THEORY AND SIMULATION

Estimation of the Parameter of the Main Equation of the Glass Transition of Amorphous Polymers and Other Amorphous Substances

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Abstract—Parameter C from the main glass-transition equation $q\tau_g = C$ according to Nemilov's theory has the meaning of temperature bandwidth δT_g in which the freezing of the structure of the glass-forming liquid occurs (where q is the cooling rate of a melt and τ_g is the time of structural relaxation at the glass-transition temperature). The currently used method to estimate C results in inflated values, a circumstance that is due to the assumption of the constancy of the activation energy of the glass transition in the derivation of the calculation formula. Methods of estimation of C that are in agreement with the experimental data have been considered. A calculation of the time of structural relaxation, τ_g, on the basis of the values of the parameters of the Williams−Landel−Ferry equation has been proposed.

INTRODUCTION

Several works have been devoted to the transition of amorphous substances from the liquid (highly elastic) state to the solid glassy state. Despite this, the problem has not been completely solved (see, e.g., [1−3]).

From the viewpoint of relaxation theories [4−7], a decisive role in the process of the glass transition of a liquid is played by the ratio between the time of structural relaxation, τ_g, and the cooling rate of a melt, $q = dT/dt$. In this regard, the equation that determines the relationship between the indicated variables,

$$q\tau_g = C \qquad (1)$$

is sometimes called the main equation of the glass transition of liquids (polymers) [8, 9]. Here, τ_g is the relaxation-time value at glass-transition temperature T_g. Empirical parameter C has the dimension of temperature.

Equation (1), proposed by Bartenev [4], was successfully used to obtain the dependence of glass-transition temperature T_g on cooling rate q [4, 10]. Furthermore, Eq. (1) in the relaxation spectrometry of polymers [8] is the condition of feasibility of a structural relaxation transition at $T = T_g$ and is similar to the situation when there is a condition during mechanical relaxation at which the maximum mechanical loss is observed. Equation (1) is additionally used to explain other relaxation processes ($q\tau_i = C_i$, where τ_i is the relaxation time of the ith relaxation process), e.g.,

thermostimulated electrical depolarization of amorphous polymers [8, p. 144].

Nemilov [7] obtained a similar relationship after generalization of the relaxation theories of the glass transition [5, 6]:

$$q\tau_g = \delta T_g. \qquad (2)$$

From this, it follows that parameter C of the Bartenev equation has the meaning of temperature bandwidth δT_g in which the freezing of the structure of the liquid under cooling occurs: $C = \delta T_g$.

Recently, an interpretation of C within the model of delocalized atoms was proposed [11]. It was found that C is determined by glass-transition temperature T_g and the part of the fluctuation volume $f_g = (\Delta V_e/V)_{T=T_g}$ frozen at the temperature $T = T_g$ [12]:

$$C = \frac{f_g}{\ln\left(1/f_g\right)} T_g. \qquad (3)$$

The fluctuation volume of the amorphous system, $\Delta V_e = N_e \Delta v_e$, occurs as a result of thermal fluctuations of particles from equilibrium positions (N_e is the number of delocalized (displaced) atoms, and Δv_e is the elementary fluctuation volume necessary for delocalization of an active atom, its displacement from the equilibrium position).

Calculation of C of the main equation of the glass transition for amorphous organic polymers and sodium silicate glasses (Na_2O-SiO_2)

Amorphous substance	T_g, K	C_1	C_2, K	$C = \dfrac{C_2}{C_1}$, K	$f_g = \dfrac{1}{C_1}$	C, K (according to formula (3))	τ_g, s (according to formula (18))
Amorphous polymers [17]							
Polyisobutylene	202	38	104	2.7	0.026	1.4	54
Polyvinyl acetate	305	36	47	1.3	0.028	2.4	26
Polyvinyl chloroacetate	296	40	40	1.0	0.025	2.0	20
Polymethyl acrylate	276	42	45	1.1	0.024	1.8	22
Polyurethane	238	36	33	0.9	0.028	1.9	18
Natural rubber	300	38	54	1.4	0.026	2.1	57
Methacrylate polymers:							
ethyl	335	40	65	1.6	0.025	2.3	32
n-butyl	300	39	97	2.5	0.026	2.1	50
n-octyl	253	37	107	2.9	0.027	1.9	58
Sodium silicate glasses [18]							
[Na_2O], mol % 15	782	36	430	12	0.028	6.1	240
20	759	36	390	11	0.028	5.9	220
25	739	35	355	10	0.028	5.8	200
30	721	35	322	9	0.028	5.6	180
33	712	35	304	9	0.028	5.6	180
35	705	35	291	8	0.028	5.5	160

The estimation of C through the use of Eq. (3) and the data on values of f_g and T_g results in the following values (table) for amorphous organic polymers,

$$C \approx (1.5{-}2.5)\,\mathrm{K}, \qquad (4)$$

and for inorganic sodium silicate glasses,

$$C \approx (5{-}6)\,\mathrm{K}. \qquad (5)$$

However, since 1955 [10], values of C of approximately $10{-}20$ K, which are significantly higher than the values given by estimations (4) and (5), have been used in the main equation of the glass transition [8, p. 143; 13, p. 21; 14, p. 138].

The present article is devoted to the examination of the divergence in estimations of the parameter of Bartenev equation (1) and to the search for a more correct way of its calculation. This is of certain interest because the main equation of the glass transition had begun to receive attention, especially after its justification by Nemilov [7], in the form of equality (2).

THEORY

Traditional Way to Estimate the Parameter of the Main Equation of the Glass Transition

In the theory of Vol'kenstein−Ptitsyn [5], molecules of the glass-forming system may occur in ground and excited states, and their dynamics is characterized by relaxation time τ. The change in concentration n of the particles in the excited state is determined via the kinetic equation

$$\frac{dn}{dT} = -\left(\frac{1}{q\tau}\right)(n - n_0),$$

where n_0 is the equilibrium value of n. Analysis of the solutions of this equation leads to the conclusion that, at certain temperature T_g, the freezing−glass transition of the liquid occurs. Moreover, the condition of the transition from the liquid state to the solid glassy state is expressed by the equation

$$\left(\frac{d\tau}{dT}\right)_{T=T_g} = -\frac{1}{|q|}. \qquad (6)$$

Because of the absence of a generally accepted theoretical formula for the peculiar temperature dependence of structural relaxation time, $\tau(T)$, in the liquid–glass transition range, the authors of [5] limited themselves to the simplest case, in which it was assumed that this dependence was to a first approximation described by the Frenkel equation [15]:

$$\tau = \tau_0 \exp\left(\frac{U}{kT}\right), \tag{7}$$

where the activation energy of the glass-transition process, U, does not depend on temperature,

$$U = \text{const}, \tag{8}$$

and τ_0 is the period of molecular fluctuation around the equilibrium position.

Substitution of dependence (7) into glass-transition criterion (6) under condition (8) leads to the following result [5]:

$$q\tau_g = \left(\frac{kT_g^2}{U}\right).$$

In this approach, the parameter of the main equation of the glass transition has the following physical meaning:

$$C = \left(\frac{kT_g}{U}\right)T_g. \tag{9}$$

In [8, 10, 13, 14] the above relationship was adopted to calculate C. Ratio (kT_g/U) was determined from relaxation-time equation (7) at the values of constants of $\tau = \tau_g \approx 10^2$ s, $\tau_0 \approx 10^{-12}$ s, and $T = T_g$:

$$\left(\frac{kT_g}{U}\right) = \frac{1}{\ln\left(\dfrac{\tau_g}{\tau_0}\right)} \approx \text{const} \approx 0.03.$$

The estimation of $C \approx 0.03T_g$ gives the following values [8, 10, 13]: for organic amorphous polymers ($T_g \approx 300$ K),

$$C \approx 10 \text{ K}, \tag{10}$$

and for inorganic silicate glasses ($T_g \approx 700$ K),

$$C \approx 20 \text{ K}, \tag{11}$$

which are significantly higher than the presented results obtained through (4) and (5). These data, $C \approx 10-20$ K, are currently in use.

The Role of the Temperature Dependence of Activation Energy in the Glass-Transition Range

It is known that the activation energy of the process of glass transition dramatically increases near T_g [8, 9]. In this regard, the assumption of the constancy of activation energy (8) in the derivation of calculation formula (9), in our opinion, leads to inflated values of C in (10) and (11).

Then, if the above procedure is repeated with allowance made for the temperature dependence of activation energy, $U(T)$, it is possible to attain main equation of the glass transition (1), in which C is determined through the equation

$$C = \frac{kT_g^2}{U_g}\left[1 - \frac{T_g}{U_g}\left(\frac{dU}{dT}\right)_{T_g}\right]^{-1}, \tag{12}$$

where U_g is the activation energy of the glass transition at $T = T_g$. The derivative in brackets is negative because the activation energy increases ($(dU/dT)_{T_g} < 0$) during cooling of the melt ($dT < 0$). This circumstance shows that the expression in square brackets is greater than one, which means that the above estimation of $C \approx 10-20$ K according to (9) is inflated.

In our previous work [16], we used the empirical Williams–Landel–Ferry equation [17]

$$\ln\frac{\tau(T)}{\tau(T_g)} = -C_1\frac{T - T_g}{T - T_g + C_2}, \tag{13}$$

which successfully describes the temperature dependence of relaxation time, $\tau(T)$, in the glass-transition range.

Substituting $\tau(T)$ into condition of the liquid–glass transition (6) from Eq. (13) leads to the main relationship of the glass transition:

$$q\tau_g = \frac{C_2}{C_1}, \tag{14}$$

from which C is determined via the ratio of the parameters of the Williams–Landel–Ferry equation,

$$C = \frac{C_2}{C_1}. \tag{15}$$

Estimation of C according to this formula on the basis of the known values of C_1 and C_2 for amorphous polymers and sodium silicate glasses (table) gives, respectively,

$$C \cong (1-3) \text{ K} \tag{16}$$

and

$$C \cong (8-10) \text{ K}. \tag{17}$$

These values agree well with the calculated results (see Eqs. (4), (5)) (table). The temperature dependence of the activation energy of the glass transition process in the liquid–glass transition range is implicitly taken into account in the Williams–Landel–Ferry equation.

In the theory of Nemilov [7], temperature range δT_g, which is equal to C, is determined through the formula

$$\delta T_g = -\left(\frac{\partial T}{\partial \ln \eta}\right)_{T=T_g}.$$

The δT_g value is taken to be equal to the temperature range in which viscosity $\eta(T)$ changes by an order from 10^{13} to 10^{12} Pa s: $\delta T_g = (T_{12} - T_{13})$, T_{12} and T_{13} are the temperatures that correspond to $\log \eta = 13$ and 12, respectively. The δT_g value turns out to be narrow. For example, when the content of PbO in inorganic lead borate glasses $PbO-B_2O_3$ is changed in a wide range (from 18 to 71 mol %), δT_g fluctuates within narrow limits [7]: 6−10 K, which coincides with the data obtained above for C for inorganic sodium silicate glasses (see (17)).

Narrow temperature range δT_g is consistent with the classical concepts of Simon [19] on the narrow bandwidth of temperatures within which the freezing of the structure of the liquid occurs. However, δT_g does not coincide with the macroscopic area of glass, ΔT_g, where the physical properties change most sharply [8, 9]; usually, $\Delta T_g > \delta T_g$. However, they should apparently be close to each other in order of magnitude.

In our opinion, the estimation based on the values of the parameters of the Williams−Landel−Ferry equation with the use of formula (15) is the most preferable of the above methods to calculate C of the main equation of the glass transition.

We can calculate the time of structural relaxation, τ_g, at a standard cooling rate of $q = 3$ K/min = 0.05 K/s via Eq. (14) [10, 16]; e.g., for sodium silicate glasses (table),

$$\tau_g = \frac{C_2}{C_1 q} = (1-2) \times 10^2 \text{ s.} \tag{18}$$

Maxwell's formula leads to the same estimation of τ_g for alkali silicate glasses (see [7]):

$$\tau_g = \frac{\eta_g}{G}, \tag{19}$$

where G is the instantaneous shear modulus, $\eta_g \approx 10^{12}$ Pa s is the viscosity at standard cooling rate q and a standard glass-transition temperature (see [16]). For the most common inorganic oxide glasses, $G \approx 10$ GPa. Equation (19) was introduced by Maxwell as a postulate that introduced an exponential law of release of elastic stresses generated in the body and the appearance of its viscosity. It was assumed that instantaneous shear modulus G changes little with temperature. Indeed, for the inorganic oxide glasses at the glass-transition temperature, it is only 3−5% lower than that at room temperature [7]. The structural-relaxation time is often considered to coincide with the Maxwell relaxation time in Eq. (19) [7, 15].

Relaxation time τ_g of amorphous organic polymers (table),

$$\tau_g = \frac{C_2}{C_1 q} \approx (20-60) \text{ s} \tag{20}$$

is significantly lower than that of silicate glasses, a circumstance that, at a constant $C_1 q$ value, is due to the low value of $C_2 = f_g/\beta_f$, where the f_g values of amorphous polymers and inorganic glasses are the same (table), while the coefficient of thermal expansion of the fluctuation volume $\beta_f = (df/dT)_{T=T_g}$ is significantly higher for polymers than that for silicate glasses [11, 20]. Low values of the structural-relaxation time of amorphous polymers, τ_g, can additionally be explained by Maxwell's formula (19), because these systems have lower elastic moduli G than those of the silicate glasses. The vast majority of the amorphous substances have $\eta_g \approx$ const $\approx 10^{12}$ Pa s [2, 7].

At typical values of $q = 0.05$ K/s and $\tau_g = (1-2) \times 10^2$ s for alkali silicate glasses, the product

$$q\tau_g = (5-10) \text{ K}, \tag{21}$$

agrees satisfactorily with the values $C_2/C_1 \approx 6-12$ K for sodium silicate glasses (table).

CONCLUSIONS

The results of calculating parameter C of the main equation of the glass transition for amorphous organic polymers according to the model of delocalized atoms and according to the values of the universal parameters of the Williams−Landel−Ferry equation agree well with each other and amount to $C \approx 1.5-2.5$ K and $C \approx 1.0-2.5$ K, respectively (table). These values are significantly lower than the currently used value $C \approx 10$ K. The main cause of the obtainment of the inflated values of C is the assumption of the constancy of the activation energy of the process of glass transition. The same statement is true for the silicate glasses. The structural-relaxation times at glass-transition temperatures were calculated for both amorphous organic polymers and for sodium silicate glasses and were equal to $\tau_g \approx 20-60$ s and $\tau_g \approx 150-250$ s, respectively.

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