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Influence of the glass transition on the secondary relaxation of an epoxy resin

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The dynamics of diglycidyl ether of bisphenol-A (DGEBA) was studied by employing broadband dielectric spectroscopy over a wide temperature range extending from below to above the glass-transition temperature. Dielectric spectra reveal the existence of two relaxation processes: the structural relaxation, slowing down for decreasing temperature and freezing at T_g, and a secondary process present in both liquid and glassy phase. Above the glass transition the temperature behavior of the structural relaxation time is properly described by a Vogel-Fulcher-Tamman equation with the singularity at $T_0=234$ K. The analysis of the variation of the relaxation strength versus temperature of both processes clearly shows the onset of the structural relaxation at $T_{\mathrm{on}}\approx 350$ K. Below this temperature the two relaxations progressively separate their time scales and change their shapes. The occurrence of the glass-transition phenomenon is markedly evidenced by the changes of the relaxation strength and of the low-frequency slope of the secondary relaxation. [S0163-1829(97)08830-9]

INTRODUCTION

The glass transition is no longer considered a distinguishing feature of a few systems but rather a physical phenomenon which can occur in every material provided that the melt is cooled at sufficiently high rate. In fact, as a melt is cooled, the relaxation processes progressively slow down and, if the cooling rate becomes faster than the relaxation rate, nonequilibrium structures can be eventually frozen and a glassy solid obtained.

In recent years many efforts have been devoted to find an unified description of the complex behavior of supercooled liquids going through the glass transition. Much of the theoretical approaches, such as Adam and Gibbs' free volume, or more recent percolation models[1–3] and the scaling form discussed by Dixon,[4] deal with the dynamics of the structural relaxation only, though it is experimentally well known that secondary relaxations and splitting of the single high-temperature process into at least two processes (a slow cooperative process and a faster secondary one) is a very common scenario in both glass-forming simple liquids[5,6] and polymeric systems.[7] Such subglass relaxations are generally characterized by an Arrhenius temperature behavior of the relaxation time and have been associated with localized motions of different origin.[8–11]

A special interest in such phenomena was induced by the mode coupling theory[12,13] (MCT) which, since its early formulation, predicted the bimodal relaxation as a main feature of the glass transition.

Moreover, a bifurcation of two relaxation processes was experimentally found in some systems close to the critical temperature, T_c, of the MCT.[14] More generally, recent dielectric investigations have shown that the decoupling of structural and secondary relaxations is a crucial feature of the relaxation of both glass-forming simple liquids and polymeric systems for temperatures higher than the glass transition.[7,15]

In this paper we analyze the dielectric behavior of structural and secondary relaxation of dyglycidyl ether of bisphenol-A (DGEBA) epoxy resin, a system which shows a secondary relaxation strong enough to be easily detected in the whole region from the decoupling of the structural relaxation down to temperatures below the glass transition, in the glassy state. Dielectric measurements were made in a wide frequency and temperature interval and the temperature behavior of the whole set of dielectric parameters, i.e., relaxation times, relaxation strengths, and shape parameters, is analyzed to have an insight into the splitting phenomenon and into the characteristics of the dynamics of the system near the glass transition.

EXPERIMENT

The epoxy resin used in this study was a commercial sample (EPON828 by Shell Co.) of a low molecular weight liquid diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight of about 190. The complex dielectric constant of the sample was measured over a frequency range spanning from 10^3 to 10^{10}Hz, by using two different techniques. In the low-frequency interval (10^3-10^7 Hz) the impedance analyzer HP4194A was employed. The apparatus and the measurement procedure were previously described.[16] In the high-frequency interval (10^7-10^{10} HZ) measurements were carried out via Hewlett-Packard Network Analysers (HP8753A and HP8720C). Dielectric spectra were collected for temperatures ranging from 163 to 363 K.

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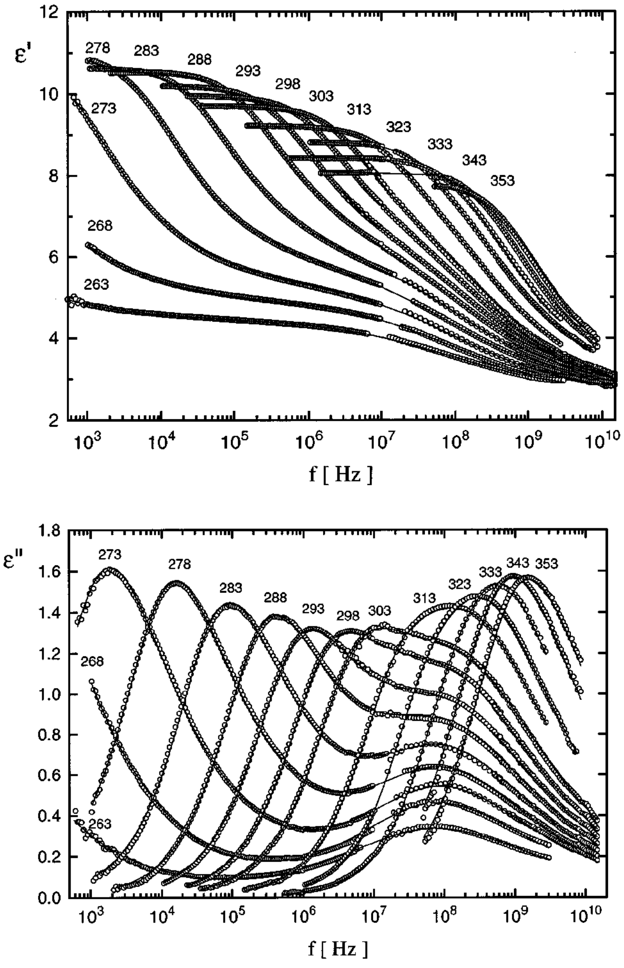

FIG. 1. Dielectric spectra of ε' and ε'' vs frequency for the epoxy resin at different temperatures. Solid lines from fitting equation.

RESULTS AND DISCUSSION

Some representative dielectric spectra of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant for DGEBA at different temperatures are shown in Figs. 1(a) and 1(b), respectively. They confirm the existence of two relaxations: the structural relaxation (or α) and one secondary process which, in this system, is referred as a γ relaxation. In fact, in DGEBA systems the β relaxation was assigned to the molecular group including the hydroxyl group, which in EPON828 gives a negligible contribution being present one in a ten molecules only. The discussion on these assignments has been presented elsewhere.[17,18] As the temperature increases, the α relaxation shifts toward higher frequencies, where it merges into the γ peak whose position slightly depends on temperature. The spectra of our system show a non-Debye and asymmetric behavior of both main and secondary relaxations as it is expected for the relaxations in complex systems. In fact, both low and high molar mass supercooled systems shows a non-Debye behavior and there is no evidence of the existence of an universal law described by a common fitting function. Among the several phenomenological equations proposed to describe the observed behaviors, the Kohlrausch-Williams-Watts (KWW),[19] in the time domain, and the Havriliak-Negami (HN),[20] in the frequency domain, are the most widely employed. Both were introduced to describe the dielectric behavior of amorphous polymers, and successively recognized also suitable to fit the relaxation behavior of low molar mass glass-forming liquids. The HN equation is a generalization of both the Cole-Cole and Cole-Davidson equations which account for the dielectric behavior of many simple liquids. Concerning the claimed universality of the KWW function, consider the work of Jonscher[21] who analyzed 100 systems and found no experimental evidence of the universality of the KWW function at low frequencies, and the analysis of Havriliak and Havriliak[22] for nearly 1000 compounds who came to the same conclusion using a different method. On the other hand, Alvarez *et al.*[23] compared the relaxation time distributions of KWW and HN functions and demonstrated that each value of the stretching parameter in KWW corresponds to a specific pair of shape parameters in the HN function. This result was confirmed more recently by Havriliak and Havriliak[24] using a direct fitting procedure. It has been shown that for representing the dielectric relaxation data the HN function is more general than the KWW, being the additional parameter necessary to take into account for the behavior of both of low- and high-frequency slopes of the relaxation.[22] About the matter, a model which related the high- and low-frequency slopes of the relaxation with intra- and intermolecular interactions (large- and small-scale modes), respectively, was proposed[2,25] and confirmed by the experimental analysis of the behavior of low molar mass and polymeric systems.[2,26] In a system where a bimodal relaxation is found, the most suitable fitting function is a superposition of two relaxation functions. In the case of our system the experimental data were conveniently fitted by a superposition of two Havriliak-Negami functions:

$$\varepsilon(\omega)-\varepsilon_2=\frac{(\varepsilon_0-\varepsilon_1)}{[1+(i\omega\tau_1)^{1-\alpha_1}]^{\beta_1}}+\frac{(\varepsilon_1-\varepsilon_2)}{[1+(i\omega\tau_2)^{1-\alpha_2}]^{\beta_2}}, \tag{1}$$

where $\epsilon(\omega)$ is the complex dielectric constant; ε_0 is the completely relaxed dielectric constant; ε_2 is the unrelaxed dielectric constant of the γ relaxation; ε_1 is the unrelaxed (relaxed) dielectric constant with respect to the $\alpha(\gamma)$ relaxation; $\alpha_1,\ \beta_1,\ \tau_1$ and $\alpha_2,\ \beta_2,\ \tau_2$ are the shape parameters and the relaxation times of the α and γ relaxation, respectively. The fitting equation was suggested by the behavior of the relaxations when their time scales were sufficiently apart, i.e., just above the glass-transition temperature; then Eq. (1) was maintained up to the high temperature except for the two highest temperature measurement points where a single HN function was employed. The use of a simple superposition of two relaxations could not be satisfactory especially in the splitting region, where the two relaxations can couple, and a different model equation could be considered. A suitable model equation was very recently proposed by Arbe *et al.*[27] who described the dielectric response in the splitting region of polybutadiene on the basis of the low temperature main and secondary relaxation processes and recovered the agreement between viscosity and the characteristic time of the main relaxation around the splitting region. This interesting approach leads to results appreciably different from those obtainable from Eq. (1) only when the time scales of the two relaxations are closer than two decades. In our case this con-

TABLE I. The dielectric parameters and their standard deviations calculated by fitting the experimental data at different temperatures T by Eq. (1).

T (K)	ε_0	ε_1	ε_2	1-α_1	1-α_2	β_1	β_2	τ_1 (s)	τ_2 (s)
163		2.45 ± 0.01	2.73 ± 0.01		0.30 ± 0.02		0.92 ± 0.15		$(3.1\pm2.1)\times10^{-6}$
173		3.49 ± 0.01	2.74 ± 0.02		0.33 ± 0.01		0.88 ± 0.13		$(1.10\pm0.57)\times10^{-6}$
183		3.52 ± 0.01	2.75 ± 0.03		0.36 ± 0.01		0.82 ± 0.14		$(5.12\pm0.90)\times10^{-7}$
193		3.56 ± 0.01	2.77 ± 0.03		0.4 ± 0.01		0.76 ± 0.13		$(2.61\pm0.90)\times10^{-7}$
203		3.60 ± 0.01	2.77 ± 0.05		0.40 ± 0.01		0.77 ± 0.15		$(1.04\pm0.40)\times10^{-7}$
213		3.64 ± 0.01	2.77 ± 0.08		0.43 ± 0.01		0.74 ± 0.17		$(4.74\pm1.90)\times10^{-8}$
233		3.72 ± 0.01	2.76 ± 0.08		0.46 ± 0.01		0.75 ± 0.15		$(1.4\pm0.46)\times10^{-8}$
243		3.79 ± 0.02	2.68 ± 0.03		0.49 ± 0.01		0.67 ± 0.06		$(7.3\pm3.0)\times10^{-9}$
253		4.00 ± 0.02	2.71 ± 0.03		0.51 ± 0.02		0.67 ± 0.07		$(5.6\pm2.0)\times10^{-9}$
263	11.9 ± 0.5	4.66 ± 0.05	2.68 ± 0.03		0.49 ± 0.01		0.74 ± 0.06	$(1.10\pm0.35)\times10^{-1}$	$(3.58\pm0.69)\times10^{-9}$
268	11.6 ± 0.4	5.07 ± 0.03	2.65 ± 0.03		0.52 ± 0.01		0.72 ± 0.05	$(3.62\pm0.93)\times10^{-3}$	$(3.20\pm0.49)\times10^{-9}$
273	11.30 ± 0.05	5.30 ± 0.03	2.65 ± 0.02	0.83 ± 0.01	0.53 ± 0.01	0.48 ± 0.01	0.70 ± 0.04	$(1.78\pm0.05)\times10^{-4}$	$(2.95\pm0.30)\times10^{-9}$
278	11.05 ± 0.01	5.50 ± 0.04	2.67 ± 0.02	0.84 ± 0.01	0.55 ± 0.01	0.49 ± 0.02	0.70 ± 0.04	$(2.07\pm0.06)\times10^{-5}$	$(2.60\pm0.23)\times10^{-9}$
283	10.75 ± 0.01	5.70 ± 0.07	2.65 ± 0.02	0.87 ± 0.02	0.57 ± 0.02	0.45 ± 0.02	0.68 ± 0.05	$(3.67\pm0.10)\times10^{-6}$	$(2.20\pm0.22)\times10^{-9}$
288	10.54 ± 0.02	5.97 ± 0.13	2.69 ± 0.02	0.87 ± 0.02	0.56 ± 0.02	0.46 ± 0.05	0.70 ± 0.05	$(8.84\pm0.31)\times10^{-7}$	$(1.70\pm0.18)\times10^{-9}$
293	10.23 ± 0.01	6.07 ± 0.21	2.65 ± 0.02	0.86 ± 0.02	0.57 ± 0.03	0.47 ± 0.04	0.69 ± 0.06	$(3.03\pm0.15)\times10^{-7}$	$(1.58\pm0.18)\times10^{-9}$
298	9.98 ± 0.01	6.28 ± 0.29	2.59 ± 0.03	0.88 ± 0.02	0.59 ± 0.03	0.47 ± 0.04	0.67 ± 0.07	$(1.10\pm0.06)\times10^{-7}$	$(1.01\pm0.17)\times10^{-9}$
303	9.74 ± 0.01	6.30 ± 0.27	2.60 ± 0.03	0.88 ± 0.01	0.60 ± 0.02	0.48 ± 0.05	0.70 ± 0.06	$(4.45\pm0.31)\times10^{-8}$	$(8.0\pm1.4)\times10^{-10}$
313	9.24 ± 0.01	6.55 ± 0.38	2.56 ± 0.05	0.92 ± 0.03	0.69 ± 0.04	0.49 ± 0.09	0.60 ± 0.12	$(1.13\pm0.16)\times10^{-8}$	$(6.1\pm1.9)\times10^{-10}$
323	8.84 ± 0.02	6.90 ± 0.58	2.60 ± 0.05	0.98 ± 0.04	0.76 ± 0.03	0.47 ± 0.14	0.53 ± 0.06	$(4.73\pm0.68)\times10^{-9}$	$(4.2\pm0.9)\times10^{-10}$
333	8.45 ± 0.01	7.20 ± 0.45	2.50 ± 0.19	0.99 ± 0.05	0.80 ± 0.03	0.53 ± 0.18	0.51 ± 0.07	$(2.09\pm0.49)\times10^{-9}$	$(3.0\pm0.8)\times 10^{-10}$
343	8.08 ± 0.03	7.49 ± 0.34	2.40 ± 0.01	1.0 ± 0.1	0.81 ± 0.01	0.53 ± 0.25	0.51 ± 0.03	$(9.99\pm5.10)\times10^{-10}$	$(2.17\pm0.40)\times10^{-10}$
353		7.71 ± 0.20	2.40 ± 0.06		0.83 ± 0.01		0.48 ± 0.02		$(1.40\pm0.08)\times10^{-10}$

dition is approached for a few experimental points only, for the temperatures higher than 313 K; consequently the temperature behavior of the parameters would be, in any case, slightly affected by that treatment.

On this basis, the fitting procedure was simultaneously performed on both ε' and ε'' data by Eq. (1). Since the dielectric relaxation function depends nonlinearly on the parameters, we used a fitting procedure based on the Levenberg-Marquardt method.[28] The values of the dielectric parameters obtained by the fitting procedure are listed in Table I. The dielectric measurements were mainly affected by the calibration procedure so that the errors are not normally distributed and an estimate of the accuracy of the dielectric parameters (errors of the parameters) could be obtained by means of the bootstrap Monte Carlo method.[28]

The relaxation times, $\tau_1$and τ_2 of the α and γ relaxation, respectively, have been reported in Fig. 2 as a function of the reciprocal temperature. The temperature dependence of the average structural relaxation time τ_1 is non-Arrhenius, with an apparent activation energy that increases with decreasing temperature. This behavior has been described by the empirical Vogel-Fulcher-Tamman equation, that can be written in the following form:[29]

$$\tau_1 = \tau_{01}\,\exp\left(\frac{DT_0}{T-T_0}\right), \tag{2}$$

where τ_{01} is the relaxation time in the high temperature limit; T_0 is the temperature of the structural blocking. Some authors identify T_0 with the Kauzmann temperature.[30,31] D is the fragility parameter which controls the departure from the Arrhenius law and is useful to distinguish between strong (high D) and fragile (low D) glasses. The values of the parameters obtained by fitting Eq. (2) to the relaxation time τ_1 are

$$\tau_{01} = (1.2\pm0.3)\times10^{-12}\ \text{s}; \quad D = (3.1\pm0.1);$$

$$T_0 = (234.2\pm0.6)\ \text{K}.$$

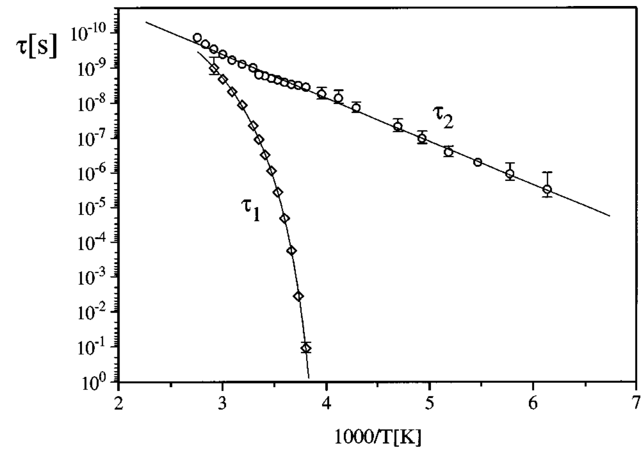

FIG. 2. Relaxation times, τ_1 and τ_2, of the α and γ relaxation, respectively, vs reciprocal temperature $1/T$. Solid lines from fitting equations. Error bars smaller than the symbol size are omitted.

The glass-transition temperature T_g can be conventionally defined as the temperature at which τ_1 becomes 10^2 s, i.e., comparable to the maximum reasonable measurement time in a relaxation experiment;[32] accordingly the value $T_g=257$ K was calculated by Eq. (2). Such T_g value is about 23 K greater than T_0 and is consistent with previously reported calorimetric measurements.[33,34]

The characteristic time of the γ relaxation below and above T_g were fitted by the Arrhenius equation:

$$\tau_2(T)=\tau_{02}\exp\left(\frac{E_a}{RT}\right), \tag{3}$$

where E_a is the activation energy per mole and R is the gas constant; τ_{02} is the relaxation time in the high temperature limit. The following values of the parameters were obtained:

$$\tau_{02}=(7.0\pm 2.7)\times 10^{-14}\ \text{s};\qquad E_a=(5.7\pm 0.2)\ \text{K cal/mol}.$$

The data of secondary relaxation in Fig. 2 show a perceptible change of the slope at the glass-transition temperature but the accuracy of the experimental data is not sufficient to support any specific conclusion on this point. We limit ourselves to point out that, in some systems, a change of the activation energy of secondary relaxations at the glass transition was observed[35] while, in other systems, the activation energy was found stable.[8] More evident changes have been observed for the temperature behavior of ε_0, ε_1, and ε_2 near the glass transition as described in the following.

The temperature dependence of the relaxed dielectric constant ε_0 is described by the Kirkwood-Fröhlich equation, which, under the assumption that orientational effects linearly superimpose, can be written[36]

$$\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2}=\frac{4\pi}{9KT}\sum N_i\left\langle\mu_i^2\right\rangle. \tag{4}$$

This equation exploits the Onsager internal electric field and relates the relaxed, ε_0, and completely unrelaxed, ε_∞, dielectric constants to the volume concentration of dipoles, N_i, and to the mean square dipole moment of each dipolar species $\langle\mu_i^2\rangle$. Equation (4) predicts that the quantity on the left-hand side, indicated in the following as $f(\varepsilon_0)$, depends linearly on the reciprocal temperature and approaches zero at very high temperatures. The experimental results plotted in Fig. 3 confirm the theoretical predictions of Eq. (4) except for the intercept for $f(\varepsilon_0)=0$ which occurs at $T\approx 700$ K. Here the ε_∞value was calculated from the optical refractive index $n=1.5$. The zeroing of the overall strength at a finite temperature was also observed in other systems and it was generally ascribed to the dipole-dipole interactions not completely taken into account by the model.[37,38]

The α-relaxation strength, $\Delta\varepsilon_1=(\varepsilon_0-\varepsilon_1)$, behaves as the overall relaxation strength, $(\varepsilon_0-\varepsilon_2)$(Fig. 4), but with a different slope. It zeros at the temperature $T_{\text{on}}\approx 350$ K, where the onset of α relaxation occurs. The existence of an onset for the α-relaxation strength has been recently reported for the poly(n-alkylmethacrylate)s[7,35] and for polybutadiene,[27] the linear increase of the α-relaxation strength with decreasing temperature has been also verified by simulations with a modified Fredrickson model.[15]

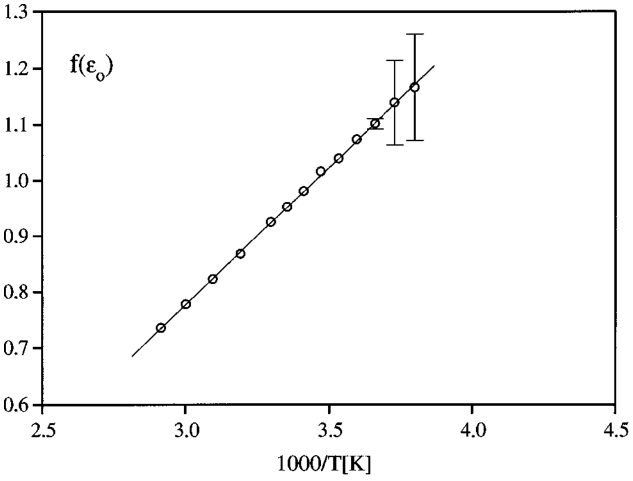

FIG. 3. Dielectric function $f(\varepsilon_0)$ plotted vs reciprocal temperature 1/ T. Solid line from linear fit equation.

Theγ-relaxation strength, $\Delta\varepsilon_2$, was found to increase with temperature both below and above the glass transition (Fig. 4); its slope markedly changes through the glass transition. The $\Delta\varepsilon_2$ data well above and well below T_g can be fitted by two different linear equations which cross together at the temperature $T_x\approx 238$ K, which lies in between the glass transition and the Kauzmann temperature. This result clearly points out that not only the structural relaxation but also the secondary one is markedly sensitive to the glass transition. Near the glass-transition temperature, secondary processes are located in a time scale more easily accessible to spectroscopic investigations than to the structural relaxation whose characteristic time attains values too long to be experimentally detected. This means, in particular, that during the measurement the secondary relaxation strength can be considered as an equilibrium quantity, the related relaxation time being much shorter than the measurement time. Consequently, the observed change of the slope of the secondary relaxation strength could be useful to characterize the glass-transition temperature itself. The relaxation strength of the secondary process, $\Delta\varepsilon_2=(\varepsilon_1-\varepsilon_2)$, equals the overall relaxation

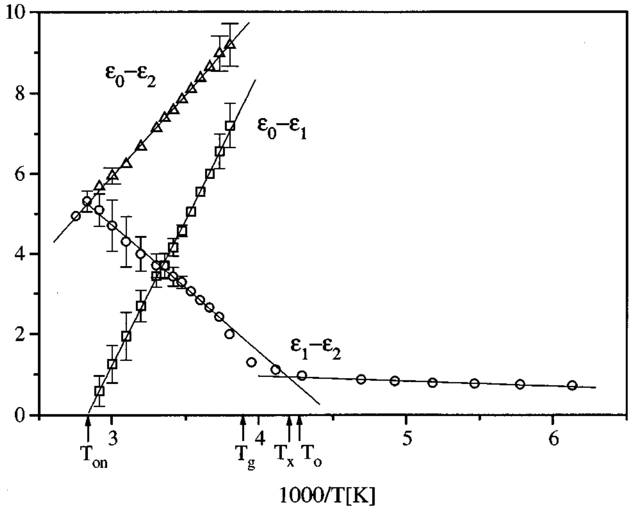

FIG. 4. Dielectric strengths plotted vs reciprocal temperature 1/ T. Solid lines from linear fit equations.

strength for temperatures higher than T_{on}. As the two relaxations have merged, i.e., above the onset temperature, it could be meaningless to distinguish between α and γ relaxation; in fact, in principle the relaxation is no more the same as below the merging temperature, even if it could be very close to either the main or secondary relaxation, depending on which is the bigger one. Accordingly, on the basis of our experimental data we conclude that the relaxation at temperatures above the onset temperature seems to be mainly related to the previous γ relaxation.

To the best of our knowledge, at the present time there are no models of the glass transition which involve secondary relaxation and their temperature behavior. Moreover, none of the numerous models that have been developed to treat relaxation phenomena is able to completely model the dynamics of the systems, i.e., positions and intensities of all of their relaxations as functions of the temperature and frequency, starting from the molecular structure.[39–42]

Concerning the strength of dielectric subglass relaxations for temperatures below T_g, a molecular model has been developed to account for the increase of $\Delta\varepsilon_2$ for increasing temperatures in polymers,[43] by assuming that below T_g an isolated-chain model is adequate to calculate the relaxation strength. Such a model describes the subglass motional modes by two states of unequal energy; consequently, the temperature dependent population of the states leads to a relaxation strength which increases with temperature. At higher temperatures, the increase of the strength of secondary relaxations above T_g was observed in many other experiments.[6,35,44–46] However, we found no indications concerning how the total relaxation strength is apportioned between the structural and the secondary relaxations. It is reasonable to think that local motions can couple with diffusive motions dominating at temperatures higher than T_g and continue with even larger frequencies; it is expected that the effect of the coupling can vary greatly from system to system so that, in principle, the strength of the secondary relaxation can both increase (as in the case here discussed) and decrease. To this respect, experimental data describing how the total relaxation strength above T_g is divided between the α and subglass relaxations have to be considered a critical test for detailed molecular models.

Further significant information can be obtained from the analysis of the shape parameters: $m_1=1-\alpha_1$, $n_1=(1-\alpha_1)\beta_1$ and $m_2=1-\alpha_2$, $n_2(1-\alpha_2)\beta_2$; they represent the low- and the high-frequency tails of their respective relaxation spectra:[47,48]

$$\varepsilon''\propto\omega^{m_{1,2}} \quad \text{for} \quad \omega\ll\omega_{01,2},$$

$$\varepsilon''\propto\omega^{-n_{1,2}} \quad \text{for} \quad \omega\gg\omega_{01,2},$$

where $\omega_{01,2}$ are the angular frequencies at the maxima of ε'' for the α and γ relaxation, respectively. The observed temperature dependence of these parameters [Figs. 5(a) and 5(b)] means that the time-temperature scaling law does not apply to this system in the whole range analyzed; in particular $m_1$and m_2 display a stronger temperature dependence than n_1 and n_2. The failure of this scaling law proves that the simplified MCT does not apply to our system; an extended version of the MCT theory,[13] though specifically developed for polymers, might be considered and this analysis will be probably carried out in future investigation. The monotonic increase of m_1 and n_1 with increasing temperature agrees with the predictions of the model relating the high-frequency part of the dielectric loss curve to the local-chain dynamics and the low-frequency one to the correlation of segments of different molecular chains.[2] In fact, this model predicts that the increase of m_1 with the temperature is produced by the corresponding reduction of the intermolecular interactions and the hindrance of the local chains. The corresponding increase of n_1 is originated by the increase of the mobility of local chains. In the system here considered, the parameter m_2 of the γ relaxation [Fig. 5(b)] features a linear dependence on the reciprocal temperature below $T_g$and shows a marked change of the slope near the glass-transition temperature. This result demonstrates that, besides the strength, also the shape of the secondary relaxation is modified by the glass transition. Moreover, it has to be noticed that m_2 and n_2 are getting the same value as temperature decreases; this means that the secondary relaxation at low temperatures is approaching the Cole-Cole behavior as observed in many other glass-forming systems.[44] For the system here considered, the coupling between motions associated to the main and secondary relaxations can give a rationale of the observed be-

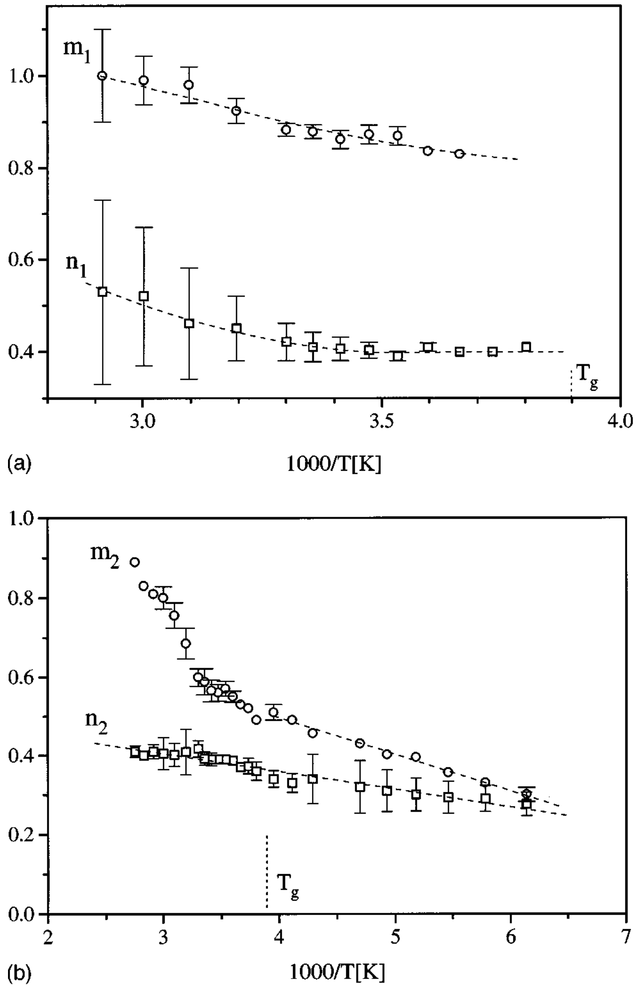

FIG. 5. Shape parameters, m and n, for (a) the main relaxation and (b) the secondary relaxation. Dashed lines are guides for the eyes.

havior. However, further investigations on different systems are needed to clarify this point.

CONCLUSIONS

In this paper broadband dielectric spectroscopy has been exploited for studying the dynamics of diglycidyl ether of bisphenol-A (DGEBA). Two relaxation processes have been evidenced: the structural relaxation freezing at T_g, and a secondary process present in both liquid and glassy phase. The fitting procedure of the experimental data was based on the superposition of two Havriliak–Negami functions and provided all the parameters describing the relaxations. The full analysis of the temperature behavior of relaxation times, relaxation strengths, and shape parameters of both processes was performed. In particular, the onset of the main relaxation occurs well above the glass transition ($T_{\mathrm{on}}=350$ K); while, as the glass-transition temperature was crossed, a change of the shape parameters and the relaxation strength of the secondary relaxation was observed. The temperature behavior of all parameters was exploited to discuss a possible scenario describing the temperature evolution of the main and secondary relaxation and their relationships. The correlation of the fitting parameters with the physical behavior of the system is satisfactory; the analysis we adopted to describe the behavior of this glass forming system provided reliable results and a deeper insight in the secondary relaxation behavior near the glass transition.

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