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Relation between structural and secondary relaxation in glass formers: the ratio between glass transition temperature and activation energy

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The relation between structural and secondary dynamics is one of the most recently considered and possibly important issue of the dynamics in glass formers. One relation of interest is the ratio between the activation energy of the secondary relaxation and RT_g , where T_g is the glass transition temperature and R is the gas constant. This relation has been recently rationalized by the Coupling Model in terms of many body dynamics and it was applied to the intermolecular Johari-Goldstein secondary relaxation. The scope of this article is to investigate the pressure dependence of this ratio and to verify the validity of the Coupling Model prediction in such conditions.

1 Introduction

Relaxation dynamics of glass formers presents a complex scenario, characterized by many processes occurring over a time scale of more than 10 decades. Studies devoted to the understanding of the glass transition were usually focused on the slow relaxation process, called structural process, which was considered the most important molecular mechanism leading to the glass transition. However, already from the pioneering work of G.P. Johari and M. Goldstein [1] it was suggested that a secondary process, faster than the structural, can be identified in all the glass formers originating from localized motion of the whole molecule. The relevance of such process, nowadays called Johari-Goldstein, JG, secondary relaxation [2], has been underestimated for a long time. Recently some experiments proved that in non-rigid glass formers, like in the rigid glass formers in the initial study by Johari and Goldstein, a secondary relaxation reflecting the localized motion of the whole molecule really exists [3-6]. Also the structural process involves the motion of the whole molecule, but differently from the secondary process, it is cooperative. Since the former process occurs after the latter and they both reflect the motion of the whole molecule a connection between them is not totally unexpected. In fact, many studies evidenced the existence of such relation [7-12]. In particular one of these relations is the ratio $E_a/(RT_g)$ first examined by A. Kudlik and co-workers [13]. Here E_a is the activation energy of the secondary relaxation time in the glassy state, T_g is the glass transition temperature, and R is the gas constant. Not all secondary relaxations considered by A. Kudlik et al. are JG secondary relaxations. The ratio was examined exclusively for JG secondary relaxations by K.L. Ngai and S. Capaccioli and it was derived from the Coupling Model (CM) to be given by [8]

$$E_a/(RT_g) = 2.303 [(1-n) \cdot \log \tau_\alpha(T_g) + n \cdot \log t_c - \log \tau_\infty] \quad (1)$$

where $\tau_{\alpha}(T_g)$ is the structural relaxation time at T_g , $t_c \approx 2$ ps is the characteristic time of the CM for molecular liquids, and n is the coupling parameter appearing in the Kohlrausch correlation function, $\exp\{-(t/\tau_{\alpha})^{1-n}\}$, for the structural relaxation. Such relation connects the temperature dependence of the JG relaxation below T_g as represented for its relaxation time by $\tau_{JG} = \tau_{\infty} \exp[E_a/(RT)]$ to the structural process (represented by n , $\tau_{\alpha}(T_g)$, and T_g). The validity of this relation has been proven true for many JG secondary relaxations at ambient pressure [8].

In the recent years, the investigations of dynamics by varying pressure P and temperature turn out to be instrumental for testing the validity of models and relations among the different parameters [11,12,14,15]. A property of the α -relaxation is that n is invariant to different combinations of P and T that maintain τ_{α} constant [16], which is also consistent with the CM. This consistency was previously discussed in Ref. [16] where readers can find more details. Hence Eq.(1) would predict the ratio $E_a/(RT_g)$ to be constant provided $\tau_{\alpha}(T_g)$ is uniformly defined to be the same for all pressures. Slight variation of τ_{∞} with pressure may alter somewhat the expected constancy of the ratio $E_a/(RT_g)$. The aim of this paper is to test the validity of the relation in Eq. (1) in mixtures and neat glass formers studied at different pressure conditions.

2 Experiment

The systems herein considered are three neat glass formers, namely polyphenylglycidylether (Aldrich, $T_g=262$ K), dipropyleneglycol dibenzoate (Aldrich, $T_g=220$ K), diglycidylether of bisphenol-A (Aldrich, $T_g=254$ K), and three different mixtures containing 5% of quinaldine (Aldrich, $T_g=180$ K) in tristyrene (Polymer Standard Service, $T_g=234$ K), 5% QN-3Styr, 10% of quinaldine in tristyrene, 10% QN-3Styr, and 5% of quinaldine in oligostyrene with molecular weight 800 g/mol (Scientific Polymer Product, $T_g=282$ K), 5% QN-PS800.

Dielectric spectroscopy measurements were performed in the frequency interval 10^{-2} Hz -10 MHz, using the Novocontrol Alpha Analyzer. Dielectric spectra were measured isothermally, after stabilizing the temperature within 0.1 K. For measurements at ambient pressure the sample was placed in a parallel plate cell (diameter 30 mm, gap 0.1 mm) and the temperature was controlled with a precision better than 0.1 K by using a conditioned dry-nitrogen stream. For measurements at high pressure different cells have been used according to the sample to be investigated. The cell was inserted inside a pressure chamber where pressure variations, generated by a manual pump, were transmitted through a hydraulic circuit filled with silicon oil. During high pressure measurements the temperature was controlled in the interval 353-233 K within 0.1 K through a liquid thermal bath connected to a thermal jacket wrapped around the pressure chamber.

3 Results and discussion

In the glassy state of the neat glass formers herein considered, there are two secondary relaxations, and in the case of mixtures there is only one. In the experiments on binary mixtures of rigid polar molecule (QN) in apolar matrices (3Styr and PS800) we probed selectively the relaxation dynamics of polar QN molecules. In fact, the dipole moment, μ , of the latter is about a factor 10 larger than that of the host component whose contribution to the dielectric signal is consequently negligible (in fact, the dielectric relaxation strength is $\propto \mu^2$). On the basis of dynamic properties, such as the correspondence of the JG relaxation time to the relaxation time of the primitive process of the CM and the pressure sensitivity [2,7], it was already pointed out that the observed secondary process in mixtures and the low frequencies secondary process in the neat glass formers are of JG type [12,17-21]. In the remainder of the article we will consider the JG relaxation and hence only the slower secondary relaxation of the neat glass formers.

By decreasing the temperature under isobaric condition, the relaxation time of the structural process, τ_{max}^{α} , above T_g increases as usual and reaches the conventional value of 100 s at T_g (Fig. 1(a) reports τ_{max}^{α} in the Arrhenius plot for PPGE). τ_{max}^{α} is the relaxation time corresponding to the frequency of the α - loss peak. The increase of pressure produces an increase of density of the system and an increase of the value of T_g . The pressure dependence of the glass transition temperature, $T_g(P)$, has been tentatively interpreted in terms of entropy theories or simple fitted by some polynomials functions of the pressure [22-27]. In the case of our systems a second order polynomial is necessary to take into account the data in the full investigated pressure interval (Fig. 1(b)). The effect of pressure on secondary processes in general is less universal than on the structural and some of them are affected by pressure variations whereas some others are not. However, it is accepted that the JG secondary processes, reflecting the local motion of the whole molecule, are sensitive to pressure variations [2]. Since the increase of pressure produces a densification (a reduction of free volume) in the material it hinders the JG secondary relaxation. The temperature dependence of τ_{JG} in the glassy state is still described by the Arrhenius equation but with pressure dependent parameters (Fig. 1(b)), τ_{JG} is the analogous of τ_{max}^{α} for the JG process). In particular, it is expected that the increase of pressure hinders the local motion and consequently produces an increase of its activation energy (Tab. (1)). According to this consideration both activation energy and glass transition temperature are expected to increase with pressure but, to the knowledge of the authors, a connection between them is not provided by any theory but the CM. The verification of the pressure dependence of the ratio $E_a/(RT_g)$ is then interesting both to evidence any connection between the two parameters, and consequently between structural and secondary dynamics, and to verify the validity of the prediction of the CM, Eq. (1).

In all the systems the experimentally calculated value of $E_a/(RT_g)$ is almost constant and in the worst case the value is scattered within an error of 10% (Tab. 1), which is reasonable because the activation energy at high pressure can be estimated by data covering only three or two time decades resulting in a large uncertainty. The activation energy of DiPGDB at 530 MPa seems somewhat underestimated and this is the reason of such low value of the ratio (Tab. 1). However, we did not find any experimental reason to reject this value. The agreement of the experimentally determined values of $E_a/(RT_g)$ with those estimated by Eq. (1) is satisfactory over the whole pressure interval investigated (Tab. 1). It is evident that a connection between the JG secondary and structural relaxation: the vitrification of the system and the temperature dependence of the JG relaxation dynamics below T_g are strictly related. Eq. (1) can also help to explain the constancy, or the weak pressure dependence of the ratio $E_a/(RT_g)$. Since the value of n at $T_g(P)$ is constant, as commonly observed for Van der Waals liquids [16] with rare exception [28], as a direct consequence of Eq. (1) we obtain that the pressure variation of $E_a/(RT_g)$ is strictly related to the variation of $\log \tau_{\infty}$. Whenever the latter is constant the former is also constant, but even a variation with pressure of τ_{∞} of two orders of magnitude reflects in a variation of $\log \tau_{\infty}$ of two units, i.e. usually about 10% of $E_a/(RT_g)$. This variation is within the experimental error of the data.

Accordingly to this weak pressure dependence plotting the logarithmic of τ_{JG} as a function of $T_g(P)/T$ would result in collapsing all the data collected in different isobaric conditions on a single master curve. In fact we would obtain $\tau_{JG} = \tau_{\infty}(P) \cdot \exp[E_a(P)/(RT_g(P))] \cdot T_g(P)/T \approx a \cdot \exp[b \cdot T_g(P)/T]$, where a , b are pressure independent and in this expression we evidenced the pressure dependence of the parameters. In Fig. (2) the scaled data of PPGE are reported showing the predicted superposition.

Finally, it is to note that the agreement with Eq. (1) does not apply to all secondary relaxations. In fact Eq. (1) can be applied only to those secondary processes whose relaxation times at T_g correspond to the primitive relaxation time of the CM, i.e. the true JG β -relaxations. A straightforward test can be done in the neat systems here investigated. Using the data from literature for the fast (γ -) relaxation of DGEBA and PPGE at ambient pressure, it can readily calculated that $E_a/(RT_g)$ is about 13 for both systems and the value calculated from Eq. (1) is 21 [29], and for the γ - process of DiPGDB the predicted value is 23 to be compared with the

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experimentally obtained 17. This disagreement is a direct consequence of the intramolecular origin of the γ -process, i.e. they are not of JG type and their relaxation time at T_g differs from the primitive relaxation time. In fact it is usually believed that the fast secondary relaxation in DGEBA and in PPGE reflect local orientation of the epoxy group [30], and for DiPGDB we can suppose that it originates from the local motion of benzoate groups [17]. It would be interesting to investigate the pressure dependence of the ratio $E_a/(RT_g)$ for the non-JG process, but the data for this are still lacking.

4 Conclusion

The relation between secondary (JG) and structural relaxation process has been verified in the form of a relation between the glass transition temperature and the activation energy of the JG relaxation in the glassy state. The data of six different glass formers evidenced that such relation exist and for each system there is a characteristic value of $E_a/(RT_g)$ that weakly depends on pressure. Such value is found to be in agreement with that provided by the CM through the Eq. (1). The results from experiment are strictly valid for JG processes, and confirm the existence of a relation between structural and secondary JG dynamics in glass formers, as well as the validity of the CM description of such relation.

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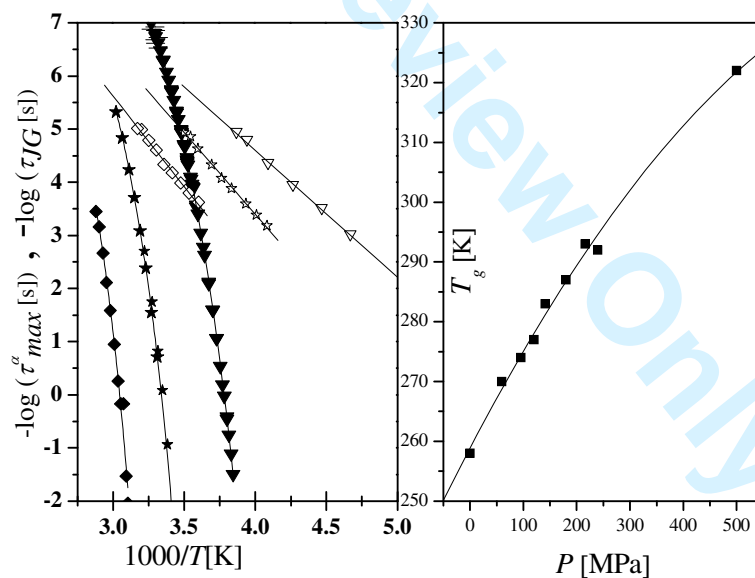


Fig. 1 (a) Arrhenius map of PPGE showing the structural (τ_{max}^{α} , closed symbols) and JG- secondary (τ_{JG} , open symbols) relaxation time as a function of inverse temperature for three different pressures: 0.1 MPa (triangles), 240 MPa (stars), and 500 MPa (diamonds). The lines are Vogel-Fulcher-Tammann and Arrhenius fit to the data. (b) Pressure dependence of the glass transition temperature ($\tau_{max}^{\alpha}(T_g) = 100$ s) for PPGE. Similar pressure dependence is characteristic for the other investigated systems.

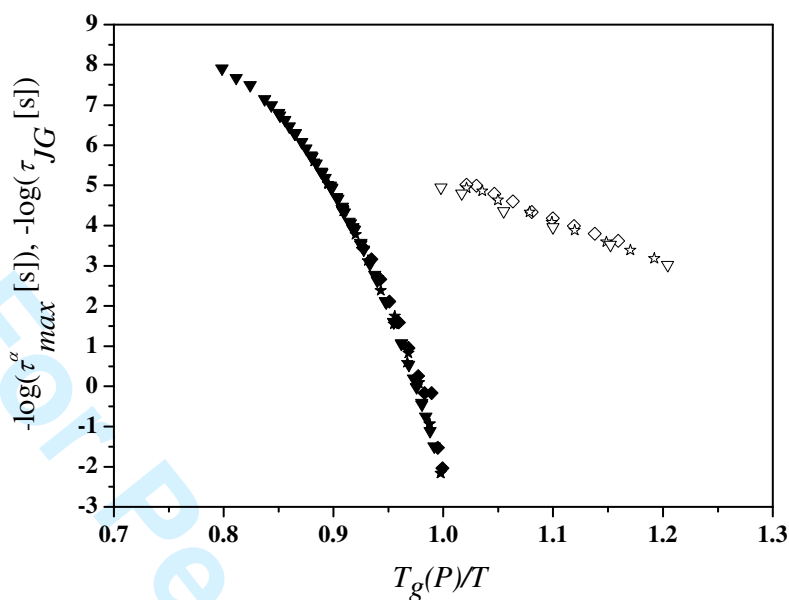


Fig. 2 Structural (closed symbols) and secondary (open symbols) relaxation time of PPGE as a function of inverse scaled temperature $T_g(P)/T$ for three different pressures: 0.1 MPa (triangles), 240 MPa (stars), and 500 MPa (diamonds). The meaning of the symbols is the same as in Fig. 1(a).

Table 1. Value of the ratio $E_a/(RT_g)$

	P [MPa]	$\log(\tau_c)$ [s]	E_a [kJ/mol]	T_g [K]	$E_a/(RT_g)_{exp}$	$E_a/(RT_g)_{Eq.1}$
DiPGDB	0.1	-14.7	50	220	27	26
	270	-17.2	66	269	29	31
	530	-14.0	56	300	22	24
PPGE	0.1	-14.1	46	258	21	19
	240	-15.6	59	294	24	23
	500	-15.8	66	322	24	23
DGEBA	0.1	-14.3	47	255	22	22
	400	-13.9	54	308	21	21
5% QN-3Styr	0.1	-16.9	52	226.0	28	27
	550	-17.0	71	300.0	28	27
10% QN-3Styr	0.1	-19.7	64	221.5	35	34
	180	-19.7	73	253.8	35	34
	380	-20.2	82	279.0	35	35
5% QN-PS800	0.1	-19.0	64	263.0	29	29
	180	-18.8	72	293.8	29	29
	350	-18.5	78	319.0	29	28

Tab. 1 Ratio $E_a/(RT_g)$ as calculated by Eq. (1) and by the experimental values of activation energy (fourth column) and glass transition temperature (fifth column). The values in column sixth and seventh are affected by an uncertainty ranging between 5-10%.