [23] (obtained by the curve fitting technique of calorimetric data, Table 2).

Fig. 7 shows the temperature dependence of normalized volume relaxation rate of arsenic sulfide glass for the length dilatometric data reported by Málek [36]. This $R_F(\Delta T)$ dependence (points: □) was calculated from the inflectional slope of $\delta(\log t)$ plots using Eq. (12) for $\Delta\alpha=2.22\times10^{-4}$ K^{-1} and T_g=188°C [16,36]. This value of dilatometric T_g was found by extrapolation of $\log(t_m/t_0)$ vs. T plot. The full line in Fig. 7 was calculated using Eq. (15) for TNM parameters [36] (obtained by the curve fitting technique of isothermal dilatometric data). In this case Eq. (15) gives a very good prediction of the normalized relaxation rate up to ΔT=40°C. Unfortunately, the comparison with calorimetric data cannot be made in this case because there are no such data available at the moment (at least as far as we know).

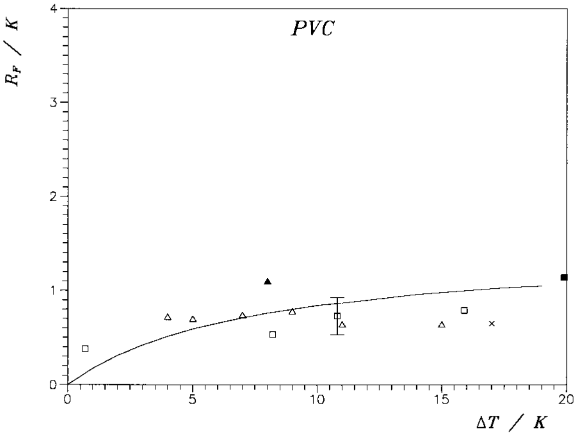

Fig. 6. The normalized relaxation rate as a function of ΔT for poly(vinylchloride). Points correspond to dilatometric data: (□) Greiner and Schwarzl [4]; (Δ) Lee and McGarry [33]; (×) Struik [6] and calorimetric data: (■) Pappin et al. [34]; (▲) Gomez Ribelles et al. [35]. The full line was calculated using Eq. (15) for TNM parameters shown in Table 2.

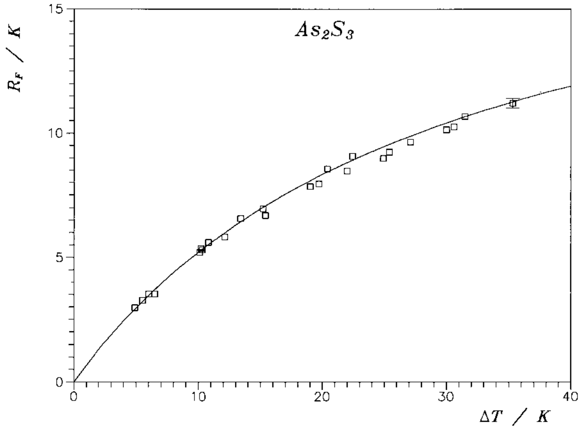

Fig. 7. The normalized relaxation rate as a function of ΔT for As_2S_3 glass. Points correspond to the length dilatometric data: (□) Málek [36]. The full line was calculated using Eq. (15) for TNM parameters shown in Table 2.

It was found that for all non-crystalline materials discussed above the normalized enthalpy and volume relaxation agree reasonably within the limits of experimental errors, particularly at lower temperature departures from T_g. This would mean that the TNM parameters in these materials are in fact very similar for both volume and enthalpy relaxation, at least at lower ΔT. Discrepancies observed for PVA, PS and PMMA for higher ΔT can be a consequence of an underestimation caused by the fact that the true inflectional slope was not reached within the experimental time scale. Another possible explanation could be that these systems become thermorheologically complex for higher ΔT and therefore the parameter β may be slightly temperature-dependent [15]. Nevertheless, these conclusions are not definitive and they should be tested in the case of inorganic glasses which exhibit higher relaxation rates and therefore lower relative errors in R_F can be expected. Another study is in progress in this respect.

It is well known that TNM parameters are strongly correlated. Approximate linear correlation between β and x was explained [37] on the basis of the Adam–Gibbs concept of increasing size of relaxing groups [38]. The inverse relation between x and Δh^* [39] follows directly from the Adam–Gibbs expression for relaxation time [23]. On the other hand, there are other correlations between TNM parameters which can be found experimentally. The TNM parameters for about 30 different non-crystalline materials have been collected in Ref. [15]. An interesting feature of these data is an inverse correlation between β and $(1-x)\theta$ parameters (see also Section 2.3). Such empirical correlations are always somewhat speculative because they may be affected partially by the data analysis procedure (the curve fitting procedure inevitably brings such problems). Nevertheless, it is reasonable to admit that a certain type of parameter correlation really exists and that it can be incorporated into the concept of the normalized relaxation rate. Assuming correlation of TNM parameters in the form $1/\beta \approx (1-x)\theta$, Eq. (15) can then be expressed in a simplified form:

$$R_f = \frac{1}{a + b \cdot (1-x)\theta} \tag{16}$$

where a and b are parameters dependent on ΔT. It is expected that these parameters should be constant for many non-crystalline materials and they can be evaluated, e.g. using TNM parameters summarized in Table 2. For ΔT=10 K one can find the following values of these parameters: a=0.12 and b=0.68.

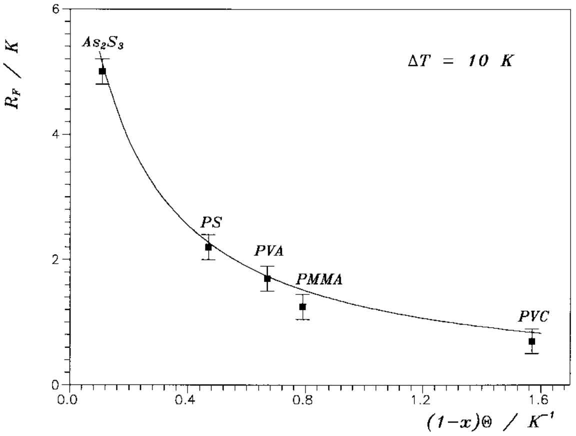

Fig. 8. The normalized relaxation rate R_F (10) as a function of parameter $(1-x)\theta$. The full line was calculated using Eq. (16) for a=0.12 and b=0.68. Points correspond to the normalized relaxation rate of non-crystalline materials obtained from volume relaxation measurements.

Fig. 8 shows the R_F vs. $(1-x)\theta$ dependence calculated using Eq. (16) for these values of parameters a and b (full line). Typical experimental values of normalized volume relaxation rates for As_2S_3, PS, PVA, PMMA and PVC are shown as points. It is seen that for all these materials there is very good agreement with theoretical prediction based on the TNM model. For materials with a relatively high value of θ and a low value of non-linearity parameter x (e.g. for vinylic polymers) one can expect a very slow relaxation rate. The value of $R_F(10)$ is lower than 1.7 K for $(1-x)\theta > 0.7$, being practically constant within the limit of experimental errors, as anticipated in Section 2.3. In contrast, the materials with low values of parameter $(1-x)\theta$ (e.g. inorganic glasses) will exhibit considerably higher relaxation rates ($R_F(10) > 3$).

4. Conclusions

The normalized volume and enthalpy relaxation rate R_F is defined and analyzed for the Tool–Narayanaswamy–Moynihan phenomenological model. It is shown that the temperature-dependent R_F can be described by a simple Eq. (15) and it is controlled mainly by the parameter $(1-x)\theta$, where $\theta = \Delta h^*/RT_g^2$. This equation was tested using previously reported volume and enthalpy relaxation data for various non-crystalline materials (As_2S_3 glass, PS, PVA, PMMA and PVC). Materials with higher values of parameter $(1-x)\theta$ (PVA, PMMA and PVC) exhibit a low relaxation rate. In contrast, a high relaxation rate is observed for materials with lower value of $(1-x)\theta$ parameter.

It is shown that the normalized enthalpy and volume relaxation agree well within the limits of experimental error rates for non-crystalline materials discussed here. This would suggest that the TNM parameters in these materials are in fact very similar for both volume and enthalpy relaxation, at least at lower ΔT. Discrepancies observed for PVA, PS and PMMA for higher ΔT can be explained by the fact that the true inflectional slope was not reached within the experimental time scale which may cause an underestimation of R_F. Another possible explanation could be that these systems become thermorheologically complex for higher ΔT. Further comparative study is in progress to verify these conclusions on inorganic glasses.

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