Dynamic Light Scattering and Ultrasonic Investigations During the Cure Reaction of an Epoxy Resin

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SYNOPSIS

Brillouin scattering (BS), photon correlation spectroscopy (PCS), and ultrasonic (US) measurements were conducted to study the curing process of diglycidyl ether of bisphenol A with butane-1,4-diol at a curing temperature of 100°C. The experimental techniques probe the primary glass–rubber transition during the curing reaction. The primary relaxation time τ obtained from the BS and US velocity and absorption increases with curing time and hence the BS experiment measures τ at earlier stages of cure than the US experiment. The relaxation times at a different extent of reaction and for different measuring temperatures are consistent with BS, US, PCS, and DSC measurements and conform to a single reduced Vogel–Fulcher–Hesse–Tamann equation. Furthermore, the US experiments show evidence of secondary relaxations in the epoxy system.

INTRODUCTION

With the increasing use of epoxy resins, especially for composite materials, it is very critical to develop *in situ* methods applicable during the curing reaction. In a series of papers[1-3] we have demonstrated that investigations of longitudinal ultrasonic properties can be successfully applied to study the influence of chemical composition, curing temperature, and catalyst on the curing process and the fully cured samples. From the time dependence of the ultrasonic absorption α and velocity v, it was possible to estimate the gelation time, the effect of primary glass–rubber transition, and the final stage of curing.

From Brillouin experiments during the polymerization process[4] it is known that the change to solidlike properties can be observed at hypersonic frequencies. Rayleigh–Brillouin spectroscopy has also been employed during the hardening process of epoxy systems.[5-7] In the earlier study,[5] the sound velocity v and attenuation α remained virtually constant during gelation, whereas in a very recent investigation[6] these quantities changed considerably during copolymerization. In the initial stages, the measured v and α correspond to the low frequency values and, as the curing proceeds, they go over to the high frequency values. Dusek et al.[7] have attempted to account for the changes in Brillouin shift and the line width by viscoelasticity and/or by scattering of phonons by stationary heterogeneities. The analysis of Brillouin spectra can be, however, supported by complementary ultrasonic measurements.

In the course of curing the sample changed from a liquid mixture of low molecular weight components to a highly crosslinked polymer network. The characteristic relaxation time τ, associated with these structural changes, continuously increases as the reaction proceeds. At constant temperature T and probing frequency ω a crossover from the fast ($\omega\tau \ll 1$) to the slow ($\omega\tau \gg 1$) relaxation limit should be observed. For a given epoxy system and constant T, the crossover is expected to appear at earlier stages of the experiment if higher ω is used. Ultrasonic and hypersonic (Brillouin scattering) techniques respectively in MHz and GHz frequency range can be employed to measure the dispersion in v and α caused mainly by structural relaxation. These sound properties might also be influenced by interactions between sound waves in the fluid and elastic waves

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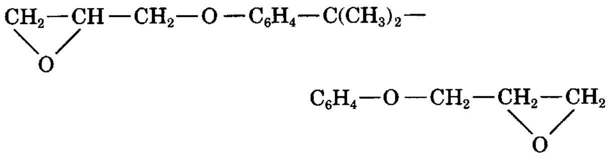
in the gel,[8-10] which are formed during the curing reaction of the epoxy resins.

In the present investigation we have employed hypersonic spontaneous Brillouin scattering, photon correlation spectroscopy, and ultrasonic measurements to study structural changes during the curing reaction[2] of diglycidyl ether of bisphenol A:



(DDGE)

with 1,4-butanediol in the presence of catalyst $Mg(ClO_4)_2$.

EXPERIMENTAL

Brillouin Scattering

The polarized Brillouin spectra were taken at a scattering angle of 90° using a spectrometer as described elsewhere.[11] The light source was an argon ion laser (Spectra Physics 2020) operating at a single mode at 488 nm with a power of 100 mW. The scattered light was spectral analyzed by a piezoelectrically scanned Fabry–Perot interferometer. The operating finesse was between 50 and 60 and the spectra were taken over a free spectral range of 23.08 GHz. A Burleigh DAS-10 stabilization system was used to maintain finesse and stabilize cavity separation. Experimental Brillouin spectra were fitted to a Lorentzian function considering the overlap of neighboring orders. After subtraction of the instrumental linewidth (0.42 GHz), the full width $2\Gamma_B$ and the shift f_B were obtained. The linewidths are reproducible to better than 10%, whereas the uncertainty in f_B is better than 3%. The relationships between the Brillouin linewidth $2\Gamma_B$ (full width at half height in Hz), the shift f_B, and the sound parameters are

$$\alpha = 2\pi\Gamma_B/v \qquad (1)$$

$$v = f_B\lambda_0/[2n\sin(\theta/2)] \qquad (2)$$

where λ_0 is the wavelength of the incident light, n is the refractive index, and θ is the scattering angle. The Brillouin spectra of the epoxy sample were recorded at 100°C during the curing reaction. The curing was slow enough to record the Brillouin spectrum (200 s) at a practically constant extent of reaction. A second sample was measured at a temperature of 25°C after cooling the sample from the curing temperature of 100°C, in order to slow down the structural relaxation. After recording the Brillouin spectra the curing of this sample was continued at 100°C.

Ultrasonic Measurements

The ultrasonic pulse-transmission method[1] modified for investigation of the curing process has been described in detail elsewhere. The frequency of the longitudinal waves was 1 MHz. The measured values are the ultrasonic velocity v and the absorption coefficient α. The relative ultrasonic absorption $\Delta\alpha = [\ln A(t=0) - \ln A(t)]/x$ was calculated from the amplitudes of the first pulse at the beginning of the measurement $A(t=0)$ and during curing $A(t)$. x is the acoustic path length in the sample. The curing reaction was monitored in the measuring cell at 100°C. The absolute error of the sound velocity is about 5% whereas the relative error is about 1‰. For the initial product (20 min curing), a product after 170 min curing and a fully cured sample the frequency dependence of c and α was measured at 25°C by a recently developed Fourier transform ultrasonic technique[12] from 4 to 25 MHz. The accuracy of the sound velocity for this method was better than 1‰.

Photon Correlation Spectroscopy

The time correlation function of the polarized light scattered intensity for the fully cured sample at 135°C was measured at a scattering angle of 90°. The time correlation function over 8 decades in time was measured with a 256 channel full correlator (ALV-5000) in one run. The analysis of the experimental time correlation function is described elsewhere.[13]

Preparation of the Sample

The reaction mixtures contain a molecular ratio of diglycidyl ether (DDGE) : butane-1,4-diol = 1 : 0.25. As a catalyst we used 3 mol % $Mg(ClO_4)_2$. The melted DDGE (~ 40°C) was mixed with a known weight of butane-1,4-diol and heated to 100°C. Then the reaction was started ($t = 0$) by adding the $Mg(ClO_4)_2$ and stirring the sample for 20 min. This initial product was used for all the measurements. All samples were then stirred for a total of 100 min in the first stage of curing. The first Brillouin spectrum was taken for the initial product 20 min after adding the catalyst and the stirring was continued by a stirring bar in the measuring cell; hereafter the rapid increase of the viscosity precluded further stirring. For the ultrasonic measurements the same product was stirred outside the measuring cell and then the sample was transferred into the cell.

RESULTS AND DISCUSSION

Curing Process

Figure 1 shows the dependence of ultrasonic and hypersonic velocity v and the corresponding absorption α on the curing time at 100°C. In the course of curing, the sample changes from a low molecular liquid mixture to a highly crosslinked polymer network as shown by the variation of the sound velocity. In an intermediate curing stage, when the structural relaxation time is comparable to the probe frequency (f_{us} or f_B) the absorption should exhibit a maximum whereas the velocity should further increase. From the ultrasonic investigations (see Refs. 1–3 and references therein), it seems to be established that the absorption maximum and the step in velocity can be connected to the pass through of the primary glass–rubber relaxation (dynamic glass transition) through the measuring frequency at a given curing temperature.

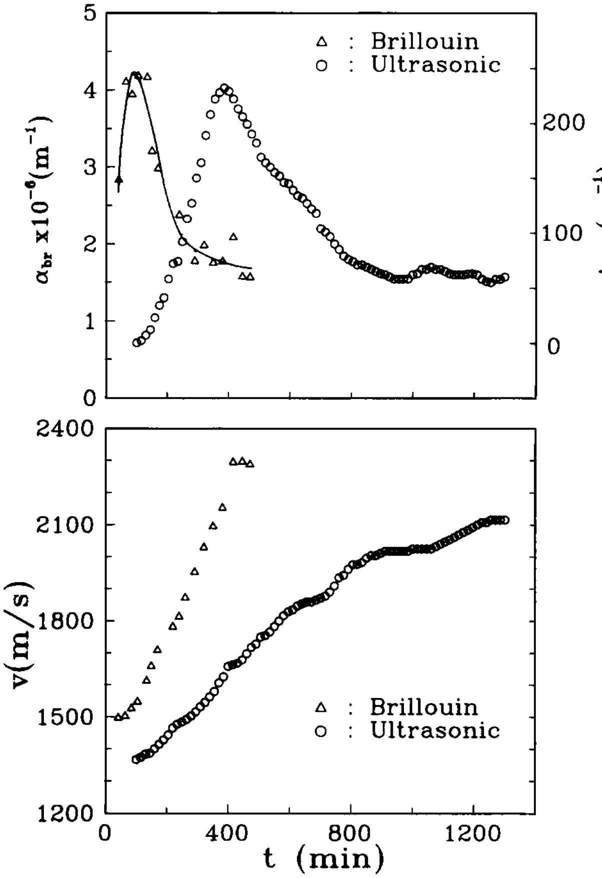


Figure 1 Sound absorption and velocity versus time of cure for an epoxy sample of DDGE with butane-1,4-diol from ultrasonic (1 MHz) and Brillouin scattering measurements at the curing temperature of 100°C.

From the frequency–temperature dependence of the primary relaxation (usually expressed by a WLF or the equivalent Vogel–Fulcher–Hesse–Tamann (VFHT) expression), it is expected that at a given temperature the crossover occurs at earlier times of cure for higher probe frequencies. (A schematic representation is given in Figure 5, see below). This is in accord with the findings of Figure 1. The assumption that in both experiments the same structural changes are detected can be supported by the relative changes in absorption and the similar values for the sound velocity at the beginning and the final stage of curing. The small differences in the later values can be attributed to additional processes between the MHz and GHz frequency region (see below). The shoulder and the small maxima in the absorption and the structure in the sound velocity for the ultrasonic experiment at higher curing times can be attributed to secondary relaxations. These relaxations are not so clearly indicated in systems without co-components (e.g., without diols) and for different catalysts (see Ref. 3), because of the simpler network structure of those systems. It should be, however, noted that the BS experiment alone cannot provide evidence of the presence of secondary relaxations.

The gel point of the system has been estimated by viscosity measurements to occur at about 170 min, which is in agreement with the initial increase in the ultrasonic absorption and the changes in ultrasonic velocity.[1–3] The small effect of the gelation on the ultrasonic velocity can be rationalized only if the system is highly crosslinked. However, for a more detailed analysis of the ultrasonic data at the gelpoint (e.g., for a quantitative test of Bacris theory[9,10]) measurements with a logarithmic accuracy and samples with a better separation of gelation and structural relaxation are needed.

The effect of the network on the hypersonic dispersion has theoretically been considered by Margusee and Deutch.[8] They suggested that the density fluctuations propagating through the medium as sound waves will suffer an additional scattering from the relative fixed elastic network. This scattering will lead to a shorter lifetime of the density fluctuations and to a spectral broadening. However, there is no indication of linewidth broadening or frequency shift at times above the gelpoint for our system (see Figs. 1 and 2). The system considered here is a highly crosslinked epoxy, i.e., the condition[8] that the light wavelength is large compared to the mean distance separating network regions ($M_c \sim 200$ g/mol) is fulfilled. But there is another complication for the application of this theory, because of the fact that the matrix is frozen in for the hypersonic frequency. As we have shown above, the main glass–rubber transition occurs much earlier for the Brillouin experiment than the frequency independent gel point. Therefore, the model of Margusse and Deutch,[8] where an elastic network is invaded by a liquid, is not fulfilled for our system. For the frequency scale of the hypersonic wave, the elastic polymer network must be considered to be in the surrounding of a frozen in solid glass. In contrast, for the length and frequency scale of ultrasonic experiments, the same system can be considered as a polymer network in a concentrated solution of its own reaction bath, i.e., as a network in a fluid. This is in agreement with the finding of Patterson[14] that the primary variable which affects the hypersonic properties of polymeric systems is the local structural relaxation and long range or other slow processes are often not observable at hypersonic frequencies. Even for typical gels[14] (Polyepoxide gel in 40% solution), no effect of crosslinking was measurable in the hypersonic properties.

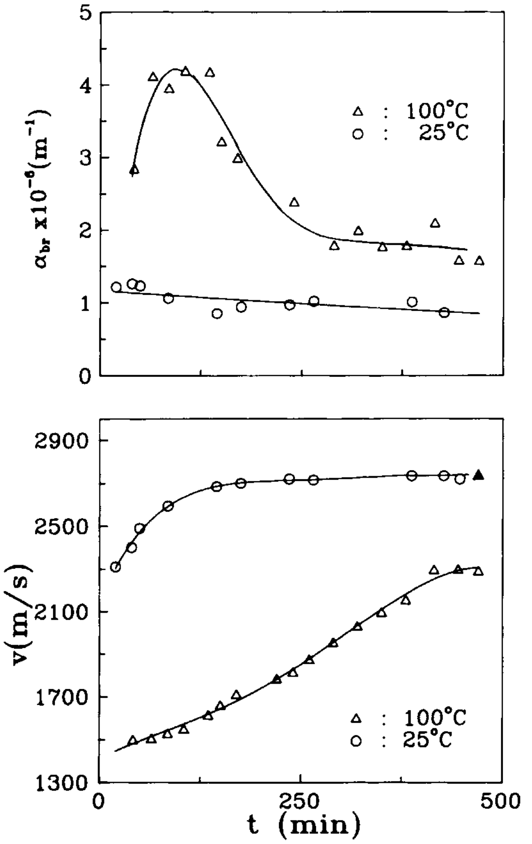


Figure 2 Hypersonic absorption and velocity Brillouin scattering versus time of cure for an epoxy sample of DDGE with butane-1,4-diol at 100°C (△) and 25°C (○). The first sample (△) was cured and measured at 100°C. The second sample (○) was cured at 100°C and the Brillouin spectra were recorded after cooling the sample to 25°C. The symbol (▲) denotes the final curing stage from the first sample measured at 25°C.

In order to check the consistency of the hypersonic dispersion of Figure 1 we have investigated the same system at 25°C. Figure 2 displays the hypersonic dispersion for the system measured during curing at 100°C and a system cured at 100°C but measured after cooling the sample to 25°C. Unlike the situation at 100°C no maximum in the hypersonic absorption is observed at 25°C; only an increase in v and small changes in α are observed with increasing conversion. As discussed above, v and α were not affected by the gelation. The behavior displayed in Figure 2 is in accord with the much slower structural relaxation time at 25°C. At this temperature the Brillouin spectrum corresponds to the high frequency limit ($\omega_B \tau \gg 1$). Thus the velocity reaches rapidly the limiting high frequency velocity v_∞ as compared to the velocity data at 100°C. In this context it is interesting to note the nice agreement between the velocities for both final products measured at 25°C (symbols ○ and △ in Fig. 2). The hypersonic attenuation at 25°C remains low as expected ($\omega_B \tau \gg 1$).

SOUND DISPERSION

To investigate the slow structural relaxation at 25°C for the initial product (20 min curing) we have employed a Fourier transform ultrasonic technique. In Figure 3 the ultrasonic absorption α/f^2 from 4 to 25 MHz and the corresponding hypersonic absorption is plotted versus frequency. Despite the relatively small ultrasonic frequency range we attempt to represent the absorption data α/f^2 by the Fourier transform of the derivative of the Kohlrausch–Williams–Watts (KWW) relaxation function $\Phi(t) = \exp[-(t/\tau)^\beta]$, according to

$$\frac{\alpha}{f^2} = \frac{\pi M''}{g v^3 f}, \quad M'' = M_r \int_0^\infty \Phi(t) \cos(\omega t)\, dt \qquad (3)$$

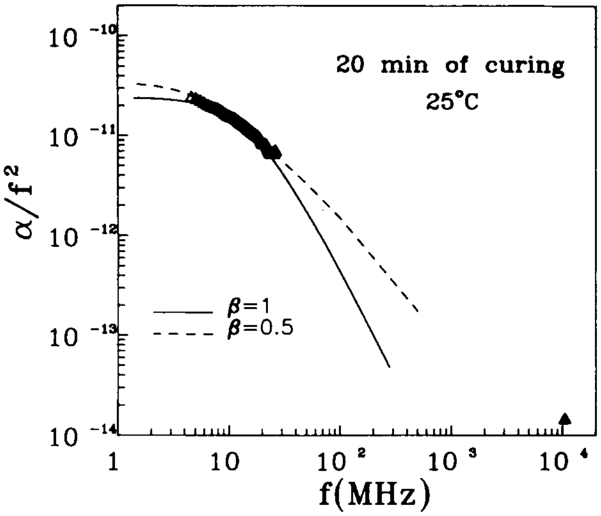


Figure 3 Frequency dependence of the ultrasonic (△) and hypersonic (▲) absorption α/f^2 of the initial product (20 min curing) at 25°C. The dashed line corresponds to a single relaxation and the solid line corresponds to a transformed KWW function ($\beta = 0.5$).

Here $\omega = 2\pi f$, M'' is the imaginary part of the complex longitudinal modulus, and M_r is its relaxation strength. For the distribution parameter $\beta = 1$ eq. (3) represents a single-valued spectrum, which yields $\tau = 1.1 \times 10^{-8}$ s. A slightly better fit of the α/f^2 data was obtained with $\beta = 0.5$ and $\tau = 5.3 \times 10^{-9}$ s; the hypersonic α/f^2 value can be considered as the high frequency limiting value $(\alpha/f^2)_\infty$.

Both values of τ, clearly support the notion that the Brillouin spectrum of the initial product at 25°C, which is only 35 K above the glass transition temperature $(T_g)^1$ is close to the $(\omega\tau \gg 1)$ relaxation limit. However, the velocity data of Figure 2 still increases after 20 min curing and reaches the limiting value v_∞ only after about 150 min of reaction time. This behavior can be due either to further slowing down of τ with time or to an additional (secondary) relaxation process. To discriminate between these possibilities, we have considered the dispersions in the sound velocities at different curing stages at 25°C, shown in Figure 4. For the initial product ($T_g = 260$ K),[1] the observed dispersion between ultrasonic and hypersonic frequencies can be ascribed mainly to the primary glass-rubber relaxation (see also Fig. 3). After 170 min curing, the system is in the glassy state ($T_g \sim 305$ K)[1] and the only way to account for the observed dispersion is to assume secondary relaxation processes. This is in agreement with the shape of the ultrasonic curves for extended curing times in Figure 1 and with the finding from other techniques.[15-17] Even in the fully cured epoxy ($T_g = 380$ K) the velocity steadily increases with frequency.

Transition Map of the Curing Process

It is well known that the primary relaxation time conforms to the free-volume Vogel–Fulcher–Hesse–Tamann (VFHT) temperature equation:

$$\tau = \tau_0 \exp[B/(T - T_0)] \qquad (4)$$

Equation (4) is equivalent to the WLF equation[18] with $T_0 = T_g - C_2$ and $B = 2.303 \cdot C_1C_2$ where C_1 and C_2 are the WLF coefficients. During curing, the material steadily changes with reaction time t_{cure}. T_g usually increases with t_{cure} and a few relationships between T_g and extent of cure were recently proposed.[16,19,20] On the other hand, C_2 and B are taken to be rather insensitive to the degree of cure.[20] During the initial stage of cure, like our initial product, the local structure of the reaction product changes rapidly and therefore B and C_2 may depend on t_{cure}.

To compute the parameters τ_0, B, and C_2 in eq. (4), which essentially describes the local segmental mobility, we complement the BS and US measurements (Fig. 1) with a photon correlation spectroscopic (PCS) study of the fully cured sample. At 135°C, the relaxation function $\Phi(t)$ was represented by the KWW decay function with $\tau = 6.5 \times 10^{-3}$ s and $\beta = 0.25 \pm 0.03$. Parenthetically, the low value

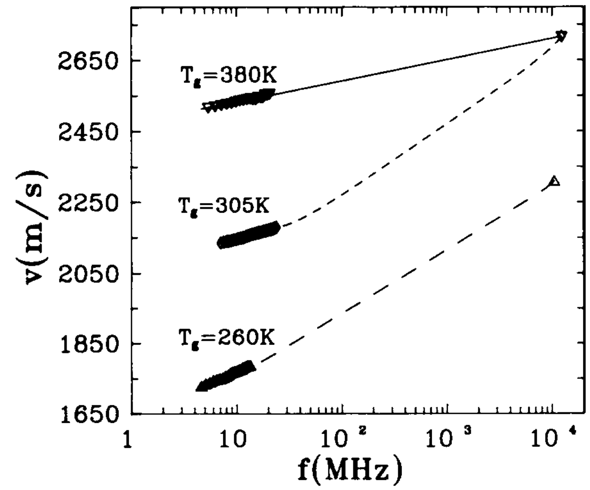


Figure 4 Frequency dependence of the ultrasonic and hypersonic velocity v for the initial product [(△) 20 min curing at 100°C], after 170 min (◇) and for a fully cured sample (▽).

of β indicates the contribution of more than one relaxation process; for the primary relaxation in amorphous polymers[13] β is typically 0.35. In a recent dielectric study[21] for a similar system diglycidyl ether of bisphenol A with diaminodiphenyl-methane the normalized dielectric loss was represented by the KWW equation with a β value between 0.2 and 0.3. Using now the primary relaxation times $\tau = 2.2 \times 10^{-11}$ s at 100°C ($t_{\text{cure}} = 112$ min, $T_g = 294$ K) obtained from BS, $\tau = 1.6 \times 10^{-7}$ s at 100°C ($t_{\text{cure}} = 385$ min, $T_g = 331$ K) obtained from US and the forementioned τ value for the fully cured sample ($T_g = 380$ K) from PCS experiment, we computed the parameters $\tau_0 = 5 \times 10^{-17}$ s, $B = 1142$ K, and $C_2 = 10$ K.

Figure 5 shows the Arrhenius plot of these relaxation times along with the time obtained from the absorption in the initial product (Fig. 3). The latter deviates from the prediction of eq. (4) using $T_g = 260$ K. This situation is also shown in the insert of Figure 5, which shows a linearized plot according to eq. (4). With T_0 being a function of t_{cure}, the deviation of the shortly cured initial product from the "reduced" VFHT equation (5) should not be surprising. At the initial stage of cure, T_g changes rapidly with t_{cure} and, moreover, the activation parameter has not yet attained the corresponding value of B in the polymeric material. In fact, lower B value improves the comparison. The segmental mobility of the material during curing is given by the shaded area of Figure 5 (insert) estimated by considering "typical uncertainties" of 5 K in T_g's.

Concluding Remarks

We have conducted dynamic light scattering [Brillouin (BS) and photon correlation spectroscopy (PCS)] and ultrasonic (US) measurements to study the curing process of diglycidyl ether of bisphenol A with butane-1,4-diol. The primary relaxation time τ can be measured by BS at earlier stages of curing and by ultrasonic experiments at longer curing times. By conducting frequency-dependent ultrasonic absorption measurements an estimate of τ can be obtained even for the initial product below the curing temperature.

The structural relaxation time obtained from US, BS, and PCS at different measuring temperatures and extent of cure reaction follows a single "reduced" Vogel-Fulcher-Hesse-Tamann equation, which describes the segmental mobility of the material during the curing reaction. For advanced curing times, the

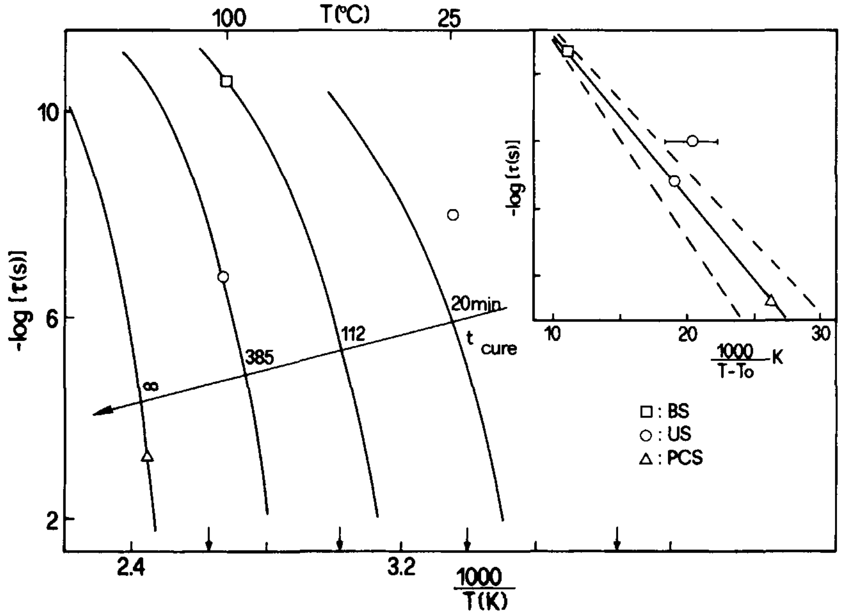


Figure 5 Representation of the structural relaxation during curing time in an Arrhenius diagram. The T_g values[1] for different curing times, corresponding to the Brillouin [112 min (□)], the ultrasonic [385 min (○)], and PCS [fully cured system (△)] relaxation times are indicated by arrows. The solid lines are calculated from the VFHT equation [eq. (4)] for the different curing times. This "reduced VFHT equation" is plotted in the insert. The shaded area corresponds to uncertainties in T_g's of 5 K.

sound velocity at ultrasonic and hypersonic frequencies suggest the presence of additional secondary relaxations indicated also by the shape of ultrasonic properties versus time.

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