

Rheological Study of the Isothermal Reticulation of an Epoxy Resin

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Synopsis

The complex modulus of shearing $G^* = G' + jG''$ was measured during the isothermal hardening of several epoxy resins. The gelation induces a slowing down of the rate of growth of viscous modulus $v'' = d(\log G'')/dt$ between two zones where this rate is constant. This slowing down of growth rate varies with the temperature and is null for $T = T_{C_{gel}}$: $v''_2 - v''_1 = K(1/T_{C_{gel}} - 1/T)$. We have shown that the two phenomena of gelation and vitrification stay perfectly distinct at all temperatures and in particular at $T_{C_{gel}}$. So the decrease of the rate v'' associated with gelation disappears at this temperature without the vitrification being responsible.

INTRODUCTION

The mechanical properties of a composite material are determined by the elastic modulus of the matrix, which can be very high, due to the use of thermosetting resins. Moreover, the characteristics of a resin at the end of cure essentially depends on the cure temperature or, more generally, on the chosen cure cycle which determines the reacting mechanism. From the point of view of rheology, the crosslinking of a resin necessarily induces an important increase of the viscoelastic modulus, between the initial state, which is a liquid, and the final state, usually vitreous.

Two macroscopic phenomena, the gelation and the vitrification, generally mark the steps of hardening of the resin. Thus, it is important to be able to define these two phenomena on the variation curve of the complex modulus, and to know their evolution as a function of the experimental conditions. The use of torsional braid analysis, proposed by Gillham,¹ or equivalent systems, brings out evidence of the existence of these two phenomena by a rheological method, and allows measurement of the time at which they appear. However, the presence of an inert support (generally braids or glass fibers) complicates the measuring of the viscoelastic modulus characteristic of the resin. A new group of mechanical instruments (Instron or Rheometrics rheometers) perfected during the last few years permits a direct access to the resin complex modulus, for example, by shear measurements between parallel plates. Considering the extent of variation of the modulus (in the order of 10 decades) it is not possible to proceed with continued measurements covering the entire phase of hardening. In an earlier article,² we have shown how, by using different plate dimensions, one can build up the complete variation curve of the viscoelastic modulus during the cure of the resin. We have also shown

through isothermal experiments, that gelation appears directly on the variation curve of the viscous modulus G'' , by diminution in the growth of this modulus.

This first study has been done on mixtures DGEBA/mPDA (diglycidyl ether of bisphenol A purified by crystallization/metaphenylene diamine) and DGEBA/DDM (diaminodiphenylmethane) in stoichiometric concentration. We also report here the measurements done with the hardener DDS (diaminodiphenylsulfone) more currently used in industry, again in stoichiometric concentration. The first results are still valid with this formulation; moreover, the gelation phenomenon is more noticeable because, besides a decrease of the G'' growth rate, is added a shoulder on the G'' curves.

New informations will be obtained from variations of some parameters taken from kinetic curves $\log(G', G'') = f(t)$ such as the speed of variation of the viscous modulus and the value of this modulus and of the elastic modulus at the gelation point and at the vitreous transition.

EXPERIMENTAL PROCEDURE

The prepolymer DGEBA was purified by crystallization from the industrial compound DOW DER 332 LC, and was mixed in stoichiometric quantity with one of the following three hardeners, mPDA, DDM, or DDS.

The complex shear modulus $G^* = G' + jG''$ was measured with the aid of the Instron 3250 Rheometer by sinusoidal shearing between two parallel plates. One plate experiences an angular deformation while the other attached to the measurement cell furnishes the torque transmitted by the sample. The manipulation is entirely automatic: A Hewlett-Packard 9845 calculator controls a frequency generator Solartron (Schlumberger) through an HPIB interface, which relays a signal to the motor to create the sinusoidal motion of the first plate. The torque transmitted by the viscoelastic sample is analyzed by the Solartron and compared to the imposed deformation signal. The calculator finally supplies the real part G' and imaginary part G'' of the viscoelastic modulus of the sample.

For the highest values of the modulus (resin in glassy state), a correction is made to compensate the compliance of the lower plate and of the measurement cell. This compliance correction in torsion is inherently elastic.

A temperature regulation allows all work at a temperature above the ambient, under inert atmosphere (nitrogen). The measurement cell is isolated and temperature-compensated (ambient temperature). The temperature is read through a thermocouple attached under the lower plate. Experiments were set up to control the difference in temperature existing between the inside of the sample and the attachment point of the thermocouple.

The viscoelastic modulus of the resin varies over a large range (approximately 10 decades for G'); it will be the same for the torque transmitted by the sample. To conserve a torque value inside the measurement scale of the instrument, it is necessary to use several systems of different sized plates. Three different sizes of discs and samples were used: (a) diameter $\phi = 4$ cm for the beginning of the kinetics, (b) $\phi = 2$ cm, and (c) $\phi = 0.5$ cm to study the final phases. The thickness of the sample is about 1 mm.

The three parts of the curves $\log G'$ and $\log G'' = f(t)$ coincide properly only if several parameters are kept constant:

(a) the shear frequency is maintained constant ($\omega = 30$ rad/s) for most measurements;

(b) the angular amplitude of shearing $\alpha_m = 0.533^\circ$;

(c) the kinetics are unvaryingly isothermal. The reactions of polycondensation create heat flow which increases when the kinetics are rapid (the case of mPDA and of DDM in particular). The low thermal conductivity of the resin, and even of the steel plates, means that the temperature is neither constant nor homogeneous at the core of the sample. When the oven is set at 100°C , for example, the core temperature of the sample resin shows a maximum of 104°C with the large plates in the case of mPDA, while this temperature variation is negligible with the small plates. To avoid these variations and maintain a constant average temperature in the sample (within 0.5°C), the oven temperature was controlled at each measurement.

(d) The mixture of the two resin components must be new. Chemical analysis was made³ in order to measure the rate of advancement of the reaction immediately after mixing the two components, and after 6 days in the freezer. While the epoxy/equivalent of the DGEBA $n = 0$ pure is 170 g, the chemical analysis adds up to 172.4 g immediately after mixing with the mPDA. The dosage made in an identical sample that was held at -16°C for 6 days shows an epoxy/equivalent of 176.9 g. The comparison shows a slow but clear evolution of the resin during its stay in the freezer. Moreover, we know that the hydroxyl function which appears after the first substitutions on amine functions act as catalysts for the reaction. This shows the importance of these first reactions on the kinetics curves. In order to eliminate this supplementary parameter, we have always worked on samples that have been newly prepared.

Under the conditions described above, the experimental curves $\log(G', G'') = f(t)$ are reproducible and the three sections determined with the plates of differing dimensions reach approximate coincidence.

Remark. The uncertainty about the time cannot be entirely eliminated because the time necessary to position a sample (at 20°C) between the plates (preheated to the processing temperature) varies obviously from one measurement to another, with the result that the plates, which cool off during this operation, are not always at the same temperature at zero time when the measurement is started.

Sometimes, in spite of great care, some measurements on the smaller plates give a time shift compared with the two other plates. These measurements therefore were not taken under consideration, or, if the time shift was small, were added to data relating to the large plates.

EXPERIMENTAL RESULTS

Figures 1–3 present several experimental curves $\log(G', G'') = f(t)$, which were obtained at different temperatures of cure, with each of the three hardeners. These curves are given here on a reduced scale but the calculator helps enlarge the scale to facilitate readings.

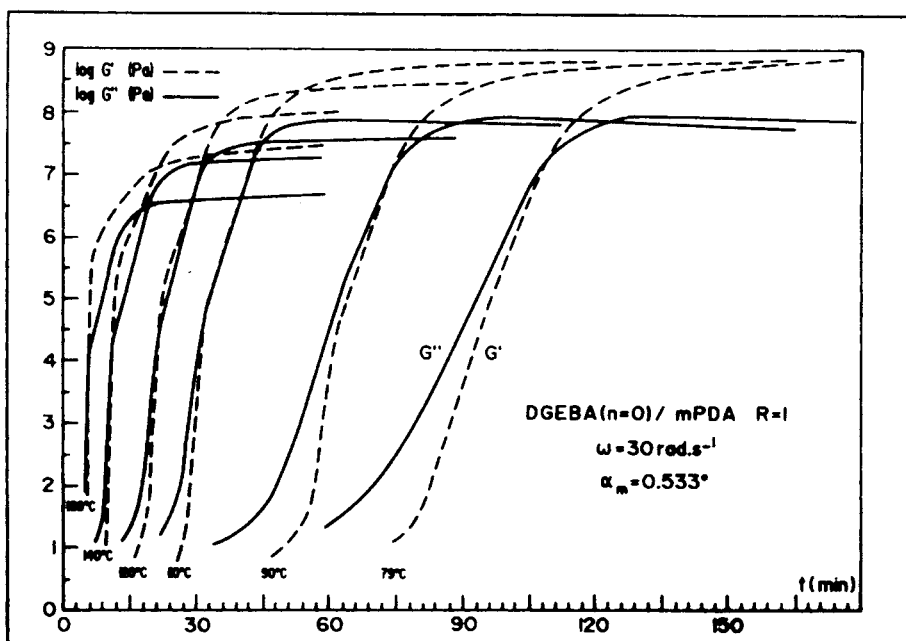


Fig. 1. Kinetics of hardening for DGEBA $n = 0$ /mPDA $R = 1$: (---) $\log G'$ (Pa); (—) $\log G''$ (Pa); $\omega = 30 \text{ rad s}^{-1}$; $\alpha_m = 0.533^\circ$.

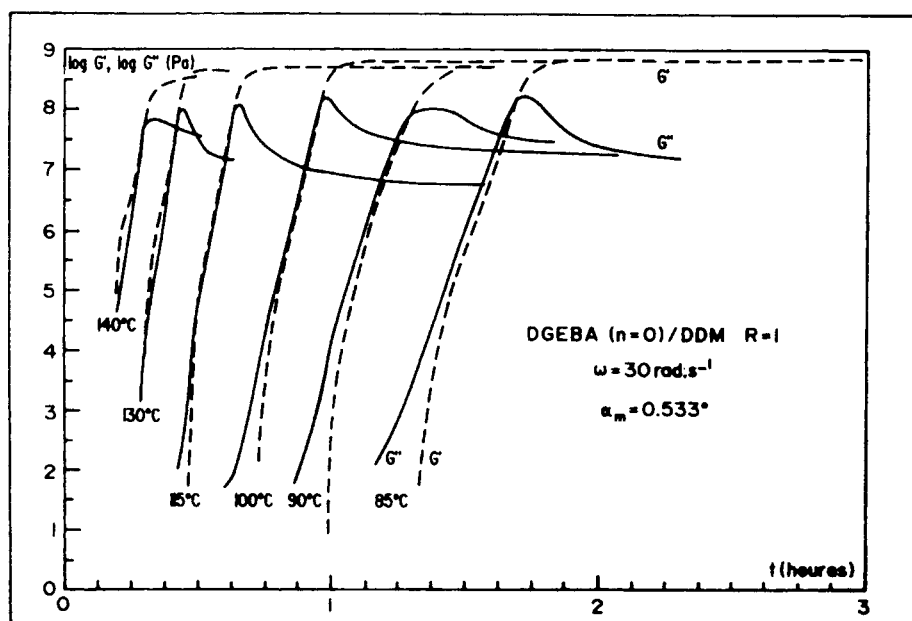


Fig. 2. Kinetics of hardening for DGEBA $n = 0$ /DDM $R = 1$: (---) $\log G'$ (Pa); (—) $\log G''$ (Pa); $\omega = 30 \text{ rad s}^{-1}$; $\alpha_m = 0.533^\circ$.

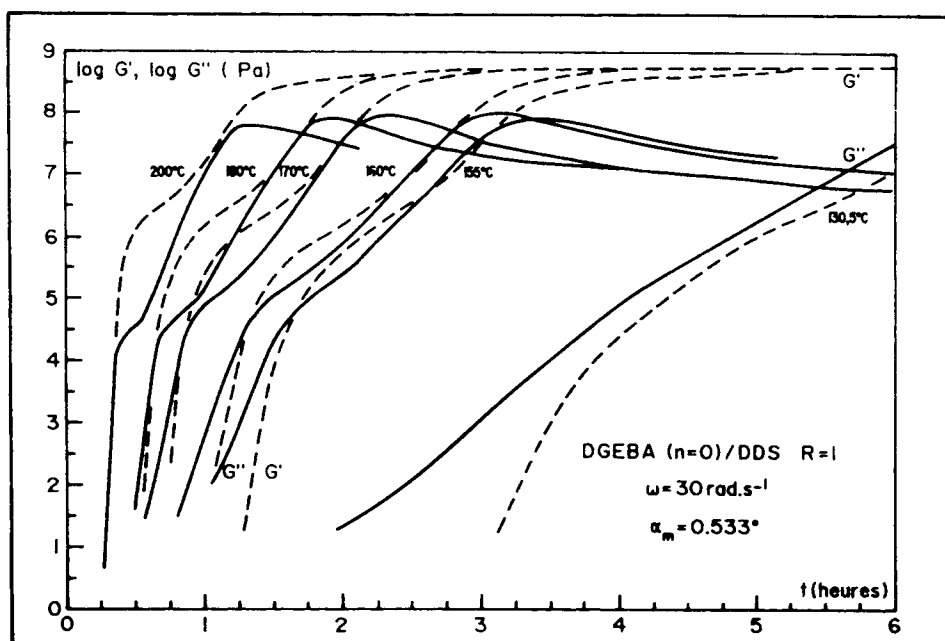


Fig. 3. Kinetics of hardening for DGEBA $n = 0$ /DDS $R = 1$: (---) $\log G'$ (Pa); (—) $\log G''$ (Pa); $\omega = 30 \text{ rad s}^{-1}$; $\alpha_m = 0.533^\circ$.

Gelation

We will rather discuss the variation curve of the viscous modulus G'' . It can be tied to the viscosity of the matrix $\eta' = G''/\omega$ and shows two linear parts at all temperatures. On Figure 1, for example (hardening agent mPDA), one can see, in all cases, a growth of $\log G''$, fairly slowly at first, then more and more rapidly until the curve becomes linear. One can define the rate of increase of the modulus as formula $v'' = d(\log G'')/dt$. When $\log G''$ has reached a value in the order of 4.5, the curve bends and one notes a second zone of linear increase of $\log G'' = f(t)$. The modulus next touches a maximum before diminution.

We have shown in a previous study² how to determine the gelation point by the point of the curve $\log G'' = f(t)$, which corresponds to the change in slope between the two linear parts. Times to gelation, so defined, are independent of experimental parameters such as the amplitude and frequency of shearing. They obey an Arrhenius law when the temperature of cure is varied, as has been shown elsewhere with other location methods for the gelation point.⁴⁻⁶ The viscous modulus G'' and therefore the viscosity at the gelation point depend on the temperature of cure as shown on Figures 8–10. The value of the viscosity stays, however, in the order of 10 000 P, the value established by some authors⁷ to locate the gel point. Others authors⁸ propose the location of the gelation by the point at which $\tan \delta = G''/G' = 1$. Figures 1–3 show that effectively $\tan \delta$ is equal to one close to the change of slope of $\log G'' = f(t)$, but for $T > 100^\circ\text{C}$ only. In fact, Figures 8–10 show that the viscous modulus G''_{gel} varies with the temperature while the elastic modulus G'_{gel} stays

about constant. As a result, $\tan \delta$ varies also at the gel point with the temperature of cure. This definition of the gel point gives results which are in approximate agreement with previous definitions and seems justifiable to us, since it is attached to an experimental phenomenon.

We can see, moreover, that Enns and Gillham⁹ have obtained times to gelation and to vitrification in agreement, with TBA and with a Rheometrics spectrometer, locating, in this case, the gelation by a shoulder on the curve $\log G'' = f(t)$. The experimental conditions are, however, a bit different than ours since, in order to measure the modulus from the beginning state to the final, these authors chose to reduce the deformation during measurement rather than to reduce the dimensions of the plates. In reducing the temperature of cure, they observed that the shoulder of G'' obtained with the spectrometer disappeared before the corresponding peak given by TBA.

At high temperature ($T \geq 125^\circ\text{C}$ with the mPDA), this decrease of the slope $d(\log G'')/dt$ is followed by a shoulder on the G'' curves. Figures 2 and 3 show the same kind of behavior with other hardening agents but the shoulder of G'' shows up better with DDM for $T \geq 120^\circ\text{C}$, and is very clearly shown with the DDS for $T \geq 135^\circ\text{C}$. The curves obtained at high temperatures with this last hardening agent are more like the curves obtained with TBA^{1,4} or with a prepreg.¹⁰ One should note that, in these last cases, the presence of an inert support on which the resin is laid means that the viscoelastic modulus measured varies in a relatively tight range (2 or 3 decades approximately), thus allowing a clear presentation of G'' maximum associated with the gelation. However, during the study of the resin by itself, the maximum of G'' overtakes the rapid increase of the modulus due to crosslinking. The phenomenon loses its clear definition and we can see only a shoulder of G'' .

Note that elsewhere, according to Schneider and Gillham,¹⁰ the loss peak attached to the gelation is much less remarkable with a prepreg than with a glass braid covered with resin. Moreover, the height of the peak increases with the number of folds of prepreg added. This shows the important influence of the support used and explains why there is no true peak of G'' at the gelation in parallel plane geometry since there is no support used.

So, the gel point has been located on the curve $\log G'' = f(t)$: (1) at low temperature, by the point on the curve that corresponds in time to the decrease of slope between two linear parts; (2) at high temperature, by the point at which the first linear variation ends, or approximately on the shoulder of G'' (Fig. 7).

Vitrification

The vitreous transition is located generally by the maximum of G'' (point M on Fig. 7) or by the maximum of the loss factor $\tan \delta = G''/G'$. The viscous modulus G'' reaches at point M a value independent of the temperature, since one can obtain $\log G''_M = 7.8 \pm 0.1$ (Pa) in the case of mPDA (with $T \leq 110^\circ\text{C}$ since the vitreous transition is not complete for the higher temperatures) $\log G''_M = 8.1 \pm 0.1$ (Pa) with the DDM and $\log G''_M = 7.9 \pm 0.1$ (Pa) with the DDS.

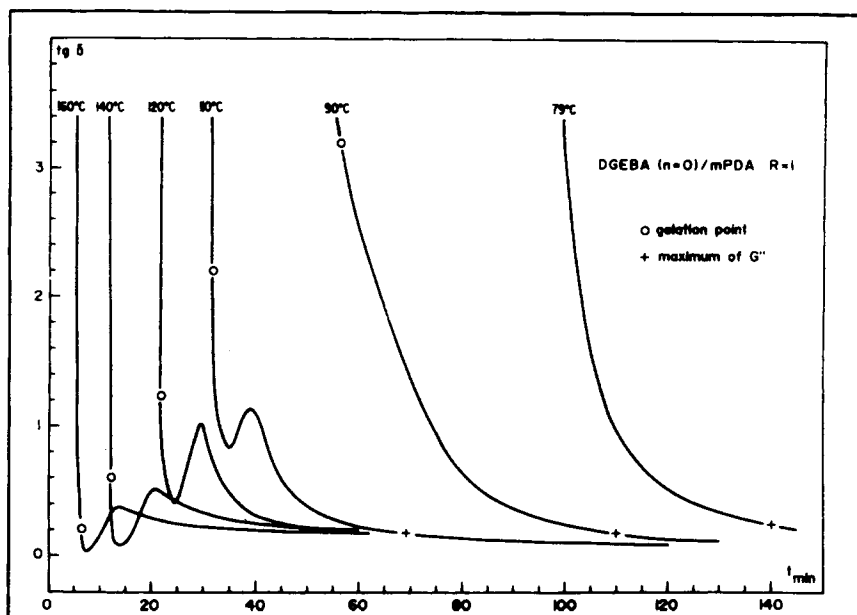


Fig. 4. Variation of the $\tan \delta$ kinetic with curing temperature for DGEBA $n = 0$ /mPDA $R = 1$: (○) gelation point; (+) maximum of G'' .

The variation curves of $\tan \delta = G''/G'$ with the temperature are shown in Figures 4–6. The values of $\tan \delta$ vary between infinite at the initial time (viscous liquid, zero elasticity) to a value very near zero at the end of reticulation (vitreous solid). They show a clear minimum followed by a maximum, except at low temperatures. On the curves 4, 5, and 6, we have marked the gel point and M point which corresponds to G'' maximum. One notes that the gel point does not show up any change in the variation of $\tan \delta$. The peak that appears is therefore linked with the vitreous transition. The progressive disappearance of this peak towards the lower temperatures, even though the vitrification obviously exists (maximum of G'' is clearly shown) is probably due to a slowing down of the kinetics. The maximum of $\tan \delta$, when present, is always anterior to the maximum of G'' . However, we know that these points indicate rather the vitreous transition already in process. In order to compare the zones of gelation and vitrification, we also tried to locate the beginning of the vitreous transition on the experimental curves.

The beginning of this transition does not show up on the curve of $\log G'' = f(t)$ but could be established arbitrarily at minimum $\tan \delta$, which is confirmed upon examining the curves of $\log G' = f(t)$. The curves obtained with the hardening agent DDS at high temperatures (Fig. 3) show up two levels, more or less clear according to the temperature. The second level corresponds to the vitrification relaxation. One can locate arbitrarily its beginning either at the inflexion point I in $\log G' = f(t)$ between the two levels, or at the point obtained by projection on the curve $\log G'' = f(t)$ at the same time. Figure 6 shows that this point is close to minimum $\tan \delta$, although it is always displaced towards positive time. Figure 14, in which are the values of G' and

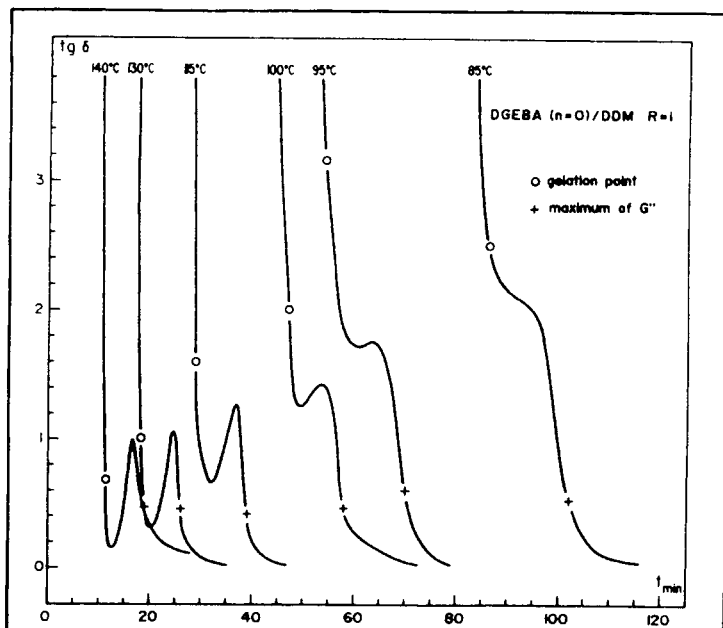


Fig. 5. Variation of the $\tan \delta$ kinetic with curing temperature for DGEBA $n = 0$ /DDM $R = 1$: (○) gelation point; (+) maximum of G'' .

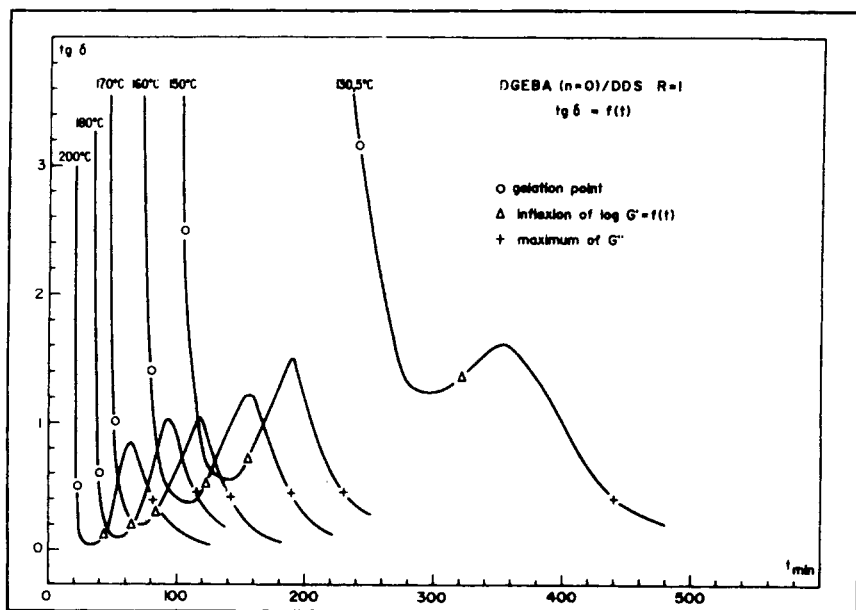


Fig. 6. Variation of the $\tan \delta$ kinetic with curing temperature for DGEBA $n = 0$ /DDS $R = 1$: (○) gelation point; (+) maximum of G'' ; (Δ) inflexion of $\log G' = f(t)$.

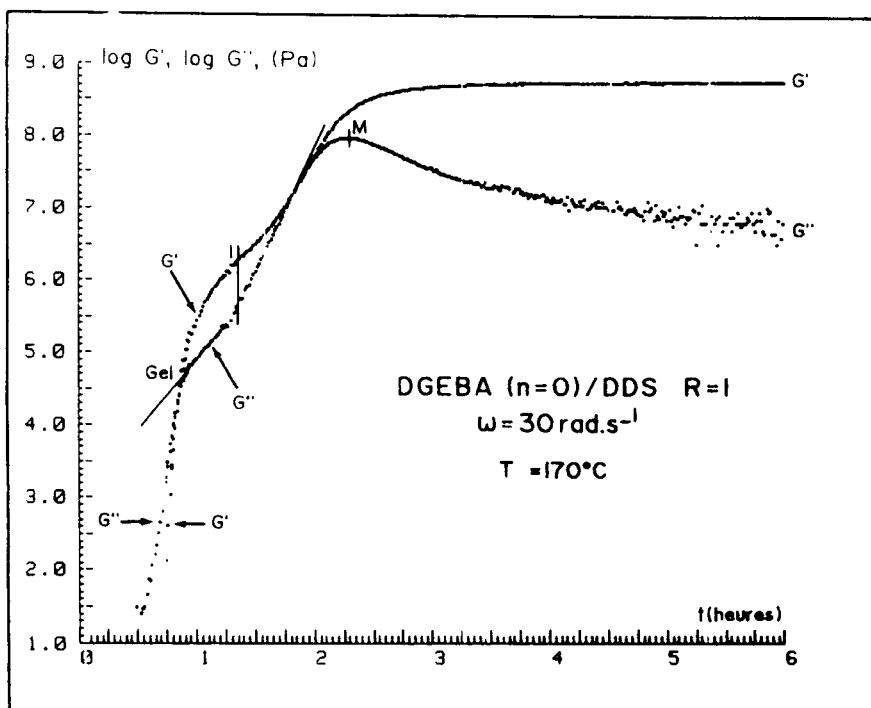


Fig. 7. Example of experimental curve: definitions of the gelation point and the vitrification range.

G'' at minimum $\tan \delta$ and at point I , reveals that the results are hardly different between these two points; and vary in the same manner in function with the temperature. The result obtained is, for example, $\log G' \sim 6$ (Pa), a practically constant value.

Nielsen¹¹ reports that the rubber modulus of a resin varies with the degree of reticulation between $\log G' = 5.9$ (Pa) for a resin with low degree of crosslinking, and $\log G' = 8.6$ (Pa) for a highly crosslinked resin. For a resin which is not crosslinked, one cannot observe a true rubbery stage. The value 5.9 would then be the maximum value for the rubbery stage or the minimum value for the beginning of the vitreous transition.

So, it appears that the beginning of the vitreous transition seems to correspond to the minimum of $\tan \delta$ when it exists; since this point is not far from the inflexion point of curves $\log G' = f(t)$ and brings about a satisfactory value in the elastic modulus.

The experimental values of times, elastic modulus, and viscous modulus at gel point and at the vitreous transition have been grouped in an appendix.

Critical Temperature for Gelation

Starting from values of $v'' = d(\log G'')/dt$ measured in the linear parts of the experimental curves on each side of the gel point, we have indicated on Figures 8–10 the variations of $\ln v'' = f(1/T)$. For each of three systems, one obtains very precisely linear variations before and after gelation. At a given

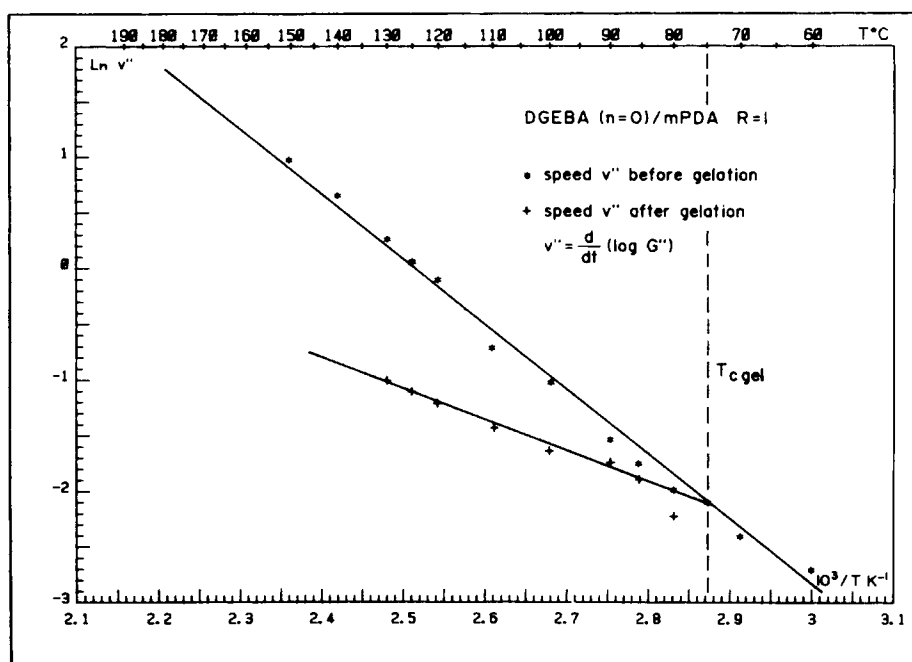


Fig. 8. Variations of $\ln v''$ before and after gelation with curing temperature for DGEBA $n = 0$ /mPDA $R = 1$: (*) speed v'' before gelation; (+) speed v'' after gelation; $v'' = d(\log G'')/dt$.

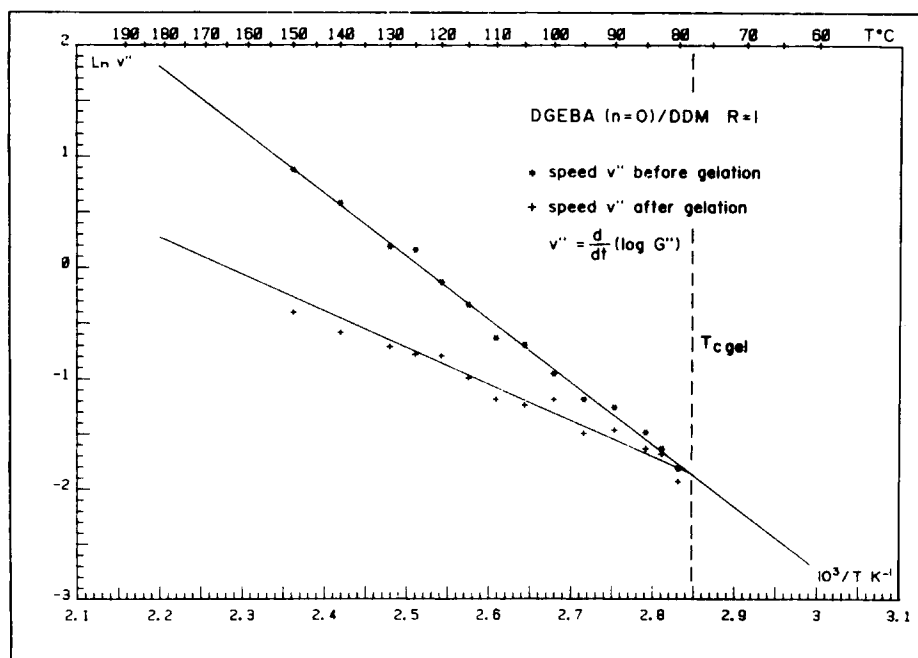


Fig. 9. Variations of $\ln v''$ before and after gelation with curing temperature for DGEBA $n = 0$ /DDM $R = 1$: (*) speed v'' before gelation; (+) speed v'' after gelation; $v'' = d(\log G'')/dt$.

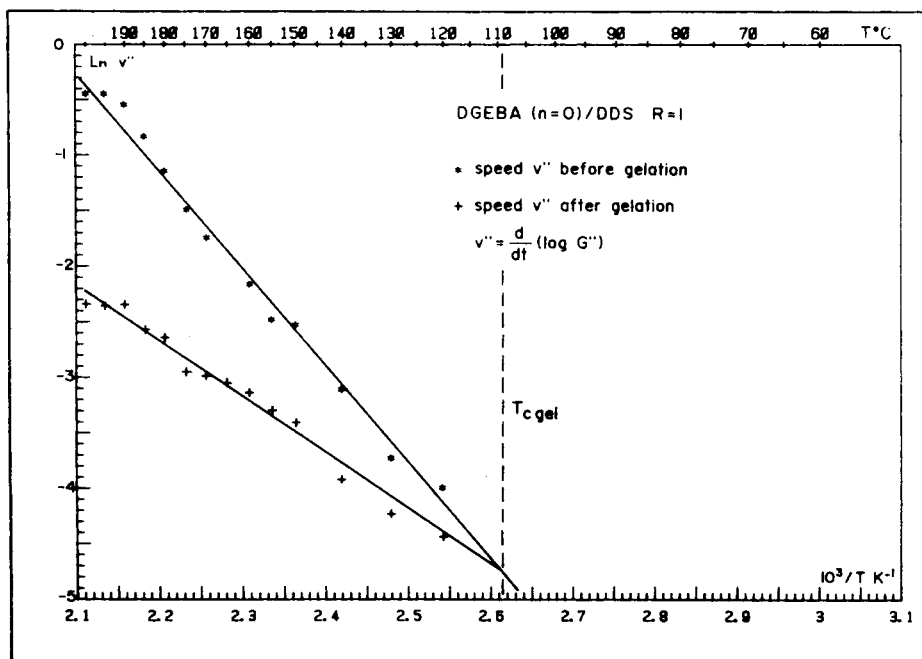


Fig. 10. Variations of $\ln v''$ before and after gelation with curing temperature for DGEBA $n = 0/\text{DDS } R = 1$: (*) speed v'' before gelation; (+) speed v'' after gelation; $v'' = d(\log G'')/dt$.

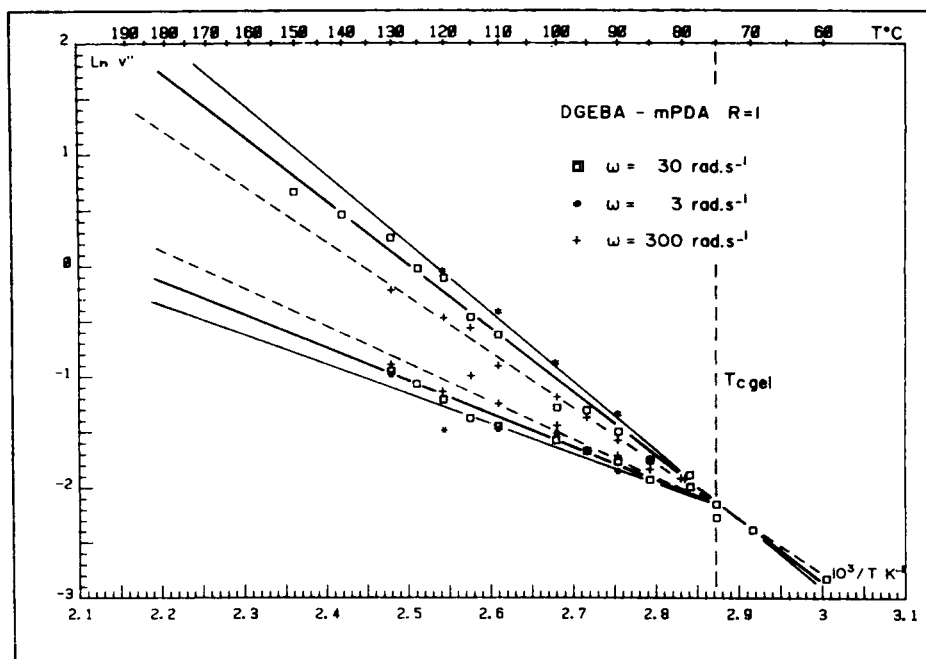


Fig. 11. Influence of the shearing frequency on the $\ln v'' = f(1/T)$ curves: (\square) $\omega = 30 \text{ rad s}^{-1}$; (*) $\omega = 3 \text{ rad s}^{-1}$; (+) $\omega = 300 \text{ rad s}^{-1}$.

temperature this diagram shows evidence of a variation in the slope $v'' = d(\log G'')/dt$, which characterizes the gelation transition. This variation is as important—the gelation is very marked—as the temperature is high. Inversely, there is a critical temperature for the gelation $T_{C \text{ gel}}$ below which there is no observable change in slope (unique value of v''); one obtains

$$\begin{aligned} T_{C \text{ gel}} &\sim 75^\circ\text{C} && \text{with mPDA} \\ &\sim 78^\circ\text{C} && \text{with DDM} \\ &\sim 109^\circ\text{C} && \text{with DDS} \end{aligned}$$

These temperatures represent, for each system, values below which there are no signs of gelation on the rheological curves. But these values were determined from the curves $\log G'' = f(t)$ obtained for a determined frequency ($\omega = 30 \text{ rad s}^{-1}$). Moreover, we know that the viscoelastic modulus depends on the frequency of measurement. We then tried to know if the critical temperature $T_{C \text{ gel}}$ depends on the frequency or represents a value that is particular to the system. We then studied, with the DGEBA/mPDA system, the influence of the frequency of shearing.

Influence of the Frequency of Shearing

The curves $\log(G', G'') = f(t)$ were determined at three different frequencies; $\omega = 3 \text{ rad s}^{-1}$, $\omega = 30 \text{ rad s}^{-1}$, and $\omega = 300 \text{ rad s}^{-1}$, keeping the same angular amplitude $\alpha_m = 0.533^\circ$. These curves are different since the mechanical properties of the initial mixture (liquid) are determined by its viscosity $\eta^* = -jG^*/\omega$ while the reticulated resin (solid) is characterized by its viscoelastic modulus.

We have already shown² that the shearing does not affect the chemical kinetics, at least in this frequency range, since the times used are identical (a) when the sample is sheared permanently at $\omega = 300 \text{ rad s}^{-1}$ and (b) when it is left to set during part of the heating time. Even so, the times to gelation are independent of the values of ω , although the modulus G''_{gel} are functions of ω .

Therefore, the speeds of variation of the viscous modulus $v'' = d(\log G'')/dt$ before and after gelation are different according to the frequency of measurement; but the experimental points measured at each frequency define new straight lines in the plane $(\ln v'', 1/T)$. These straight lines form a cluster and coincide in a very limited area of this plane. One might suppose that the

TABLE I
Variation with Curing Temperature of the Gap of Time between Gelation and Beginning of Vitrification for the DGEBA-DDS $R = 1$ System
(This Work)

T ($^\circ\text{C}$)	t_{gel} (min)	$t_{\text{min, tan } \delta}$ (min)	$\Delta t = t_{\text{min, tan } \delta} - t_{\text{gel}}$
200	21	30	9
180	37	55	18
170	51	75	24
160	79	110	31
150	110.5	140	29.5
130.5	244	295	51

dispersion around the point of concurrence is due to the uncertain position of each straight line. Figure 11 shows, in effect, that all these straight lines pass visibly through the same point. The abscissa of this point represents the critical temperature of gelation $T_{C\text{ gel}}$, which is independent of the frequency of measurement and depends only on the nature of the system. One notes that the ordinates of this point is also independent of ω . Thus the rate of variation

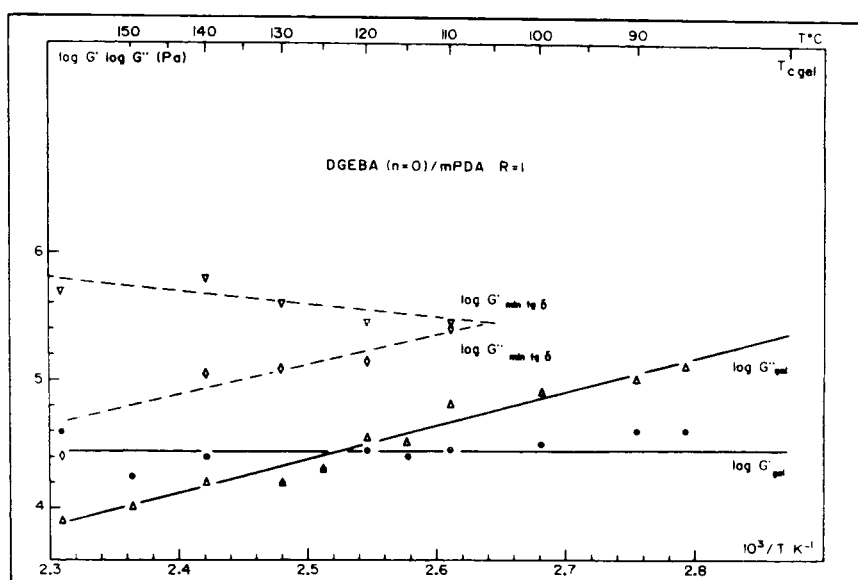


Fig. 12. Variation of the viscoelastic modulus at gelation and vitrification with curing temperature for DGEBA $n = 0$ /mPDA $R = 1$.

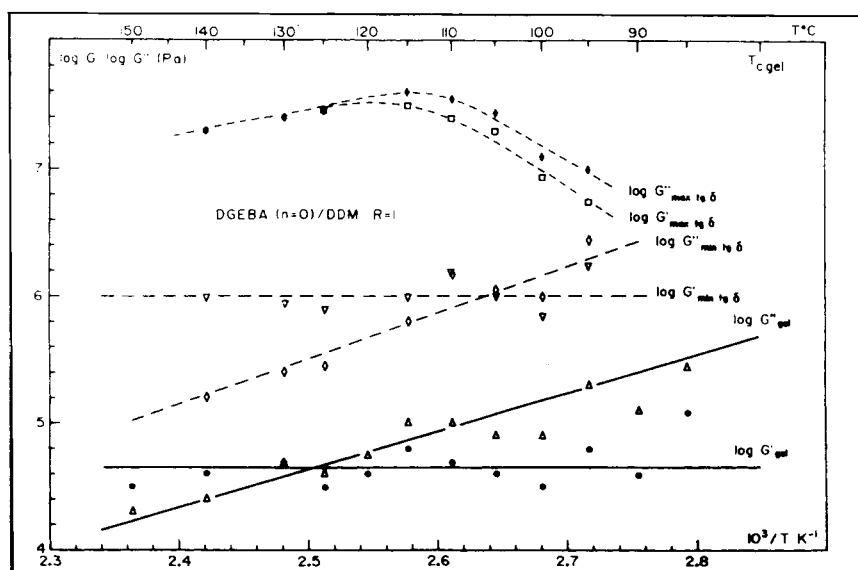


Fig. 13. Variation of the viscoelastic modulus at gelation and vitrification with curing temperature for DGEBA $n = 0$ /DDM $R = 1$.

v'' of the viscous modulus at temperature $T_{C\text{ gel}}$ is also representative of the system studied.

DISCUSSION

According to Gillham and Benci,⁴ the gelation would not appear below T_{gg} , the temperature at which the vitrification coincides with the gelation. For $T < T_{gg}$, the vitrification would happen before the gelation, blocking this transition. The two phenomena can be characterized (1) by the time at which they appear or (2) by the value of the viscoelastic modulus at that moment.

Table I allows a comparison of times to gelation and to beginning of vitrification: One notes that the gap between these times grows regularly when the curing temperature is lowered. By extrapolation to $T_{C\text{ gel}}$, one notes that the two phenomena remain perfectly distinct, even at the critical temper-

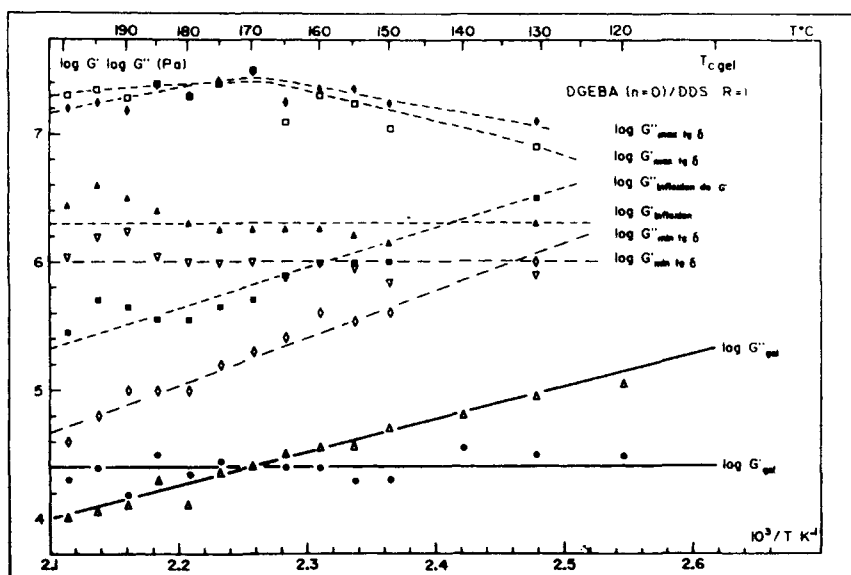


Fig. 14. Variation of the viscoelastic modulus at gelation and vitrification with curing temperature for DGEBA $n = 0$ /DDS $R = 1$.

TABLE II
Variation with Curing Temperature of the Gap of Time between Gelation and Vitrification
for the EPON 828 (DGEBA)-PACM 20 System⁹ by TBA

T (°C)	t_{gel} (min)	t_{vit} (min)	$\Delta t = t_{\text{vit}} - t_{\text{gel}}$
110	6	14	8
89	12	24	12
70	30	46	16
65	38	57	19
39	141	203	62
17	375	641	266
5	820	1544	724
-5	1223	2948	1725

TABLE III
Variation with Curing Temperature of the Gap of Time between Gelation and Vittrification
for EPON 828¹² by TBA^a

$T(^{\circ}\text{C})$	t_{gel} (min)	t_{vit} (min)	$\Delta t = t_{\text{vit}} - t_{\text{gel}}$
170	30	140	110
150	65	210	145
130	130	400	270
110	300	750	450

^aValues issued from a diagram.

TABLE IV
Variation with Curing Temperature of the Gap of Time between Gelation and Vittrification
for the Tetraglycidylmethlene Dianiline-DDS-BF₃ System¹³ by TICA^a

$T(^{\circ}\text{C})$	t_{gel} (s)	t_{vit} (s)	$\Delta t = t_{\text{vit}} - t_{\text{gel}}$
195	200	900	700
175	600	1600	1000
155	1400	2500	1100
135	2300	5300	3000

^aThe vittrification times are defined on maximum $\tan \delta$.

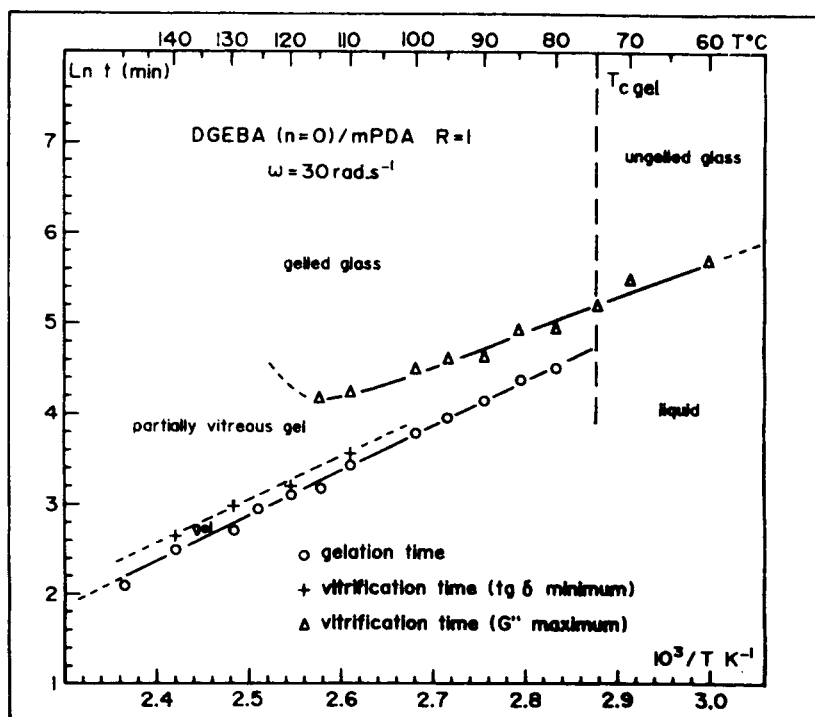


Fig. 15. Isothermal time-temperature-transformation cure diagram for DGEBA $n = 0$ /mPDA $R = 1$: (○) gelation time; (+) vittrification time ($\tan \delta_{\text{min}}$); (Δ) vittrification time (G''_{max}).

ature $T_{C\text{ gel}}$, where gelation no longer appears. It seems, then, that there is no temperature at which the two phenomena can appear simultaneously.

The same conclusion can be drawn from the analysis of the values of the viscoelastic modulus, (Figs. 12–14). With the hardening agents DDM and DDS the elastic modulus keep a constant value (allowing for a margin of error) for the gel point and beginning of vitrification point, whatever the temperature, and so cannot coincide at $T_{C\text{ gel}}$. The same is true for the viscous modulus which vary the same way, showing a difference between gelation and vitrification of one decade, if we start the vitrification at minimum $\tan \delta$, or 1.5 decades if we consider the inflexion point on the curve $\log G' = f(t)$.

We deduce that if the gelation does not appear with rheology below temperature $T_{C\text{ gel}}$, the vitrification is not responsible since it appears in all cases later than the gelation. One must look at the phenomenon of gelation itself for the disappearance, at $T_{C\text{ gel}}$, of the change in slope of $\log G'' = f(t)$, and we have seen that the amplitude of this change in slope $\Delta v'' = v''_2 - v''_1$ varies linearly with $1/T$: $\Delta v'' = K(1/T_{C\text{ gel}} - 1/T)$ to annul at $T_{C\text{ gel}}$. It seems then that it is not necessary to suppose that gelation and vitrification coincide at temperature $T_{C\text{ gel}}$. In every case vitrification represents a posterior phase to the gelation in the hardening of the resin.

This conclusion seems contrary to the interpretation of Gillham, but in fact does not oppose the experimental results presented by him and by others authors. In fact, the tables of values, obtained with the torsional braid analysis or torsion impregnated cloth analysis (forced oscillation) depending on the case and presented in Tables II–IV, clearly show that the gap in time between gelation and vitrification grows when the temperature is lowered.

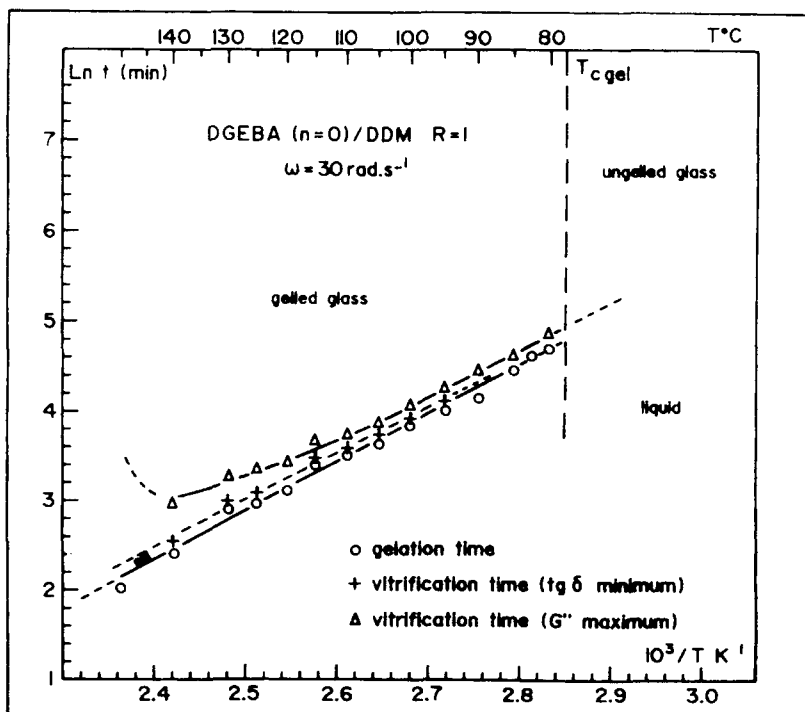


Fig. 16. Isothermal time-temperature-transformation cure diagram for DGEBA $n = 0$ /DDM $R = 1$: (○) gelation time; (+) vitrification time ($\tan \delta_{\min}$); (Δ) vitrification time (G''_{\max}).

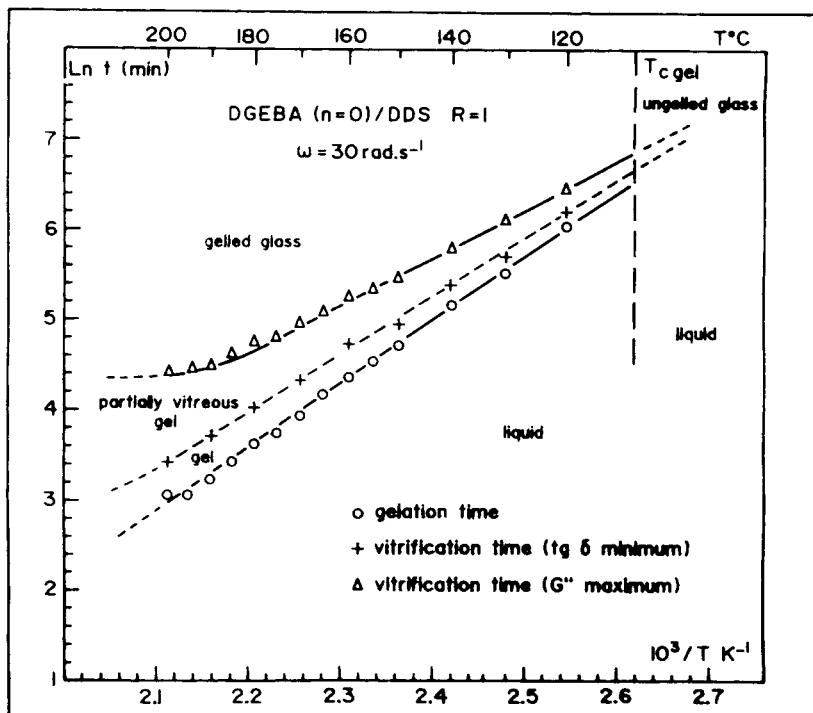


Fig. 17. Isothermal time-temperature-transformation cure diagram for DGEBA $n = 0$ /DDS $R = 1$: (○) gelation time; (+) vitrification time ($\tan \delta_{\min}$); (Δ) vitrification time (G''_{\max}).

The two phenomena stay distinct and separate at all temperatures.

On Figures 15–17, we have reported the log variations of (1) time to gelation and (2) time to vitrification (located by the minimum of $\tan \delta$ and the maximum of G'') as a function of the inverse of the temperature with all three hardening agents. This representation has the advantage of giving a linear gelation curve (law of Arrhenius), but the curve of vitrification which seems linear within the limits of temperature studies is in reality an S-curve as Gillham^{4,14} showed: The times increase very rapidly at the approach of maximum temperature $T_{g\infty}$; and tend towards zero near T_{g0} , value relative to the initial mixture. Figures 15–17 show that, although the gap in times increases towards lower temperatures, the gap between logs of time to gelation and to vitrification diminishes. An approximate extrapolation of these curves would seem to show that they cross at low temperatures. In fact, we have seen that, on one hand, the gap in time increases within the temperature range studied (i.e., under $T_{C \text{ gel}}$) and, on the other hand, the gelation curve should not be extrapolated beyond $T_{C \text{ gel}}$ since the transition is no longer apparent. The curves stay distinctly separate.

Temperature T_{gg} was determined by Babayevsky and Gillham¹⁵ as being the lower limit at which the gelation peak is barely observable, with TBA, on the three systems studied by us. So determined, this temperature should be a close neighbor of $T_{C \text{ gel}}$, the temperature from which gelation starts to be observable on our own curves. Table V presents the obtained results.

The results are in satisfactory agreement in the case of mPDA only. In fact, the temperature of 110°C (DDM) and 130°C (DDS) would better represent

TABLE V
Comparison of T_{gg} Temperatures¹⁴ and $T_{C\text{ gel}}$ Temperatures (This Work)

	T_{gg} ($^{\circ}\text{C}$) ¹⁴	$T_{C\text{ gel}}$ ($^{\circ}\text{C}$)
DGEBA-mPDA	70	75
DGEBA-DDM	110	78
DGEBA-DDS	130	109

the limiting temperatures for which the increase of G'' associated with the gelation appears on our curves: approximately 120°C (DDM) and 135°C (DDS), but do not represent to our mind the lower temperature limits of gelation.

CONCLUSION

The rheology in parallel plates geometry, although relatively unused in the study of composites, is a fruitful technique for studying the kinetics of resin reticulation. The gelation appears by diminishing the rate of growth of the viscous modulus $v'' = d(\log G'')/dt$ between two zones where this rate is constant. The decrease in rate $v''_2 - v''_1$ is linear as a function of the temperature inverse and is null for critical temperature $T_{C\text{ gel}}$. $T_{C\text{ gel}}$ is independent of the frequency of shearing and has been measured for the three systems studied. At high temperatures a shoulder of G'' adds to the change in slope of the viscous modulus. The vitrification expresses itself with maximum G'' and usually of $\tan \delta$. Our discussion shows that the two phenomena of gelation and vitrification stay perfectly distinct at all temperatures. The vitreous transition is therefore totally independent of the fact that gelation is no longer present at temperatures below $T_{C\text{ gel}}$.

APPENDIX: Variations of the gelation time, vitrification time, and viscoelastic modulus at these points with curing temperature. r_{gel} and r_{sit} (min). G' and G'' (Pa).

TABLE VI
DGEBA $n = 0/\text{mPDA}$ $R = 1$

T ($^{\circ}\text{C}$)	t_{gel}	$\log G'_{\text{gel}}$	$\log G''_{\text{gel}}$	$\tan \delta_{\text{gel}}$	t_{vit} ($\tan \delta_{\text{min}}$)	$\log G'$ ($\tan \delta_{\text{min}}$)	$\log G''$ ($\tan \delta_{\text{min}}$)	t_{vit} (G'_{max})
60								300
70								240
75								180
80	92							140
85	81	4.6	5.1	3.2				137
90	65	4.6	5.0	2.5				102
95	53	4.5	4.9	2.5				100
100	44	4.5	4.9	2.5				90
110	30.5	4.45	4.8	2.2	35	5.45	5.35	69
115	24	4.4	4.5	1.25				65
120	22	4.45	4.55	1.3	24.5	5.45	5.15	
125	19	4.3	4.3	1.0				
130	15	4.2	4.2	1.0	19.5	5.6	5.1	
140	12	4.4	4.2	0.6	14	5.8	5.0	
150	8	4.25	4.0	0.6				
160	6	4.6	3.9	0.2	7	5.7	4.4	

TABLE VII
DGEBA $n = 0$ /DDM $R = 1$

T ($^{\circ}\text{C}$)	t_{gel}	$\log G'_{\text{gel}}$	$\log G''_{\text{gel}}$	$\tan \delta_{\text{gel}}$	t_{vit} ($\tan \delta_{\text{min}}$)	$\log G'$ ($\tan \delta_{\text{min}}$)	$\log G''$ ($\tan \delta_{\text{min}}$)	t_{vit} (G''_{max})
80	111.5							131
85	86	5.1	5.45	2.3				102
90	63	4.6	5.1	3.2				85
95	55.5	4.8	5.3	3.2	61	6.25	6.45	70
100	46	4.5	4.8	2.0	49	5.8	6.0	58
105	37.5	4.6	4.9	2.0	42	6.0	6.05	48
110	33	4.7	5.0	2.0	36	6.2	6.2	42
115	29.5	4.8	5.0	1.6	32	6.0	5.8	39
120	22	4.6	4.75	1.4				30.5
125	19.5	4.5	4.6	1.25	22	5.9	5.45	28
130	18	4.7	4.7	1.0	20	5.95	5.4	26
140	11	4.6	4.4	0.6	12.5	6.0	5.2	19
150	7.5	4.5	4.3	0.6				

TABLE VIII
DGEBA $n = 0$ /DDS $R = 1$

T ($^{\circ}\text{C}$)	t_{gel}	$\log G'_{\text{gel}}$	$\log G''_{\text{gel}}$	$\tan \delta_{\text{gel}}$	t_{vit} ($\tan \delta_{\text{min}}$)	$\log G'$ ($\tan \delta_{\text{min}}$)	$\log G''$ ($\tan \delta_{\text{min}}$)	t_{vit} (G''_{max})
120	410	4.5	5.05	3.55	490			630
130.5	244	4.5	4.95	2.8	295	5.9	6.0	440
140	172	4.55	4.8	1.8	220			320
150	110.5	4.3	4.7	2.5	140	5.8	5.6	230
155	93	4.3	4.55	1.8		5.95	5.5	204
160	79	4.4	4.55	1.4	110	6.0	5.6	189
165	64	4.4	4.5	1.3		5.85	5.4	162
170	51	4.4	4.4	1.0	75	6.0	5.3	141
175	42	4.45	4.35	0.8		6.0	5.2	120
180	37	4.35	4.1	0.6	55	6.0	5.0	115
185	30.5	4.5	4.3	0.6		6.05	5.0	99
190	25	4.2	4.1	0.8	40	6.25	5.0	87
195	21	4.4	4.05	0.4		6.2	4.8	84
200	21	4.3	4.0	0.5	30	6.05	4.6	81

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