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Temperature Dependence of the Behavior of a Reactive Epoxy−Amine System by Means of Dynamic Rheology. 2. High-T_g Epoxy−Amine System

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ABSTRACT: A high-T_g epoxy−amine system based on diglycidyl ether of bisphenol A (DGEBA) and 4,4′-methylenebis[3-chloro-2,6-diethylaniline] (MCDEA) was studied near the gel point in isothermal conditions from 80 to 180 °C by means of a rheological method, thus, below and above the glass transition temperature of the fully cured network, $T_{g\infty}$ ($T_{g\infty} = 177$ °C). The lower limit of this temperature range is close to ${}_{gel}T_g$ (${}_{gel}T_g = 50$ °C), the temperature at which gelation and vitrification occur simultaneously. Close to the gel point, the power laws relating viscosity, η, to ϵ^{-k} and the storage shear modulus, G', to ϵ^{z} ($\epsilon = |x - x_{gel}|/x_{gel}$) are verified above 150 °C. The scaling law $\partial(\log G^*)/\partial t$ proportional to $\omega^{-\kappa}$ is verified only at 170 °C ($\kappa = 0.25$) and 180 °C ($\kappa = 0.18$). The exponents k and Δ are constant above 150 °C ($k = 1.43 \pm 0.03$, $\Delta = 0.69 \pm 0.01$) and are very close to those found in the Rouse percolation model. Below 150 °C, these exponents diminish as the curing temperature decreases. The exponent z is frequency dependent at a given temperature, and its value z_0 for $\omega = 1$ rad/s decreases with temperature. z_0 and κ are found to be more sensitive to the vitrification phenomenon than the parameters k and Δ. At 180 °C, thus above $T_{g\infty}$, the values of exponents k, z_0, Δ, and κ are in good agreement with those derived from the percolation theory with macromolecular chains obeying the Rouse model. Below 150 °C, this behavior is no longer observed. These results are compared to those obtained for a low-T_g epoxy−amine system for which only the gelation phenomenon occurs.

Introduction

The rheological behavior of chemical and physical gels has been studied theoretically[1−4] and experimentally[5−23] by many authors. It appears that the gelation process is a critical phenomenon which obeys the percolation laws.[24−28] Near the gel point, viscosity, η, and equilibrium modulus, G, can be described as power laws of the relative distance from the gel point, ϵ ($\epsilon = |x - x_{gel}|/x_{gel}$, where x and x_{gel} are the extends of reaction at time t and at the gel point, respectively).

At the gel point, the frequency dependence of the storage shear modulus, G', and the loss shear modulus, G'', can be represented by a power law over a large angular frequency range:

$$G'(\omega) = A_{G'}\,\omega^{\Delta} \qquad G''(\omega) = A_{G''}\omega^{\Delta} \tag{1}$$

This fact can be used to determine the gel time from the crossover of the tan δ curves at various angular frequencies[30] since

$$G''/G' = \tan\delta = \tan(\pi\Delta/2) \tag{2}$$

The different critical exponents can be related using the Rouse model where the hydrodynamic interactions are screened to the space and fractal dimensions of the gel system.[1−4,31]

The values of the exponents obtained from a three dimensional percolation model and from an electrical analogy were reported in the first part of the study[32] (see Table 1 of ref 32). In this previous paper, a low-T_g epoxy−amine system based on diglycidyl ether of 1,4-butanediol (DGEBD) and 4,9-dioxa-1,12-dodecanediamine (4D) has been studied near the gel point at constant cure temperature in a temperature range from 40 to 70 °C. The curing temperatures are in all cases above the maximum glass transition temperature of the fully cured network of this system ($T_{g\infty} = -12$ °C). Above 50 °C, it was found that the reaction medium, which is a polydisperse self-similar distribution of polymeric fractals, behaves as the Rouse model. The parameters describing the dependence of the viscosity, η, and of the shear modulus, G, on the relative distance to the gel point, ϵ ($\epsilon = |x - x_{gel}|/x_{gel}$) were found to be 1.44 ± 0.03 (k exponent) and 2.65 ± 0.02 (z exponent), respectively. In the same way, the shear relaxation modulus, $G(t)$ (or $G(\omega)$), and the derivative of the logarithm of the complex modulus, G^*, were found to be describe by power laws with exponents equal to 0.70 ± 0.02 (Δ exponent) and 0.24 ± 0.02 (κ exponent), respectively. These results well agree with those found on similar reactive systems[12,14−17] investigated above the maximum glass transition temperature, $T_{g\infty}$.

Lairez et al.[18] studied the system based on the diglycidyl ether of bisphenol A (DGEBA) and 4,4′-diaminodiphenyl sulfone at 160 °C, thus at a temperature lower than the glass transition temperature of the fully cured network ($T_{g\infty} = 200$ °C). The Δ exponent was found to be 0.63 ± 0.01. This low value for the Δ exponent can be associated to the fact that the isothermal curing temperature is below $T_{g\infty}$ even if these authors considered that the gelation occurs without major interference with vitrification at this temperature. More recently, Miaoling et al.[15] showed that the growth of the system based on DGEBA and ethylenediamine (EDA) does not exhibit a scaling behavior at 40 °C which is below $T_{g\infty}$ ($T_{g\infty} = 105$ °C).

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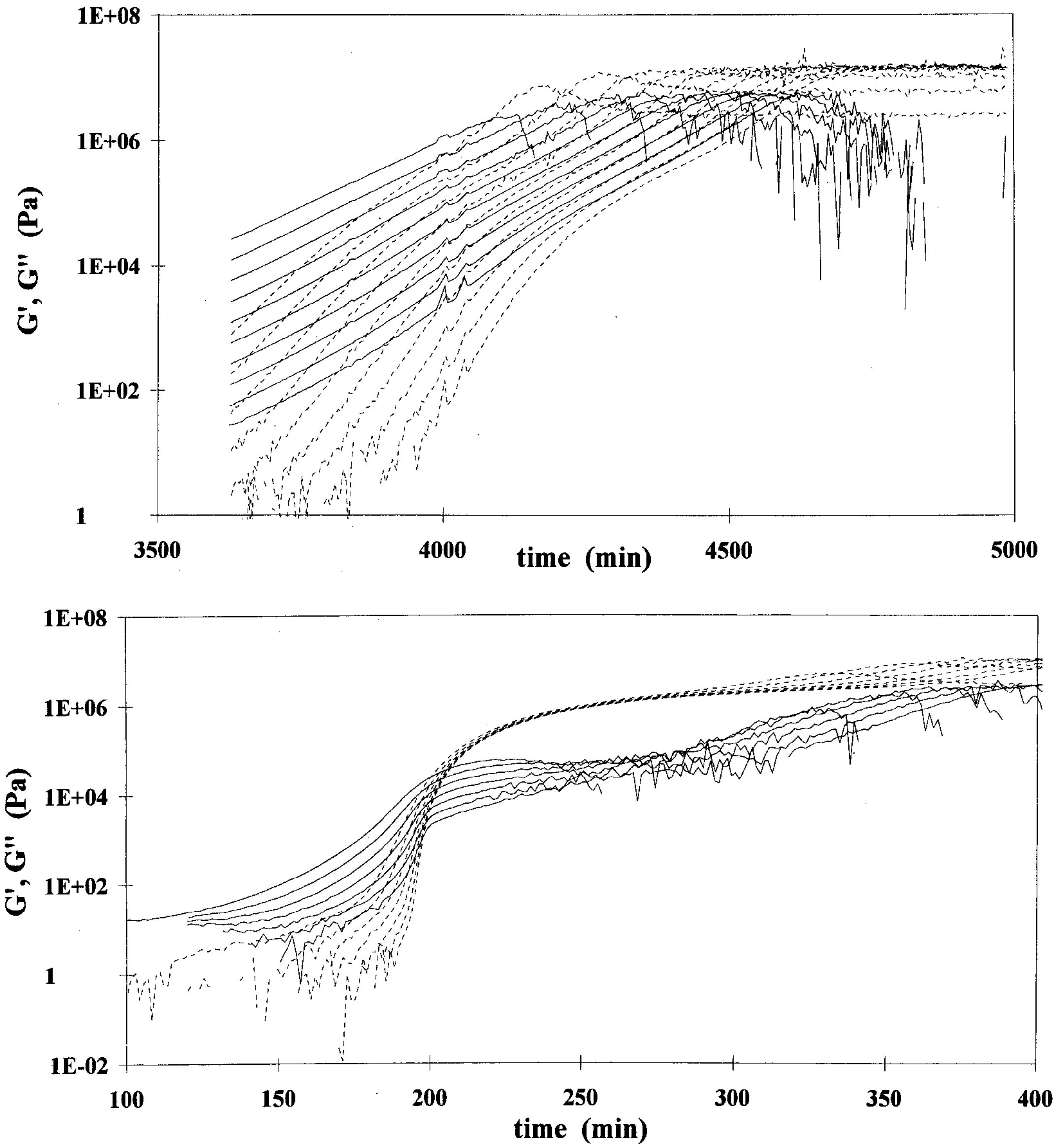
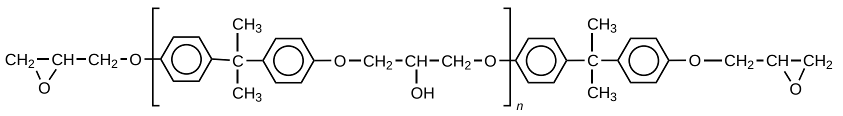
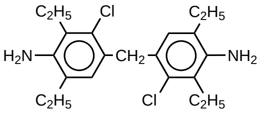


Figure 1. Experimental curves of storage shear modulus, G' (- - -) and loss modulus, G'' (—), versus time of reaction for isothermal curings at 80 °C (a, top) and 150 °C (b, bottom) for various angular frequencies (from 1 to 100 rad s^{-1}).

Table 1. Characteristics of Monomers

name	chemical formula	supplier
DGEBA ($n = 0.02$)		Dow Chemical DER 332
MCDEA		Lonza

In the present paper, a systematic study of a high-T_g epoxy−amine reactive system is made in order to allow us a better understanding of its behavior near the gelation threshold. For this purpose, a reactive system based on diglycidyl ether of bisphenol A (DGEBA) and 4,4′-methylenebis[3-chloro-2,6-diethylaniline] (MCDEA) with a maximum glass transition temperature $T_{g\infty} = 177$ °C is considered.[33] Isothermal polymerizations were done from 80 to 180 °C, thus including curing temperatures below and above $T_{g\infty}$. The lower limit of this temperature range is near ${}_{gel}T_g$ (${}_{gel}T_g = 50$ °C), the temperature at which gelation and vitrification occur simultaneously.

Experimental Part

Reagents. The chemical formulas of the monomers are listed in Table 1. All reagents were used as received and the amino hydrogen-to-epoxy ratio, r, is equal to 1. MCDEA and DGEBA were mixed at 90 °C for 10 min. At the end of this step, the conversion of the epoxy groups is less than 3%.[33]

Experimental Techniques. The dynamic mechanical spectra of the DGEBA/MCDEA reactive system were measured upon curing at a constant temperature ranging from 80 to 180 °C. A Rheometrics dynamic analyzer (RDA II) equipped with

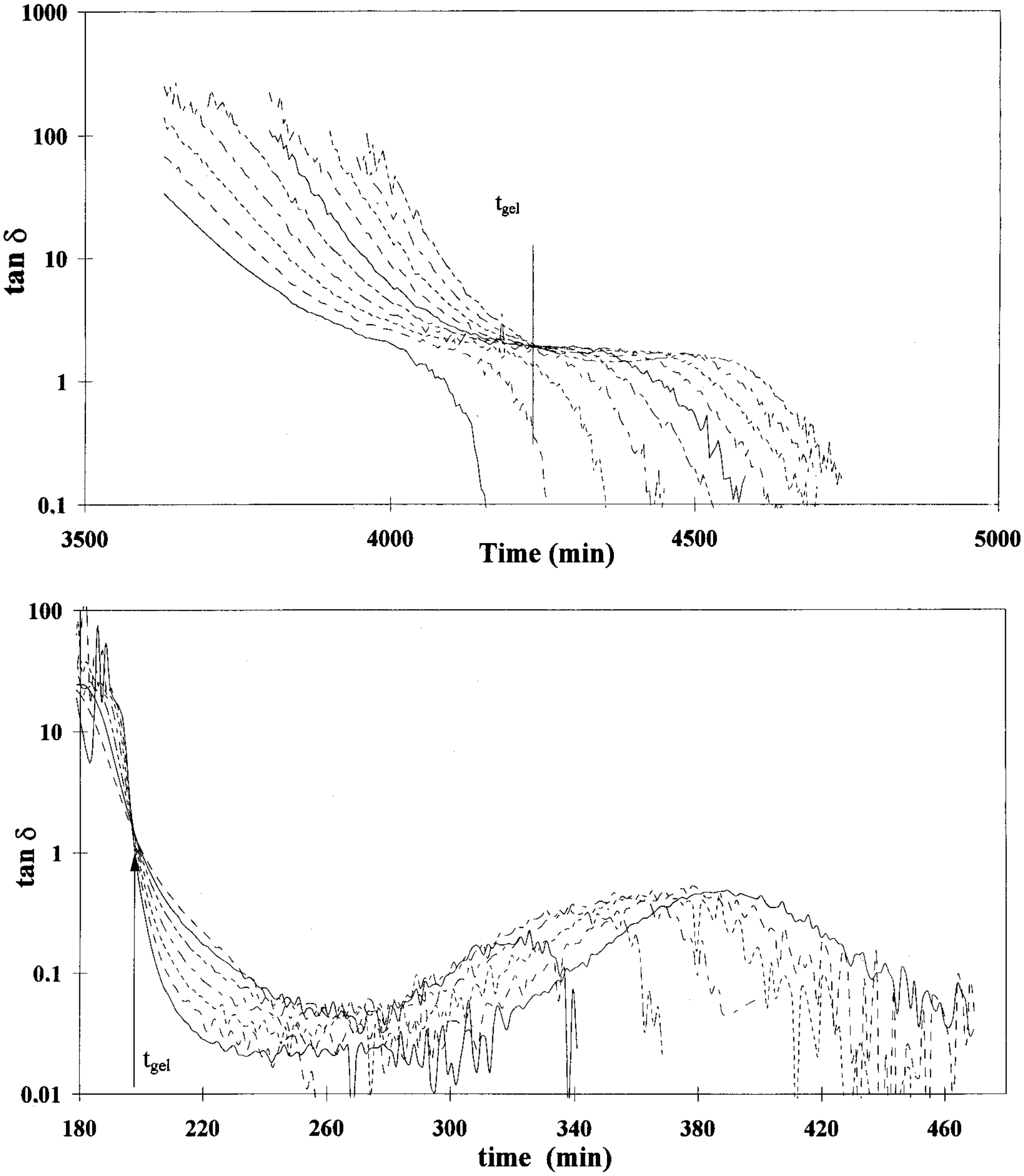


Figure 2. Experimental curves of loss factor, tan δ, versus time of reaction for isothermal curings at 80 °C (a) and 150 °C (b) for various angular frequencies (from 1 to 100 rad s^{-1}).

Table 2. Lower Limits of the Frequency Range for Rheological Measurements Performed at Various Temperatures of Curing Calculated from Ref 11

	T (°C)									
	80	90	105	110	120	135	150	160	170	180
lower limit (rad s^{-1})	0.1	0.1	0.1	0.1	0.2	0.4	1	2	2	2

parallel plates was used. The plate diameter was 40 mm, and the thickness close to 1.5 mm. The angular deformation varies from 50% in the liquid state to 1% in the solid state. The high value of the deformation in the liquid state allows us to obtain accurate values of the real part of the dynamic viscosity, η', at the beginning of the curing. A strain sweep was carried out to be sure that such a deformation remained within the linear viscoelastic region of the sample. The frequency range considered was varied with the curing temperature, T_i. In fact, in the frequency sweep mode, measurements were made at different times, and at every frequency, the reaction kept going on during the measurement time. Therefore, the reaction rate needs to be slow in order to consider that the change of modulus during testing is negligible. Izuka et al.[11] proposed the following condition:

$$(1/G^*)(\partial G^*/\partial t)(2\pi/\omega) < 0.1 \qquad (3)$$

This requirement was evaluated for all the experimental data at the gel time for which the derivative of the logarithm of the complex modulus, G^* is close to its maximum value. This equation allows us to determine the range for the frequency sweep. The lower limits of this frequency range are given on Table 2 for all temperatures.

Results

The kinetics of the DGEBA/MCDEA reactive system was reported previously by Girard-Reydet et al.[33] These authors reported from kinetical models that the reactivity ratio, n, of the primary amine to the secondary one is equal to 0.65. In the first part of this paper,[32] it was demonstrated that it is possible to calculate the theoretical extent of the reaction at the gel point. By applying the same method to the kinetics reported in ref 32, the theoretical extend at gelation, x_{gel}, is equal to 0.59. This value is very close to those obtained experimentally by the authors.[33]

The experimental curves of the storage shear modulus, G', and loss shear modulus, G'', versus time at 80 and 150 °C are given in Figure 1a,b, respectively. The experimental curves of the loss factor, tan δ, versus time are also reported at the same temperatures (80 and 150

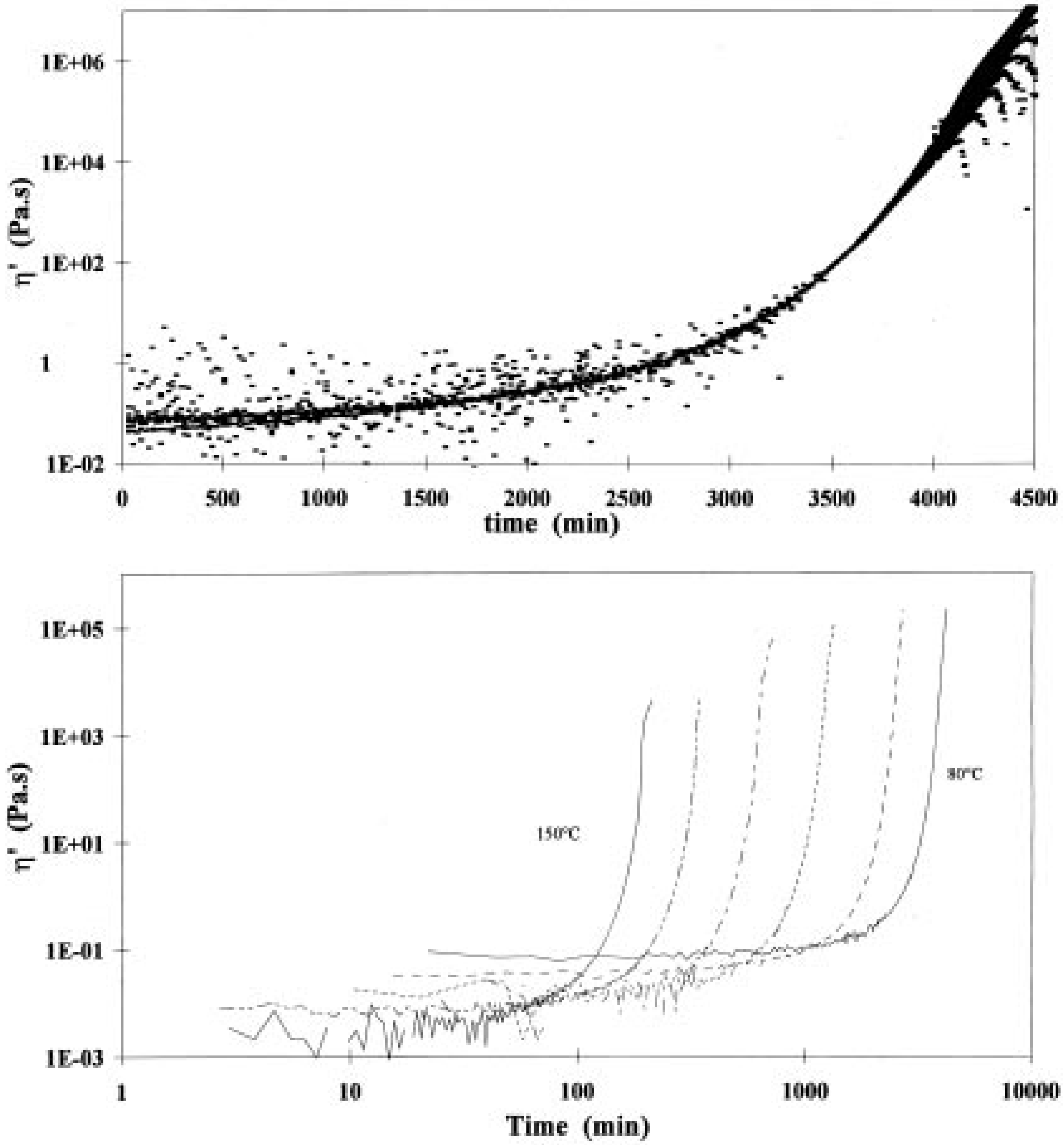


Figure 3. (a, top) Experimental curves of the real part, η', of dynamic viscosity versus time of reaction at 80 °C (various angular frequencies were used: from 1 to 100 rad s^{-1}). (b, bottom) Dependence of the real part of dynamic viscosity, η', with time of reaction obtained from experimental results at 80, 90, 105, 120, 135,and 150 °C.

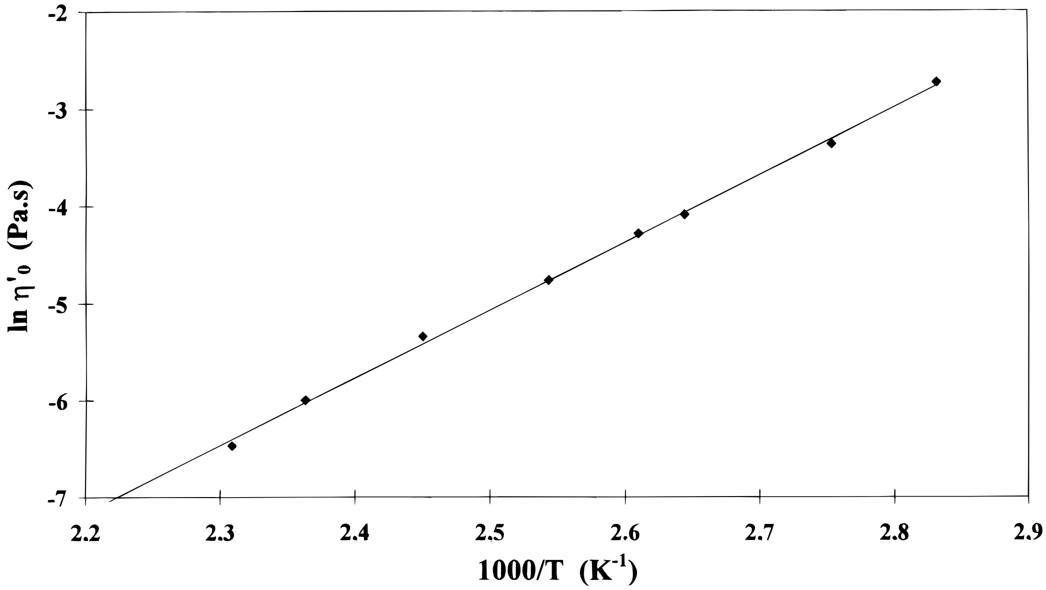


Figure 4. Arrhenius plot of the real part of dynamic viscosity at the initial time, η'_0.

°C) in Figure 2a,b, respectively. It can be observed that the gelation process is more and more disturbed by the vitrification phenomenon as the temperature decreases. This effect can be associated to the difference between

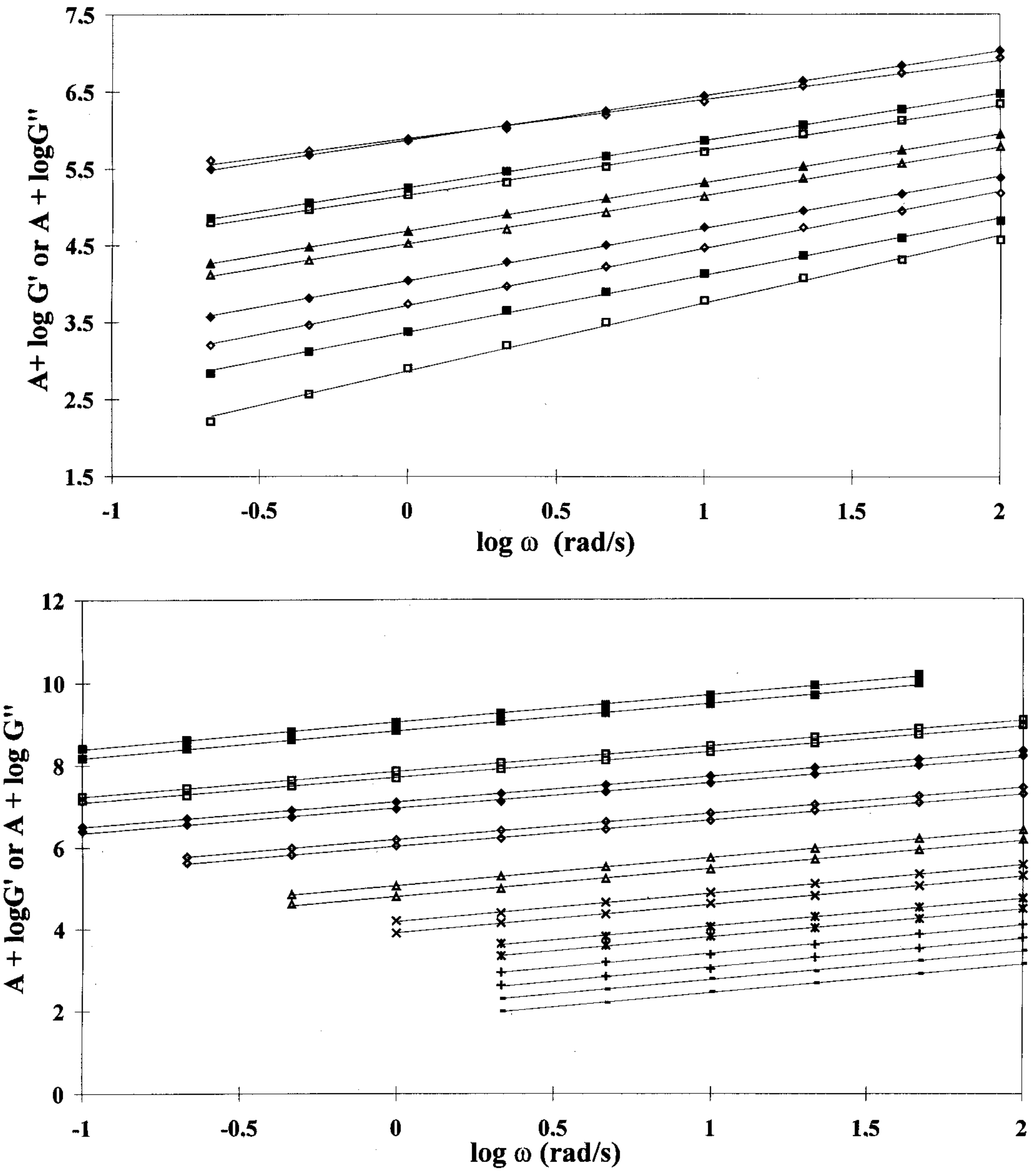


Figure 5. (a, top) Evolution of the log G' and log G'' with log ω near the gel point at 120 °C. (■) $A = 0$, 626 min; (□) $A = 0.5$, 630 min; (◆) $A = 1$, 634 min; (◇) $A = 1.5$, 636 min; (△) $A = 2$, 640 min. (b, bottom) log G' and log G'' as a function of the angular frequency at the gel point for various isothermal curing temperatures: (■) $A = 4$, 90 °C; (□) $A = 3.5$, 105 °C; (◆) $A = 3$, 110 °C; (◇) $A = 2.5$, 120 °C; (△) $A = 2$, 135 °C; (X) $A = 1.5$, 150 °C; (*) $A = 1$, 160 °C; (+) $A = 0.5$, 170 °C; (—) $A = 0$, 180 °C.

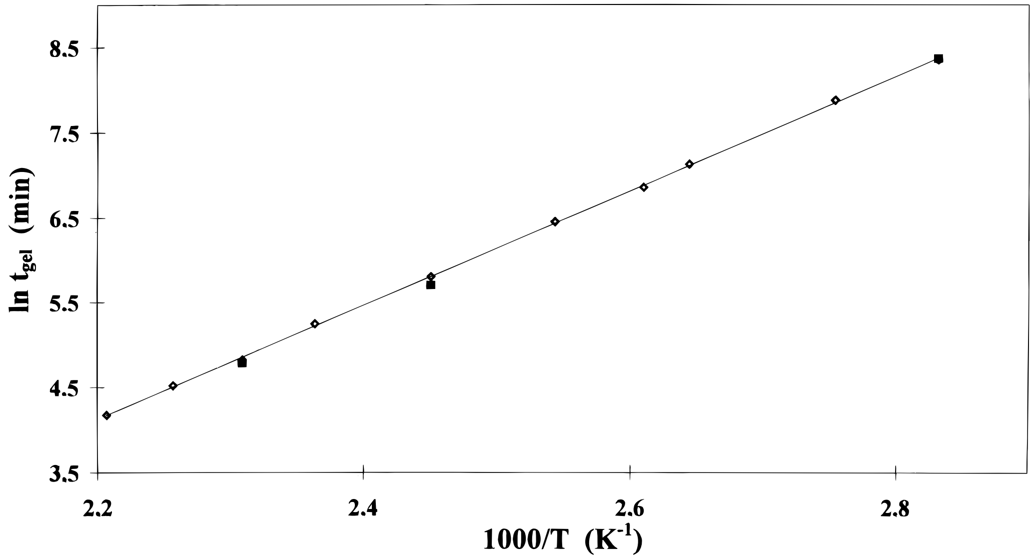


Figure 6. Arrhenius plot of gel times found from the rheological measurements.

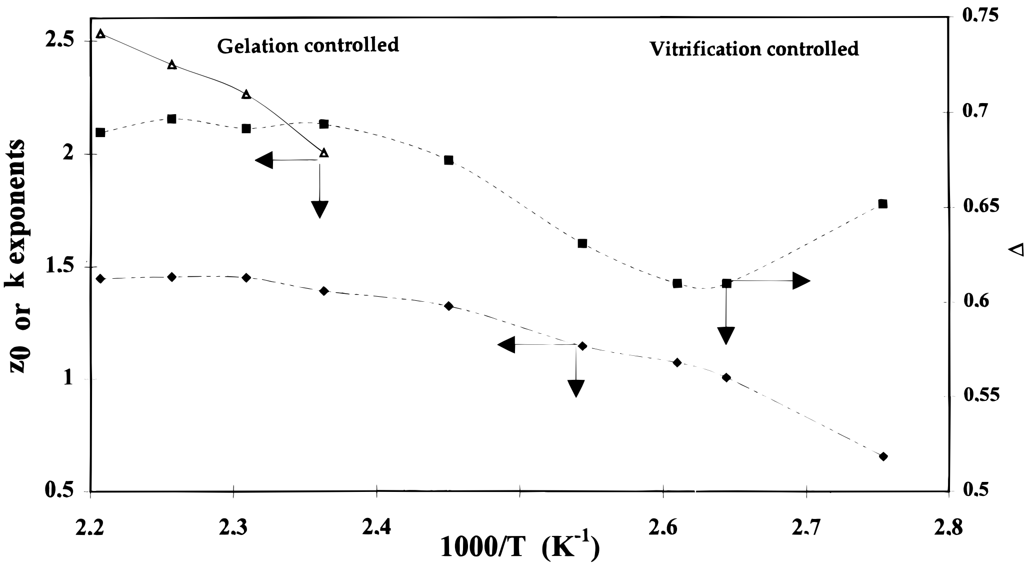


Figure 7. Critical exponents *k* (◆), z_0 (△), and Δ (■) versus reciprocal temperature of reaction.

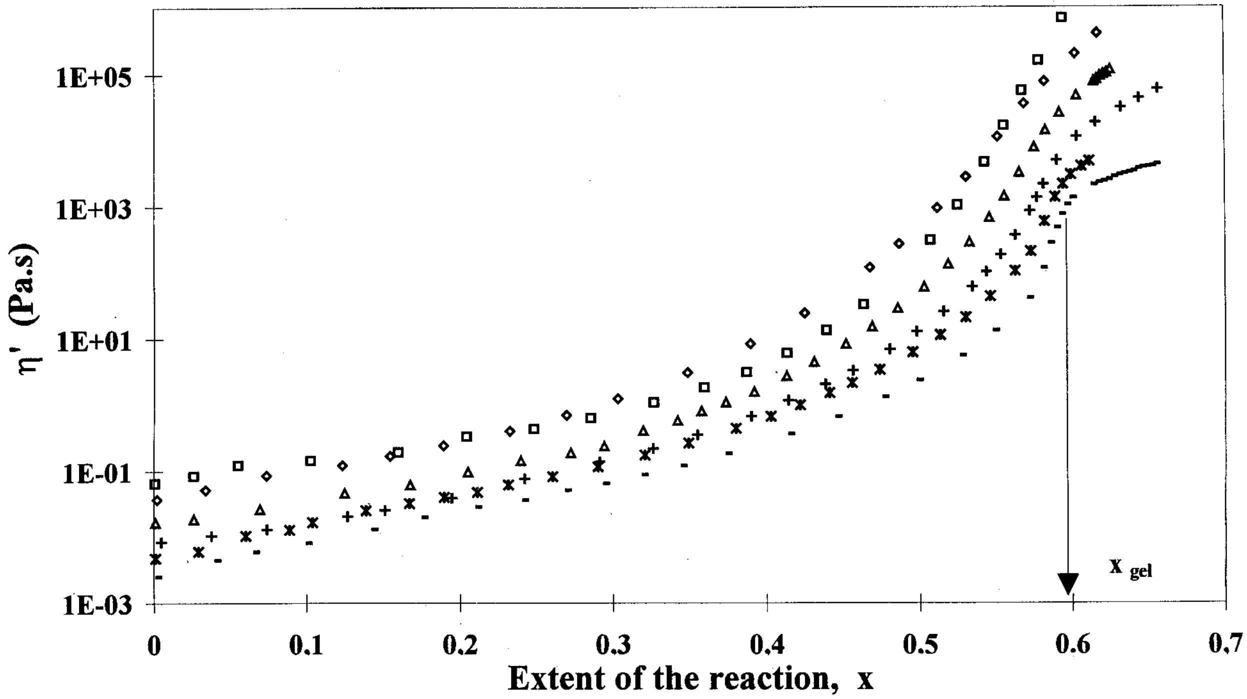


Figure 8. Real part of the dynamic viscosity, η', as a function of the extent of reaction *x*. (□) 80 °C; (◇) 90 °C; (△) 105 °C; (+) 120 °C; (*) 135 °C; (—) 150 °C.

Table 3. Critical Exponents Found from Rheological Measurements at Various Temperatures of Curing

	T (°C)									
	80	90	105	110	120	135	150	160	170	180
tan δ	1.82	1.63	1.4	1.43	1.52	1.74	1.92	1.95	1.9	1.9
$\Delta' = 2\delta/\pi$	0.68	0.65	0.605	0.611	0.63	0.668	0.694	0.698	0.692	0.692
Δ	0.59	0.652	0.61	0.61	0.631	0.675	0.694	0.683	0.697	0.687
k		0.65	1	1.07	1.15	1.32	1.39	1.45	1.45	1.44
a^a							−0.145	−0.141	−0.147	−0.148
$z_0{}^a$							2	2.22	2.4	2.54
κ									0.18	0.25

[a] From $z = z_0 + a \log \omega$.

gelation and vitrification times (thus, the difference in conversions) which decreases as the temperature decreases. Nevertheless, the crossover of the tan δ versus time curves recorded at various frequencies, which characterizes the gel point, exits for all the temperatures considered. At low temperature, the highest frequency curve does not participate in this crossover. The values of tan δ measured at this crossover point are listed in Table 3. Table 3 contains also the values of relaxation exponent, Δ′, calculated using eq 2 .

The dependence of the real part of the complex viscosity, η' ($\eta' = G''/\omega$), on the reaction time is reported in Figure 3a at 80 °C. It can be seen that for the gelation, the value of η' is the same whatever the frequency. Thus, the loss shear modulus, G'', is proportional to the angular frequency, ω, and the reaction medium behaves as a newtonian fluid.[30] Assuming this behavior, the curves η' versus time are obtained at all temperatures before the gel point (Figure 3b).

The initial values of the real part of dynamic viscosity, η'_0, measured at time zero are represented versus inverse temperature between 80 and 160 °C in Figure 4. These values of η'_0 are taken as viscosities of initial mixture from the monomers. Since the viscosity of the initial monomer mixture decreases as the temperature increases, it is difficult to obtain accurate values of η'_0 above 160 °C. η'_0 obeys an Arrhenius law in the temperature range considered. The apparent activation

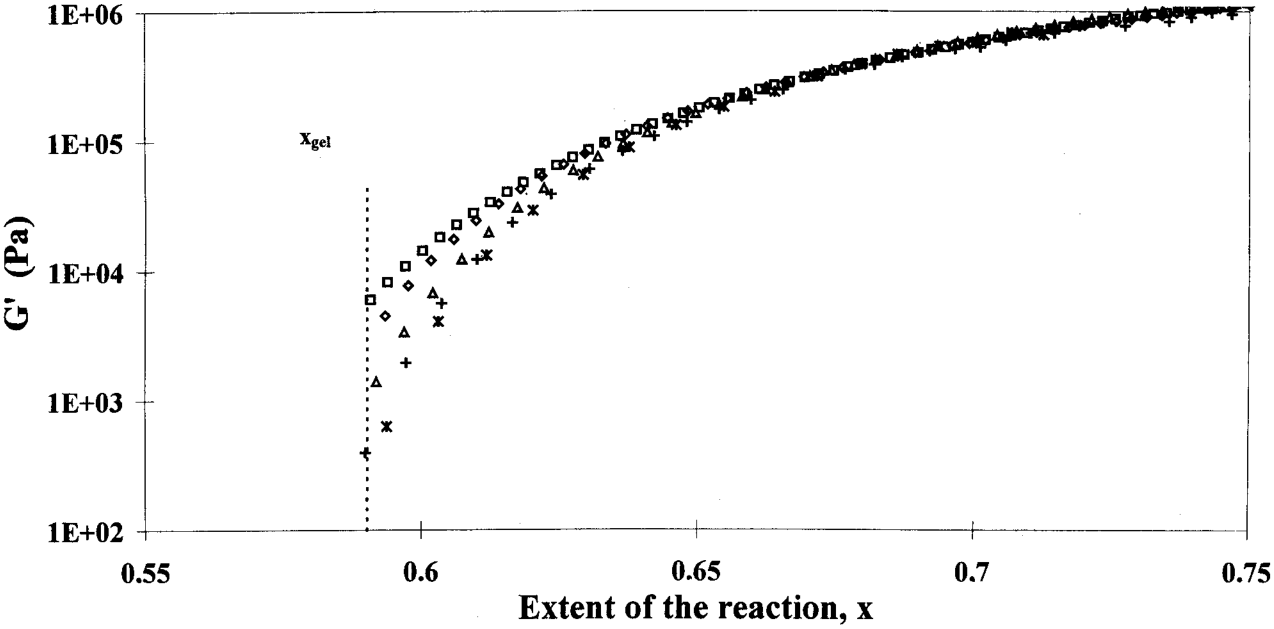


Figure 9. Storage shear modulus, *G*′, as a function of the extent of reaction, *x*, for an angular frequency of 10 rad s^{-1} at various temperatures of curing: (□) 135 °C; (◇) 150 °C; (△) 160 °C; (+) 170 °C; (*) 180 °C.

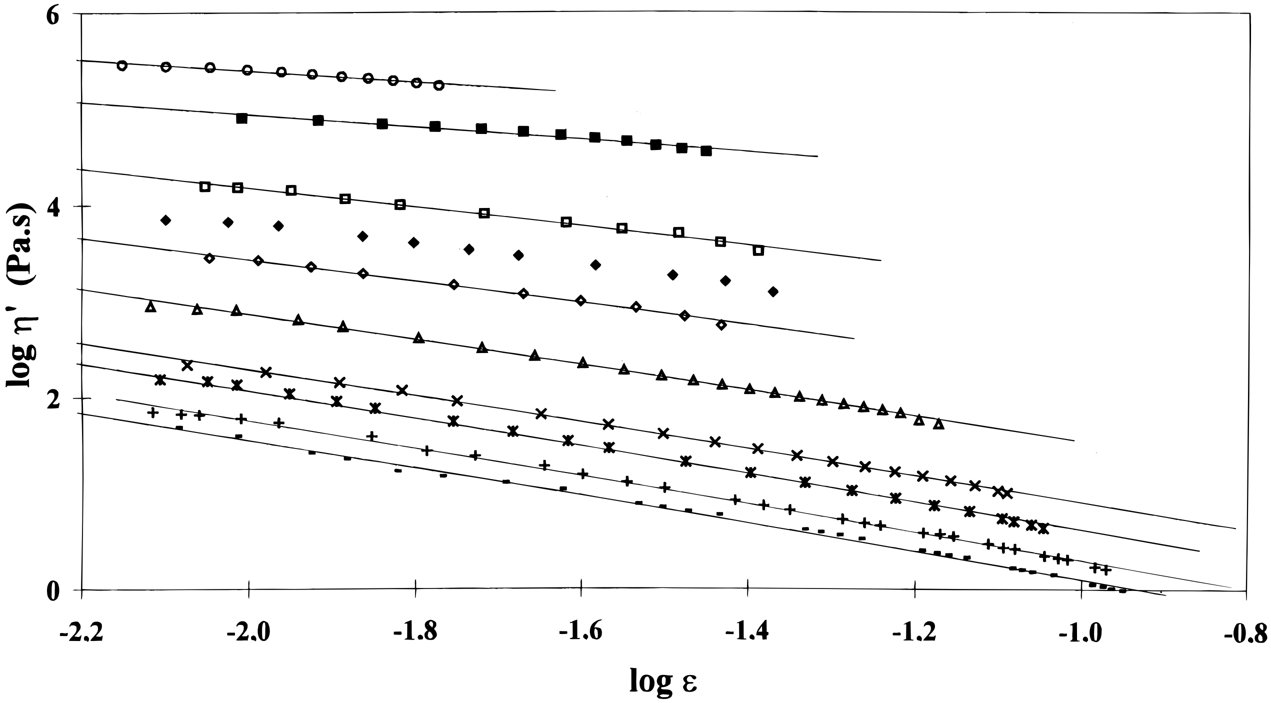


Figure 10. η' versus the relative distance from the gel point, ϵ ($\epsilon = |x_{gel} - x|/x_{gel}$) (○) 80 °C; (■) 90 °C; (□) 105 °C; (◆) 110 °C; (◇) 120 °C; (△) 135 °C; (X) 150 °C; (*) 160 °C; (+) 170 °C; (−) 180 °C.

energy (57.9 kJ mol^{-1}) is similar to those found from the gel times (57.2 kJ mol^{-1}).[33]

In the first part of this work,[32] a method was used to determine the relaxation Δ exponent from the logarithmic curves of storage and loss shear moduli, *G*′ and *G*″, respectively, versus angular frequency at various times of reaction. The same method was applied to the DGEBA/MCDEA reactive system, and Figure 5a gives the results obtained at 120 °C. It can be seen that the dependencies of log *G*′ and log *G*″ versus log ω are linear in for times close to the gel point. The critical behavior of $G'(\omega)$ and $G''(\omega)$ are reported in Figure 5b for the temperature range from 90−180 °C. Applying this method to the data for an isothermal curing at 80 °C is difficult due to the fact that the experimental results are disturbed by the vitrification phenomenon near the gel point. Figure 5b shows that the curves log *G*′ and log *G*″ versus log ω curves have the same slopes at the gel point.

This behavior is different that the one observed by Miaoling et al.[15] on the DGEBA/EDA reactive system. Considering the results of these authors, it is noticed that the lower limit of their measurement frequency range is 0.01 Hz. This value is too small in comparaison to the gel time found for this system at 40 °C (about 60 min). In this work, the lower limit calculated from the requirement proposed by Izuka is 2 rad s^{-1} (0.3 Hz) at 180 °C, the temperature at which the gelation occurs at 64 min.

Table 3 reports the values of Δ exponents obtained from the slopes of the linear parts of log *G*′ and log *G*″ vs angular frequency. These values are in all the cases

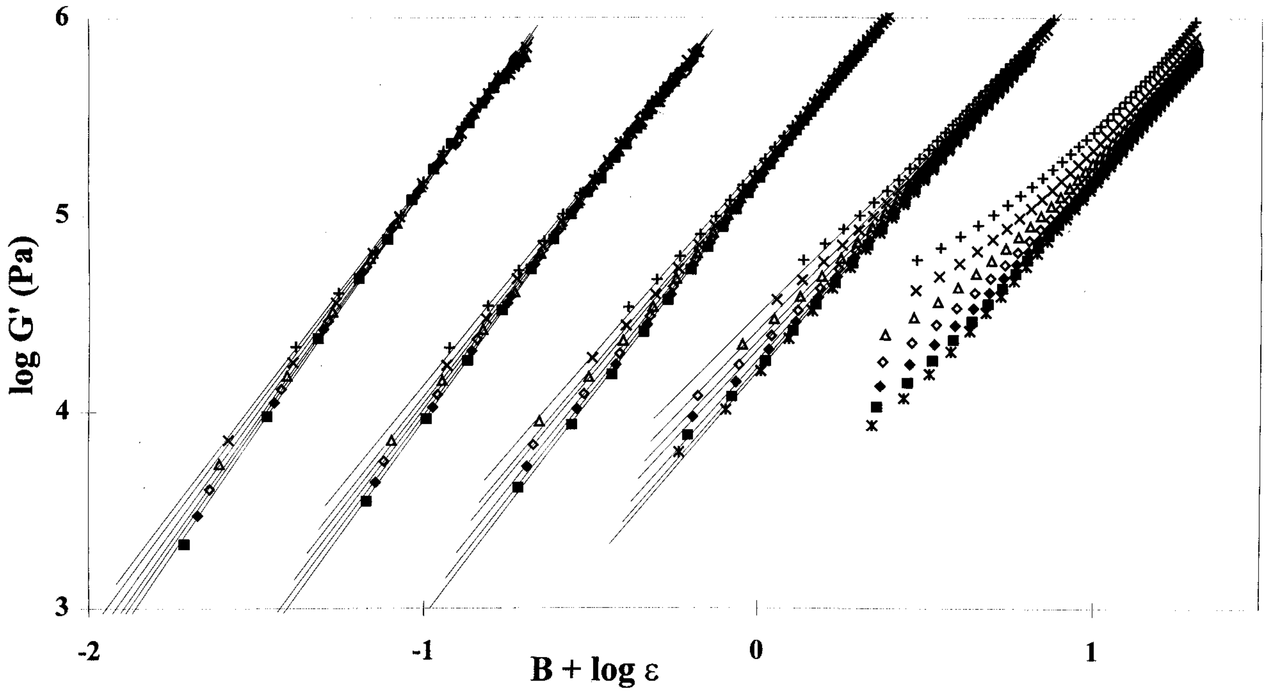


Figure 11. G' versus the relative distance from the gel point, ϵ ($\epsilon = |x_{gel} - x|/x_{gel}$); $B = 0$, 180 °C; $B = 0.5$, 170 °C; $B = 1$, 160 °C; $B = 1.5$, 150 °C; $B = 2$, 135 °C.

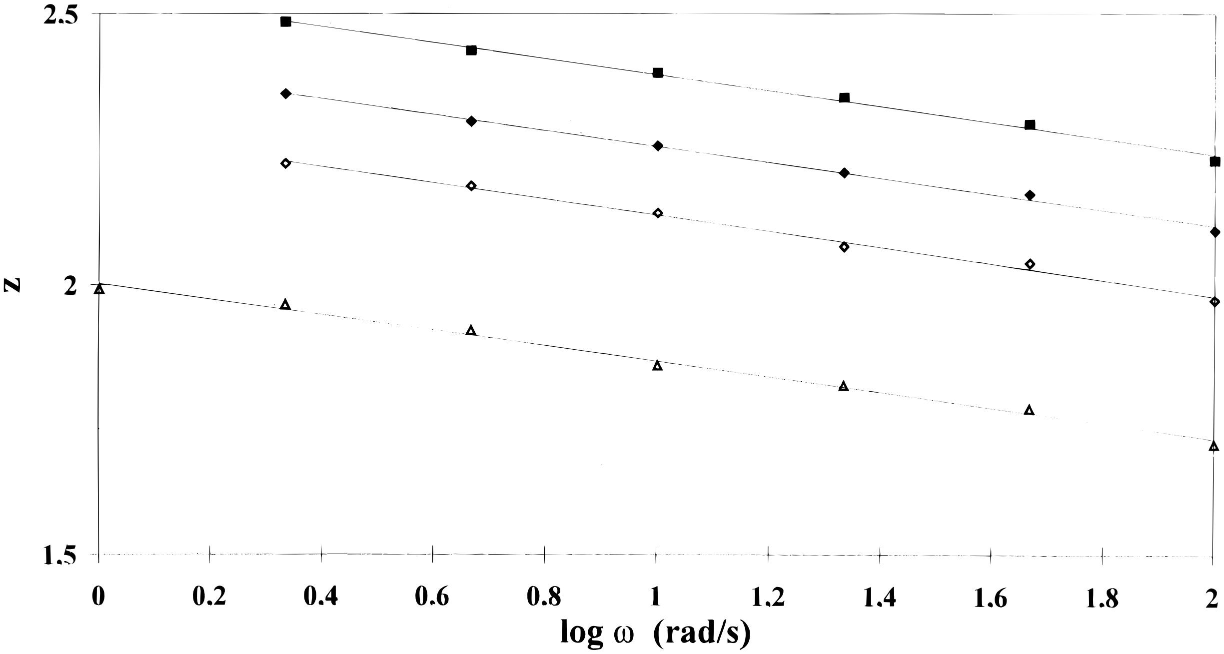


Figure 12. Dependence of the z exponent with the angular frequency at various temperatures for curing versus log ω: (■) 180 °C; (◆) 170 °C; (◇) 160 °C; (△) 150 °C.

Table 4. Gel Times (in minutes) of the DGEBA/MCDEA System at All Temperatures

	T (°C)									
	80	90	105	110	120	135	150	160	170	180
t_{gel} (min)	4250 4300[a]	2642	1252	951	634	332 300[a]	190	124 120[a]	92	64

[a] From insoluble fraction in tetrahydrofurane (see Girard-Reydet et al.[33]).

higher than 0.6 and similar to the values found for Δ' calculated from tan δ at the crossover. Thus, for all the curing temperatures, the gelation occurs before G' and G'' crossover. The Δ exponents are represented in Figure 7 versus reciprocal temperature. The times for gelation found from this rheological method are reported in Table 4. Theses values are similar to those found by measuring the time at which insoluble fractions appear in a solvent (tetrahydrofuran).[33] This latest observation leads to the conclusion that these gel times correspond to the extent of the reaction calculated previously. Since the conversion at the gel point is constant whatever the curing temperature, the gel time obeys an Arrhenius law with an activation energy of 55.9 kJ mol^{-1} (Figure 6).

Combining the experimental dependences of real part of the dynamic viscosity, η', and storage shear modulus, G', with reaction time and the kinetic equation, extent of reaction vs time, leads to the dependence of η' and G' on conversion, x, for all the curing temperatures. Figure 8 represents the η' vs x curves at 80, 90, 105, 120, 135, and 150 °C. The evolution of the storage shear modulus, G', vs conversion, x, is given in Figure 9 for

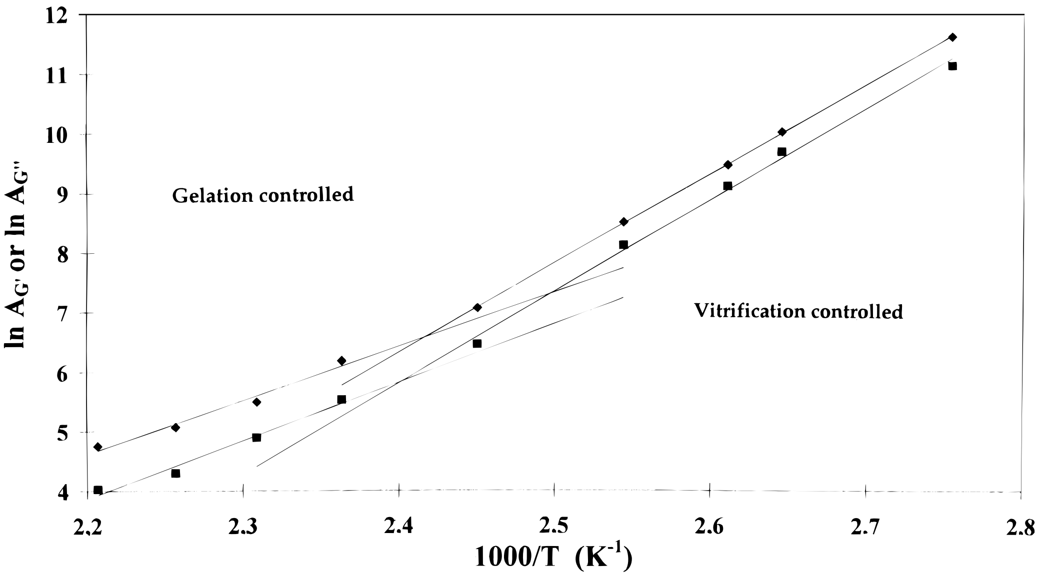


Figure 13. Arrhenius plot of preexponential factors $A_{G'}$ (■) and $A_{G''}$ (◆).

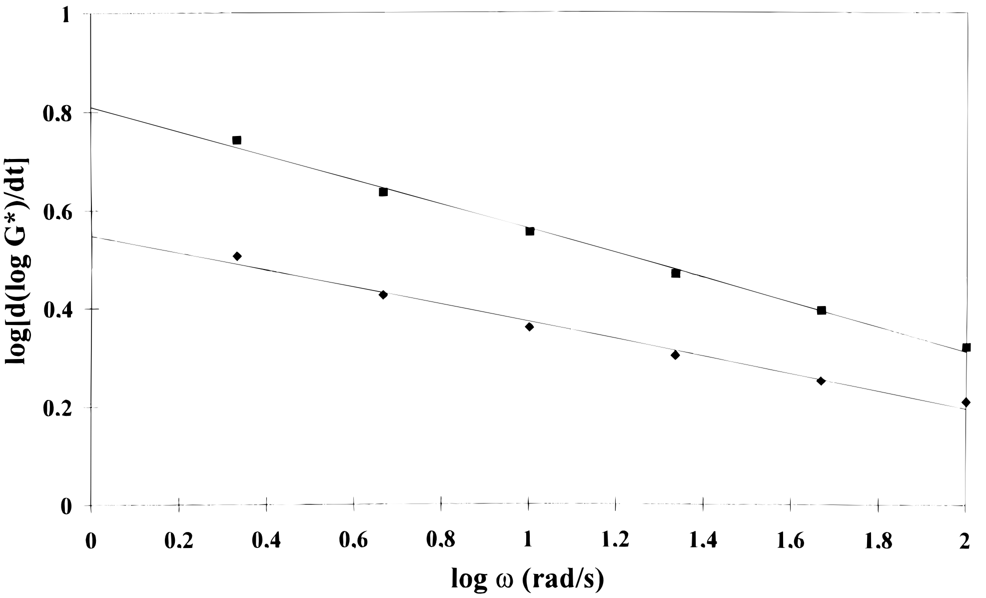


Figure 14. log[∂(log G^*)/∂t] versus the angular frequency, ω, at 180 °C (■) and 170 °C (□).

various temperatures from 135 to 180 °C and for the angular frequency, ω, equal to 10 rad/s. It is observed that η' and G' increase as the temperature decreases.

The dependences of log η' versus log ϵ (where $\epsilon = |x_{gel} - x|/x_{gel}$) are represented for the different curing temperatures in Figure 10. A domain for the distance with the gelation, ϵ, can be determined near the gel point. This ϵ domain is defined as the range within which the curves are linear. The lower the temperature, the more narrow this domain is

$$0.12 \text{ to } 7 \times 10^{-3} \text{ at } 180\ °C$$

$$0.017 \text{ to } 7 \times 10^{-3} \text{ at } 80\ °C$$

Values of the k exponent are listed in Table 4, and Figure 7 gives its dependence versus reciprocal temperature. Similarly, Figure 11 represents the dependence of log G' versus log ϵ. These curves are fitted using a linear fit above 150 °C and give the exponent, z, from the slopes (Figure 12). It can be seen that the dependence of z with the reciprocal temperature are linear curves. Thus, the exponent z verifies the following equation:

$$z = z_0 + a \log \omega \tag{4}$$

The values of a and z_0 are reported in Table 3 and in Figure 7. It could be observed that the coefficient a remains constant, whereas z_0 decreases as the temperature decreases.

Discussion

The temperature dependence of the critical exponents k, z_0, and Δ is reported in Figure 7. The preexponential factors, $A_{G'}$ and $A_{G''}$, obtained from eq 1 are represented in Figure 13 versus the reciprocal temperature. From these temperature dependences, it appears that the behavior of the reaction medium of the DGEBA/MCDEA system changes between 135 and 150 °C. In fact, the exponents k and Δ remain constant in the curing temperature range (from 150 to 180 °C), while their values decrease as the curing temperature decreases below 150 °C. Similarly, Arrhenius plots of $A_{G'}$ and $A_{G''}$ exhibit two linear domains: the first range occurring between 150 and 180 °C and the second one below 150 °C.

As the isothermal curing temperature decreases, the gelation process becomes more and more disturbed by the vitrification phenomenon as ${}_{\mathrm{gel}}T_{\mathrm{g}}$ approaches. ${}_{\mathrm{gel}}T_{\mathrm{g}}$ is equal to 50 °C for the DGEBA/MCDEA system considered. Lairez et al.[18] found an exponent Δ equal to 0.63 for an isothermal curing at 160 °C, i.e., at 80 °C over ${}_{\mathrm{gel}}T_{\mathrm{g}}$ (for the DGEBA/DDS system, ${}_{\mathrm{gel}}T_{\mathrm{g}}$ is equal to 79 °C).[33] This value for Δ is the same for the system DGEBA/MCDEA for a curing at 120 °C, thus at 70 °C over ${}_{\mathrm{gel}}T_{\mathrm{g}}$.

Both preexponential factors, $A_{G'}$ and $A_{G''}$, increase as the temperature decreases. Thus, as the temperature decreases, the reaction medium becomes more and more glassy. G^* at low temperatures is of the same order of magnitude as the value of the rubbery plateau. On one hand, approaching the glassylike state increases more the storage shear modulus, G', than the loss shear modulus, G''. Therefore, the value of the loss factor decreases drastically as the temperature decreases. This effect is consistent with the decrease of the exponent Δ observed for curing temperatures below 150 °C (Figure 7). On the other hand, the large relaxation times are of the same order of magnitude as the measurement time in the vicinity of the glassy state. The macromolecular chains which correspond to these relaxation times behave as in the glassy state. For isothermal curing temperatures of 80 and 90 °C, gelation and vitrification are very close, thus the exponent Δ obtained at these temperatures tends toward 0.5 (solid like behavior; Figure 2a).

Below 150 °C, exponent k decreases with temperature (Figure 7). Similarly, it is observed in Figure 10 that the domain where log η' is linear vs log ϵ, becomes narrower when the temperature decreases. These observations show that applying the scaling law defining the relation between the viscosity and the distance from the gel point is more and more difficult as the temperature decreases. Therefore, the reaction medium of DGEBA/MCDEA system is no longer a polydisperse self-similar distribution of polymeric fractals as the curing temperature decreases. This behavior was foreseeable if one recalls that the large clusters behave as in the glassy state. In the temperature range from 150 to 180 °C, the exponents Δ and k remain constant with the average values of 0.69 ± 0.01 and 1.43 ± 0.03, respectively. These values are similar to those found from the Rouse percolation model taking into account the accuracy of the determination ($\Delta = 0.67$ and $k = 1.33$). The dependence of the equilibrium modulus, G, with the distance to the gel point (G proportional to ϵ^z) is verified only for curing temperatures from 150 to 180 °C (Figure 11). This behavior confirms the disappearence of the fractality at low temperatures. The values of exponent z_0 increase while Δ and k remain constants as the temperature increases from 150 to 180 °C. These temperature dependences of the critical exponents are not contradictory since z_0 is more sensitive to the occurrence of the vitrification than the Δ and k exponents. In fact, z_0 describes the behavior of the polymolecular medium beyond the gel point, whereas k is determined before the gel point and Δ, at the gelation threshold. For a curing at 180 °C, i.e., for a temperature above the glass transition temperature of the fully cured network, $T_{\mathrm{g}\infty}$, z_0 is close to 2.54 which is close to the value predicted by the Rouse percolation model ($z = 2.67$).

The log [$\partial(\log G^*)/\partial t$] vs log ω curves are linear only at 170 and 180 °C (Figure 14). This behavior indicates that the power law relating the derivative of the complex modulus to angular frequency[8,31] is no longer obeyed as the temperature decreases. The exponent κ is equal to 0.25 and 0.18 at 180 and 170 °C, respectively. This important decrease of κ from 180 °C (i.e., for a temperature above $T_{\mathrm{g}\infty}$) to 170 °C (i.e., for a temperature below $T_{\mathrm{g}\infty}$) indicates that κ is more disturbed by the vitrification phenomenon than the exponent Δ. The value 0.25 found at 180 °C is predicted by the Rouse percolation model.

Conclusion

The rheological behavior of the DGEBA/MCDEA system has been studied near the gel point in the temperature range between 80 to 180 °C with a viscoelastic method. The results obtained lead to the followings observations.

(i) The equations $G' = A_{G'}\omega^{\Delta}$ and $G'' = A_{G''}\omega^{\Delta}$ are followed above 90 °C.

(ii) The scaling laws $\eta' \propto \epsilon^{-k}$ and $G' \propto \epsilon^{-z}$ are well confirmed above 150 °C. The ϵ domains for which the scaling laws are verified become narrower as the curing temperature decreases.

(iii) The scaling law $\partial(\log G^*)/\partial t \propto \omega^{-\kappa}$ is verified only at 170 and 180 °C.

(iv) The exponents k and Δ exhibit the same behavior. They are constant between 150 and 180 °C. Below 150 °C (i.e., at a curing temperature 100 °C above ${}_{\mathrm{gel}}T_{\mathrm{g}}$), their values decrease as the temperature decreases.

(v) The exponents z_0 and κ are not constant and decrease as the curing temperature decreases.

The values of k (1.44), z_0 (2.54), Δ (0.687), and κ (0.25) found at 180 °C, lead to the assertion that the system DGEBA/MCDEA is a polydisperse self-similar distribution of polymeric fractals which obeys to the Rouse percolation model at this temperature. This temperature is above $T_{\mathrm{g}\infty}$. This behavior is similar to the one observed on the system DGEBD/4D studied above $T_{\mathrm{g}\infty}$ in the first part of this work.[32]

When temperature decreases, the values of k and Δ show that the reaction bath is closed to the Rouse percolation model before and at the gel point up to 150 °C. Exponents z_0 and κ are more sensitive to vitrification than k and Δ.

Below 150 °C, except for Δ, the scaling laws are no longer well verified for exponent k, z_0, and κ. The reaction medium does not obey to percolation near the gel point.

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