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Structural relaxation process in glass-forming liquids: a comparison between the optical Kerr effect and dielectric spectroscopy

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ABSTRACT

We present a comparative analysis of dielectric spectroscopy and optical Kerr effect measurements of relaxation processes in glass-forming phenyl glycidyl ether. In particular we focus our attention on the structural α -relaxation process and the most important finding is the existence of a constant scaling factor between the characteristic times obtained by the two experiments in the high-temperature region.

§ 1. INTRODUCTION

The glass transition phenomenon has become, during the last few years, one of the most important topics of condensed-matter physics. The richness in phenomenology of the glass transition and especially the large dynamic range involved in this process make it difficult to describe all aspects completely, either from the experimental or from the theoretical point of view. In this context the main feature to take into account is the increase in relaxation times characterizing the molecular motion of the glass-forming systems. In particular, concerning the structural relaxation process, often called α relaxation, in fragile glass formers the temperature dependence of the characteristic time deviates from the Arrhenius behaviour $t_0 \exp(\Delta E/k_B T)$ (T is the temperature, k_B is the Boltzmann constant, ΔE is the activation energy and t_0 is a characteristic time), showing a greater increase. For a typical decrease in the temperature of about 100 K below the melting point the relaxation times increase by about 15 decades.

In the last few years the improvement in experimental techniques has extended the accessible dynamic range of study, leading to wide superposition in the time–frequency regions of measurements so that a direct comparison of these data is now possible. These comparisons have not yet been the subject of an exhaustive experi-

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mental and theoretical work and only a few previous studies exist (Comez *et al.* 1999, Schneider *et al.* 1999, Wuttke *et al.* 2000). In particular a comparison of data can be worked out from optical Kerr effect (OKE) and dielectric spectroscopies. The difficulty of this kind of comparative analysis originates from several aspects. First of all these techniques are sensitive to the glass dynamics through different probes (i.e. induced and static dipoles in the present case) that could be connected to the molecular degrees of freedom in a different way. Indeed, according to some relevant approximations, the experimental response could be characterized by only the single-molecule orientational dynamics, but even in this case the two responses (optical and dielectric) are defined by different orders of the Legendre polynomials. Despite these difficulties a direct comparison of the relaxation times obtained by these spectroscopies and of their temperature dependence is an interesting task; in fact, it can give valuable information about the universal or non-universal nature of glass dynamics.

In this paper we present a comparison of the relaxation times characterizing the α process in the epoxy resin phenyl glycidyl ether (PGE) observed by the time-resolved OKE and dielectric spectroscopy techniques. The presence in the PGE molecules of the epoxy and phenylic rings makes it particularly suitable for both dielectric and optical study. To our knowledge this is the first comparative analysis between these two techniques.

§2. OPTICAL KERR EFFECT EXPERIMENT

The time-resolved OKE spectroscopy measures the birefringence relaxation of the system directly in the time domain. For a molecule characterized by anisotropic polarizability the birefringence response is mainly due the orientational degrees of freedom of the system. The response function, measured in a OKE experiment, can be written in the following form (Hellwarth 1977, Yan and Nelson 1987, McMorro *et al.* 1988):

$$R(t) \propto -\frac{\partial}{\partial t} \Phi(q, t), \quad (1)$$

where

$$\Phi(q, t) = \frac{\langle \varepsilon_{xy}(q, t) \varepsilon_{xy}(-q, 0) \rangle}{\langle |\varepsilon_{xy}(q, 0)|^2 \rangle} \quad (2)$$

is the correlation function of the dielectric constant. Recently this technique has proved to give interesting information in the study of glass-former dynamics (Torre *et al.* 1998, 1999, 2000). The present study is performed with experimental equipment and a laser system which has been described in detail elsewhere (Bartolini *et al.* 1999). With respect to the experimental procedure reported there, we must note that in the present case we have introduced an improvement in measuring the long-time part of the relaxation process. The measurements in this temporal region are made with stretched pulses of about 1 ps which allow us to transfer a larger quantity of energy to the system without increasing the instantaneous intensity of the pulse. This larger quantity of energy is then released in the signal detected, which is characterized by a better signal-to-noise ratio (Bartolini *et al.* 2002).

The OKE data are collected at different temperatures from 265.3 to 352.5 K covering a temporal region up to 4 ns. In figure 1(a) we show all the signals in a log-log plot; in the first few picoseconds they are characterized by oscillatory

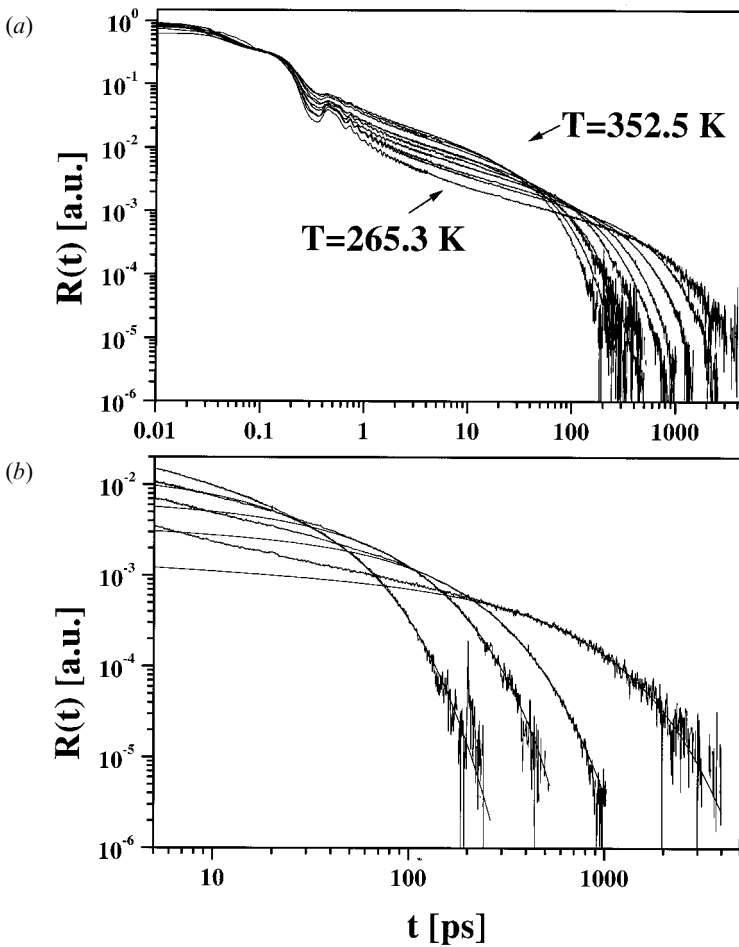


Figure 1. (a) OKE signals; (b) long-time region of four OKE signals with the corresponding fit to the KWW law. From top to bottom the curves correspond to $T = 352.5, 312.9, 293.1$ and 265.3 K.

dynamics due to the excitation of intramolecular vibrational degrees of freedom at $\nu \approx 245$ and 332 cm^{-1} . Also we note that two temporal regions are present; in the first we observe a moderate dependence of the signals on the temperature; finally, in the second region, which takes place at a long time, the signals exhibit a slow relaxation clearly dependent on temperature and extending to a longer time as the temperature is lowered. This last region reproduces the α -relaxation process which is of interest in this paper. It is well known that the structural relaxation process in glass-forming liquids cannot be described by a simple exponential decay. Usually this relaxation in a glass former is properly described by the Kolrausch–William–Watts (KWW) law (Williams and Watts 1970). So the correlation function of interest becomes

$$\Phi(t) = \Phi_0 \exp \left[- \left(\frac{t}{\tau_{\text{KWW}}} \right)^{\beta_{\text{KWW}}} \right], \quad (3)$$

where τ_{KWW} is the characteristic time of the process, β_{KWW} is the stretching parameter and Φ_0 is an amplitude parameter. Indeed this is a phenomenological function, also called a stretched exponential, that has found a theoretical basis in the framework of the mode coupling theory (Götze and Sjögren 1992). Since the OKE experiment measures the derivative of the correlation function of the dielectric constant (see equations (1) and (2)), to reproduce the long-time part of the signals we use the time derivative of the KWW law. Moreover a complete analysis of the optical signals from the first few picoseconds is beyond the aim of the present paper and will be presented in a forthcoming article (Bartolini *et al.* 2002). In figure 1 (a) we show in a log–log plot the long-time region of four experimental curves with the relative fit obtained from the KWW derivative; it should be noted that this function reproduces very accurately the experimental curves in the slower temporal region.

§ 3. DIELECTRIC EXPERIMENT

Dielectric spectroscopy measures the relaxation process of the polarization produced by the reorientation of the static dipole moment of the molecules. Dielectric measurements, performed in the frequency domain, permit us to obtain the spectra of the dielectric constant $\varepsilon(\omega)$ which is related to the Laplace transform of the correlation function of the dielectric dipole ($\gamma(t) = \langle \mu_i(0) \sum_j \mu_j(t) \rangle / \langle \mu_i(0) \sum_j \mu_j(0) \rangle$) (Böttcher and Bordewijk 1978). Measurements on PGE were carried out using the frequency-domain reflectometry technique, by employing two different experimental apparatuses that assure a wide superposition among the spectral ranges; the network analysers HP8753ES, with a capacitor cell characterized by an empty capacitance $C_0 \approx 3.5$ pF, and HP8722D, with $C_0 \approx 0.15$ pF, were employed in the frequency ranges 5×10^4 – 1.8×10^9 and 5×10^7 – 4×10^{10} Hz respectively. The measurements are collected in the frequency interval between 100 kHz and 30 GHz and were carried out at temperatures between 243.1 and 353.1 K. More details about the experimental apparatuses have been reported elsewhere (Wei and Sridhar 1989, Fioretto *et al.* 1994, Kremer and Arndt 1997, Corezzi *et al.* 1999). In the investigated temperature range, the spectra of the dielectric constant $\varepsilon(\omega)$ (figure 2) clearly show the presence of the α relaxation, which shifts towards lower frequencies as the temperature decreases, in agreement with the α -relaxation behaviour in the optical measurements. Indeed in the frequency range covered by these measurements, no signature of further relaxation processes is present. In order to reproduce the α -relaxation process in the frequency domain a Fourier-transformed KWW function is required. Since this cannot be computed in an analytic form, very often the experimental curves were fitted to the phenomenological Cole–Davidson (CD) function (Böttcher and Bordewijk 1978):

$$\varepsilon(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon}{(1 + i\omega\tau_{\text{CD}})^{\beta_{\text{CD}}}}, \quad (4)$$

where ε_∞ is the high frequency limit of $\varepsilon(\omega)$, β_{CD} is a shape parameter stating the non-exponentiality of the process, $\Delta\varepsilon$ is the strength and τ_{CD} is the characteristic relaxation time. The CD function is a good approximation for the KWW Fourier transform even if some differences are present. The KWW and CD parameters can be connected according some appropriate phenomenological relations (Lindsey and Patterson 1980):

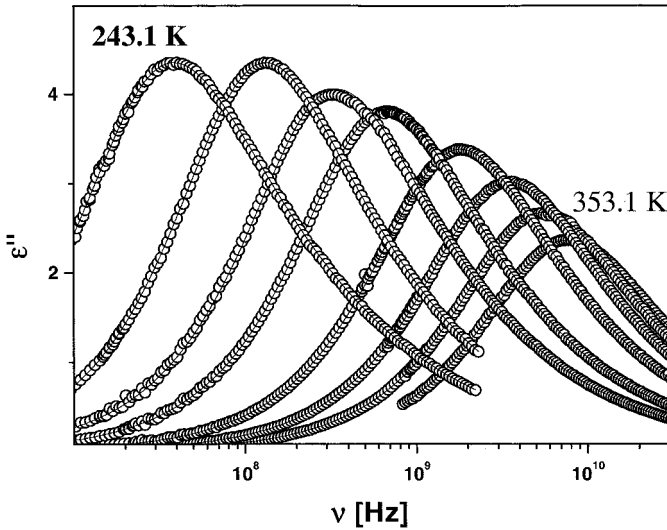


Figure 2. Dielectric spectra (○) with corresponding fit to the CD function (—).

$$\tau_{\text{KWW}} = \tau_{\text{CD}}(1.184\beta_{\text{CD}} - 0.184), \quad (5)$$

$$\beta_{\text{KWW}} = 0.683\beta_{\text{CD}} + 0.316, \quad 0.6 < \beta_{\text{CD}} < 1.0. \quad (6)$$

Also in the present case, experimental curves corresponding to different domains have been fitted using different theoretical functions: the KWW law in the time domain for optical measurements and the CD function in the frequency domain for the dielectric results. Then we report the CD fitting parameters to the KWW values using equations (5) and (6). Finally a comparison between all the fitting parameters has been carried out according to the KWW law. In the following we call $\tau_{\text{KWW}}^{\text{o}}$ and $\beta_{\text{KWW}}^{\text{o}}$ the parameters of the KWW functions obtained from the OKE measurements and $\tau_{\text{KWW}}^{\text{d}}$ and $\beta_{\text{KWW}}^{\text{d}}$ those from the dielectric measurements.

§4. DISCUSSION

In figure 3 we show the characteristic time of the α -relaxation process from the analysis of the two types of measurement. The values of $\tau_{\text{KWW}}^{\text{d}}$ are smaller than $\tau_{\text{KWW}}^{\text{o}}$ in the whole temperature range investigated, meaning that the relaxation process probed by the optical spectroscopy technique is slower than that investigated by the dielectric technique. This result contrasts with some classical theoretical predictions concerning the simple liquid dynamics, among these the Debye rotational diffusion theory (Böttcher and Bordewijk 1978). According to this model the characteristic time of the dielectric processes would be three times that from optical spectroscopy. This scaling factor is defined by the different orders of the Legendre polynomials characterizing the response functions probed by the two experiments. However, the disagreement between theory and experiment is not surprising because, in the present case, the relaxation times refer to molecular glass-forming dynamics that cannot be interpreted by simple Debye diffusion theory. Moreover it can be noted that the two time scales superimpose, multiplying one of them by a temperature-independent scaling factor (figure 3). In particular we have found that $\tau_{\text{KWW}}^{\text{d}} = 0.58\tau_{\text{KWW}}^{\text{o}}$ in the temperature range from 265.3 to 352.5 K, which is almost entirely above the

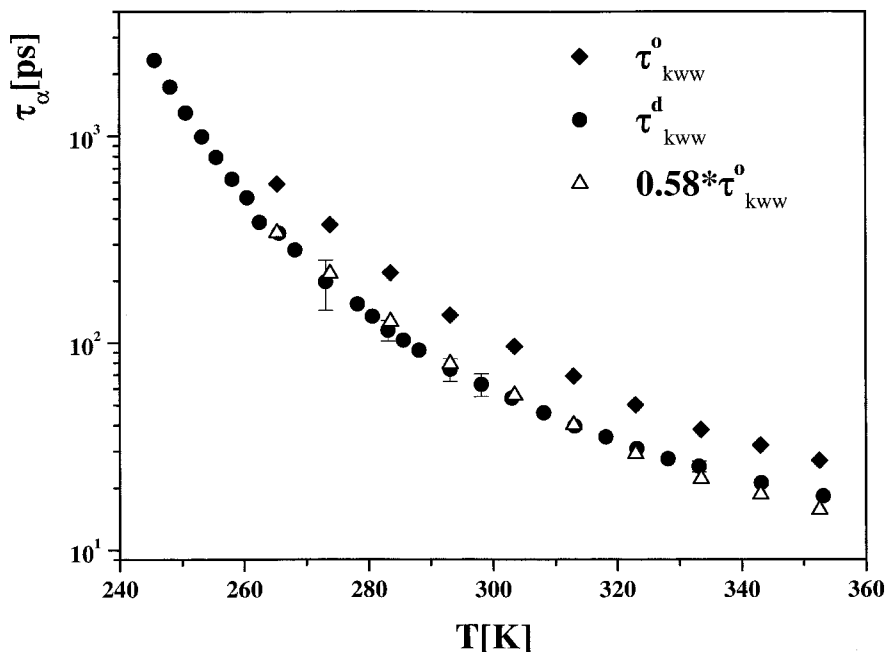


Figure 3. α -relaxation time of the KWW function obtained from OKE measurements (\blacklozenge) and dielectric spectra (\blacksquare) fit (for the procedure see the text). It should be noted that OKE relaxation times rescaled for a constant factor (\triangle) superimpose on the dielectric values.

melting point of the system: $T_m = 276.6$ K. This finding of an almost constant scaling factor ($\tau_{\text{KWW}}^{\text{d}}/\tau_{\text{KWW}}^{\text{o}} \approx k$) in the high-temperature region ($T \gg T_g$) seems to be a general result. Indeed very similar results have been even found in previous studies comparing the relaxation processes of propylene carbonate (PC) (Schneider *et al.* 1999) and diglycidyl ether of bisphenol-A (DGEBA) (Comez *et al.* 1999) measured by dielectric spectroscopy and light scattering experiments. However, it should be noted that, according to Schneider *et al.* (1999), in a PC glass former the α processes are characterized by faster relaxation times in the light scattering spectra with respect to the dielectric spectra with a scaling factor of about three, while in the DGEBA sample, according to (Comez *et al.* 1999), the α -relaxation time scales are longer from optical spectroscopy than from the dielectric technique with a scaling factor of about 0.13. In these comparisons all the tested glass formers (PC, DGEBA and PGE) have very similar dynamic behaviours concerning the slowing down of the α processes; however, the epoxy resins DGEBA and PGE show a scaling factor $k < 1$, while PC has a factor $k > 1$. Definitely epoxy resins and PC are characterized by different molecular structure: the first are quite complex molecules whereas the second is relatively simple. Probably the molecular structure of the system under analysis plays an important role in the definition of the absolute time scale of relaxation measured by different spectroscopic techniques, although it does not modify the features of α dynamics substantially. Nevertheless a more detailed and extended analysis has to be made before some conclusions are drawn.

Concerning the stretching parameters we note that the two set of values present different behaviours. $\beta_{\text{KWW}}^{\text{o}}$ (figure 4) does not show any temperature dependence in

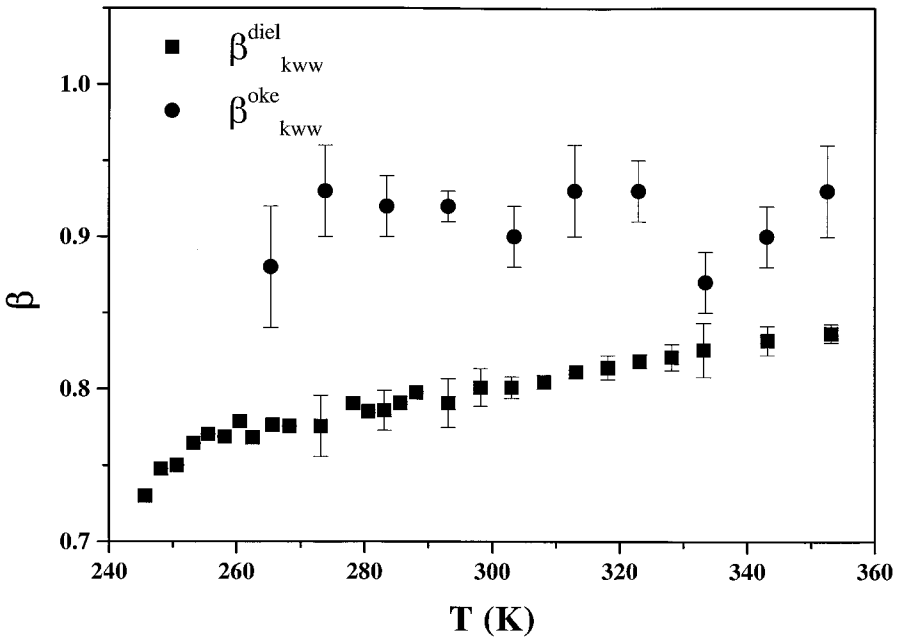


Figure 4. Stretching parameters of the KWW function obtained from OKE measurements (●) and dielectric spectra (■) fit.

the interval explored; in fact, all the values are consistent although the spread is wide, except that at 333.4 K. The mean value of these data results in $\beta_{kww}^o = 0.91$. On the other hand it can be seen that β_{kww}^d shows a decreasing behaviour as the temperature is lowered, varying by about 13% in the whole temperature range. This difference could be due to the larger temperature range investigated by dielectric spectroscopy or to a different influence of the temperature on the relaxation process obtained by the two spectroscopies. However, concerning the former hypothesis it can be noted that, even in the temperature region where data from both experiments are available, β_{kww}^d presents a more pronounced decreasing behaviour. At this moment it is therefore difficult to explain the reason for this difference and a more extended analysis is required.

In this paper we have presented the comparison of relaxation times obtained from dielectric and OKE spectroscopies on a fragile glass former. A complex scenario appears from this preliminary analysis. In the temperature range studied, the relaxation times show identical temperature dependences even if their time scales are different. This common temperature behaviour of the relaxation processes indicates the universal nature of dynamics in glass formers. In contrast, the different time scales that these two probing techniques measure have to be attributed to the molecular aspect of the relaxation processes. In fact, a comparison with previous work on different glass formers suggests a strong connection of the probed relaxation time scales from the molecular structure. Undoubtedly, the comparative analyses of experimental results are really a key issue in the comprehension of glass transition phenomena, since they permit us to distinguish the universal and probe-dependent features. Moreover this is a very open topic which only in the last few years has

begun to be considered and it will require many further theoretical and experimental studies in the future.

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