

Dielectric and mechanical relaxation in epoxy systems with molecules of differing topology

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 9511

(<http://iopscience.iop.org/0953-8984/12/45/312>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 06:58

Please note that [terms and conditions apply](#).

Dielectric and mechanical relaxation in epoxy systems with molecules of differing topology

Marian Paluch

Max-Planck-Institut für Polymerforschung, Postfach 31 48, 55021 Mainz, Germany

and

Institute of Physics, Silesian University, ulica Uniwersytecka 4, 40-007, Poland

E-mail: paluch@mpip-mainz.mpg.d

Received 12 April 2000, in final form 24 July 2000

Abstract. Two epoxy systems with molecules having different topologies and functionalities, i.e. bifunctional linear and trifunctional star-like molecules, are characterized by means of both dielectric and mechanical spectroscopy methods in order to detect segmental and molecular relaxation rates as functions of temperature. The dielectric method is also used to determine the ionic conductivity effects in both systems. An effect of pressure at a constant temperature on the segmental relaxation times and on the conductivity is also investigated. We also examined coupling between the dc-conductivity relaxation process and α -relaxation process. As a result it was found that the dependence of the dc-conductivity relaxation time on the α -relaxation time can be described by means of the fractional Debye–Stokes–Einstein power-law relation. Like for our previous high-pressure results on other glass formers, it turns out that the pressure dependence of the α -relaxation time systematically deviates from the exponential form on approaching the glassy state.

1. Introduction

One of the most commonly used experimental methods for studying the molecular dynamics of supercooled liquids and glasses is broad-band dielectric spectroscopy. The reason for the success is the extremely wide range of probe frequencies, which allows one to track the evolution of the α -relaxation process over a time range exceeding 14 decades [1–4]. On the basis of such measurements, it has been demonstrated that on approaching the glass transition, the characteristic relaxation time (τ) of the α -process fails to obey simple activated behaviour as expressed by the Arrhenius form [2, 3]. This temperature dependence of τ is usually parametrized by means of the Vogel–Fulcher–Tammann (VFT) equation. However, the VFT law is useful for fitting the relaxation times only over a limited range of temperatures [5, 6].

It was also found from measurements of dielectric responses that the shape of the relaxation spectra of supercooled liquids is different from the Debye form as regards frequency and exponential decay in the time domain [7–10]. Therefore, experiments on the relaxation phenomena in glass-forming systems focus not only on the relaxation time but also on the shape of the spectra. Among other things, a great deal of effort has gone into the exploration of the scaling behaviour of the relaxation function for the α -process [11–15]. It was shown that the dielectric relaxation data for various liquids and temperatures could be successfully superimposed onto a master curve by a suitable scaling of the abscissa and ordinate [11, 15]. Although some controversy arose concerning the universality of such an approach [16–18],

this procedure has been frequently employed in the analysis of dielectric responses of low-molecular-weight glass-forming systems.

The relaxation spectra of glass-forming liquids obtained by means of dielectric methods are usually wider than that of the Debye process. The observed broadened shape of the dielectric spectra is considered to be related to the interactions arising from the close proximity of atoms and molecules in condensed matter. The interpretation of this phenomenon usually involves such concepts as relaxation time distributions and cooperative relaxation [19–22]. On the whole, the relaxation processes observed in condensed matter are a physical manifestation of dynamical properties of molecules.

In the present paper dielectric spectroscopy is employed to study the molecular dynamics of two epoxy systems with different topologies. We compare the dielectric relaxation behaviour of three-arm star-like molecules of glycerol propoxylate triglycidyl ether (EP3) and the low-molecular-weight linear polymer poly(propylene glycol)-bis(2, 3-epoxypropyl ether) (EP2). It is also of interest to examine how the differences in topology of these epoxies affect the dynamics of the α -relaxation process. Apart from the α -mode, we also observe an additional relaxation process in the dielectric spectrum of EP3, which is only visible in the high-temperature range. In order to understand the nature of this additional mode, mechanical measurements over the widest possible range of frequency were also carried out. Moreover, the effect of high pressure on the behaviour of the dielectric relaxation in EP3 is examined.

2. Experimental procedure

2.1. Samples

The poly(propylene glycol)-bis(2, 3-epoxypropyl ether) ($M_n = 380$) and glycerol propoxylate triglycidyl ether (Epoxye equivalent weight 620–680) were obtained from Aldrich Chemicals and were used as received. The chemical formulae of the two compounds are shown in figure 1. The glass transition temperature determined by means of differential scanning calorimetry is 197 K for EP2 and 203 K for EP3.

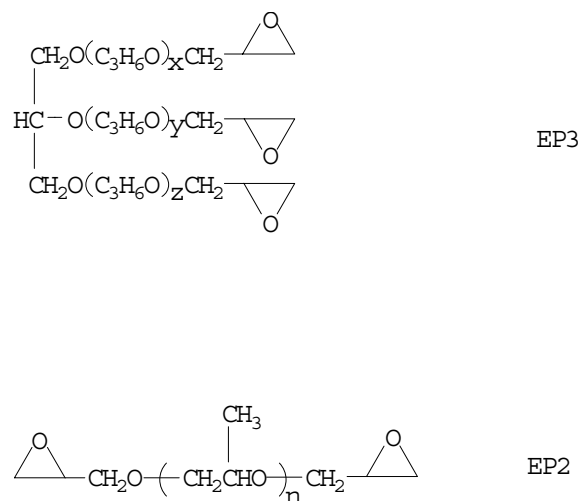


Figure 1. The chemical structures for the epoxies studied.

2.2. Dielectric spectroscopy

The temperature-dependent dielectric measurements were carried out using the experimental set-up made by Novo-Control GmbH. This system was equipped with a Solartron frequency response analyser SI 1260 and broad-band dielectric converter. We measured the complex permittivity: $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ over the frequency range of 10^{-2} – 10^6 Hz by placing the sample in a parallel-plate cell (diameter 20 mm, thickness 0.1 mm). The samples are in the liquid state at room temperature. Temperature was controlled using a nitrogen-gas cryostat and the temperature stability of the sample was better than 0.1 K.

For high-pressure studies we used a pressure system constructed by UNIPRESS with a home-made special flat parallel capacitor described in detail in [23]. The pressure-transmitting liquid was a mixture of hexane and silicone oil and pressure was measured by a Nova Swiss tensometric pressure meter with a resolution of 0.1 MPa. The sample tested was totally isolated from the medium delivering pressure and was in contact only with stainless steel, Teflon and quartz. The temperature was controlled within 0.1 K by means of a liquid flow provided by a thermostatic bath.

2.3. Mechanical spectroscopy

Dynamic mechanical measurements were performed by means of the Rheometrics RMS 800 mechanical spectrometer. Shear deformation was applied under conditions of controlled deformation amplitude, always remaining in the range of the linear viscoelastic response of the samples studied. The frequency dependencies of the storage (G') and loss (G'') shear moduli were measured at various temperatures. The parallel-plate geometry was used below 25 °C, with plate diameters of 6 mm. In the case of the plate–plate geometry, the gap between the plates (sample thickness) was about 1 mm. Experiments were performed under a dry nitrogen atmosphere.

The frequency dependencies of G' and G'' measured within the frequency range of 0.1–100 rad s⁻¹ at various temperatures were used to construct master curves representing a broad range of frequency dependencies of these quantities. Only shifts along the frequency scale were performed. This procedure provided a temperature dependence of the shift factors ($\log a_T$ versus T). The low-frequency range of the master dependence of G'' (with $G'' \sim \omega$, indicating the Newtonian flow range) was used to determine the zero shear viscosity at the reference temperature ($\eta_0(T_{ref}) = G''/\omega$). Viscosity values related to other temperatures were determined using $\eta_0(T) = \eta_0(T_{ref}) + \log a_T$. The relaxation time corresponding to the transition between the Newtonian flow range at low frequencies and the glassy range at high frequencies at the reference temperature has been determined as $\tau(T_{ref}) = 1/\omega_c$, where ω_c is the frequency at which the G' - and G'' -dependencies cross each other. Relaxation times at other temperatures are given by $\tau(T) = \tau(T_{ref}) + \log a_T$.

3. Results and discussion

In figure 2 the dependence of the dielectric loss ε'' on the frequency for supercooled EP3 at various temperatures is shown. For this material we observe a broad asymmetric peak corresponding to the α -relaxation process which is related to the dynamic glass transition. The primary relaxation process occurring in the dielectric spectra of both systems studied is mainly due to the orientation of the same polar group, the epoxy ring that carries a permanent dipole moment (2.1 D) [24]. At low frequencies, the conductivity process associated with mobility of ions in liquid gives rise to a steep increase in the dielectric loss in accordance with the

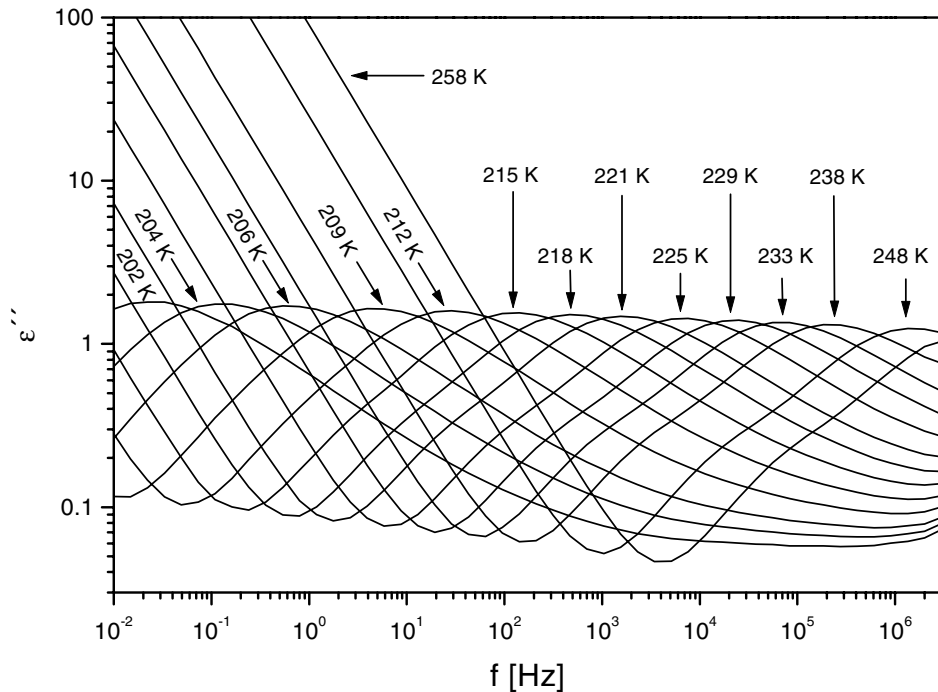


Figure 2. The frequency dependence of the dielectric loss ε'' for EP3 at the labelled temperatures. An additional relaxation process is visible in the low-frequency wings of the α -relaxation peak. The solid lines represent experimental data.

electrodynamic relation $\varepsilon'' = \sigma_0/\varepsilon_0\omega$, where σ_0 and ε_0 denote the dc electrical conductivity and the permittivity of vacuum, respectively. It can also be observed in figure 2 that an additional relaxation process takes place and we will call this the α' -mode below. This process with relatively small amplitude occurs on the low-frequency wing of the primary relaxation in the high-temperature range and is no longer observed in the vicinity of the glass transition. The disappearance of this additional relaxation process can most probably be attributed to a weaker temperature dependence of $\tau_{\alpha'}(T)$ in relation to $\tau_{\alpha}(T)$. Therefore, on approaching the glass transition, the faster α -relaxation process overlaps with the slower α' -mode. It is worth stressing that dielectric spectra of EP2 do not display the α' -mode at all. The molecular origin of this additional mode will be discussed in the remainder of this work.

A direct comparison of dielectric spectra of the two systems tested is presented in figure 3. In order to analyse the data in detail, $\varepsilon''(\omega)$ was fitted by means of a superposition of two Havriliak–Negami functions and a conductivity contribution:

$$\varepsilon'' = \frac{\sigma_0}{\varepsilon_0\omega} + \text{Im} \sum_{i=1}^2 \left(\varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1 + (i\omega\tau_{HN})^{\alpha}]^{\gamma}} \right) \quad (1)$$

where α_{HN} and γ_{HN} are the shape parameters which characterize the symmetric and asymmetric broadening of the spectrum.

The solid lines in figure 3 represent the fit according to equation (1). Although the above function provides an excellent fit to the experimental data, it is rather difficult to extract an unequivocal set of parameters due to strong overlap between α - and α' -modes. The following shape parameters were obtained from the fitting procedure: $\alpha_{HN} = 0.82 \pm 0.01$,

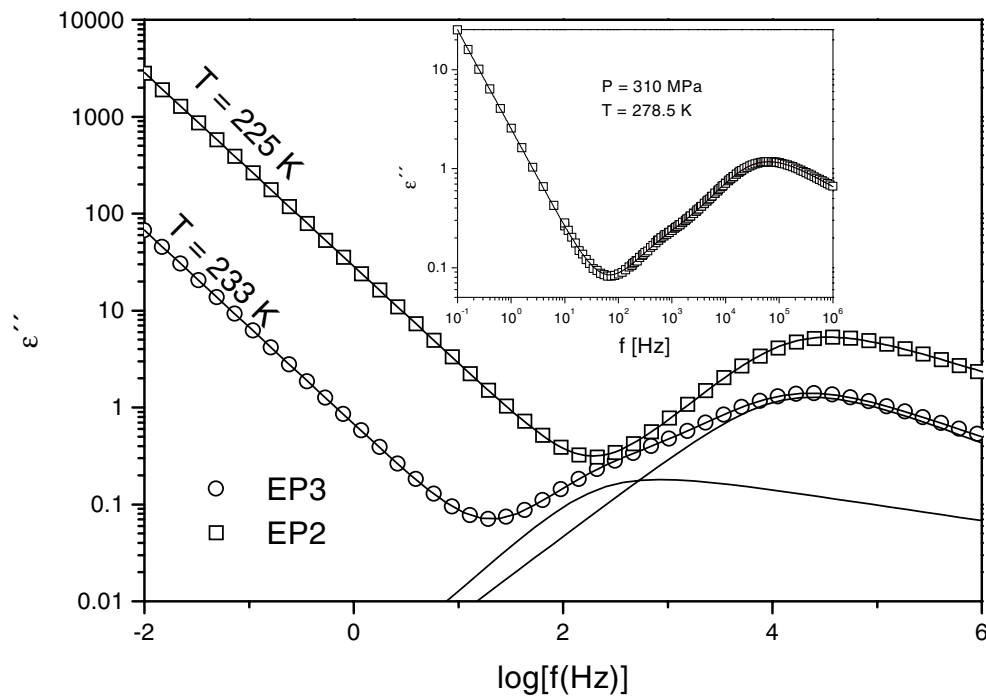


Figure 3. A comparison of the dielectric spectra of EP2 and EP3. The inset shows the frequency dependence of the dielectric loss ϵ'' measured under high pressure. The solid lines show the fits using equation (1).

$\gamma_{HN} = 0.5 \pm 0.02$ for the α -process and $\alpha_{HN} = 0.94 \pm 0.02$, $\gamma_{HN} = 0.17 \pm 0.05$ for the α' -process in EP3, and $\alpha_{HN} = 0.84 \pm 0.01$, $\gamma_{HN} = 0.48 \pm 0.02$ for the processes in EP2. As a result we found that the shapes of the absorption peaks of the α -processes are similar for the two systems examined and are almost temperature independent. A slight broadening of the primary relaxation was observed with decreasing temperature.

In a high-pressure study, the sample (EP3) was compressed from atmospheric pressure up to 0.35 GPa at different temperatures. Spectra were obtained that were analogous to those from the temperature-dependent measurements at ambient pressure. An example of the dielectric loss $\epsilon''(\omega)$ measured under high pressure is shown in the inset of figure 3. As before, the dielectric spectrum $\epsilon''(\omega)$ is fitted by means of equation (1) which provides a good description of the experimental data. The dielectric spectra of EP3 obtained under isothermal and isobaric conditions have the same shape. This suggests that the distribution function of the relaxation times is independent of temperature and pressure.

Evident differences in α -relaxation behaviour between EP2 and EP3 are only observed in the strength of relaxation. EP2 shows relaxation two times stronger than that of EP3. This result can be explained by the different packing of the molecules of EP2 with respect to that for EP3. The complex structure of the three-arm star-like molecules hinders the arrangement of dipoles, which contribute to the total dielectric response. There is also another possible explanation of the observed differences in strength of relaxation. Assuming the same value of density for the two liquids, the number of dipole moments in unit volume is much greater for EP2 than EP3. Therefore one can expect the total polarization of the sample to be larger for EP2.

Additional information on the α' -mode in EP3 was obtained from mechanical relaxation measurements. From the frequency dependence of the dynamic shear modulus G , one can determine the timescale of the local mobility of polymers as well as the motions of the whole polymer chain [25, 26]. The nature of the α' -mode can be better understood by a direct comparison of results from mechanical and dielectric relaxation experiments for EP3. However, when comparing data obtained from different spectroscopic techniques, a homogeneous representation has to be chosen to get a correct result [27, 28]. In the linear response regime the dielectric and mechanical responses are completely characterized by dynamic susceptibilities, i.e. mechanical shear compliance, J^* , and dielectric susceptibility, ε^* . Dynamic results can also be represented by means of a quantity called rigidity. In this case the relevant quantities are the mechanical modulus, G^* , and the dielectric modulus, M^* . In the frequency domain these quantities are related to each other by the following simple equations:

$$\varepsilon^* = \frac{1}{M^*} \quad (2)$$

$$J^* = \frac{1}{G^*}. \quad (3)$$

Although, in principle, the two representations are equivalent, there is no consensus as to whether the dynamic susceptibility or the modulus is appropriate for analysing relaxation data. In this context it is worth noting that susceptibilities refer to a retardation process whereas the modulus is related to a relaxation process [29]. Therefore, the characteristic time constants determined from the susceptibility data are retardation times, whereas the modulus representation can provide direct information on the relaxation times. Now, it is also obvious that a homogeneous representation has to be chosen to get correct results from comparison of data measured by different spectroscopic techniques. In order to compare the dielectric and mechanical data we used the modulus representation. Therefore, the dielectric spectra of the epoxies studied have to be converted to moduli by using equation (2). In figure 4 we show the master curves for G' , G'' and M' , M'' for EP3 which were constructed just by horizontal shifts of frequency spectra measured at various temperatures. The frequency dependencies of the storage (G') and loss (G'') moduli exhibit two relaxation modes. The α -process is visible at higher frequencies, whereas at lower frequencies, at a distance of about two decades, another process occurs which is believed to be related to a mobility of the whole EP3 molecule. These two relaxations correspond to the relaxation modes observed in the dielectric spectrum of M'' . Therefore, we believe that the α' -mode, which is observed in the dielectric spectrum of EP3, represents the overall motion of a three-arm star-like molecule. Thus, the dielectric measurements provide complementary information about the motion of a whole molecule as well as the mobility of the terminal epoxy groups as shown in EP3.

From figure 4 or 5, it is worth noting that the dc-conductivity relaxation in the electric modulus representation occurs now in the form of a Debye peak which is positioned at $\omega = \sigma_0/\varepsilon_s\varepsilon_0$ [30, 31]. Additionally, the spectrum of $M''(f)$ measured at the high pressure $P = 270$ MPa is also superimposed on the master plots in figure 4. The maximum of M'' , which corresponds to the dc process, is shifted towards higher frequencies in relation to identical peaks obtained at ambient pressure. This may be an indication that the dc relaxation process is not coupled in the same way with the α -process for the two thermodynamical variables: T and P .

An analysis analogous to that for EP3 was conducted for EP2. The master plots created for EP2 are depicted in figure 5. In that case, only the α - and σ -modes are observed in the dielectric modulus whereas segmental relaxation associated with the dynamic glass transition is visible in the mechanical modulus.

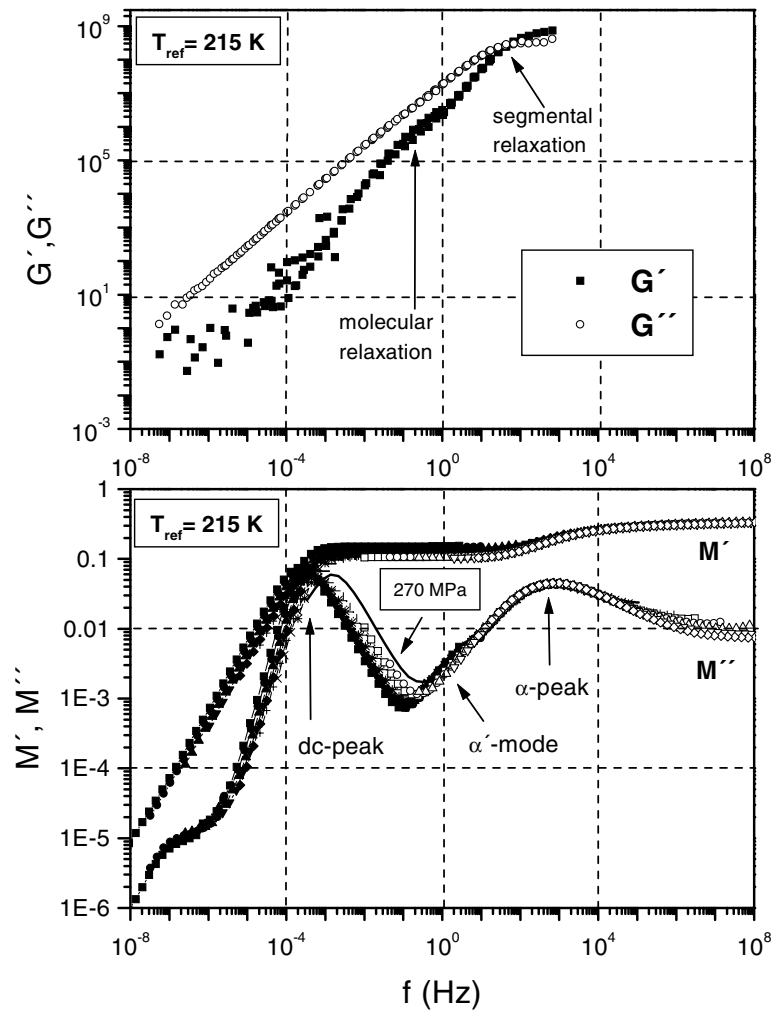


Figure 4. Top panel: the frequency dependences of G' and G'' (master curves) for EP3. Bottom panel: the master curves of M' and M'' constructed by shifting frequency spectra measured at various temperatures. The solid curve represents the dielectric spectrum obtained from high-pressure measurements.

The plots of the temperature dependences of all relaxation times determined for EP2 and EP3 are shown in figure 6. The characteristic time constants were determined from the modulus data as $\tau_\sigma = (2\pi f_\sigma)^{-1}$, $\tau_\alpha = (2\pi f_\alpha)^{-1}$, $\tau_\alpha^G = (2\pi f_\alpha^G)^{-1}$ where f_σ , f_α denote the frequency of the maximum of M'' for the dc and α -relaxation processes, respectively, and f_α^G is the frequency of the crossing point of G' and G'' . These dependencies exhibit clearly a non-Arrhenius behaviour over the whole temperature range studied. The relaxation times are found to evolve with temperature according to the VFT law: $\tau = \tau_0 \exp(D_T T_0 / T - T_0)$ [32]. The values of the VFT parameters obtained from the fitting procedure are collected in table 1. We can observe that nearly the same values of the strength parameters D_T for the processes considered were obtained for EP3. However, an analogous convergence was not found in the case of EP2. On the other hand, one can note that the temperature dependencies for the dc

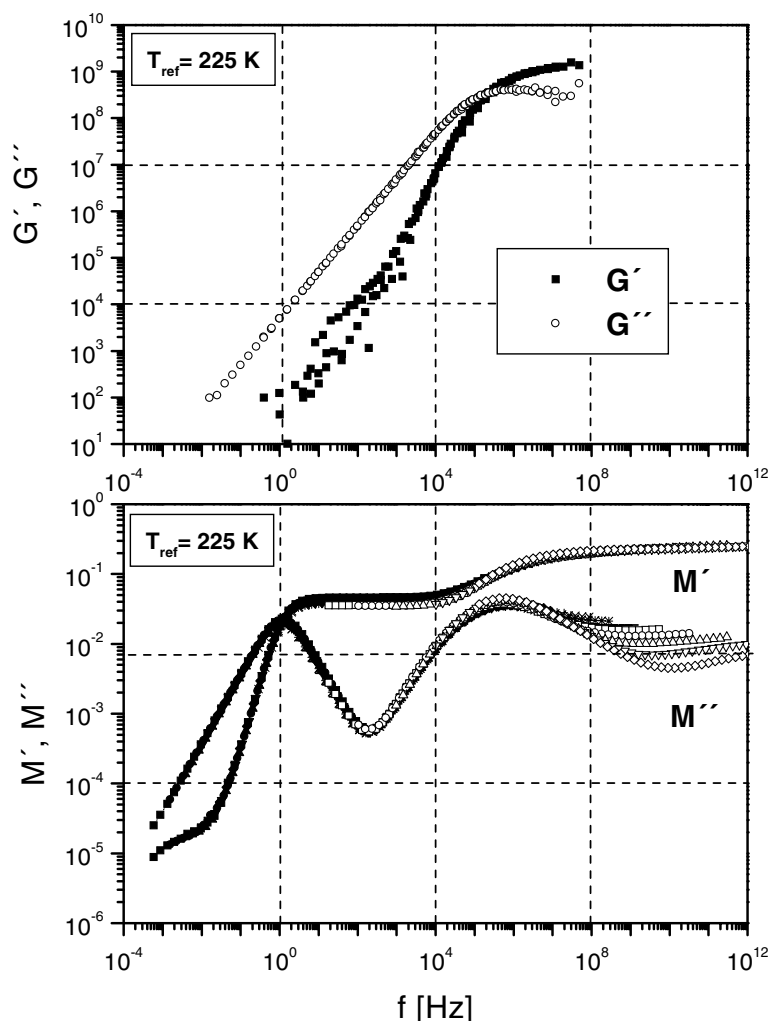


Figure 5. Top panel: the master curves of the frequency dependences of G' and G'' determined at various temperatures for EP2. Bottom panel: the frequency dependences of M' and M'' (master curves).

process in the two systems examined are very similar. This suggests that conductivity relaxation is weakly sensitive to differences in molecular topology. Owing to the low value of the strength parameter D_T for the α -process, both EP2 and EP3 can be classified as fragile systems.

The molecular dynamics of glass-forming liquids can be also controlled by changing the pressure. By using pressure as an additional thermodynamical variable, the effect of compression on molecular mobility in EP3 is analysed. In figure 7 we present relaxation times obtained for the dc and α -relaxation processes as functions of pressure. It can be observed that the α -relaxation is more pressure sensitive than the dc conductivity. Both pressure dependencies can be reproduced very well with a phenomenological expression [33–35]:

$$\tau = \tau_a \exp\left(\frac{D_P P}{P_0 - P}\right) \quad (4)$$

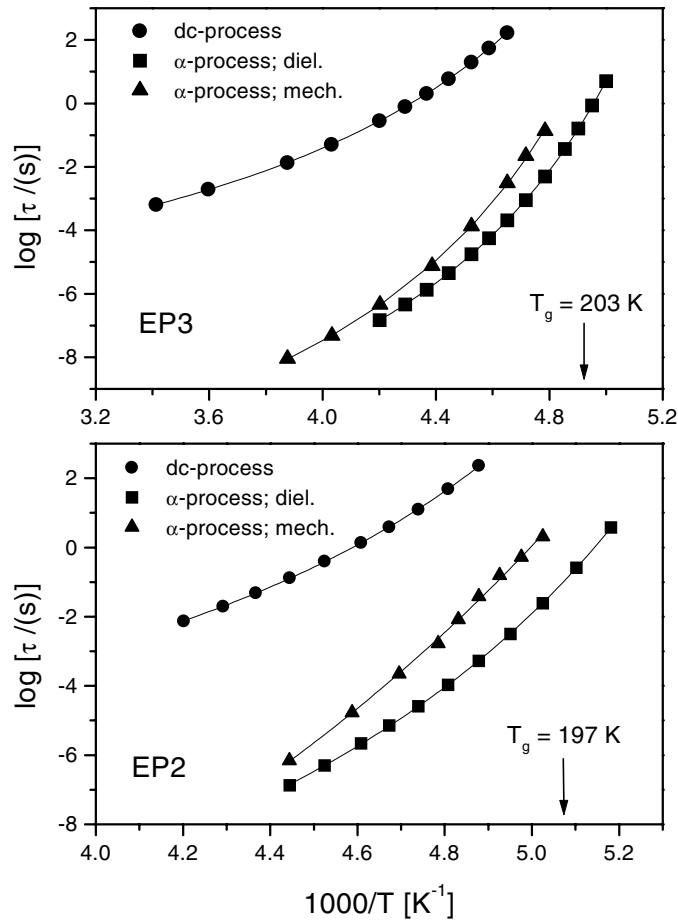


Figure 6. The temperature dependences of different relaxation processes determined from dielectric and mechanical measurements for EP2 and EP3. The experimental data were fitted to the temperature VFT law.

Table 1. Fitting parameters for the data in figure 6, using the temperature VFT law.

Relaxation process	$\log \tau_0$	D_T	T_0 (K)	Sample
dc process	-8.3 ± 0.2	7 ± 0.4	159 ± 1	EP2
	6.8 ± 0.1	6.5 ± 0.2	164 ± 0.5	EP3
α -process (dielectric)	-16.3 ± 0.2	10.5 ± 0.3	152 ± 1	EP2
	-13.5 ± 0.1	6.5 ± 0.1	167 ± 0.5	EP3
α -process (mechanical)	-24 ± 4	32 ± 12	128 ± 13	EP2
	-13.9 ± 0.4	6.9 ± 0.4	170 ± 2	EP3

where τ_a is the relaxation time at atmospheric pressure, P_0 is the pressure of an ideal glass transition and D_P is the isothermal fragility parameter. In table 2 the values of the parameters τ_a , D_P , P_0 extracted from fitting equation (2) to the data shown in figure 7 are compiled. On

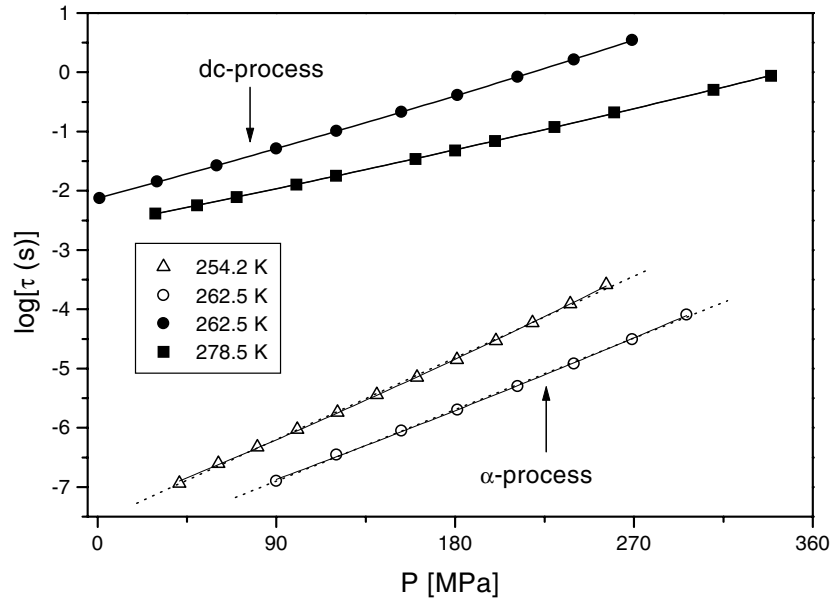


Figure 7. The pressure dependences of the relaxation times corresponding to the dc and α -relaxation processes of EP3. The solid line is a fit using equation (4). The dashed line represents a fit to the activation form (equation (5)).

Table 2. Fitting parameters obtained from equation (4) for the data in figure 7.

Relaxation process	$\log \tau_0$	D_P	P_0 (GPa)	Isotherm (K)
dc process	-2.12 ± 0.01	26 ± 2.5	2.87 ± 0.23	262.5
	-2.59 ± 0.01	24 ± 3.5	3.56 ± 0.43	278.5
α -process	-7.39 ± 0.02	23 ± 2.5	1.80 ± 0.17	254.2
	-7.79 ± 0.02	18 ± 2.0	1.76 ± 0.13	262.5

the other hand, the almost linear dependencies of the dc and α -relaxation rates suggest the applicability of a simple activation form [36–40]:

$$\tau = \tau_A \exp\left(\frac{PV^*}{RT}\right). \quad (5)$$

From the above equation one can calculate the activation volume V^* :

$$V^* = 2.303RT \left(\frac{\partial \log \tau}{\partial P} \right)_T. \quad (6)$$

To this end we differentiate the experimental data from figure 7. The activation volume versus pressure for the relaxation processes discussed is depicted in figure 8. This method is also very useful for checking the validity of equations (4) and (5) [41]. As a result we found that V^* increases slightly with increasing pressure. However, according to equation (3) the constant value of the activation volume is to be expected. Only for a limited pressure range can the pressure dependencies of the relaxation processes studied be correctly represented by a simple activation form as expressed by equation (5). Therefore, we can only define the mean activation

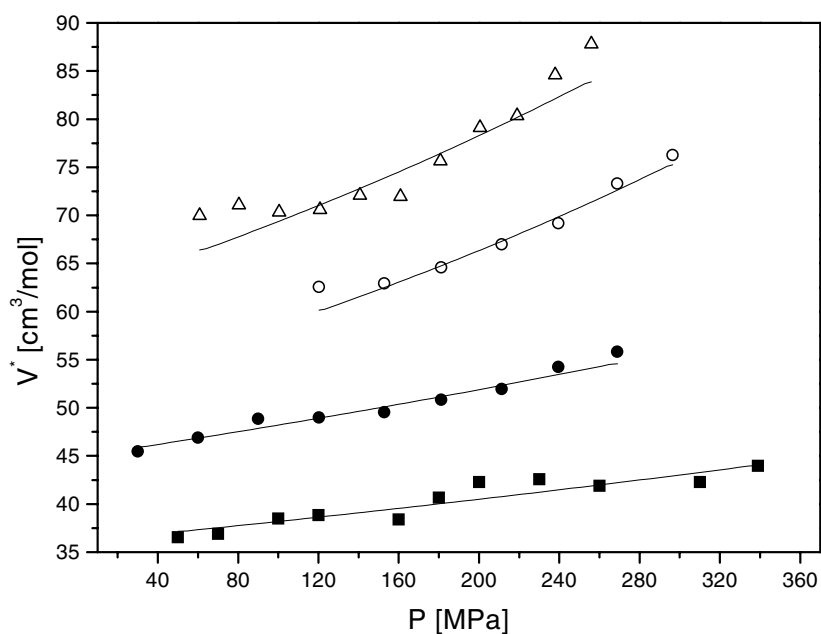


Figure 8. Activation volume plotted as a function of pressure (the key to the symbols is the same as for figure 7). The solid lines were determined from equation (4) and equation (6).

volume. The corresponding values of V^* for the α -relaxation process are $72 \text{ cm}^3 \text{ mol}^{-1}$ and $65 \text{ cm}^3 \text{ mol}^{-1}$ at $T = 254.2 \text{ K}$ and $T = 262.5 \text{ K}$, respectively. Much smaller values of the mean activation volume were found for the dc relaxation process: $49.5 \text{ cm}^3 \text{ mol}^{-1}$ and $39 \text{ cm}^3 \text{ mol}^{-1}$ at $T = 262.5 \text{ K}$ and $T = 278.5 \text{ K}$, respectively. If the relaxation process is considered to be an activated process, V^* reflects the volume requirements for the relaxation. The values of V^* for the primary relaxation indicate that relaxation of the epoxy rings at the ends of the molecule of EP3 is basically observed in the dielectric spectrum. Analysing the effect of temperature on V^* , one can note that the mean activation volume decreases with increasing temperature. This behaviour has been attributed to the increase of the cooperativity at lower temperatures and was found in several different polymer melts as well as low-molecular-weight glass-forming liquids [40, 42].

As was mentioned above, from comparison of the dielectric spectra for different pressures and temperatures one can expect the dc and α -processes to be differently coupled for the isothermal and isobaric studies. This is demonstrated clearly in figure 9 by plotting the dc relaxation times versus the α -relaxation time. The plots for the isothermal and isobaric data do not produce the same curve. In addition they have different slopes. In the last few years a number of experimental works provided evidence that the dependence of τ_σ on τ_α for fluids having very high viscosity can be described by means of a fractional Debye–Stokes–Einstein (FDSE) power-law relation [24, 43, 44]

$$\tau_\sigma \tau_\alpha^n = \text{constant} \quad (7)$$

with the fractional exponent n less than unity. Our experimental results obtained for EP3 also support the applicability of the FDSE relation. A linear dependence of $\log \tau_\sigma$ on $\log \tau_\alpha$ is observed. As indicated in figure 9, different values of the fractional exponent n characterize isobaric and isothermal dependencies. This exponent is often considered to correspond to the

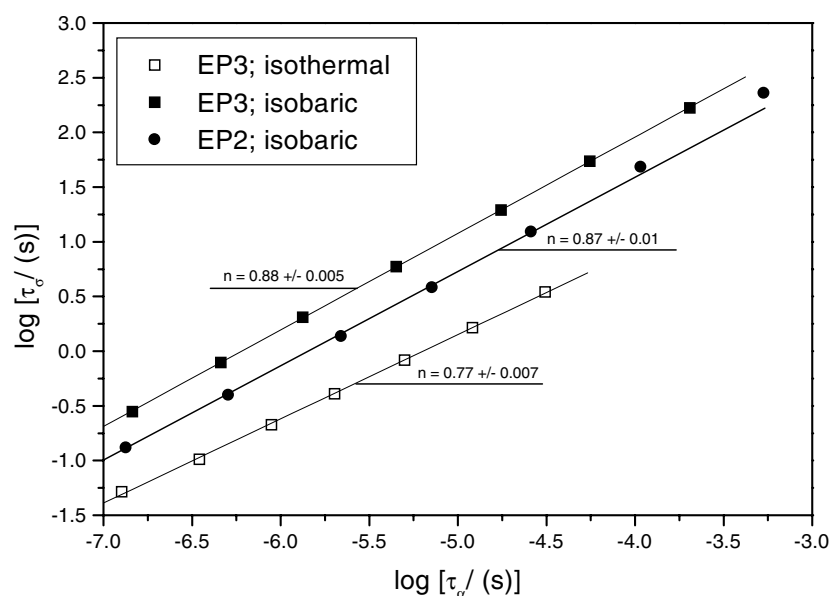


Figure 9. The logarithm of the dc-conductivity relaxation time against the logarithm of the relaxation time of the α -process. The solid lines represent the FDSE law (equation (7)).

ratio between the critical free volume for the ionic transport and the critical free volume for the dipolar orientation. The relationship between τ_σ and τ_α has been also examined for EP2. A log–log plot of τ_σ versus τ_α is shown in figure 9. A good agreement with the FDSE relation is observed in the higher-temperature range. The points slightly deviate from a straight line on approaching the glassy state. The value of the fractional exponent ($n = 0.87$) for this polymer is similar to that for EP3.

Now, we return to the question of whether the observed α -relaxation process is affected by the differences in molecular topology. These differences could only be reflected in the shape of the response function and in the temperature dependence of the characteristic relaxation time. However, the results of our analysis indicate that there are no significant differences in the dynamics of the α -relaxation process for molecules with different topologies. Similar values of the shape parameters of the dielectric response function and the steepness index [45], which describes the deviations of the liquid relaxation times from an Arrhenius behaviour, were found for both systems studied.

4. Conclusions

The relaxation behaviours of two epoxy compounds, with different topologies, were studied by means of dielectric and mechanical spectroscopy. In dielectric spectra of EP3, we observed an additional relaxation process (α' -mode) which is slower than the primary relaxation process (α -mode). On the basis of mechanical measurements it was recognized that the α' -mode originates from the molecular relaxation. We also used dielectric spectroscopy to study the dc-conductivity relaxation process. The temperature dependencies of the dc-conductivity relaxation times are nearly the same for the two epoxies. On the other hand, it was found that the dc-conductivity process in EP3 is more coupled to the α -relaxation process for the isothermal path than for the isobaric one. In both cases, the dependence of the dc-conductivity

relaxation time versus the α -relaxation time can be well described by means of the FDSE law. Moreover, we analysed the effect of hydrostatic pressure on the evolution of the relaxation rates for both the α -process and dc conductivity. Like for our previous high-pressure results on other glass formers, it turns out that the pressure dependence of the characteristic relaxation time systematically deviates from the exponential form on approaching the glassy state. From the analysis of the $\tau_\alpha(P)$ and $\tau_\sigma(P)$ dependencies, we determined the mean values of the activation volume for both relaxation processes.

Acknowledgments

We thank Professor T Pakula, Professor J Ziolo, Dr Z Dendzik, Dr P Habdas and Dr T Sriksirin for helpful discussions. We are also grateful to A Hanevald for his assistance with the mechanical measurements. The work was partly supported by the Committee for Scientific Research, Poland (grant No 2P03B 02015)

References

- [1] Lunkenheimer P, Piemenov A and Loidl A 1997 *Phys. Rev. Lett.* **78** 2995
- [2] Schneider U, Lunkenheimer P, Brand R and Loidl A 1999 *Phys. Rev. E* **59** 6924
- [3] Schönhals A, Kremer F, Hofmann A, Fisher E W and Schlosser E 1993 *Phys. Rev. Lett.* **70** 3459
- [4] Alegria A, Colmenero J, Mari P O and Campbell I A 1999 *Phys. Rev. E* **59** 6888
- [5] Stickel F, Fisher E W and Richert R 1996 *J. Chem. Phys.* **104** 2043
- [6] Hansen C, Stickel F, Richert R and Fisher E W 1998 *J. Chem. Phys.* **108** 6408
- [7] Hofmann A, Kremer F, Fisher E W and Schönhals A 1994 *Disordered Effects on Relaxation Processes* ed R Richert and A Blumen (Berlin: Springer) p 309
- [8] Richert R and Wagner H 1998 *Solid State Ion.* **105** 167
- [9] Leheny R and Nagel S R 1997 *Europhys. Lett.* **39** 447
- [10] Leheny R and Nagel S R 1998 *J. Non-Cryst. Solids* **235–237** 278
- [11] Dixon P K, Wu L, Nagel S R, Williams B D and Carini J P 1990 *Phys. Rev. Lett.* **65** 1108
- [12] Leslie-Pelecky D L and Bridge N O 1994 *Phys. Rev. Lett.* **72** 1232
- [13] Menon N and Nagel S R 1995 *Phys. Rev. Lett.* **74** 1230
- [14] Chamberlin R V 1996 *Europhys. Lett.* **33** 545
- [15] Dendzik Z, Paluch M, Gburski Z and Ziolo J 1997 *J. Phys.: Condens. Matter* **9** 339
- [16] Paluch M, Dendzik Z and Gburski Z 1998 *J. Non-Cryst. Solids* **232–234** 390
- [17] Schönhals A, Kremer F and Schlosser E 1991 *Phys. Rev. Lett.* **67** 999
- [18] Kudlik A, Benkhof S, Lenk R and Rössler E 1995 *Europhys. Lett* **32** 511
- [19] Alvarez F, Alegria A and Colmenero J 1991 *Phys. Rev. B* **44** 7306
- [20] Schäfer H, Sternin E, Stannarius R, Arndt M and Kremer F 1996 *Phys. Rev. Lett.* **76** 2172
- [21] Dissado L A and Hill R M 1983 *Proc. R. Soc. A* **390** 131
- [22] Schönhals A and Schlosser E 1989 *Colloid Polym. Sci.* **267** 125
- [23] Urbanowicz P, Rzoska S J, Paluch M, Sawicki B, Szulc A and Ziolo J 1995 *Chem. Phys.* **201** 575
- [24] Corezzi S, Ampani E, Rolla P A, Capaccioli S and Fioretto D 1999 *J. Chem. Phys.* **111** 9343
- [25] Ferry J D 1980 *Viscoelastic Properties of Polymers* (New York: Wiley)
- [26] Pakula T, Geyley S, Edling T and Boese D 1996 *Rheol. Acta* **35** 631
- [27] Faivre A, Niquet G, Maglione M, Fornazero J, Jal J F and David L 1999 *Eur. Phys. J. B* **10** 277
- [28] Deegan R D, Leheny R L, Menon N, Nagel S R and Venerus D C 1999 *J. Phys. Chem. B* **103** 4066
- [29] Richert R and Wagner H 1998 *Solid State Ion.* **105** 167
- [30] Wu L 1991 *Phys. Rev. B* **43** 9906
- [31] Paluch M and Ziolo J 1998 *Europhys. Lett.* **44** 315
- [32] The temperature dependence of the relaxation time for polymers is often analysed by means of the Williams–Landel–Ferry (WLF) equation. However, It can be shown that the WLF equation is equivalent to the VFT law; e.g. see Richert R and Blumen A 1994 *Disordered Effects on Relaxation Processes* (Berlin: Springer) p 17
- [33] Paluch M, Rzoska S J, Habdas P and Ziolo J 1997 *J. Phys.: Condens. Matter* **9** 5485
- [34] Paluch M, Rzoska S J, Ziolo J and Habdas P 1998 *J. Phys.: Condens. Matter* **10** 4131

- [35] Paluch M, Dendzik Z and Rzoska S J 1999 *Phys. Rev. B* **5** 2979
- [36] Fytas G, Dorfmueller Th and Wang C H 1983 *J. Phys. Chem.* **87** 5041
- [37] Naoki M, Endou H and Matsumoto K 1987 *J. Phys. Chem.* **91** 4169
- [38] Forsman H 1989 *J. Phys. D: Appl. Phys.* **22**1582
- [39] Leyser H, Schulte A, Doster W and Petry W 1995 *Phys. Rev. E* **51** 5899
- [40] Fludas G, Gravalides C, Reisinger T and Werner G 1999 *J. Chem. Phys.* **111** 9847
- [41] Stickel F, Fischer E W and Richert R 1995 *J. Chem. Phys.* **102** 6251
- [42] Fytas G, Dorfmueller Th and Wang C H 1983 *J. Phys. Chem.* **87** 5041
- [43] Corezzi S, Capaccioli S, Gallone G, Lucchesi M and Rolla P A 1999 *J. Phys.: Condens. Matter* **11** 10297
- [44] Koike T 1999 *Adv. Polym Sci.* **148** 139
- [45] Boehmer R, Ngai K L, Ngai C A, Angell C A and Plazek D J 1993 *J. Chem. Phys.* **99** 4201