Brillouin light scattering from shear waves in an epoxy resin through the glass transition

Brillouin light scattering from shear waves in an epoxy resin through the glass transition

L Comez†, D Fioretto†, L Verdini† and P A Rolla‡

† INFM, Unità di Perugia, Dipartimento di Fisica dell' Università, Via Pascoli, I-06100 Perugia, Italy
‡ INFM, Unità di Pisa, Dipartimento di Fisica dell' Università, Piazza Torricelli 2, I-56126 Pisa, Italy

Abstract. The temperature dependences of the characteristic frequency and lifetime of hypersonic transverse acoustic waves in the epoxy system EPON 828 have been probed by means of the Brillouin light scattering technique. Evidence has been found of a very broad dispersion region, together with a discontinuity close to the glass transition temperature T_g. For temperatures higher than T_g, the shear loss data obtained from Brillouin spectra are in quantitative agreement with dielectric data for the same system. For lower temperatures, the Brillouin data deviate from the dielectric ones, the former being more sensitive to the secondary relaxation processes.

1. Introduction

One of the primary features of the liquid–glass transition is the cessation of viscous flow and the development of shear elasticity [1]. This transition occurs over a wide temperature region, whose width depends on the cooling (or heating) rate and on the frequency of the elastic wave. It is well known that transverse acoustic waves can propagate in a liquid, provided that their frequency is higher than the reciprocal of the relaxation time. This condition can be attained in supercooled liquids and tested by Brillouin light scattering measurements [2]. Brillouin scattering offers a substantial advantage over ultrasonic techniques, since the frequencies involved are higher, and shear waves can be observed up to temperatures much higher than T_g. Depolarized Brillouin spectra of supercooled systems arise from shear acoustic waves and from anisotropy fluctuations. In the viscous liquid region the shear wave is overdamped and, if the liquid consists of optically anisotropic molecules, orientational fluctuations couple to the shear modes and can produce a depolarized quasi-elastic spectrum with a dip in the central peak due to interference effects [3]. On approaching the glass transition region, the shear modes become underdamped and give rise to a Brillouin doublet, of very weak intensity as compared with the central peak. Recently, renewed interest in light scattering spectroscopy of the liquid–glass transition has been stimulated by the development of the mode-coupling theory, which predicts an ergodic–non-ergodic transition on cooling the liquid towards T_g [4, 5]. Yet, most light scattering studies deal with the behaviour of the quasi-elastic peak or of the longitudinal acoustic modes [6]. There is a lack of recent experimental work on transverse acoustic (TA) modes, probably due to the low cross section of these modes.

In this paper a Brillouin light scattering study of the TA modes through the glass transition of an epoxy resin is reported. Back-scattering measurements have been made on a sample supported by an optically polished opaque substrate. This geometry has proved to be particularly appropriate for investigating shear waves in glass-forming systems. The temperature behaviour of the dynamic shear modulus obtained from Brillouin spectra is discussed and compared with the results of dielectric measurements.

2. Experiment

The epoxy resin examined here is a commercial sample (EPON 828 from Shell Co. Ltd) of liquid diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight of about 190. The sample was filtered through a 0.22 μm membrane, and a film about 1 mm thick was placed on a optically polished silicon substrate. Brillouin spectra were taken in the temperature range 213–313 K, using a p-polarized 40 mW light beam from an Ar$^+$ laser, operating on a single mode of the 514.5 nm line. The depolarized back-scattered light was analysed by means of a Sandercock-type $(3 + 3)$-pass tandem Fabry–Perot interferometer [7], characterized by a finesse of about 100 and a contrast ratio greater than 5×10^{10}.
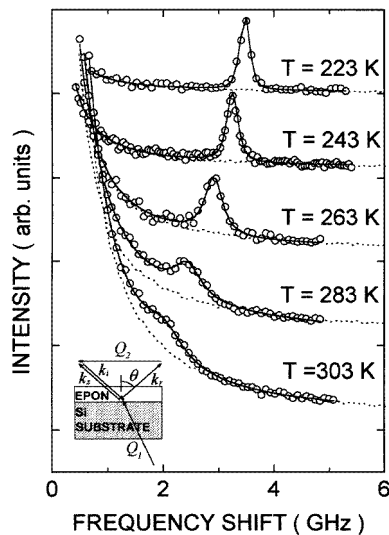

Figure 1. Brillouin spectra of EPON 828 at different temperatures: ($\circ$) I_{VH}-spectra of the supported sample; ($\cdots$) I_{QE}-spectra of the bulk sample; and (—) the best fit according to equations (1)–(3). In the inset the geometry of the interaction is shown.

The structure of the sample, consisting of a transparent thick film on an opaque substrate, was chosen in order to produce a greater amount of information from a single spectrum. In fact, as shown in the inset of figure 1, two interaction mechanisms are possible in our experiment: (i) direct coupling between the incident light of wavenumber k_i and modes with wavenumber $Q_1 = 2nk_i$, lying in the direction of k_i in the film; and (ii) coupling between the incident light and modes with wavenumber $Q_2 = 2k_i \sin\theta$, parallel to the surface.

Figure 1 shows depolarized spectra obtained at five different temperatures for the incidence angle $\theta = 45°$. The intensity $I_{VH}(\omega)$ of the scattered light in these spectra

consists of two main contributions:

$$I_{VH}(\omega) = I_{QE}(\omega) + I_{TA}(\omega) \tag{1}$$

corresponding to the quasi-elastic line and to the transverse acoustic modes, respectively. $I_{QE}(\omega)$ arises from polarizability fluctuation due to rotational diffusion of optically anisotropic molecules in the sample [3]. It has been shown that the relaxation processes responsible for the observed quasi-elastic light scattering are q-independent in the small-wave-vector limit of Brillouin scattering [8]. In order to selectively determine the behaviour of $I_{QE}(\omega)$, we thus performed depolarized back-scattering measurements for bulk samples. The experimental spectra are reported in figure 1 as dotted lines. In diluted solutions the spectrum of these fluctuations would be a Lorentzian peak centred at zero frequency with a linewidth proportional to the rotational diffusion constant. In bulky systems, such as glass-forming systems near the glass transition, a single Lorentzian is inadequate for interpolating experimental data due to the presence of a distribution of relaxation times [9]. In the present case, $I_{QE}(\omega)$ could be properly interpolated by means of a 'stretched' Lorentzian function:

$$I_{QE}(\omega) = \frac{I_{QE}^0}{\omega} \operatorname{Im} m\{[1 - i\omega\tau]^{-\beta}\} \tag{2}$$

where τ is the relaxation time and β is the shape parameter of the Cole–Davidson relaxation function. The inelastic part of the spectrum, $I_{TA}(\omega)$, originates from thermally activated TA modes. The coupling between TA modes and the refractive index of the medium can occur both through the orientational fluctuations of optically anisotropic molecules, and via the photoelastic (Pockel's) effect. The first effect is the only one to be present in ordinary liquids, and is responsible for the characteristic dip at $\omega = 0$ in depolarized spectra of liquid systems [3, 10]. The second effect is typical of solid systems and has been proved to be dominant also in the intermediate situation of systems near the glass transition (see reference [9] and references therein). The presence of the TA mode in our spectra is allowed by the interaction geometry adopted here. In fact, it is well known that, in the back-scattering geometry, from bulk isotropic systems, where only phonons with wave vector Q_1 can contribute, there is no scattered light from transverse phonons. In contrast to this, in our case transverse phonons with wave vector Q_2 parallel to the surface can contribute to the scattered light, giving rise to the well defined peaks in the spectra. This interaction geometry has already been introduced to study polymeric films by the Brillouin scattering technique [11, 12]. In that case the thickness of the films was comparable with the phonon wavelength, so an acoustic mode guided by the film, i.e. the longitudinal guided mode, could be revealed together with the longitudinal acoustic mode. In the present case, the thickness of the EPON sample is much larger than the phonon wavelength, and the TA mode is simply a bulk mode travelling parallel to the film. The main advantages of the back-scattering geometry proposed here are that: (i) the same optical system is used both to focus and to reveal the scattered light; (ii) the phonon wave vector Q_2 does not depend on the refractive index n and thus it does not depend on temperature; and (iii) the phonon wave vector can be varied by a simple rotation of the sample. The intensity of the light scattered by TA modes can be written as

$$I_{TA}(\omega) = I_{TA}^0 \frac{2\Gamma_{TA}\omega_{TA}^2}{[\omega_{TA}^2 - \omega^2]^2 + [2\omega\Gamma_{TA}]^2} \tag{3}$$

where ω_{TA}^2 and Γ_{TA} approximately correspond to the frequency position and to the linewidth of the TA peaks [13]. These quantities are frequency dependent, since they can be related

to the real and imaginary parts of the dynamic shear modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ through the relations

$$G'(\omega) = \rho\omega_{TA}^2/Q_2^2 \qquad G''(\omega) = 2\rho\omega\Gamma_{TA}/Q_2^2. \qquad (4)$$

If the Maxwell model of viscoelasticity is appropriate for describing the frequency dependence of the shear modulus, it becomes $G^*(\omega) = i\omega\tau G_\infty(1 + i\omega\tau)^{-1}$, and equation (3) assumes the form used by Tao *et al* [9], provided that I_{TA}^0 is proportional to a frequency-dependent Pockel's coefficient. In the present case of a macromolecular system near the glass transition, the single-relaxation-time approximation and the vanishing of the shear modulus at low frequencies imposed by the Maxwell model are not appropriate [14]. For this reason we do not make any *a priori* assumption as to the form of the relaxation function. Moreover, since the quasi-elastic line dominates the low-frequency part of the spectrum and the contribution of TA modes becomes dominant in a narrow spectral region around the Brillouin peaks only, it is reasonable to assume that ω_{TA}, Γ_{TA}, and I_{TA}^0 do not appreciably change in this frequency region, so their values are kept constant in equation (3).

Table 1. Frequency positions and linewidths of the transverse acoustic mode of the EPON sample, obtained by fitting equation (4) to the Brillouin spectra.

T (K)	f_{TA} (GHz)	Γ_{TA} (GHz)
213	3.54 ± 0.01	0.056 ± 0.002
223	3.49 ± 0.01	0.059 ± 0.002
233	3.41 ± 0.01	0.064 ± 0.001
243	3.25 ± 0.01	0.085 ± 0.002
253	3.07 ± 0.01	0.095 ± 0.005
263	2.91 ± 0.01	0.164 ± 0.008
273	2.71 ± 0.01	0.205 ± 0.008
283	2.47 ± 0.02	0.282 ± 0.018
288	2.32 ± 0.02	0.342 ± 0.020
293	2.21 ± 0.02	0.350 ± 0.027
298	2.09 ± 0.02	0.423 ± 0.029
303	1.94 ± 0.03	0.477 ± 0.044
313	1.65 ± 0.05	0.637 ± 0.049

In summary, the values of ω_{TA} and Γ_{TA} can be obtained by fitting the $I_{VH}(\omega)$ of equations (1)–(4) to the Brillouin spectra, where also I_{TA}^0 and I_{QE}^0 are free parameters while β and τ coincide with the values obtained for the depolarized spectra of the bulk system.

3. Results and discussion

The best fit of $I_{VH}(\omega)$ convoluted with the instrumental linewidth to the experimental spectra has been performed by means of the Levenberg–Marquardt method. This analysis could not be extended beyond 313 K since, as can be seen in figure 1, the TA peak becomes progressively hidden by the quasi-elastic line. The values of the parameters $f_{TA} = \omega_{TA}/2\pi$ and Γ_{TA} obtained by the fitting procedure are reported in table 1 and plotted in figure 2. The increase of the linewidth Γ_{TA} with temperature is due to an increasing absorption which, together with the velocity dispersion indicated by the decrease of the frequency of the peaks, clearly shows the existence of one or more relaxation processes entering the Brillouin frequency region. In some previous studies of glass-forming systems this process
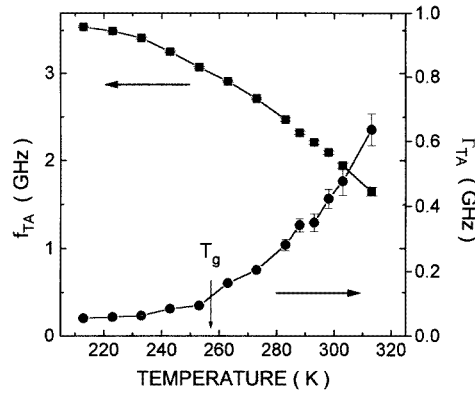
Figure 2. The temperature behaviour of the frequency position (f_{TA}) and linewidth (Γ_{TA}) of transverse acoustic modes of EPON 828.
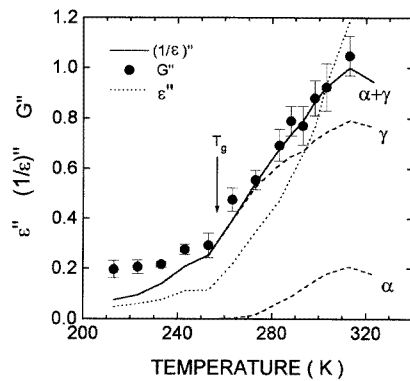

Figure 3. The imaginary part of the dielectric modulus $(1/\epsilon)''$ versus temperature, normalized to its maximum value. The contributions to the modulus from α- and γ-relaxations are shown as dashed lines. The normalized values of the transverse acoustic modulus G'', obtained from the frequency position and linewidth of the transverse acoustic modes by using equation (4), are shown as solid circles. The imaginary part of the dielectric constant is also shown for comparison.

was identified as the main or structural relaxation, whose characteristic time diverges close to the glass transition. But this interpretation does not apply to the present case, since the linewidth of the TA peaks is larger than zero even at temperatures below the glass transition temperature of the epoxy resin ($T_g = 257$ K [15]), thus suggesting contributions to the absorption to arise from diffusive processes which remain activated below T_g, i.e. secondary processes. In fact, the existence of a well defined secondary relaxation in this system was demonstrated by previous dielectric experiments [15]. The origin of the relaxation indicated by Brillouin measurements can be analysed by comparing dielectric and Brillouin results (figure 3). The imaginary part G'' of the elastic modulus has been determined from equation (4), using the values of ω_{TA} and Γ_{TA} obtained from the spectra. The imaginary part $(1/\epsilon)''$ of the dielectric modulus has been calculated by using the values of ϵ from reference ([15]), taken at the frequencies of the TA modes for each spectrum. The requirement of comparing G'' with $(1/\epsilon)''$, rather than with ϵ'', is well known in the literature [16, 17], and it is

confirmed by the temperature behaviour of ϵ'' which is also reported in figure 3 as a dotted line. The separate contributions to the dielectric loss arising from the main and secondary relaxations are also shown, as dashed lines, in figure 3.

The similarity between the temperature behaviour of G'' and that of $(1/\epsilon)''$ in figure 3 is apparent. In particular, we remark that: (i) for temperatures higher than T_g, the values of G'' and $(1/\epsilon)''$ overlap within the experimental error; (ii) the slope of the loss curves markedly changes near T_g; and (iii) for temperatures lower than T_g, the values of G'' and $(1/\epsilon)''$ remain non-zero. The close resemblance of the two curves for $T > T_g$ leads us to infer that the dynamics responsible for the dielectric relaxation is similar to that responsible for acoustic relaxation. This result supports the predictions of some theories concerning the dynamics of glass-forming systems. In particular, the mode-coupling theory [5] predicts the existence of a universal correlation function in the critical spectrum region covering the present Brillouin frequency window. On the other hand, in the temperature range analysed here, neither Brillouin data nor previous dielectric results could provide evidence for a critical temperature T_c or the validity of a time–temperature scaling law predicted by the simplified version of the theory [5]. In other cases where this discrepancy was observed, it was attributed to the occurrence of secondary relaxations not included in the simplified version of the theory [18]. Actually, the dielectric data of figure 3 show that the γ-relaxation dominates the response of the system in this frequency and temperature region. Also the change of the slope of the losses near T_g can be attributed to the secondary relaxation. In fact, a previous dielectric study of the system in this region [15] has shown a marked change in the behaviour of the strength of the γ-relaxation, which directly reflects the temperature behaviour of the loss. For temperatures lower than T_g, both elastic and electric losses are related to the γ-process, which is the only one to be activated in this region. Moreover, figure 3 clearly shows that G'' is higher than $(1/\epsilon)''$, suggesting a higher sensitivity of Brillouin data to the secondary relaxation. Secondary relaxations were also found to markedly affect density fluctuations as revealed by polarized Brillouin spectra from polybutadiene [12], polyacrylates [11, 19], and different polymeric systems [20]. In those cases an Arrhenius behaviour of the relaxation time was generally observed, which is typical of secondary relaxations, and consistent with dielectric data on the same systems.

In conclusion, for the epoxy system investigated here, at temperatures higher than T_g a quantitative agreement of the temperature behaviour of shear and dielectric losses in the GHz region has been found. The single-relaxation-time approximation has proved to be inappropriate to account for the attenuation of TA modes in this region. In fact, both structural and secondary relaxations, each of them characterized by a wide distribution of relaxation times, affect Brillouin data, giving rise to a dispersion region that extends over a temperature range much larger than that typical of acoustic or ultra-acoustic measurements [16]. The discontinuity in the slope of G'' close to T_g has been attributed to the change of the slope of the γ-relaxation strength which occurs near the glass transition. For temperatures lower than T_g, a progressive departure of shear data from the dielectric behaviour has been demonstrated, suggesting a marked sensitivity of Brillouin data to secondary relaxation processes.

References

[1] Jäckle J 1986 *Rep. Prog. Phys.* **49** 171
[2] Grimsditch M, Bhadra R and Torell L M 1989 *Phys. Rev. Lett.* **62** 2616 and references therein
[3] Berne B J and Pecora R 1976 *Dynamic Light Scattering* (New York: Wiley)
[4] Cummins H Z, Li G, Du W M, Hernandez J and Tao N J 1994 *J. Phys.: Condens. Matter* **6** A51

  [5] Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241
  [6] Champion J V and Liddell P 1982 *J. Polym. Sci.: Polym. Phys. Edn* **20** 327
  [7] Nizzoli F and Sandercock J R 1990 *Dynamical Properties of Solids* ed G Horton and A A Maradudin
       (Amsterdam: North-Holland)
  [8] Du W M, Li G, Cummins H Z, Fuchs M, Toulouse J and Knauss L A 1994 *Phys. Rev.* E **49** 2192
  [9] Tao N J, Li G and Cummins H Z 1992 *Phys. Rev.* B **45** 686
 [10] Wang C H and Zhang J 1986 *J. Chem. Phys.* **85** 794
 [11] Fioretto D, Carlotti G, Palmieri L, Socino G, Verdini L and Livi A 1993 *Phys. Rev.* B **47** 15 286
 [12] Fioretto D, Palmieri L, Socino G and Verdini L 1994 *Phys. Rev.* B **50** 605
 [13] Soltwisch M, Spiroski A, Kisliuk A, Sokolov A P, Rössler E and Quitmann D 1995 *Phil. Mag.* B **71** 683
 [14] Philippoff W 1965 *Physical Acoustics* vol IIB, ed W P Mason (New York: Academic)
 [15] Casalini R, Fioretto D, Livi A, Lucchesi M and Rolla P A 1997 submitted
 [16] McCrum N G, Read B E and Williams G 1991 *Anelastic and Dielectric Effects in Polymeric Solids* (New
       York: Dover)
 [17] Fioretto D, Livi A, Rolla P A, Socino G and Verdini L 1994 *J. Phys.: Condens. Matter* **6** 5295
 [18] Cummins H Z, Li G, Du W M and Hernandez J 1994 *J. Non-Cryst. Solids* **172–174** 26
 [19] Fioretto D, Palmieri L, Socino G and Verdini L 1994 *J. Non-Cryst. Solids* **172–174** 1130
 [20] Patterson G D 1985 *Dynamic Light Scattering* (New York: Plenum)