PHYSICAL REVIEW E VOLUME 56, NUMBER 5 NOVEMBER 1997

Dielectric relaxation of glass-forming epoxy resin under high pressure

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(Received 20 February 1997; revised manuscript received 14 July 1997)

Measurements of relaxation time in epoxy resin [poly(bisphenol *A-co*-epichlorohydrin), glycidyl end capped] in the supercooled liquid state have been carried out using dielectric spectroscopy over the frequency range from 10 mHz to 10 MHz as a function of pressure (up to $p=250$ MPa) and as a function of temperature. To our knowledge, this is the first time a two-dimensional surface of relaxation times $\tau=\tau(T,p)$ in epoxy resin has been plotted. The pressure and the temperature dependence of structural relaxation times are in good agreement with the extended Vogel-Fulcher-Tammann equation. For isobaric data, the fragility of the epoxy system reveals a tendency to decrease at elevated pressures. By using pressure as an additional variable, the influence of pressure on glass transition temperature T_g has been determined. [S1063-651X(97)07211-5]

PACS number(s): 64.70.Pf, 77.22.Gm, 65.50.+m

INTRODUCTION

It is well known that a liquid can be supercooled below its ordinary melting point. When the cooling process is continued the liquid becomes a disordered solid, i.e., a glass at some critical temperature T_g. The approach to glass is characterized by rapidly increasing viscosity and relaxation time. The temperature dependence of relaxation times near the glass temperature often shows a marked departure from the simple Arrhenius behavior with a temperature-independent activation energy [1–3]. This temperature dependence of relaxation time (or viscosity) for many supercooled liquids is usually described, at least approximately, by the Vogel-Fulcher-Tammann (VFT) equation [4]

$$\tau=\tau_0 \exp \frac{B}{T-T_0}. \tag{1}$$

At present, measurements of a relaxation time τ may extend over more than 14 decades; however, the theoretical description of the temperature dependence is still under discussion [5,6]. There is a great variety of functions for the analysis of the temperature dependence (see [7] and references therein), yet no basic theory fits the whole range of the temperature change of the relaxation time [8,9]. This situation seems to be fairly clear for polymeric [2,10] and macromolecular (for example, copolymers) glass-forming systems since the temperature dependence of the relaxation time is in good agreement with the VFT law.

The vetrification process can be induced by lowering the temperature and also by increasing the pressure at constant temperature. However, the majority of studies of liquid-glass dynamics have been performed under atmospheric pressure presumably due to the technical problems encountered at high pressures. Nevertheless, over the past few years some progress has been made in the study of the pressure evolution of the relaxation time (and viscosity) [11–19] and the scaling behavior for the pressure path [20]. Recent dielectric studies on phthalate derivatives [20], which belong to the fragile glass-forming liquids, indicate the applicability in this case of the pressure analog of the VFT relation

$$\tau=\tau_{0p}\exp\left(\frac{Ap}{p_0-p}\right), \tag{2}$$

where p_0 is the pressure of an ideal glass transition, $B=\text{const}$ and τ_{0p} denotes relaxation times in atmospheric pressure. This relation allows one to reproduce well experimental data covering over eight decades of relaxation times, particularly near the glass transition pressure p_g. However, attempts to study the temperature-pressure relaxation time ‘‘equation of state’’ for glass-forming liquids are rare. The understanding of the combined T and P dependences of relaxation time may provide more information about the influence of pressure on both fragility glass formers and glass temperature.

To analyze both the T and p dependences of τ, one can consider a generalized VFT equation in the form [21]

$$\tau=\tau_0\exp\left(\frac{B+b(p-0.1\ \text{MPa})}{T-[T_0+a(p-0.1\ \text{MPa})]}\right). \tag{3}$$

Relation (3) was obtained from Eq. (1) by applying the transformation proposed by Cohen and Grest [22],

$$B(p)\rightarrow B+b(p-0.1\ \text{MPa}), \tag{4a}$$

$$T_0(p)\rightarrow T_0+a(p-0.1\ \text{MPa}). \tag{4b}$$

Apart from preliminary studies by Leyser *et al.* [21] (using specific-heat spectroscopy) carried out for two isotherms in a limited range of τ (about three decades), the extended VFT relation has not yet been thoroughly tested.

Therefore, our chief aim is to examine the approach to glass transitions under isothermal and isobaric conditions and to test the extended VFT law. In particular, we wish to determine the influence of pressure on the glass transition temperature and the fragility parameter. In this paper, the measurements of the dielectric relaxation time in epoxy resin [Epidian 5, i.e., poly(bisphenol *A-co*-epichlorohydrin), glycidyl end capped] over a wide range pressure and temperature are presented. Epidian 5 was chosen for this study for several reasons: (i) it supercools readily, (ii) the relaxation

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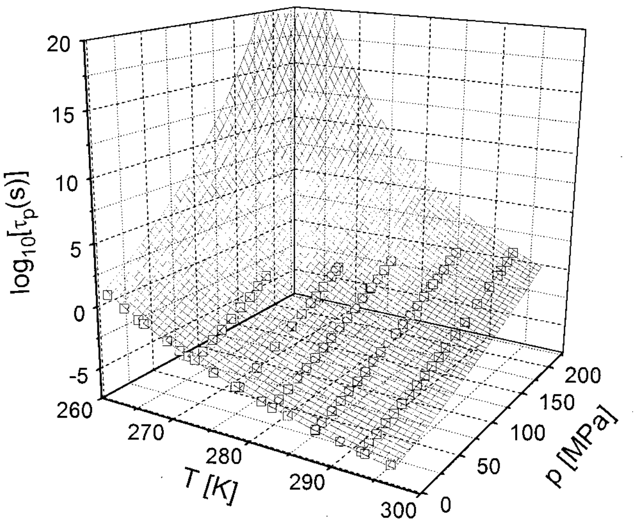


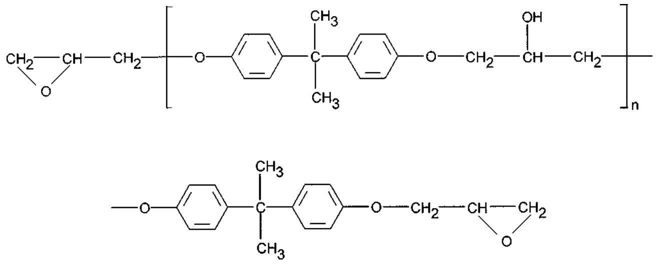
FIG. 1. Relaxation time of epoxy resin as a function of pressure and temperature. The data points describe a smooth two-dimensional surface within the range of values plotted. The wire surface is a fit of the dielectric data obtained by the extended VFT formula.

time can be varied over many orders of magnitude (a maximum of 8) over our temperature and pressure range, and (iii) it has a great dipole moment.

EXPERIMENT AND RESULTS

In order to measure the complex dielectric function $\varepsilon^*(\omega)$ in a frequency range from 10 mHz to 10 MHz, two different measuring systems, Solartron SI-1260 and Hewlett Packard 4192 A, were used. The relaxation time τ was calculated using the frequency of the maximum absorption peak. Pressure studies were performed on apparatus made by UNIPRESS. The pressure was measured by a Nova Swiss tensometric pressure meter with a resolution ± 0.1 MPa. The pressure chamber was thermostated with an accuracy better than 0.1 K. The temperature was controlled by means of a Keithely 195A with a platinum resistor (class A1, DIN 43760) that was located in the jacket of the chamber and a copper-constantan thermocouple was placed inside the pressure chamber. A more detailed description of the pressure apparatus can be found in our previous paper [23].

The measurements were conducted on Epidian 5. Epidian 5 belongs to the epoxy-resin family, which also contains other types of Epidians that differ in molecular weight. A polar glassy epoxy system, resulting from the reaction of epichlorohydrin with dian, can be generally presented as



Epidian 5 with an epoxy equivalent weight of about 390 was purchased from Sarzyna Chemical Company.

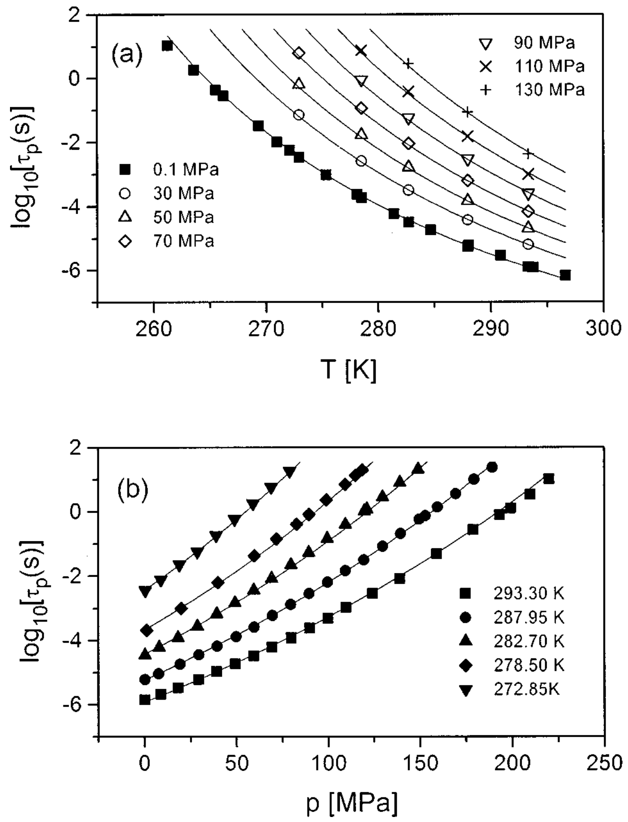


FIG. 2. (a) Isobaric and (b) isothermal data of relaxation times. Solid lines indicate the quality of the fit according to the extended VFT law.

Figure 1 shows the pressure and temperature dependences of relaxation times $\tau = \tau(p,T)$ obtained from dielectric measurements. It can be seen that data presented describe a smooth two-dimensional surface. The observed relaxation time increases with increasing pressure, similar to the divergence of τ when the glass temperature is approached by lowering the temperature at constant pressure. In Fig. 1 the wire surface is determined by the fit method according to the extended VFT equation (3). This fit produces the following value parameters: $B = 1259 \pm 60$ K, $b = 2 \pm 0.1$ K/MPa, $T_0 = 225 \pm 1$ K, $a = 0.086 \pm 0.004$ K/MPa, and $\log_{10}[\tau_0(s)] = -13.9 \pm 0.3$. In Figs. 1(a) and 2(b) the isobaric and isothermal projections of the experimentally obtained surface on τ-T and τ-p planes are shown, respectively. It can be seen that formula (3) describes the experimental points very well. Moreover, the fits of the isothermal data carried out from Eq. (2) have been included in Fig. 3 (the fits are denoted by solid lines). Fitting parameters are given in Table I.

We would like to stress that (a) relation (2) *cannot* be derived from Eq. (3); (b) in Eq. (3) one set of parameters (B,b,a,T_0,τ_0) describes the whole $\tau(pT)$ surface; (c) in general, values of pre-exponential factors τ_{0p} [in Eq. (2)] and τ_0 [in Eq. (3)] differ from each other: τ_{0p} represents relaxation time in atmospheric pressure and τ_0 is a characteristic time constant on the order of magnitude of 10^{-13} s; and (d) in Eq. (2) each isotherm requires a different set of parameters for each temperature. However, relation (2) is more convenient if isothermal data (not the whole surface) are analyzed.

It is assumed that the glassy state is entered at the glassy transition temperature T_g, characterized by a viscosity of the

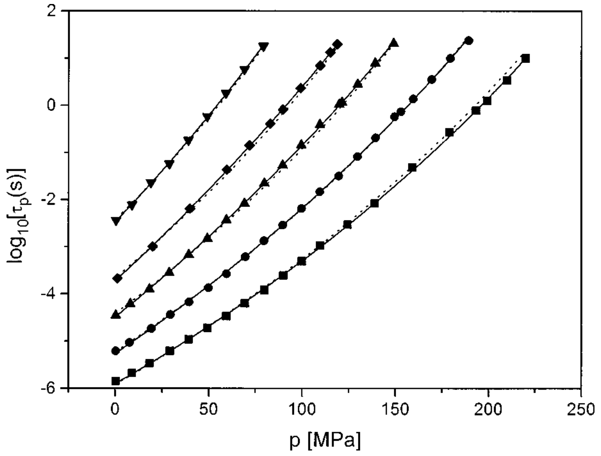


FIG. 3. Fits of isothermal data carried out from Eq. (2) (solid lines). The dashed lines are the fits according to the extended VFT law, which have already been shown in Fig. 2(b).

order of 10^{13} P, which implies a relaxation time exceeding 100 s. Assuming that $T=T_g$ for $\log_{10}\tau=2$, the values of T_g can be found for various pressures. Figure 4 shows the dependence between T_g and p obtained from experimental data. Additionally, the calorimetric glass transition temperature $T_g=260.6$ K in atmospheric pressure was determined from the middle point of the differential scanning calorimetry (DSC) scan at a 20-K/min heating rate. It is noteworthy that glass transition temperature $T_g=259.1$ K calculated from dielectric measurements is in good agreement with the one found from DSC.

The fragility parameter [24], as well as glass transition temperature, is one of the most important material constants. Considering isobaric data of τ, the extended VFT formula (3) can be rewritten as

$$\ln\tau=\ln\tau_0+\frac{DT_0(p)}{T-T_0(p)} \quad \text{for } p=\text{const.} \tag{5}$$

The material-dependent parameter D, the so-called strength parameter that appears in Eq. (5), is related to fragility. The most fragile glass-forming materials are those corresponding to small-D values (typically $D<10$). Comparing relation (5) to Eq. (3) and applying transformation (4), one can obtain a relation between parameter D and pressure, i.e.,

$$D=\frac{B+b(p-0.1\ \text{MPa})}{T_0+a(p-0.1\ \text{MPa})}.$$

TABLE I. Fitting parameters for the data in Fig. 3 using the $\tau=\tau_{0p}\exp[Ap/(p_0-p)]$ equation.

Glass former	T (K)	P_0 (MPa)	A	$\log_{10}[\tau_{\text{op}}(\text{s})]$
Epidian 5	293.30	802± 31	42± 2.5	−5.899±0.020
	287.95	789± 32	49± 2.5	−5.260±0.017
	282.70	835± 40	62± 3.5	−4.489±0.012
	278.50	885± 50	75± 5	−3.719±0.011
	272.85	733±127	72±14	−2.469±0.017

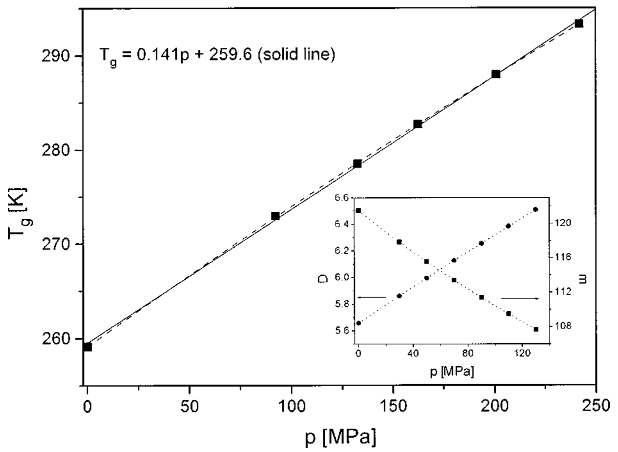


FIG. 4. Glass temperature T_g vs p for epoxy resin. The solid line is a linear approximation; however, second-order polynomial (dashed line) fits the experimental points better. The inset shows the pressure behavior of the strength parameter D (circle) and fragile parameter m (square). Dotted lines in the inset are a guide for the eye.

Another convenient measure for fragility can be introduced by focusing on the strength of the relaxation time increase at the glass transition, i.e.,

$$m=\frac{d\log_{10}\tau}{d(T_g/T)} \quad \text{for } T=T_g. \tag{6}$$

Using the extended VFT equation, a simple equation for this derivative can be achieved. The inset in Fig. 4 presents the pressure behavior strength parameter as well as the fragility parameter, which are related to each other. For tested epoxy resin under isobaric conditions, the fragility decreases slightly in high pressure. Owing to the low value of D and the observed non-Debye behavior of structural relaxation, Epidian 5 can be regarded as fragile system.

It would be interesting to follow the behavior of the shape parameters of the relaxation function and the half-width in the T-p plane. Unfortunately, above 10 MHz (out of our measurement window), a strong second relaxation process appears, which markedly influences the shape of the α relaxation peak, despite the fact that both peaks were well separated from each other in the studied range of τ. This analysis was discontinued since parameters characterizing only the α relaxation process could not be obtained (parameters that are not influenced by the second relaxation).

CONCLUSION

To our knowledge this is the first time a two-dimensional surface of relaxation times $\tau=\tau(T,p)$ in fragile epoxy resin, obtained by employing dielectric spectroscopy, has been reported. In conclusion, we have shown that the pressure and temperature dependences of the structural relaxation time are suitably described by the extended Vogel-Fulcher-Tammann equation in the whole p-T range in which the measurements were carried out. The extended VFT law is consistent with the free volume model. The good applicability of this equation for epoxy resin suggests that dynamics is governed by a simple volume-activated process. The same conclusion can be also drawn from the temperature measurements in other epoxy systems [25,26]. An additional task of this paper was to investigate of the influence of the pressure on the liquid to glass transition. The experimentally determined glass temperature seems to increase linearly with pressure only in the first approximation. It is noteworthy that the extended VFT equation (3) predicts a linear $T_g(p)$ dependence. Thus the VFT equation does a good job as long as the linear approximation of pressure dependence of T_g can be applied. In fact, second-order polynomial fits the experimental points better. Similar behavior of $T_g(p)$ for polymeric systems was also observed in p,V,T measurements that were performed by the hydrostatic method [27]. Measurements of strong glycerol reported elsewhere [28,29] in a wide pressure range exhibit a marked deviation from linearity as well. For isobaric data we noticed that the fragility of the epoxy resin reveals a tendency to drop in value at elevated pressures. Further pressure studies are clearly required to clarify this issue. Finally, we hope that the introduction of another independent variable, i.e., pressure, here and in subsequent experiments, will be reflected in theoretical research.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the State Committee for Scientific Research (KBN, Poland), Project No. 2 P03B 030 12.

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