

Rheological Behavior of an Epoxy/Amine System near the Gel Point

D. Lairez,^{*,†,‡} M. Adam,[§] J. R. Emery,[†] and D. Durand[†]

URA CNRS 509 & 807, Université du Maine, Route de Laval, 72017 Le Mans Cedex, France, and Service de Physique de l'Etat Condensé, DRECAM, CE-Saclay, 91191 Gif-sur-Yvette Cedex, France

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ABSTRACT: Experimental results are presented concerning the dynamic behavior of a cross-linking polymer near the gel point. Attention is focused on the exponents which govern the frequency dependence of the real and imaginary parts of the shear modulus. It is found that there is only one moment during the network formation at which these two exponents are identical, while this behavior is predicted during a time period including the gel point. Nevertheless, the exponent value found is not far from the percolation and Rouse model theories.

The critical behavior of the mechanical properties of cross-linking polymers near the gelation threshold is of particular interest for the question of the universality of such systems.¹ But experimental results are widely scattered, according to different authors.

The growing clusters, which appear as the connectivity increases, may be described in terms of the fractal geometry in the length scales between the monomer size and the correlation length of connectivity ξ . These length scales, with respect to the mechanical properties of the material, correspond respectively to two limits of the viscoelastic behavior: a very high frequency ω_0 and a crossover frequency ω^* . In practice, rheological properties are probed at low frequencies far below ω_0 , and thus the frequency dependence of the modulus observed at a frequency ω is governed essentially by the frequency ω^* .

In the viscoelastic pattern, that is for $\omega^* < \omega$, a power law behavior is observed² for the complex modulus $G^* = G' + iG''$

$$G^* \sim (i\omega/\omega_0)^u \sim (\omega/\omega_0)^u e^{iu\pi/2} \sim (\omega/\omega_0)^u e^{i\delta} \quad (1)$$

where $\delta = \arctan(G''/G')$ is the loss angle. This leads to the same power law frequency dependence for the real (G') and imaginary (G'') parts of the modulus

$$G' \sim G'' \sim \omega^u \quad (2)$$

and a loss angle value consistent with the exponent u , that is

$$u = 2\delta/\pi \quad (3)$$

At the gel point, ω^* tends to zero, and this frequency power law behavior is observed over all of the frequency domain. Simple electrical analogy and effective medium theory predict $u = 0.5$, as for regular and nonfractal RC (resistor-capacitor) line response.^{3,4} On the other hand, two main theoretical approaches, which take into account the fractal geometry of polymer clusters and their intrinsic irregular nature, predict a rather different exponent value.

(1) Percolation theory (conjointly with an electrical analogy) postulates that if the elasticity has a purely en-

tropic nature, the complex elastic modulus is the analogue of the conductivity of a network with randomly distributed resistors and capacitors.^{2,5} Simulations performed in three dimensions predict $u = 0.7$.⁶

(2) The Rouse model, which assumes no hydrodynamic interaction between polydisperse polymeric clusters, predicts $u = 2/3$.^{7,8}

Because of the close values for the exponent u predicted by percolation and Rouse theories, dynamic rheological experiments do not allow for distinguishing the former from the latter. With this aim in view, it is better to determine experimentally the exponents s and t , which govern the divergence of the viscosity and the emergence of the elastic modulus near the gel point, respectively.

For $\omega < \omega^*$, the material before the gel point tends to behave classically as a Newtonian liquid ($G' \sim \omega^2$ and $G'' \sim \omega^1$) and as an Hookean solid after the gel point ($G' \sim \omega^0$ and $G'' \sim \omega^1$). The gel point corresponds to the emergence of a zero-frequency shear modulus. But, in fact, measurements always have a finite duration and therefore correspond to observation of the system at a nonzero frequency ω . Because of the behavior of ω^* , which decreases as one approaches the gel point, tends to zero at the gel point, and increases as one goes further from the gel point, there is a time period, including the gel point, during which $\omega^* < \omega$. We call this period the gelation domain, in which one expects theoretically and simultaneously (1) moduli independent of the relative distance from the gelation threshold ϵ , (2) a loss angle constant and independent of the frequency, and (3) a spectrum with a constant exponent, identical for G' and G'' .

The problem of this exponent value is particularly important in deciding experimentally which theoretical model is relevant for describing the dynamic behavior of the system. Thus the gelation-domain localization is very important but is a very difficult problem for evolving systems. Some authors² have studied quenched systems for which gelation is approached by varying the stoichiometric ratio r . In such systems the critical parameter is the stoichiometric ratio, and the measurements can be allowed to take a long time and can be performed as near the gel point as desired. The frequency dependence of the modulus, with such systems, was found to be very close to that of the percolation theory. On the other hand, some papers report exponent values for evolving systems depending on the stoichiometric ratio r .^{9,10} For $r = 1$ the

[†] Université du Maine.

[‡] Present address: Service de Physique de l'Etat Condensé, DRECAM, CE-Saclay, 91191 Gif-sur-Yvette Cedex, France.

[§] DRECAM.

exponent is found to be equal to 0.5 and continuously increasing with unbalanced stoichiometric ratios. However, other authors^{8,11} report dynamic results for evolving systems which are rather different and close to the Rouse model or percolation theory predictions ($\nu \approx 0.7$). Therefore, because of these scattered results, it is difficult to decide which theoretical model is relevant and if gelation has a universal character.

One of the problems of the gelation-domain localization of such evolving systems is the nonsimultaneity of the measurements corresponding to each frequency. In such evolving systems, the relevant parameter is the advancement of the chemical reaction, which increases with time. Each measurement, performed at a given frequency, takes a finite time and thus is obtained at different degrees of connectivity. So it is not possible with a direct use of such discrete data to get a correct frequency power law and to estimate the gelation domain with sufficient accuracy. In some cases, because of this problem, the definition of the gel point was arbitrarily defined by the G' and G'' crossing.¹²⁻¹⁵

The experimental results presented here concern an epoxy/amine cross-linking system in a balanced stoichiometric ratio. Dynamic rheological measurements were performed during the course of the chemical reaction. In the case of this polymeric system, the exponents which govern the two parts of the modulus change continuously during the cross-linking reaction, and there is precisely only one reaction time at which the exponents are identical. This time does not correspond to the G' and G'' crossings.

Experimental Section

The epoxy/amine system is the diglycidyl ether of bisphenol A (DGEBA) which is cross-linked by *p,p'*-diaminodiphenyl sulfone (DDS). The DGEBA was obtained from Dow Chemical (DER 332), and the DDS was obtained from Fluka Chemical Co. The required amount of resin (DGEBA) was accurately weighed into a tall glass vial and the appropriate amount of hardener (DDS) added to give a 1:1 stoichiometric ratio. The vial containing the sample was stirred and degassed for about 7 min at which point the hardener had dissolved and the mixture appeared homogeneous. The advancement of the chemical reaction after dissolution was determined by differential scanning calorimetry (DSC) and was found to be less than 5%.

The cross-linking reaction was carried out at 160 °C, a temperature at which the gelation process occurs without a major interference with vitrification (see Figures 1 and 2). The measurements were performed in real time with a RHEOMETRICS rheometer using parallel-disk configuration. The diameter of these disks was chosen to adjust the sensitivity of the apparatus to the system modulus. Thus, 30-mm diameters were used to follow the last part of the cure process, and the gelation part was more accurately monitored with 50-mm-diameter disks over a frequency range from 0.1 to 10 Hz in five steps.

Results and Discussion

Figure 2 shows the evolution near the gel point of the real part (G') and imaginary part (G'') of the shear modulus at 1 Hz and the tangent of the loss angle ($\tan \delta = G''/G'$) obtained at different frequencies. The coincidence domain of the $\tan \delta$ curves obtained at different frequencies permits us, in a first approximation, to localize the gelation domain inside the time range between 60 and 61 min. The $\tan \delta$ value obtained in this gelation domain is clearly above 1, which indicates that G' and G'' crossing does not occur in this time domain. The estimation of the exponent value of the frequency dependence of the moduli in this domain encounters two problems.

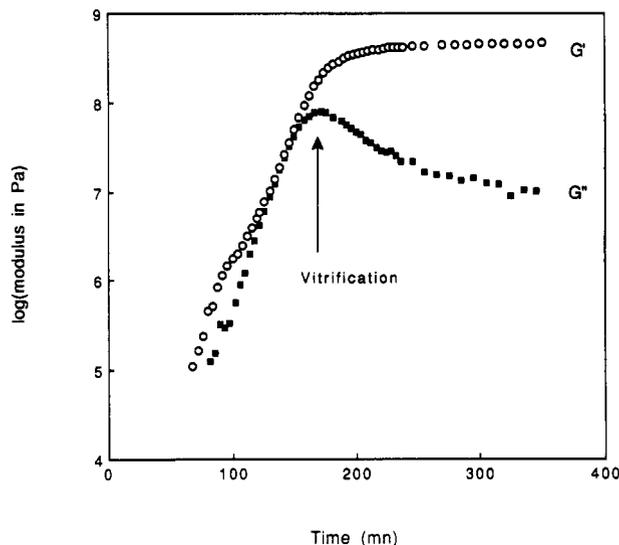


Figure 1. Variation of real (G') and imaginary (G'') parts of the elastic modulus (measured at 1 Hz) as a function of reaction time. The vitrification of the polymeric system occurs at 170 min.

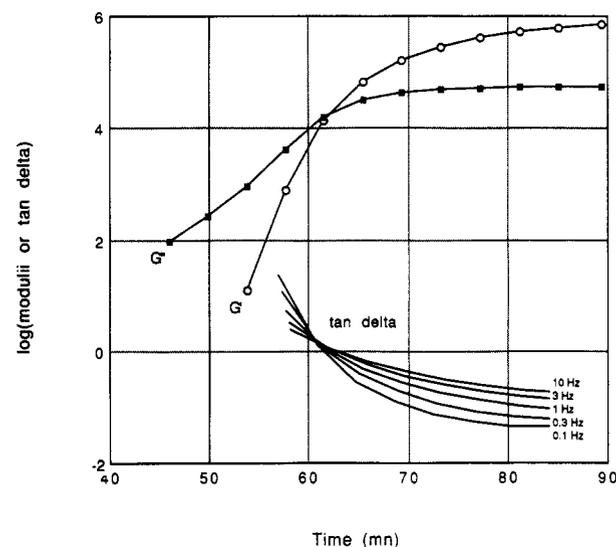


Figure 2. Evolution of G' and G'' (Pa) at 1 Hz and loss tangent ($\tan \delta$) obtained at different frequencies near the gelation threshold.

(1) The measurements which were performed at different frequencies are not obtained at the same reaction time; they are performed from the lower to the upper frequencies during a time of the order of 1 min (Figure 3). Because of the increase of the moduli during this time, this leads to overestimating the value of the exponent ν .

(2) Each set of measurements is spaced 4 min from the previous one. Figure 3 shows that the nearest set of measurements to the gel point is made just after the transition. Because of the decreasing of the exponent value with the time in this domain, this will underestimate the value of the exponent ν .

In order to deduce a correct value for the exponent ν at the gel point,¹⁴ it is necessary to interpolate the experimental data which are discrete and nonsimultaneous. Parts a-e of Figure 4 present the results which are obtained by interpolation (by means of a second-order polynomial) of the three measurement sets which are the nearest to the gel point. The evolution of the exponents characterizing the spectrum of each modulus is plotted on Figure 5 and is in agreement with results obtained on other

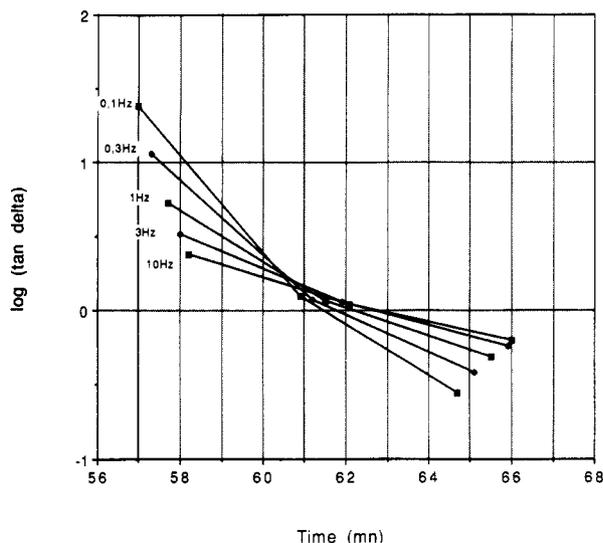


Figure 3. Evolutions of $\tan \delta$ obtained at different frequencies around the gel point. Discrete and nonsimultaneous nature of data obtained at different frequencies are displayed.

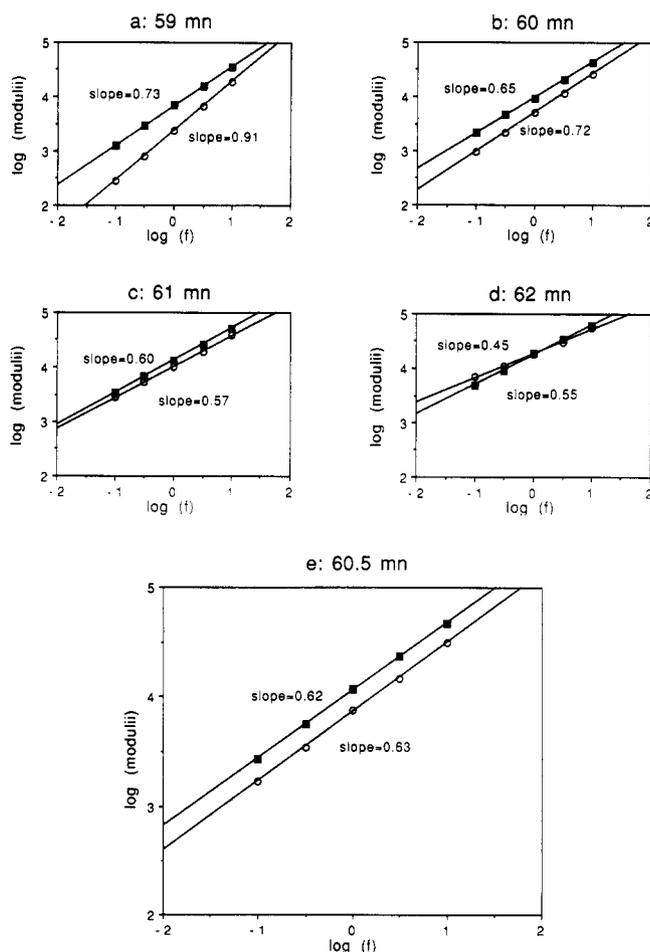


Figure 4. Spectra of G' and G'' (Pa) obtained by interpolation of experimental data at different times around the gel point: (a) 59, (b) 60, (c) 61, (d) 62, and (e) 60.5 min. Symbols: (O) G' ; (■) G'' .

systems.¹⁶ This figure clearly shows that values of exponents change drastically near the gel point and that the G' and G'' spectra obey the same power law after 60.5 min of cure. There, the value of the exponent is between 0.62 and 0.63. At the same time, the value of $\tan \delta$ obtained by interpolation of the experimental data is $\tan \delta = 1.58$; this leads to $u = 2\delta/\pi = 0.64$, which is consistent with the

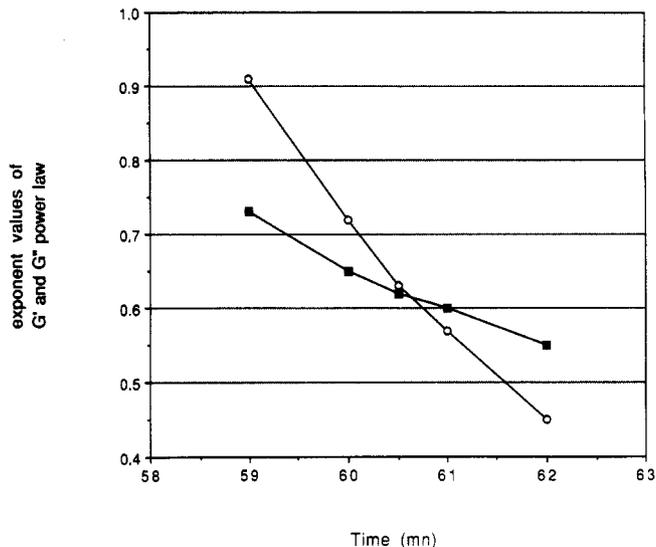


Figure 5. Variation with reaction time, near the gel point, of the exponents which govern the frequency dependence of the real and imaginary parts of the modulus.

value deduced from the spectrum.

This exponent value, for the rheological dynamic behavior of an epoxy/amine cross-linking system near the gel point, is fairly close to the value predicted by the percolation and Rouse model theories. At the gel point which is defined by a similar power law exponent for G' and G'' , the values of these two moduli are clearly different. Using G' and G'' crossing as the gel point criterion¹⁵ would lead to a wrong estimate of the exponent value. Nevertheless, if this criterion is used, the approximate evaluation of the exponent is not far from 0.5 (Figure 4d) but rather different for G' and G'' . In fact, the G' and G'' crossing criterion imposes the a priori value $u = 0.5$ (see eq 3).

Conclusion

The experimental results presented here outline the important variation of the dynamic behavior of a cross-linking system near the gel point. The gel-point localization is then very important. In addition, because of their discrete nature and of their nonsimultaneous character in the frequency domain, the experimental data have to be interpolated to make a good estimation of the exponent value which characterizes the moduli spectra. There is only one moment during the network formation at which this exponent is the same for the real and imaginary parts of the modulus. This surprising result from the theoretical point of view is due to the rapid kinetics of the chemical reaction involved in the gelation process and to the low frequencies used in the rheological study. The period of time during which the fractal nature of the polymer clusters is revealed by a particular dynamical behavior ($\omega^* < \omega$) is then very short and seems to be pointlike. Nevertheless, at this time the exponent value found is not far from those of the percolation and Rouse model theories.

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