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A comparison between the bond-strength-coordination number fluctuation model and the random walk model of viscosity

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Abstract We have studied the temperature dependence of the viscosity of some polymeric materials by using both, the bond-strength-coordination number fluctuation model and the random walk model. The results reveal that both models show an excellent agreement with the experimental data. For the random walk model, two equations corresponding to two temperature regimes (low-T and high-T) separated by the critical temperature T_c, which is difficult to determine, are needed to describe the temperature dependence of the viscosity of a fragile system, whereas for the bond-strength-coordination number fluctuation model, a single equation with clear physical meaning describes the temperature dependence of the viscosity of both, the fragile and strong systems. We have also studied the relationship between the normalized temperature range of cooperativity and the fragility index. A theoretical expression for the relationship has been derived based on the bond-strength-coordination number fluctuation model. The comparison with the experimental data shows a good agreement, leading to the conclusion that the kinetic properties of glass forming liquids and the cooperativity of molecular relaxations are correlated.

Keywords Fragility · Glass forming materials · Glass transition · Viscosity

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Introduction

The theory on the temperature dependence of dynamical properties such as viscosity in supercooled melts, polymeric materials, glasses, etc. is of a particular interest from both, the fundamental and applied science point of view. Among these, the strong-fragile concept has played an important role for the understanding of fundamental properties of these kinds of materials [1–3]. The so-called Angell's plot which is described as the logarithm of the viscosity η versus the reduced inverse temperature T_g/T (T_g being the glass transition temperature) characterizes fragile and strong systems based on the degree of deviation from the Arrhenius behavior. For highly polymerized network glass formers such as SiO_2, nearly straight lines in Angell's plot are observed (strong systems). In contrast, in systems with non-directional interatomic or intermolecular bonds such as ionic or organic liquids, deviation from Arrhenius behavior is observed (fragile systems). Although many studies have been done, the detailed microscopic mechanism responsible for the degree of fragility is still under intensive debate.

The relationship between the kinetic properties of glass forming liquids and the cooperative molecular relaxations in some polymeric materials has been studied recently by Saiter et al. [4]. They have studied the variation of the temperature difference $\Delta T = T_c - T_k$ with the fragility index m. T_c is a critical temperature that demarcates the transition from a non-cooperative relaxation process to a cooperative one as defined in the random walk model [5, 6] and T_k is the Kauzmann temperature. It has been found that the lower the fragility index, the greater the temperature range of cooperativity ΔT [4].

In the present paper, a comparative study on the temperature dependence of the viscosity in a family sample of unsaturated polyester resin is presented based on the bond-strength-coordination number fluctuation model proposed by one of the authors [7] and the random walk model [5, 6]. An analytical expression that relates the normalized temperature range of cooperativity $(T_c - T_k)/T_g$ and the fragility index m has been also derived.

Random walk model

The random walk approach used for the description of structural unit dynamics in configurational space has successfully explained the super-Arrhenius and Arrhenius-type temperature dependence of viscosity for the weakly bonded and strongly bonded melts, respectively [5, 6]. The model assumes the existence of two types of excitations in viscous liquids. The first type is the elastic excitations which neither change the microscopic structure of the liquid nor contribute to viscous flow and loss phenomena. The second type is the inelastic excitations, in which the displacements of structural units in configurational space give rise to phenomena associated with energy-dissipating processes such as the viscous flow. Due to strong interactions between molecules in viscous liquids, their movements must be highly cooperative. According to the model, the transition from a non-cooperative relaxation process to a cooperative one occurs at the critical temperature T_c, that characterizes a dynamical singularity at which the nonlinearly coupled density fluctuations vanish. This transition has been considered as a jump of the structural unit in a multidimensional configurational space.

For weakly bonded melts, two characteristic regimes separated by T_c appear in the temperature dependence of the viscosity. In the low temperature regime $(T < T_c)$, over-barrier jumps are rate-limiting and the temperature dependence of the viscosity is given by [5, 6]

$$\eta = \eta_0[\pi/2(\alpha-1)]^{1/2}\alpha^{(2\alpha-3)/2(\alpha-1)}[\Gamma(1/\alpha)]^{-1} (T_0/T)^{(2-\alpha)/2(\alpha-1)}\exp[(\alpha-1)(T_0/\alpha T)^{\alpha/(\alpha-1)}], \quad (1)$$

where η_0 accounts for the contribution of structural unit jumps via fluid states to the viscosity, α is the parameter that characterizes the fragility. Γ is the statistical Gamma function and T_0 is a temperature proportional to the width of the density of possible metastable state which is given by

$$g(E) = (\alpha/2k_B T_0)[\Gamma(1/\alpha)]^{-1}\exp[+|E/k_B T_0|^{\alpha}], \quad 1 < \alpha < \infty, \quad (2)$$

where k_B is the Boltzmann constant. For $\alpha = 2$, Eq. 2 yields a Gaussian density of possible metastable state function. On the other hand, in the high temperature regime $(T > T_c)$, it is assumed that the fluctuations in the energy landscape are enough to eliminate the energy barriers that separate the adjacent local energy minima. In this case, the temperature dependence of the viscosity is given by [5, 6]

$$\eta = \eta_0 2^{(2\alpha-1)/2(\alpha-1)}(1/\alpha)\Gamma(1/\alpha)(T_0/T)\exp[(\alpha-1) (1-2^{-1/(\alpha-1)})(T_0/\alpha T)^{\alpha/(\alpha-1)}]. \quad (3)$$

For strongly bonded melts, the energy required for bond breaking E_d has been added to the contribution of ground state energies [5, 6]. For this case, the density of possible metastable state is written as

$$g(E) = (\alpha/2k_B T_0)[\Gamma(1/\alpha)]^{-1}\exp[-|(E-E_d)/k_B T_0|^{\alpha}], \quad 1 < \alpha < \infty. \quad (4)$$

The temperature dependence of the viscosity is derived from Eq. 4 as

$$\eta = \eta_0[\pi/2(\alpha-1)]^{1/2}\alpha^{(2\alpha-3)/2(\alpha-1)}[\Gamma(1/\alpha)]^{-1} (T_0/T)^{(2-\alpha)/2(\alpha-1)}\exp[(T_d/T)+(\alpha-1)(T_0/\alpha T)^{\alpha/(\alpha-1)}], \quad (5)$$

where $T_d = E_d/k_B$. Under the condition $T_d \gg T_0$, the temperature dependence of the viscosity given by Eq. 5 becomes Arrhenius-like, particularly when $T \approx T_0$.

Bond-strength-coordination number fluctuation model

In this model, the melt is considered as an agglomeration of structural units, which give a solid physical background to understand the concept of fragility. According to the model, the viscous flow occurs when the structural units move from one position to another by breaking the bonds connecting them. Each structural unit is bound to other structural units by a certain bond strength [7]. By lowering the temperature of the system, the viscosity of the melt increases due to the increase in the connectivity between the structural units and at the glass transition temperature, the spatial distribution of structural units is frozen. From such considerations, the temperature dependence of the viscosity obtained by adopting a Gaussian distribution of binding energy E and coordination number Z is given by [7]

$$\ln(\eta/\eta_{T_g}) = \ln(\eta_\infty/\eta_{T_g}) + \frac{Cx + Cx^2\left\{\left[\ln(\eta_{T_g}/\eta_\infty)+\frac{1}{2}\ln(1-B)\right]\frac{(1-B)}{C} - 1\right\}}{1-Bx^2} - \frac{1}{2}\ln(1-Bx^2), \quad (6)$$

where

$$C = \frac{E_0 Z_0}{RT_g}, \quad B = \frac{(\Delta E)^2(\Delta Z)^2}{R^2 T_g^2} \quad \text{and} \quad x = T_g/T. \quad (7)$$

η_∞ is the viscosity at high temperature limit considered here as material independent. Based on experimental data, the value of 10^{-5} Pa s is commonly used [8]. The usual value of the viscosity at the glass transition temperature $\eta_{T_g} = 10^{12}$ Pa s is adopted [8]. C contains information about the total bond strength of the structural unit and B gives its fluctuation. E_0 is the average value of the binding energy between the structural units and Z_0 is the average value of the coordination number of the structural units. ΔE and ΔZ are the fluctuations of E and Z, respectively. R is the gas constant. According to the model, the fragility index is written as [7]

$$m_{BC} = \frac{B - C + 2\left[\ln\left(\frac{\eta_{T_g}}{\eta_\infty}\right) + \frac{1}{2}\ln(1-B)\right]}{\ln(10)(1-B)}. \tag{8}$$

Equation 8 is remarkable in that, if data of temperature dependence of the viscosity near T_g are known, information about microscopic quantities used in the present model can be extracted. This is an important step for the understanding of microscopic mechanism responsible for the degree of fragility in materials. As many studies show, the determination of the fragility index allows the characterization of different glass forming materials [9–13].

Temperature dependence of the viscosity: a comparison

From Eqs. 1 and 3 we can derive respectively, the following equations,

$$\ln(\eta/\eta_{T_g}) = [(2-\alpha)/2(\alpha-1)]\ln x + [1 - x^{\alpha/(\alpha-1)}](1-\alpha)(T_0/\alpha T_g)^{\alpha/(\alpha-1)}, \quad (T < T_c), \tag{9}$$

$$\ln(\eta/\eta_{T_g}) = \ln x + [1 - x^{\alpha/(\alpha-1)}](1-\alpha)(1-2^{-1/(\alpha-1)})(T_0/\alpha T_g)^{\alpha/(\alpha-1)}, \quad (T > T_c). \tag{10}$$

In Fig. 1 we have shown the application of these equations for the description of the temperature dependence of the viscosity for a family sample of unsaturated polyester resin (with styrene content of 25, 30, 35, and 40%W/W) [4]. The normalized crossover temperature T_g/T_c which demarcates the frontier between the low temperature regime and the high temperature regime is denoted by the dashed line. Data of α and T_0 are taken from [14] whereas the values of T_g and T_c are taken from [4]. In Fig. 1, we have also shown the behavior described by the bond-strength-coordination

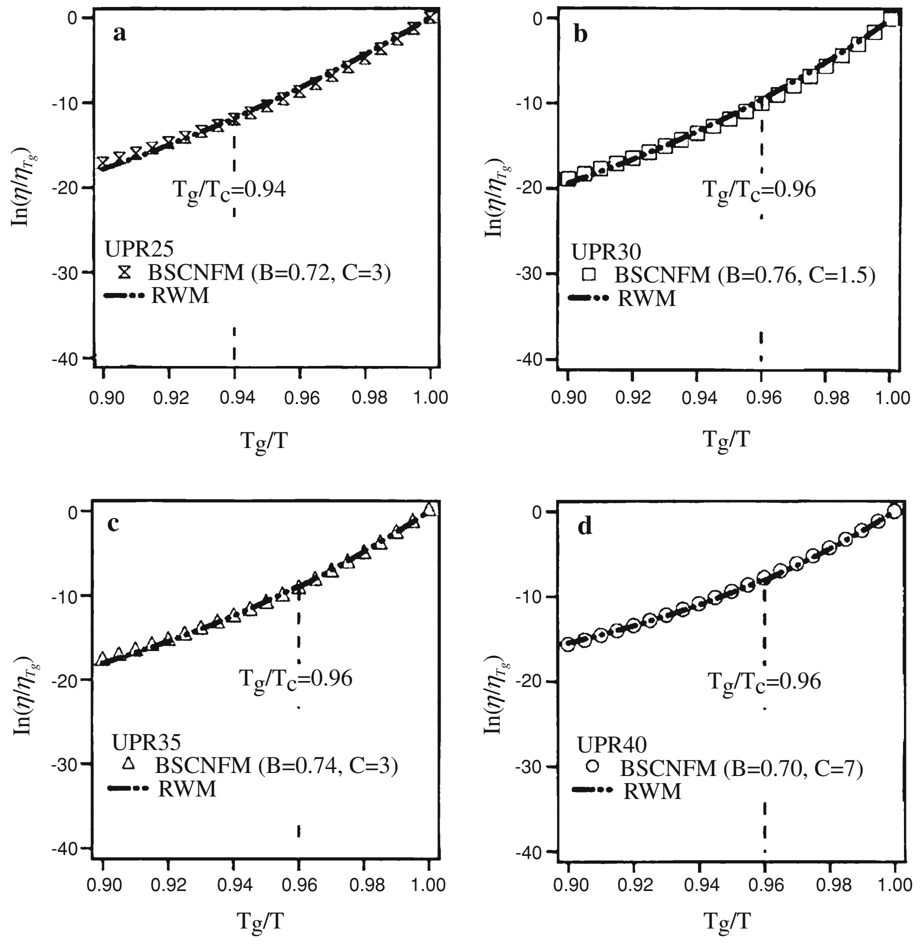

Fig. 1 Temperature dependence of the viscosity described by Eq. 6, (BSCNFM) and Eqs. 9 and 10, (RWM) for UPR25 (**a**), UPR30 (**b**), UPR35 (**c**), and UPR40 (**d**)

number fluctuation model given in Eq. 6, by choosing adequately the values of B and C. We can see that the agreement between both models is excellent. It should be noted however that, in the random walk model, two equations are needed to describe the temperature dependence of the viscosity of a fragile system. Furthermore, the determination of the critical temperature T_c is difficult [15]. On the other hand, in the bond-strength-coordination number fluctuation model, a single equation with clear physical meaning describes the temperature dependence of the viscosity of both, the fragile and strong systems. For the analysis of experimental data, the bond-strength-coordination number fluctuation model is preferable, because we do not need to invoke to two equations and because we do not need T_c. However, it is worth to mention that, strictly speaking, the values of the parameters B and C are valid in a limited temperature range due to the fact that E and Z have been assumed to be temperature independent quantities. To improve the agreement with experiments in a large range of temperature, we must take into account, without altering the physical background of the model, the temperature dependence of the binding energy between the structural units E and the coordination number of the structural units Z [16].

Relationship between the fragility index and the normalized temperature range of cooperativity

The comparison between the two models given in the previous section prompts us to investigate the temperature range of cooperativity $\Delta T = T_c - T_k$ in terms of our model. Recently [17], it has been shown that the bond-strength-coordination number fluctuation model of the viscosity, proposed by one of the authors [7], incorporates the well known Vogel–Fulcher–Tammann (VFT) relation. There, a theoretical relationship between B and C that reproduces the VFT relation has been derived,

$$\begin{aligned} C &= \frac{2\gamma(1-B)}{2\gamma + \sqrt{B}(1+\gamma^2)}\left\{\ln(\eta_{T_g}/\eta_\infty) + \frac{1}{2}\ln(1-B)\right\}, \\ \gamma &\equiv \frac{|\Delta E|/E_0}{|\Delta Z|/Z_0} = 1. \end{aligned} \tag{11}$$

Here, γ gives the ratio of the normalized bond-strength-fluctuation to the coordination number fluctuation. On the other hand, usually it is considered that the Kauzmann temperature is similar to the ideal glass transition temperature appearing in the VFT relation [18]. Based on these observations, in the present study, we have derived the following theoretical expression for the normalized temperature range of cooperativity,

$$\frac{T_c - T_k}{T_g} = \frac{1}{x_c} - \left[1 - \frac{\left(\frac{1+\sqrt{B^*}}{1-B^*}\right)C^* - \frac{1}{2}\ln(1-B^*)}{m\ln(10)}\right], \tag{12}$$

where x_c represents the reduced inverse temperature T_g/T_c. B^* and C^* denote the values of B and C that obey Eq. 11.

The behavior of the normalized temperature range of cooperativity $(T_c - T_k)/T_g$ versus the fragility index m is shown in Fig. 2. We can see that the model reproduces reasonably well the experimental values [4]. The figure indicates also that the temperature range of cooperativity and the fragility are correlated.

Discussion

The result shown in Fig. 2 follows the results reported by other authors [19–22]. In these studies, there were shown that the higher the fragility index, the lower the value of T_c/T_g. According to Angell [21], the basic properties of relaxing liquids are correlated through the fragility. Large value of temperature range of cooperativity corresponds to a small value of fragility index as has been discussed earlier [4], for the materials under consideration here. The

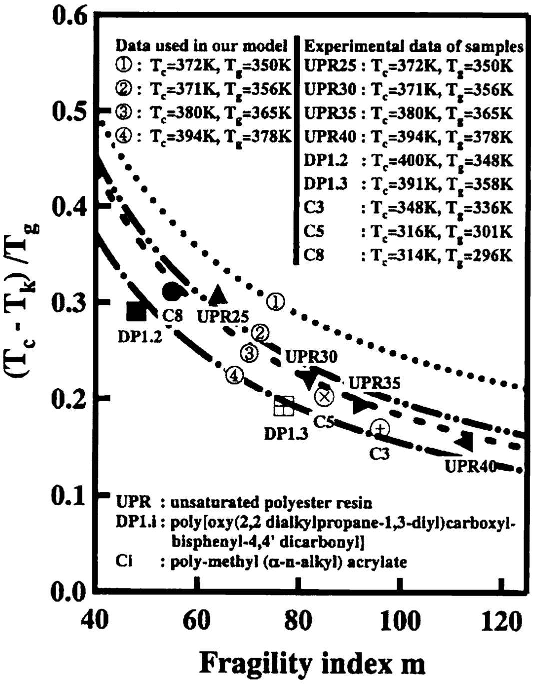

Fig. 2 The relationship between the normalized temperature range of cooperativity and the fragility index for three sample families of polymeric materials. The numbers after the name of the chemical compound represent the styrene content (in %W/W), the number of carbon atoms in the lateral chain, and the number of carbon atoms of the side chain attached to the tertiary carbon of the propyl spacer for UPR, C, and DP1, respectively

materials trend shown in Fig. 2 relates also with the chemistry of the materials. For instance, by increasing the styrene concentration, the distance between the polyester chain is increased, which results in the greater degree of freedom for molecular relaxation. Such a behavior is reflected in the value of the fragility that increases with the addition of styrene. The average barrier height that a structural unit must crossover to relax decreases when the fragility of the system increases [23]. The decrease of the interactions between the chains results also in the decrease of the temperature range of cooperative relaxation, which is the trend observed in Fig. 2. The relaxation process in the glassy state is a cooperative phenomenon and the motion of a molecule depends on neighbor's motions. The rearranging movement of one structural unit is only possible if a certain number of neighboring structural units is also moved [11, 24]. The glass transition engages cooperative molecular movements, which are time and temperature dependent. The relaxation function $\Phi(t)$ which characterizes these movements is usually represented by a normalized stretched exponential function [25, 26]

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \quad 0<\beta<1, \tag{13}$$

where β is a parameter inversely related to the width of the distribution of relaxation time τ. For UPR samples, it has been shown that β spreads between 0.1 and 0.3 [26]. The low values of β reflect a very wide distribution of relaxation times, implying the existence of a large number of potential minima available to the molecules during their relaxation. The values of the fragility index change from 64 to 113 for UPR as the styrene concentration increases (from UPR25 to UPR40), reflecting a character that becomes more fragile. For the DP1.1 samples, by changing the length of the lateral chain, from DP1.2 to DP1.3, the interactions between the main chains are changed and the values of the fragility index change from 48 to 77. Similarly, by changing the number of carbon atoms of the lateral chains in CI samples (from C8 to C3), the fragility index changes from 55 to 96, due to the change in the magnitude of the interactions between these lateral chains, the shorter the lateral chain, the weaker the interactions [4].

Conclusions

In this study, we have shown that the bond-strength-coordination number fluctuation model and the random walk model describe the same behavior if judicious parameters of B and C are to be chosen for the materials under consideration. We have also studied the fragility index dependence of the normalized temperature range of cooperativity. It is shown that the smaller the fragility index, the greater the normalized temperature range of cooperativity. This means that the kinetic properties of glass forming liquids, as given by the fragility index, and the cooperative molecular relaxations of the formed glass are correlated. An analytical expression for the relationship has been derived based on the bond-strength-coordination number fluctuation model. The results are consistent with the fact that a low value of the fragility index corresponds to strong molecular interactions, while a high value of m corresponds to weak molecular interactions.

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