Gelation Time during Polymerization by Ultrasonic Shear Waves Propagation

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In practice, a liquid is said to have gelled when it can support almost instantaneously a shear stress for a period of several seconds, and then recover its shape when the stress is removed. Theoretically, a liquid's approach to gelation is seen to be akin to a critical phenomenon[1] and is described in terms of a power law with the liquid's viscosity and related properties approaching a singularity at the gelation time, t_{gel}. Among the methods suggested for determining it, t_{gel} is seen either as the time when the real and imaginary components of the shear modulus, $G'(\omega)$ and $G''(\omega)$, respectively, at frequency ω, cross over for a stoichiometric balanced network,[2] which is not found to be generally valid,[3] or as the time at which the lines drawn near the plateau region in the plots of the 1 kHz frequency values of the imaginary component of the electrical impedance (or the real component of the electrical modulus) intersect,[4] which has serious fundamental limitations, and can be misleading.[5,6] For nonstoichiometric networks t_{gel} does not coincide with the $G'(\omega)$ -$G''(\omega)$ crossover.[2]

Gelation time can be more appropriately determined directly by using the propagation behavior of shear waves through a polymerizing liquid. To elaborate, the complex shear modulus G^* $(=G' + iG'')$ is related to the complex velocity v_s^*, by v_s^{*2}/ρ, where ρ is the density of the medium. This reduces to $v_s = (2\omega\eta_s/\rho)^{1/2}$, and the attenuation, $\alpha_s = (\omega\rho/2\eta_s)^{1/2}$, where η_s is the shear viscosity. At low viscosities the attenuation of a shear wave is extremely high, e.g. when $\rho = 1$ g/mL, $\eta_s = 1$ P, and $\omega = 12.56$ Mrad ($f = 2$ MHz); $\alpha_s = 2.6 \times 10^5$ Np/m. Thus the ultrasonic shear or transverse waves are heavily damped in liquids of low viscosity and they do not propagate more than a few wave lengths from the source. For a Hookean solid, $G'' = 0$ and G' equals the rigidity modulus, G, of the solid. For that case, $v_s = (G/\rho)^{1/2}$, and $\alpha_s = 0$. Hence when a material begins to behave in a Hookean manner, in at least the short and long time limits, α_s decreases and the shear wave propagates through a distance encompassing the sample. The time when a shear wave begins to propagate through a liquid in which a covalently bonded cluster grows may be seen as t_{gel}. With that as a criterion, t_{gel} of several diepoxide−diamine mixtures has been determined at different temperatures. The values obtained agree with t_{gel} deduced from the power law dependence of the dc conductivity of the mixtures during their polymerization.[7,8]

Ethylenediamine (EDA), propylene-1,3-diamine (PDA) hexamethylene-1,6-diamine (HMDA), and cyclohexylamine (CHA) were purchased from Aldrich Chemicals. These were 99 +% pure and were used as received. The diglycidyl ether of Bisphenol-A (DGEBA) was obtained from Shell Chemicals. Supplied to us as EPON 828, its molecular weight was 380, its calorimetric glass transition temperature, T_g, was 259 K, and the epoxide functionality was 2.0. The average number of repeat units in the molecule was 0.14. One mole of the diamine mixed with 2 mol of DGEBA, a stoichiometric composition, polymerizes to a covalently bonded network structure in which each amine molecule, devoid of its four protons, is covalently bonded to four DGEBA molecules, with the N atoms acting as junction points. One mole of monoamine mixed with 1 mol of DGEBA, also a stoichiometric composition, polymerizes to a linear chain polymer structure, with the N atom of the monoamine connecting the Bisphenol-A molecules and the amine's alkyl group becoming a side group to the linear chain. Mixtures were prepared by accurately weighing in amounts of 3 g, mechanially mixing thoroughly at 298 K, and were used within 2 min of preparation.

Two assemblies were used: (1) The first was a Matec Ultrasonic measurement assembly, model MBS 8000, which was interfaced with a personal computer.[9] It uses a phase detection technique, and allows measurements of the transit time and the intensity of the first transmitted pulse at preselected time intervals. (2) The second was a Fallon Ultrasonics Sysytem model FU1100, which is designed for measurements of amplitude and time of selected echoes. The selection of echoes was made by blocking out gates to unwanted echoes that follow the echo of interest. To allow the measurement of transit time accurately between selected echoes, the automatic gain circuit of the instrument amplifies the desired echo to a detectable limit. The system uses a spike excitation technique to generate the broad-band frequencies, detects the resonant frequency of the transducer, and uses that frequency, thus eliminating the need of a separate signal generator. The signal amplitude may be measured in millivolts or in percentage, with respect to a fixed reference within a gate when two gates are used. It automatically controls the attenuation of saturating signals, and collects data for the transit time, the amplitude of the echo, the samples' temperature, and the time of measurement, simultaneously.

A shear wave transducer (Panametrics model 5052, $f_0 = 2.25$ MHz, band-width $\Delta f = 2.0$ MHz), was used for both sending and receiving the ultrasonic pulse in a reflection mode. The ultrasonic cell assembly was similar to the one used for longitudinal wave measurements, with aluminum rods acting as buffer rods between the sample and the transducer.[9] The sample was 1.5−2 mm thick (wave propagation distance 3−4 mm), and was measured to 0.01 mm for each study. The accuracy of the transit time measurement was 5 ns from assembly 1 and 0.1 ns from assembly 2, that of the attenuation, 5% from both, and that of the temperature, 0.2 K.

Velocity of the shear wave propagating through the sample was determined by measuring the time delay, Δt, between two successive echoes,

$$v_2 = 2l/\Delta t \tag{1}$$

where l is the length of the sample. The attenuation, α, was determined from

$$\alpha = \frac{1}{2l}\left[\ln\left(\frac{A_0}{A_1}\right) + \ln\left(\frac{4v_1\rho_1v_2\rho_2}{(\rho_1v_1 + \rho_2v_2)^2}\right)\right] \tag{2}$$

where A_0 and A_1 are the heights of the successive echoes, ρ_1 is the density of Al (=2.71 g/mL) used as a buffer rod, v_1 is the velocity of the shear wave in Al (= 3.31 km/s), ρ_2 is the density of the state of the material (taken as an average value of 1.1 g/mL), and v_2 is the velocity of the shear wave through the material. Figure 1 shows

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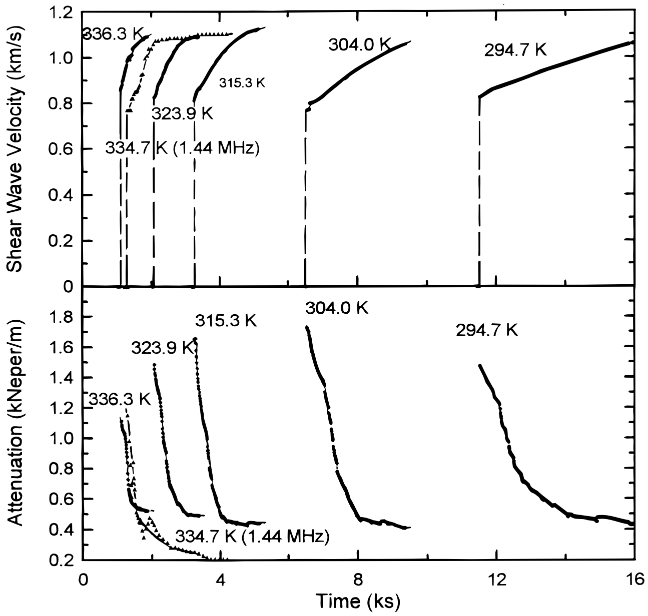

Figure 1. Typical plots of the velocity and attenuation of the 1.44 MHz (labeled) and 2.25 MHz shear wave propagating through the PDA−DGEBA mixture during its polymerization to a network structure at different temperatures, as indicated.

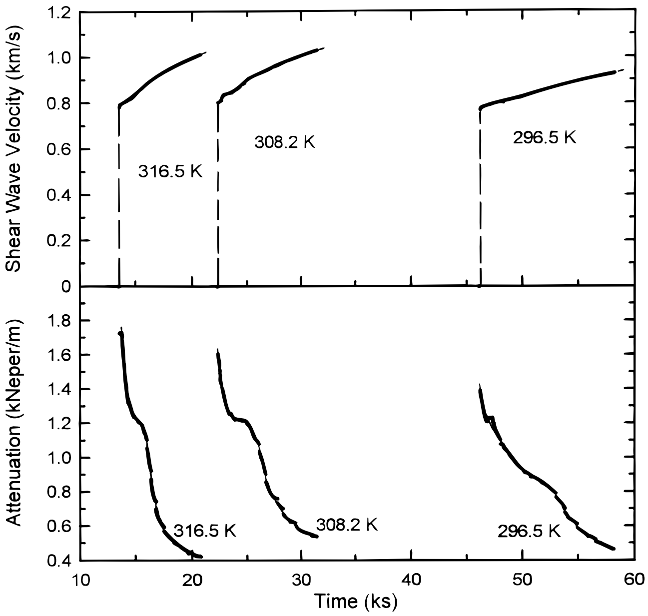

Figure 2. Typical plots of the velocity and attenuation of the 2.25 MHz shear wave propagating through the CHA−DGEBA mixture during its polymerization to a linear chain structure at different temperatures, as indicated.

typical plots of the velocity and attenuation of the ultrasonic wave against the polymerization time, *t*, of PDA-DGEBA mixture at different temperatures. The plots show that a shear wave echo could be detected until a certain time of polymerization. It appeared abruptly thereafter when Δt reached 4 −5 ms through the buffer−sample assembly (or v_2 reached 0.8−0.9 km/s), and the intensity of the received signal increased to 18% or more (or α decreased to 2×10^3 Np/m or less). For reasons already given here, the polymerization time at which the shear wave's Δt and α over a 3.2 mm distance in the sample could be measured was taken as the time, t_{gel}, when a gel-structure capable of sustaining a shear was produced in the whole sample. Measurements were made also with a shear wave of frequency 1.44 MHz at 334.7 K. The data, shown also in Figure 1, confirm that t_{gel} is independent of the frequency used for the measurements.

Table 1. Gelation Time during the Polymerization of Several Diepoxide−Diamine Mixtures at Different Temperatures

ultrasonic assembly 1		ultrasonic assembly 2		dc measurement	
T (K)	t_{gel} (ks)	T (K)	t_{gel} (ks)	T (K)	t_{gel} (ks)
		EDA−DGEBA			
296.1	11.27	296.5	11.20	296.2	12.0
305.4	6.91	305.2	6.44	305.3	7.1
314.0	3.90	313.6	3.91	313.7	4.0
324.9	2.13	324.4	2.11	324.2	2.0
335.9	1.18	335.9	1.17	335.3	1.18
		PDA−DGEBA			
295.1	12.14	294.7	11.52	294.9	12.20
303.9	6.38	304.0	6.54	303.8	6.20
315.1	3.25	325.3	3.24	315.5	3.40
323.6	2.29	323.9	2.07	323.7	2.01
334.6	1.31	336.3	1.11	335.0	1.10
		HMDA−DGEBA			
		296.5	12.49	296.5	12.20
		304.3	7.14	304.2	7.45
		312.2	4.23	312.3	4.30
		324.5	2.07	324.2	2.16
		336.2	1.30	336.5	1.26

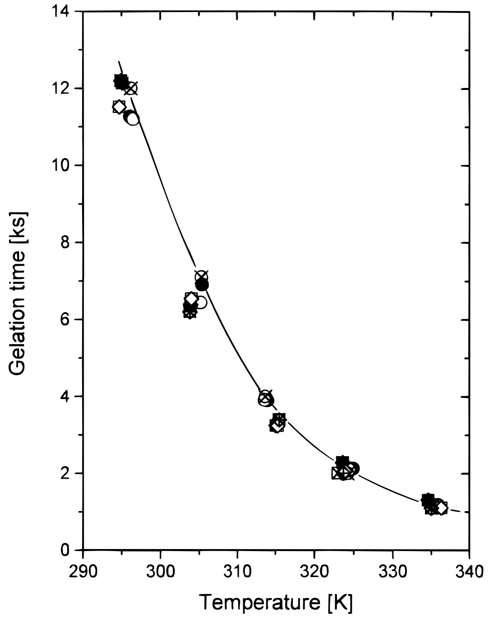

Figure 3. The Gelation time of the three network-forming mixtures plotted against the temperature. Open symbols refer to measurements made with assembly 1, solid symbols to those with assembly 2, and the symbols with a cross inside represent t_{gel} deduced from the dc conductivity data.[7,8] Squares refer to EDA−DGEBA, circles to PDA−DGEBA, and diamonds to HMDA−DGEBA mixtures. A line is drawn through t_{gel} deduced from the dc conductivity data for PDA−DGEBA.

A shear wave's echo signal can also appear abruptly when η_s has reached a certain value and that can be mistaken for the occurrence of gelation. Whether the appearance of an echo indicates gelation or high η_s may be resolved by comparing the molecular relaxation time of the material at the time of the echo's appearances. If the relaxation time is relatively short, the appearance of the echo-signal indicates gelation and t correspond to t_{gel}. If it is long, it corresponds to a high η_s as the liquid *approaches* vitrification. Using that as criterion, a set of experiments were done on the CHA-DGEBA mixture which polymerizes to a linear chain structure of the type −A−B−A−B−. (Chain entanglements may cause gelation but, as the fully polymerized sample was brittle and the dynamic mechanical measurements showed no plateau region for G', chain entanglements in it did not occur significantly.) The plots of its v_s and α_s in Figure 2 appear similar to those in Figure 1, but the polymerization time, at which the signal echo appears are at least 10-times of those in Figure 1. At this time, the average dielectric relaxation time, t_{diel}, of the EDA−DGEBA,[7,10] PDA−DGEBA[8] and HMDA−DGEBA[8] mixtures is in the 1 ns to 1 ms range, but that of the CHA−DGEBA mixture is in the millisecond range.[11] This difference in t_{diel} demonstrates that the data in Figure 1 yield t_{gel} and those in Figure 2 indicate a high viscosity.

The value of t_{gel} during the network growth of the three mixtures at different temperatures are listed in Table 1. The values measured by the two assemblies are within a few percent at comparable temperatures, but because of the improved accuracy and automation, t_{gel} measured by assembly 2 is more accurate. The t_{gel} values deduced from the dc conductivity data[7,8] are included in Table 1. These seem to be consistent with the t_{gel} measured by using ultrasonic shear waves.

Figure 3 shows the plots of t_{gel} against the temperature, where the values deduced from the power law extrapolation of the dc conductivity[7,8] are included. The plots are curved and seem to approach zero asymptotically, according to the equation; $t_{\mathrm{gel}} \propto \exp(1/T)$, as described before.[8,12] Values for t_{gel} of the three mixtures differ, increasingly more as the polymerization temperature is decreased. A discussion of t_{gel} in terms of the extent of reaction and conductivity has appeared.[13]

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