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Brillouin scattering from epoxy resins and gels

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Summary

The isothermal curing process of the system diglycidyl ether of Bisphenol A/poly(oxypropylene)diamine (Jeffamine D-400) without and in the presence of solvent (Diglyme) was investigated by Brillouin spectroscopy for the stoichiometric amounts of epoxide and amine groups. The spectroscopic data have been explained in terms of the relaxing viscosity model in the former case and by the scattering of phonons by stationary heterogeneities in the latter one. It is suggested that these heterogeneities may be small air bubles released during curing and frozen in due to the high viscosity at and above the gel point.

Introduction

Brillouin spectroscopy has been proposed as an effective method for monitoring the kinetics of thermal polymerization (e.g. 1). A number of authors (1-3) studied the kinetics of radical polymerization of styrene at temperatures below the glass transition temperature (T_g) of bulk polystyrene. For explaining the observed Brillouin shifts and line width changes during the reaction, Jackson and Stevens (1) proposed a relaxing viscosity model, where the characteristic relaxation times were dependent on the degree of polymerization. Polymerization of butyl methacrylate at 60°C above the polymer glass transition temperature has been studied in Ref. (4). Both the phonon velocity and attenuation showed a relaxing behaviour during conversion. The results of Raylegh-Brillouin spectroscopy applied to isothermal curing in two kinds of epoxy/amine systems were compared with those of torsional braid analysis (5). It has been found that the Brillouin shift increased with an increase in density. The Landau-Placzek (L-P) ratio (intensity ratio of Rayleigh line to Brillouin lines) increased remarkably at gelation, while the Brillouin shift and line width were not sensitive to the onset of gelation. They were markedly affected as the system approached the glassy state, though.

In this study isothermal curing of epoxy resins is investigated by Brillouin spectroscopy. Particularly, the behaviour of the scattered light spectra at gelation is studied. Curing of the system diglycidyl ether of Bisphenol A (DGEBA)/poly(oxypropylene)diamine (Jeffamine D 400) was examined without and in the presence of solvent (diethylene glycol dimethyl ether). The spectroscopic data have been explained in terms of the relaxing viscosity model and/or by the scattering of phonons by stationary heterogeneities.

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Theoretical considerations

The Rayleigh-Brillouin scattering of a viscoelastic polymer fluid arises mainly from local density fluctuations. The velocity and attenuation of hypersonic waves can be obtained from the Brillouin frequency shifts, ν_B, and line width, $\Delta\nu_B$. The longitudinal sound (phonon) velocity V(K) for waves of the wavevector magnitude K is given by (e.g. Ref. 6)

$$V(K) = 2\pi\nu_B/K, \qquad (1)$$

where $K = 4\pi n \sin(\Theta/2)/\lambda$, λ is the wavelength of the incident light, n is the refractive index of the medium and Θ is the scattering angle. Provided the observed Brillouin lines have a Lorentzian profile and the amplitude of the sound waves damps according to $\exp(-\alpha r)$ in space, the attenuation of the hypersonic sound per sound wavelength, $\alpha\lambda_s$, is then given by (e.g. Ref. 6)

$$\alpha\lambda_s = 2\pi\Delta\nu_B/\nu_B\ , \qquad (2)$$

with $\Delta\nu_B$ and ν_B measured in Hz.
According to the viscoelastic model of polymer fluids the sound velocity V is given by the longitudinal elastic modulus, $M(\omega)$, of the medium (7):

$$V^2 = M(\omega)/\rho, \qquad (3)$$

where $M(\omega) = K(\omega) + (4G(\omega)/3)$, $K(\omega)$ and $G(\omega)$ are, respectively, the frequency dependent compression and shear moduli, ω is the frequency and ρ is the polymer density.
The attenuation per sound wavelength is given by (1)

$$\alpha\lambda_s = 4\pi\omega\eta(\omega)/3\rho V^2\ , \qquad (4)$$

where $\eta(\omega)$ is the frequency dependent viscosity.
The simple model of relaxing polymeric fluids including only one compressional (τ_c) and one shear viscosity relaxation time (τ_s) may be used for semi-quantitative description of viscoelastic properties of polymers. The frequency dependent moduli can be written in the form (e.g. Ref. 4):

$$K(\omega) = K_o + (K_\infty - K_o)[\omega^2\tau_c^2/(1 + \omega^2\tau_c^2)]$$

and (5)

$$G(\omega) = G_\infty\omega^2\tau_s^2/(1 + \omega^2\tau_s^2)$$

where K_∞ and G_∞ are the infinite frequency values of the moduli and K_o is the zero frequency modulus.
The frequency dependent viscosity is $\eta(\omega) = \eta_s(\omega) + \eta_c(\omega)$, where η_s and η_c are the shear and volume viscosity:

$$\eta_s(\omega) = G_\infty\tau_s/(1 + \omega^2\tau_s^2)$$

and (6)

$$\eta_c(\omega) = (K_\infty - K_o)\tau_c/(1 + \omega^2\tau_c^2)$$

To understand more fully the changes of the Brillouin spectra observed during curing, a low molecular weight liquid far above its glass transition temperature and a polymer near the glass transition are examined. In the former case the Brillouin line width follows the shear viscosity, $\eta_S(\omega)$ (e.g. Ref. 6). Near T_g the Brillouin splitting is determined by the limiting high-frequency longitudinal modulus, M_∞. In typical polymeric fluids $\Delta\nu_B$ decreases as the material approaches T_g due to slowing down of relaxation proceses. The remaining hypersonic attenuation in polymer near T_g was attributed to vibrational specific heat relaxations (6). In the intermediate case, when the structural relaxation time is comparable to ν_B, $\Delta\nu_B$ should go through a maximum. A sharp increase of ν_B $(M(\omega))$ is indicated by relation (5) combined with (1) and (3).

Experimental

Materials: Diglycidyl ether of Bisphenol A (DGEBA)(CIBA-Geigy MY-790) having the number-average molecular weight $M_n =$ $= 350$, epoxy equivalent $\gamma_E = 174.5$ g/mol epoxy, and functionality $f_n = 2.0$ was used. Jeffamine D-400 (TEXACO) had $M_n = 397$ and the amino equivalent $\gamma_A = 105$ g/mol H in NH_2 which gives $f_n = 3.75$. Diethylene glykol dimethyl ether (Diglyme) was of analytical grade purity.

Sample preparation: DGEBA was dissolved in Jeffamine D 400 or Diglyme solution of Jeffamine D 400 at 45°C, stirred for 5 minutes, filtered into optical cylindrical cells and degassed at room temperature. The initial molar ratio of amine hydrogens to epoxy groups $r = 1$ $(=2[NH_2]/[EPOXY])$ was used. Two types of samples differing in the solvent content were studied: (i) epoxy samples without any solvent (E), and (ii) epoxy samples diluted with 42 wt% of Diglyme (ED). Curing took place at 60°C and 90°C for samples E and ED, respectively. Curing at these temperature was slow enough to enable one to record the Brillouin spectrum practically at a constant chemical composition.

Determination of epoxy groups: Near infrared spectra were recorded with a Perkin-Elmer-Hitachi Spectrometer 340. The relative concentration of epoxy groups was calculated from the peak height at 2207 nm and compared with the peak height at 2138 nm taken as an internal standard.

Viscosity measurement: A capillary viscometer (0.6 mm diameter) was used for viscosity measurements up to 2.5×10^{-2} Pa s. Still higher values of viscosity were determined as a function of the degree of polymerization using a falling sphere viscometer, correcting for finite length and diameter with the method of Francis (7).

Light scattering technique: The light source was an argon-ion laser operating at 488.0 nm and delivering 200-300 mW of vertically polarized single mode beam of the incident light. The light scattered at the scattering angle of 90°±1° from the sample was spectrally analyzed using a triple pass pressure scanned Fabry-Perot interferometer (8). For the Brillouin spectra reported here, the free spectral range of 30 GHz was chosen in order to provide a sufficient separation of the Brillouin doublet and the central Rayleigh line. The observation of the spectrum was made in single sweep (15 minutes) of the interferometer. The sample was held in a thermostated container with an immersion liquid (glycerol). The fluctuation of the sample temperature was below ± 0.1°C.

The Brillouin splittings, ν_B, were determined directly from the observed peak shifts, and the line width, $\Delta\nu_B$, was corrected for instrumental broadening by substracting the instrumental half-width from the observed half-width at half-height (9).

Results and discussion

The Brillouin shift ν_B and $\Delta\nu_B$, the line width of the Brillouin doublet are plotted in Fig. 1a as a function of the curing time t for sample E (cured at 60°C without solvent). The corresponding time dependence of the conversion of functional groups, ξ , is given in Fig. 1b.

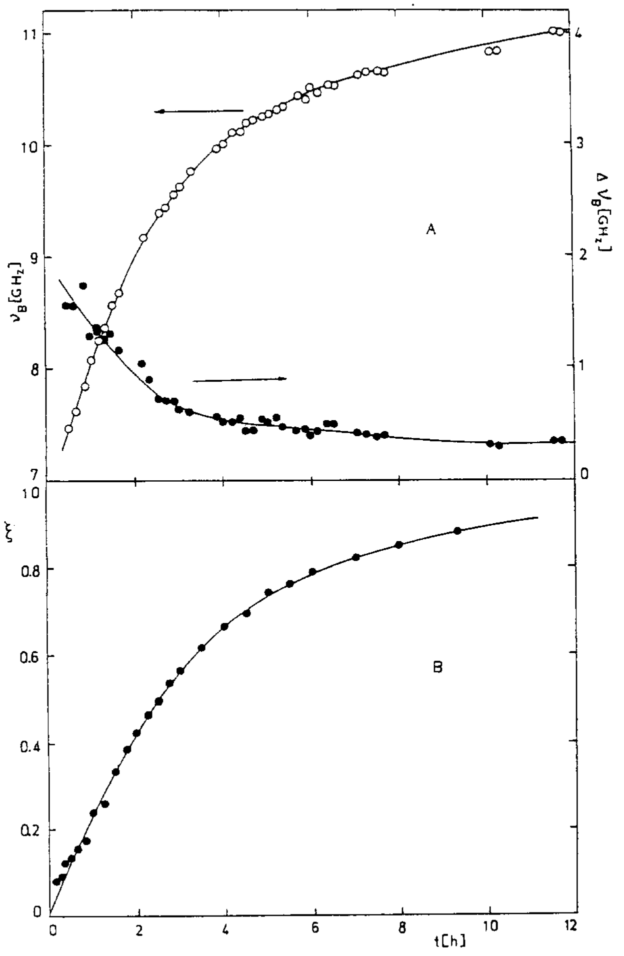

Fig. 1 Measured quantities for the system E as a function of reaction time t: (a) The Brillouin shift ν_B and the width of the Brillouin doublet $\Delta\nu_B$, (b) the conversion of functional groups ξ

The gel point for this system corresponds to a conversion $\xi \approx 0.60$ (10). The Landau-Placzek ratio (not presented here) exhibited a substantial scatter due to the speckle pattern effect at the small input aperture used in this study. Therefore, we have not been able to confirm the results of the work (5) where a remarkable increase of L-P ratio was observed upon approaching the gel point. Nevertheless, the static light scattering experiments clearly show that the scattering intensity remarkably increases prior to gelation and is nearly independent of the curing time above the gel point. This result will be discussed in detail elsewhere (11).

As for the parameters of the Brillouin lines, ν_B increases and $\Delta\nu_B$ decreases with increasing t and/or conversion. Both quantities were not affected by gelation. This is in full agreement with the main results of the work (5). The changes of both quantities with ξ can be qualitatively explained in terms of the relaxing viscosity model described in the first part of the present work. Since relaxation effect has not been observed in the t dependences of the discussed quantities (t dependences of both ν_B and $\Delta\nu_B$ are monotonous), we have supposed that the measurements in the hypersonic region were realized well above the relaxation region; $\nu_B > 1/\tau_C$, $\nu_B > 1/\tau_S$. The increase of ν_B and decrease of $\Delta\nu_B$ with increasing ξ or t can be explained by an increase of τ_S and τ_C (T_g increases with ξ (12)).

The values of ν_B and $\Delta\nu_B$, the scattered light intensity I, the zero frequency shear viscosity η_S as a function of the curing time t for the epoxy sample ED (the sample with 42 wt% of Diglyme) are shown in Fig. 2. Because conversion ξ could not be measured by infrared spectroscopy due to the high absorption of Diglyme, η_S was measured instead of ξ to obtain the gel time. Two fundamental effects were observed in the Brillouin experiments in the course of reaction (Fig. 2a): a small ($\approx$ 9%) increase in ν_B and a large ($\approx$250%) increase in the width of the Brillouin lines which in turn means a large decrease in the life-time of phonons. The above two features cannot be explained by the relaxing viscosity model without physically unrealistic changes of parameters of Eqs (5) and (6): e.g., very high values of M_0 ($\approx M_\infty$) would have to be assumed to explain the small increase in ν_B. It has been concluded therefore that a relaxational mechanism is unlikely to be responsible for the observed effects.

As an alternative the scattering of phonons by stationary scatterers has been considered. This so called scattering interpretation was successfully applied to the data of Brillouin scattering from gelatin gels (13). The scattering of phonons by scatterers results in a shortening of the life-time of the sound waves which manifest itself in an increase of $\Delta\nu_B$($\Delta\nu_B \sim 1/\tau$, where τ is the life-time of phonons). While the effect of phonon scattering on sound velocity represents a small correction only (13,14), the Brillouin width, in the absence of other attenuation effects, can be influenced substantially (the primary effect). Thus, the attenuation α in a system of N spheres of radius a (scatterers) embedded in a medium with a negligible sound attenuation was shown to be $\alpha = N\Sigma_S$, where Σ_S is the scattering cross-section of one sphere, given by (14)

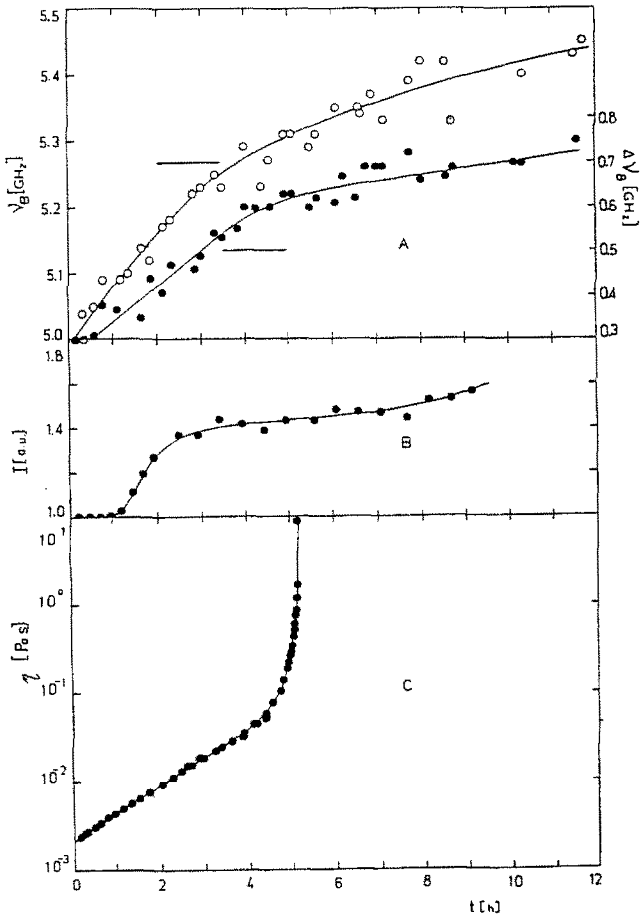

Fig. 2 Measured quantities for the system ED (sample with 42 wt% of Diglyme) as a function of reaction time t: (a) The Brillouin shift ν_B and the width of the Brillouin doublet $\Delta\nu_B$; (b) the scattered light intensity I; (c) the zero frequency shear viscosity η_s

$$\Sigma_s = (4/9)\pi a^2 (ka)^4 \left[\left| \frac{\kappa_s - \kappa_m}{\kappa_m} \right|^2 + \left| \frac{\rho_s - \rho_m}{2\rho_s - \rho_m} \right|^2 \right] , \qquad (7)$$

where ρ_s, κ_s(ρ_m, κ_m) are, respectively, the density and compressibility of the spheres (medium) and $k = 2\pi\lambda_s$. Relation (7) is formally very similar to the well-known Rayleigh relation for the intensity of light scattered by a collection of small spherical scatterers. Thus, the term in square brackets in Eq.(7) plays an analogous role as the refractive index difference in the theory of Rayleigh light scattering (15).

In the scattering interpretation the increase in $\Delta\nu_B$ (cf. Fig. 2a) suggests that some kind of density fluctuation (of the order of the hypersonic wavelength) takes place prior to gelation. This scattering interpretation of the changes in $\Delta\nu_B$ is supported by static scattering experiments which show the same scattering mechanism. Both $\Delta\nu_B$ and the scattered intensity I as a function of t are qualitatively very similar in that both increase remarkably prior to gelation (cf. Fig. 2a and 2b). Similar effects were already observed in earlier light scattering studies on epoxy resins (11,16,17). It is to be noted that the volume fraction of separated phase (of lower refractive index (17)) is of the order of 10^{-3}(11,17) and the diameter of the scatterers is ~1 µm (11). The above facts suggest that these scatterers may be small air bubles released during curing and frozen in due to the high viscosity at and above the gel point.

In conclusion it should be pointed out why the effect of the phonon scattering was not observed in samples of type E (cured without solvent). We assume that the weak phonon scattering in these samples is masked by the strong phonon absorption ($\sim \eta(\omega)$) due to the relaxational mechanism.

Conclusions

The changes of quantities I and $\Delta\nu_B$ observed near the onset of gelation do not reflect the sol-gel transition directly but only indirectly through viscosity changes. Most probably, the viscosity controls diffusion of small air bubles produced during curing out of the sample. We suppose that the changes of the L-P ratio observed in Ref.(5) can be explained analogically.

References

(1) Jackson D A, Stevens J R (1975) Mol Phys 30: 911

(2) Coakley R W, Mitchell R S, Hunt J L, Stevens J R (1976) J Macromol.Sci Phys B12: 511

(3) Alms G R, Patterson G D, Stevens J R (1979) J Chem Phys 77: 2145

(4) Champion J V, Liddell P (1980) Polymer 21:1247

(5) Kondo S, Igarashi T, Nakamura T (1981) J Appl Polym Sci 26: 2337

(6) Jarry J P, Patterson G D (1981) Macromolecules 14: 1281

(7) Van Wazer J R, Lyons J M, Kim K Y, Colwell R E, "Viscosity and Flow Measurements", Wiley, 1966

(8) Fousková A, Pavel M, Holakovský J (1988) Czech J Phys (Czech) 38: 54

(9) Leidecher H W, La Macchia J T (1967) J Acoust Soc Am 43: 143

(10) Dušek K, Ilavský M, Štokrová Š, Matějka L, Luňák S in "Crosslinked Expoxies", (Eds Sedláček B, Kahovec J) Walter de Gruyter, Berlin, New York, 1987, p. 279

(11) Grof K, Štěpánek P, Koňák Č, Jakeš J, Dušek K (1988) 9th Polymer Networks Group Meeting "Networks 88", Freiburg i.Brsg.

(12) Havlíček I, Dušek K in "Crosslinked Epoxies", (Eds Sedláček B, Kahovec J) Walter de Gruyter, Berlin, New York, 1987

(13) Bedborough D S, Jackson D A (1976) Polymer 17: 573

(14) Morse P M, Uno Ingard K "Theoretical Acoustics", McGraw-Hill, New York, 1968
(15) Kerker M "The Scattering of Light", Academic Press, New York, 1969
(16) Bogdanova L M, Belgovskii I M, Irzhak V I, Rosenberg B A (1981) Polymer Bull 4: 119
(17) Netshvoldova E M, Cakhonenko L S, Belgovskii I M, Prut E V (1987) Vysokomol Soed 29: 1269

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