

Application of the Percolation Model to Gelation of an Epoxy Resin

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Synopsis

The percolation model has been applied to the study of gelation of the TGDDM-DDS system (tetraglycidyl-diaminodiphenylmethane-diaminodiphenylsulfone) at a mass concentration of 100–30. For each temperature the experimental viscosity curves are satisfactorily described by a percolation law. Using the degree of chemical reactions, X , as a variable, a very clear change in the reaction mechanism with temperature can be shown. Then a rate of advancement of effective reactions, Y , is defined. This value only takes intermolecular-type reactions into account, and is probably the only variable on which viscosity depends in a percolation law: $\eta = B(1 - Y/Y_c)^{-p}$. We obtain $Y_c = 0.45$ and $p = 2.0$. Comparing X_c and Y_c at the gel point, we obtain information on the proportion of intramolecular reactions with temperature. It is also demonstrated that the critical percolation threshold agrees closely with the gel point determined experimentally on $\log G'' = f(t)$ curves.

INTRODUCTION

The process of gelation of a thermosetting resin is analogous to the phenomenon of percolation^{1,2} and it is currently accepted that the classical Flory³ and Stockmayer⁴ theory of gelation is identical to percolation theory according to the Bethe lattice.⁵ However, a certain amount of recent theoretical research seems to show that the phenomenon of gelation does not belong to the same class of universality as standard percolation (random 3-dimensional process).^{6–8} This means that the viscosity η before the liquid-gel transition and the elastic modulus G' after it must obey the same kind of rules as those describing standard percolation, that is to say, power laws as a function of the distance from the gel point, but with exponents that are not necessarily the same. Furthermore, from the point of view of the reaction mechanism, this means that, in a real environment, reactions do not necessarily take place at random, but are determined by certain kinetic parameters.

In this article, we have tried to apply the general percolation laws to gelation of an epoxy resin widely used in the composite materials industry: the TGDDM-DDS system (tetraglycidyl-diaminodiphenylmethane-diaminodiphenylsulfone). This system has been the object of detailed experimental study by the rheological method: the rheological kinetics has been studied both by continuous and sinusoidal shearing over a wide range of temperature⁹ (75°–180°C) and concentration¹⁰ (from $R = 0.24$ to 1.3, R being the ratio of amine functions to epoxy functions). The mechanism of the chemical reaction¹¹

and the kinetics¹² have also been studied by C¹³-NMR, FTIR, chromatography, and calorimetric analysis.

RHEOLOGICAL BEHAVIOR

Figure 1 shows an example of the curves for elastic modulus G' and loss modulus G'' , determined at 180°C by sinusoidal shearing between parallel plates at constant frequency ($\omega = 30$ rad/s) (Rheometrics RDA 700).⁹ These curves resemble those for other previously studied epoxy systems based on BADGE^{13,14} (bisphenol A diglycidyl ether), and can be interpreted in the same way. The glass transition appears towards the end of the cure through the maximum of G'' and the final plateau of G' and G'' . The gel point has been associated with decrease in the slope of $\log G'' = f(t)$ between two linear sections, and at the more or less marked shoulder of this curve which accompanies it.¹⁴ The study of various systems has shown that at this point:

- the elastic modulus G'_{gel} is practically constant at all temperatures (though the TGDDM-DDS system shows a change in behavior for $T < 120^\circ\text{C}$);
- the loss modulus G''_{gel} decreases slightly with increasing temperatures, but the dynamic viscosity $\eta^* = \sqrt{G'^2 + G''^2} / \omega$ remains close to 10^3 Pa s for all the systems studied, a value often selected in the literature to determine the gel point;
- the loss factor $\tan \delta = (G''/G')_{\text{gel}}$ also varies with temperature, but the values are all close to 1, a value which is also used by some authors to define the gel point;

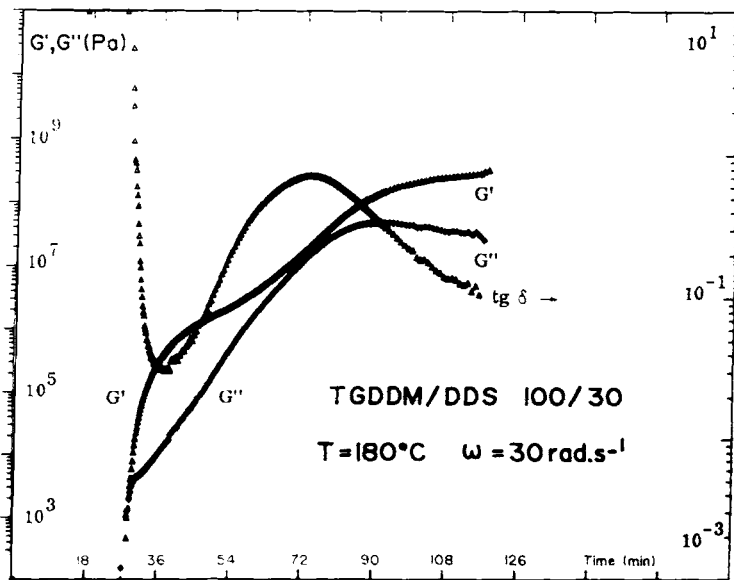


Fig. 1. Example of experimental curves $\log G'$, $\log G'' = f(t)$. TGDDM-DDS 100-30 system, $\omega = 30$ rad/s, Rheometrics RDA 700.

- the gel time is independent of the excitation frequency (whereas the rheological curves depend on it);
- the degree of advancement of chemical reactions, measured by C^{13} -NMR and FTIR on the simple BADGE-DDM¹⁵ (diaminodiphenylmethane) system, in which only the classical epoxy-amine reactions are involved, with comparable reactivities, has the value $X_{gel} = 0.59 \pm 0.02$, in excellent agreement with the theoretical value 0.58 obtained by the Flory theory³: $X_{gel} = [R(f-1)(g-1)]^{-1/2}$ with $R = 1$ for the stoichiometric concentration, $f = 2$ and $g = 4$ for a diepoxytetraamine system.

On the other hand, the gel point is very often defined in the literature as the point at which viscosity increases very rapidly. The classical theory³ indicates that viscosity under permanent shearing tends towards infinity at the gel point. This property has been used by some authors¹⁶ to define the gel time as the time for which the η_0/η ratio cancels itself out, η_0 being the initial viscosity. In fact, this method can only be applied if the η_0/η ratio varies linearly, thus facilitating extrapolation to zero. Figure 2 shows that this is not the case for the TGDDM-DDS system; the $\eta_0/\eta = f(t)$ curves determined by permanent shearing at several temperatures are not linear vs. time (or logarithm of time) throughout the entire domain (the time obtained by extrapolation of the linear section for $\eta_0/\eta = 0$ corresponds to a very low real viscosity, of the order of 10 Pa s). Thus this method is not suitable for an easy extrapolation. However, if the percolation laws can be applied to viscosity, this means in effect that its rate of variation tends towards a maximum at the percolation threshold. By means of this model it should therefore be possible to locate the gel point accurately and to confirm the interpretation which has been given for $\log G'' = f(t)$ curves.

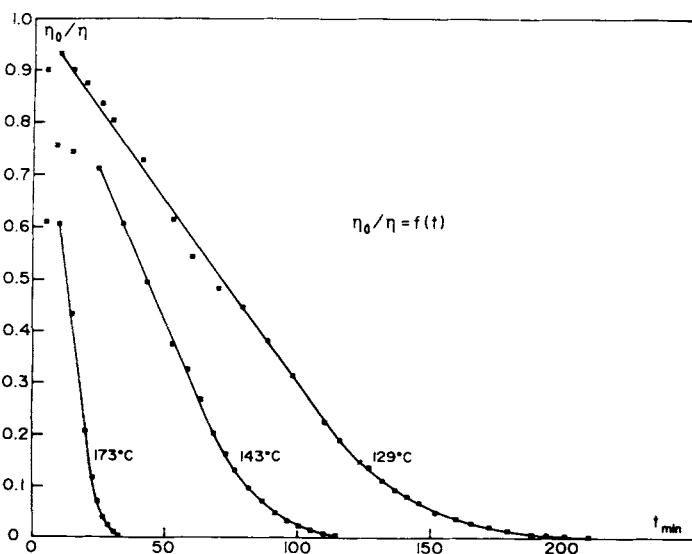


Fig. 2. Variations of the inverse of viscosity vs. time at several temperatures. TGDDM-DDS 100-30 system. Permanent shearing Rheomat 30 (Contraves).

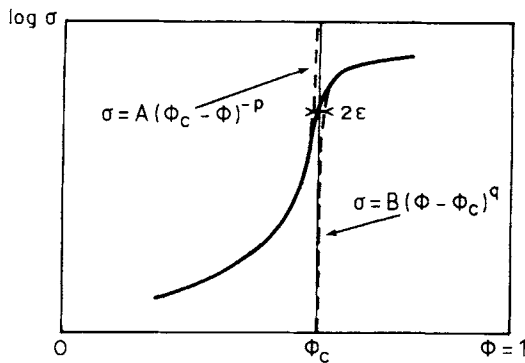


Fig. 3. Variations of electrical conductivity of a mixture of particles around the percolation threshold.

MODELING VISCOSITY VARIATION CURVES

General Percolation Laws—A Review

The percolation model has often been used to describe variations in the electrical conductivity of a mixture of two types of particle, one of which is a poor conductor, the other a good conductor, when the proportion ϕ_c of the latter increases. As Figure 3 indicates, conductivity of the mixture increases very rapidly close to a critical threshold ϕ_c known as the percolation threshold. On either side of this threshold, variations of conductivity can be described by laws of the form:

$$\begin{cases} \sigma = A(\phi_c - \phi)^{-p} & \text{for } \phi < \phi_c - \epsilon \\ \sigma = B(\phi - \phi_c)^q & \text{for } \phi > \phi_c + \epsilon \end{cases}$$

where ϵ is small and A , B , p , and q are four positive constants.

These relationships do not apply in the zone very close to the percolation threshold, for which the experiment shows that there is continuity between the two curves.

Experimental Procedure

The theory^{1,2} shows that it must be possible to apply the percolation laws to the elastic modulus G_0 beyond the gel point, to the viscosity η , and consequently to the loss modulus G'' which is proportional to it, before the gel point. But the experimental $\log G', G'' = f(t)$ curves are affected by the phenomenon of vitrification which follows gelation. The storage modulus reaches a higher plateau in the glassy state, while the loss modulus passes through a maximum before reaching the final value. Also, the viscoelastic modulus is too low to be measured in the initial phase of the cure, below 10 Pa. Consequently, the percolation laws cannot easily be tested on variations of the viscoelastic modulus. However, with permanent shearing, variations of viscosity from the beginning of cure up to a maximum value of 10^5 Pa s can be followed by modifying the shearing rate value. This study was carried out using a Contraves Rheomat 30.⁹ The system was studied at a mass concentra-

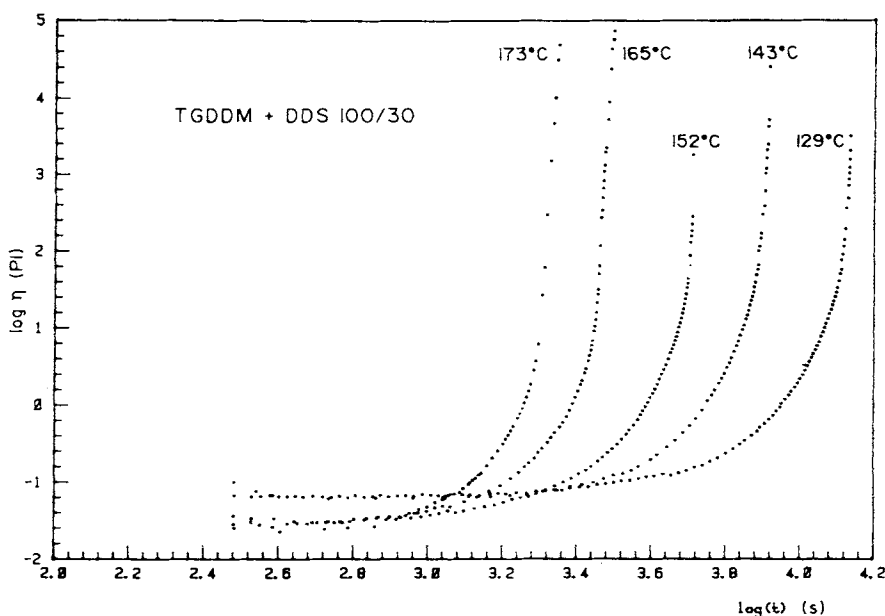


Fig. 4. Curves of viscosity $\log \eta = f(t)$ at different temperatures. TGDDM-DDS 100-30 system. (Shearing rate $10^{-2} \text{ s}^{-1} < \dot{\gamma} < 10^2 \text{ s}^{-1}$.)

tion of 100 g TGDDM for 30 g DDS, which is the concentration generally used in industry. We verified that the value measured at the beginning of the cure did represent static viscosity⁹; furthermore, several authors agree that this technique does yield static viscosity up to values of the order of 10^3 Pa s ¹⁷ or even 10^4 Pa s ,¹⁸ in other words, close to the gel point (Fig. 4).

Application of the Percolation Model

A first approach assumes that the proportion ϕ in the electric percolation model is equivalent to the extent of reaction X , which represents the proportion of chemical bonds formed in the sample, and determines the construction of the molecular network. The extent of reaction is indeed the representative parameter to describe the viscosity rise.¹⁹ So the study requires the chemical kinetics law. This is determined by calorimetric analysis. The kinetics law obtained comprises two terms which account for autocatalysis¹²:

$$\frac{dX}{dt} = K(1 - X)^2 + K_1X(1 - X)^2$$

with $\ln K = 14.13 - 6930/T$, $\ln K_1 = 25.93 - 10600/T$

where K and K_1 are expressed in h^{-1} and T in K.

This law describes the major part of the cure, from $X = 0$ to the glass transition, in the temperature range $100\text{--}180^\circ\text{C}$. We have to keep in mind indeed that the reaction is not complete for the low temperatures, because the kinetics is diffusion-controlled in the glassy transition, but this limitation does not affect the study of gelation.

TABLE I
 Values of the Parameters Deduced by Adjustment of the $\eta = A(1 - X/X_c)^{-p}$ Law
 on the Experimental Curves $\log \eta = f(t)^a$

T (°C)	$\log A$ (Pa s)	X_c	p
129	-1.25	0.35	4.13
143	-1.19	0.49	2.93
152	-1.43	0.51	2.82
155	-1.45	0.525	2.17
165	-1.505	0.56	1.96
172	-1.52	0.59	2.00
181	-1.50	0.60	1.42

^a X = extent of chemical reactions.

$\log \eta = f(X)$ curves can thus be plotted for all temperatures from the $\log \eta = f_1(t)$ curves and the chemical kinetics $X = f_2(t)$. We therefore tried to apply to them a law of the form $\eta = A(1 - X/X_c)^{-p}$, in which X_c represents the degree of critical reaction at the percolation threshold.

This expression can be written as $\log \eta = \log A - p \log(1 - X/X_c)$, and shows that variations of $\log \eta$ must be linear with $\log(1 - X/X_c)$, if the law is applicable. Experimentation does show that these variations are linear when the value of X_c selected is appropriate. So the percolationlike model can describe the increase in viscosity before gelation. The values of X_c , A , and p can then be determined by an adjustment method, this for each temperature T . The degree of accuracy of this method for calculating X_c is around ± 0.01 , but taking the other uncertainties (relating to temperature and chemical kinetics) into account, the absolute precision for X_c can be estimated at ± 0.02 . Table I presents the results obtained.

Discussion

Figure 5 shows a very good fit at several temperatures between the experimental $\log \eta = f(X)$ curves and the curves obtained by the percolation law. The agreement is satisfactory, not only in the region close to the critical threshold, but in fact practically right from the beginning of the cure. The discrepancies observed must be attributed rather to temperature stabilization problems at the beginning of the reaction. So the parameter A is near the initial viscosity η_0 of the mixture and the slight decrease observed with increasing temperature is in agreement with the WLF equation. It thus appears clearly that at each temperature, variations in viscosity can be described by a law of the type $\eta = A(1 - X/X_c)^{-p}$, from beginning of cure up to a point close to the critical threshold. It is consequently possible to identify the system's gel point at this critical threshold, where the viscosity becomes infinite.

Figure 6 shows the variations obtained for X_c at the critical point, plotted against temperature. The parameter X_c varies from around $X_c = 0.4$ at 130°C to $X_c = 0.6$ at 180°C. The theory, however, indicates that X_c should be constant at the gel point, if the reaction mechanism remains unchanged. So this variation clearly shows that the reaction mechanism changes with cure temperature. It is known that the TGDDM-DDS system can give rise to

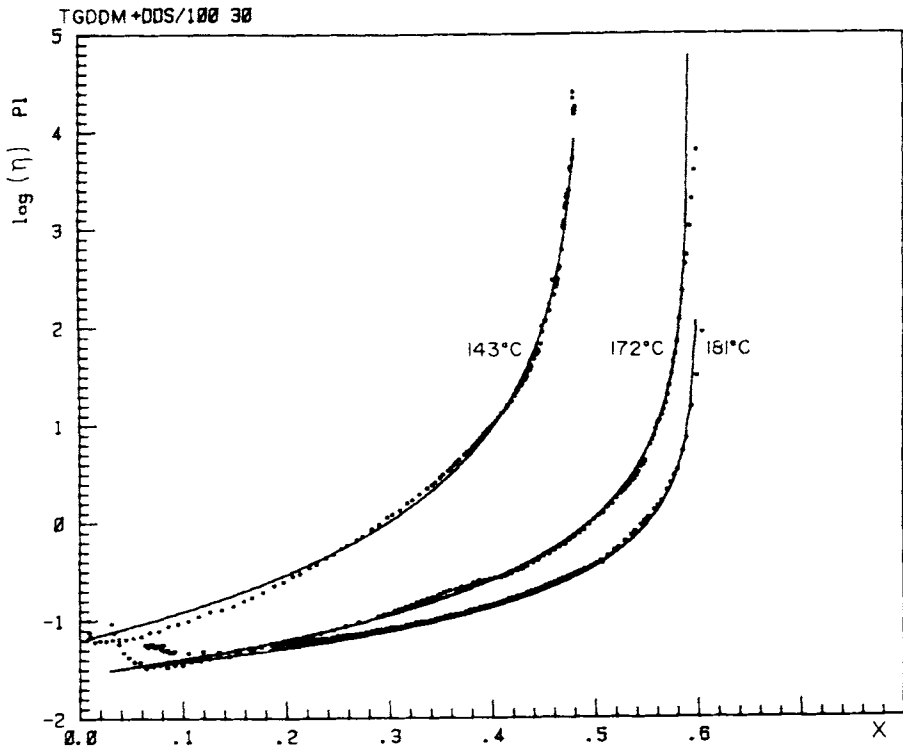


Fig. 5. Variations of viscosity vs. the extent of reaction X , at different temperatures: (···) experimental; (—) percolation.

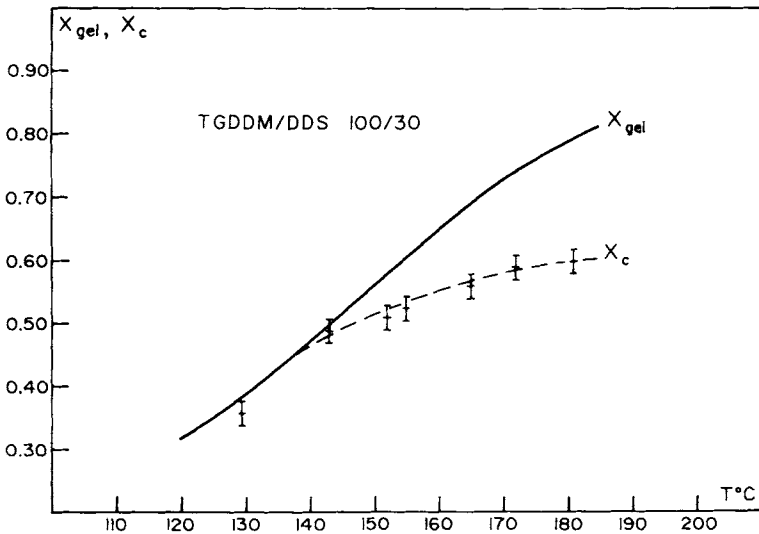


Fig. 6. Variation of the extent of reaction at the gel point, vs. temperature: (—) X_{gel} determined from the time t_{gel} measured on the rheological curves (shoulder of G'') and from the chemical kinetics $X = f(t)$; (---) X_c determined from the percolation law.

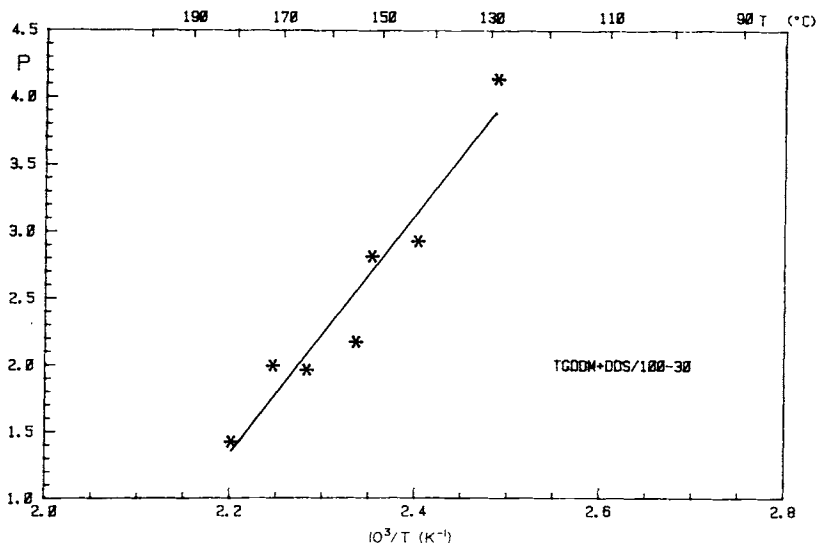


Fig. 7. Variation of the percolation exponent vs. temperature.

several reactions other than the classical primary and secondary epoxy-amine reactions.¹¹ Etherification and homopolymerisation reactions can become significant at high temperatures, and they can either be intermolecular or intramolecular. From Figure 6 it can be observed that a higher value of X is needed to reach the gel point at high temperatures, which means the reactions are less effective in building up the macromolecular network. Intramolecular-type reactions are indeed less effective at hardening, and Figure 6 suggests that they become more extensive at high temperatures.

Using Figure 6, we can also compare variations of X_c and X_{gel} with temperature. X_{gel} being determined from the gel time t_{gel} on the $\log G'' = f(t)$ curves (at the shoulder on G''), and by applying the kinetic law $X = f(t)$.²⁰ Agreement between these values is satisfactory at low temperatures (130 and 140°C), but there are increasing discrepancies towards higher temperatures. In fact, the material is not subjected to the same kind of strain in both cases, since X_{gel} is determined by low amplitude sinusoidal shearing, whereas X_c is determined by continuous shearing. According to the above interpretation, the very considerable variation of X_{gel} suggests that there are more intramolecular reactions at high temperatures in the case of alternating shearing. It has indeed been shown elsewhere²¹ that mechanical agitation, here provided by continuous shearing, favors intermolecular reactions, at the expense of the intramolecular reactions without modifying the total chemical kinetics.

Figure 7 shows a clear variation of the percolation exponent p with temperature. The decrease in p , from 4.1 for 130°C to 1.4 for 180°C, reflects a more marked curvature on $\log \eta = f(X)$ with temperature and might *a priori* be explained in two ways: either by the influence of the glass transition or by a modification of the reaction mechanism, which has already been shown. In fact only the latter explanation should be accepted. It is known that the glass transition becomes closer to the gelation transition as the temperature decreases; despite this, experimental study on the TGDDM-DDS system has

shown that the critical temperature $T_{c\text{ gel}}$ at which gelation no longer appears on rheological curves (when it is masked by vitrification) is close to 80°C,⁹ which is much lower than the temperatures used in this study. Moreover, there is little likelihood that the viscosity variation curves could be influenced by vitrification for such low values of η at the beginning of the cure.

So, although the viscosity variation curves can be modeled at any temperature by a percolation-type law as a function of the degree of chemical reaction X , the variations of parameters X_c and p with cure temperature show that the type of percolation associated with hardening of the system depends largely on temperature and/or that the extent of reaction X is not a suitable variable to account for the process of percolation.

DEFINITION OF RATE OF EXTENT OF EFFECTIVE REACTIONS

Method and Solution to the Problem

The analogy between the phenomena of gelation and percolation has led us to consider viscosity variations as a function of the number of chemical bonds which determine the construction of the macromolecular network. We know that, in the case of the TGDDM-DDS system, the polycondensation reactions involve not only intermolecular reactions, which are responsible for network construction, but also intramolecular reactions, which are present particularly at high temperatures, but play no part in the construction of the network. It is therefore clear that the total degree of advancement, X , of the chemical reactions is not the best parameter for describing the rheological evolution of the system. We have tried to define a rate of advancement of effective reactions Y , which only takes intramolecular-type reactions into account. If the percolation mechanism is the same whatever the temperature, the values of Y_c at the critical threshold and of the percolation exponent p must be constant.

This hypothesis fits in with the observation that the elastic modulus G'_{gel} as determined by experiment is constant at the gel point, allowing for experimental uncertainties, for all temperatures between 120 and 180°C. This temperature variation is relatively small on the Kelvin scale; the theory of elasticity ($G' = \phi\nu RT$ with $\phi = 1$) indicates then that the crosslinking density ν_{gel} and consequently the degree of advancement of effective reactions, Y_{gel} , which determines it are approximately constant at the gel point.

The experimental $\log \eta = f(\log t)$ curves determined at different temperatures are approximately identical, after shifting them, as shown in Figure 4. All of these curves can in this way be reduced to a master curve⁹ by using the reduced coordinates η/η_0 and t/t_{gel} , where η_0 is the initial viscosity and t_{gel} the gel time. Furthermore, the theory suggests a law of the form $\eta_{(t,T)} = B_{(T)}[1 - Y_{(t,T)}/Y_c]^{-p}$ such that the viscosity $\eta_{(t,T)}$ only depends on time through the effective rate of advancement $Y_{(t,T)}$ with Y_c and p constant, and the parameter B varying with temperature. Since the ratio $\eta_{(t,T)}/\eta_{0(T)}$ only depends on $t/t_{\text{gel}(T)} = k_{(T)} \cdot t$, this is also true for the rate $Y_{(t,T)}$, so that

$$Y_{(t,T)} = f(k_{(T)}, t)$$

TABLE II
 Values of the Parameters Deduced by Adjustment on the $\eta = B(1 - Y/Y_c)^{-p}$ Law
 on the Experimental Curves $\log \eta = f(t)$

T ($^{\circ}\text{C}$)	$\log B$ (Pa s)	p	k (h^{-1})	t_c (h)	Y_c
129	-1.47	2.28	0.223	3.82	0.46
143	-1.60	2.27	0.420	2.27	0.48
152	-1.85	2.02	0.696	1.43	0.50
155	-1.84	2.06	0.512	1.29	0.40
165	-1.87	1.92	0.816	0.82	0.40
172	-2.05	1.91	1.362	0.62	0.46
181	-2.09	1.80	1.830	0.42	0.43

^a Y = rate of advancement of effective reactions.

or

$$k_{(T)} \cdot t = F(Y)$$

$$d(k_{(T)} \cdot t) = H(Y) dY$$

Any sort of function $H(Y)$ can be considered *a priori*, and there is nothing to enable us to determine it. We will assume, in order to simplify the calculations, that $Y_{(t,T)}$ obeys a kinetic law of the second order:

$$\frac{dY_{(t,T)}}{[1 - Y_{(t,T)}]^2} = k_{(T)} \cdot dt$$

This equation can be integrated immediately to give, for the initial condition $Y = 0$ and $t = 0$,

$$Y_{(t,T)} = \frac{k_{(T)} \cdot t}{1 + k_{(T)} \cdot t}$$

We can thus obtain

$$\eta_{(t,T)} = B \left(1 - \frac{t}{t_c} \frac{1 + kt_c}{1 + kt} \right)^{-p} \quad (1)$$

The values of the parameters B , p , k , and t_c have been determined using an adjustment program on the experimental $\log \eta = f(t)$ curves. The value of the rate of effective advancement at the critical threshold (in other words, at the gel point) are then calculated using $Y_c = kt_c / (1 + kt_c)$. The values obtained are presented in Table II (see below).

Discussion

Figure 8 shows very good agreement between the viscosity variations derived from experimental $\log \eta = f(t)$ curves, and the curves obtained from the percolation law [eq. (1)]. The curves fit closely over a wide range, but not

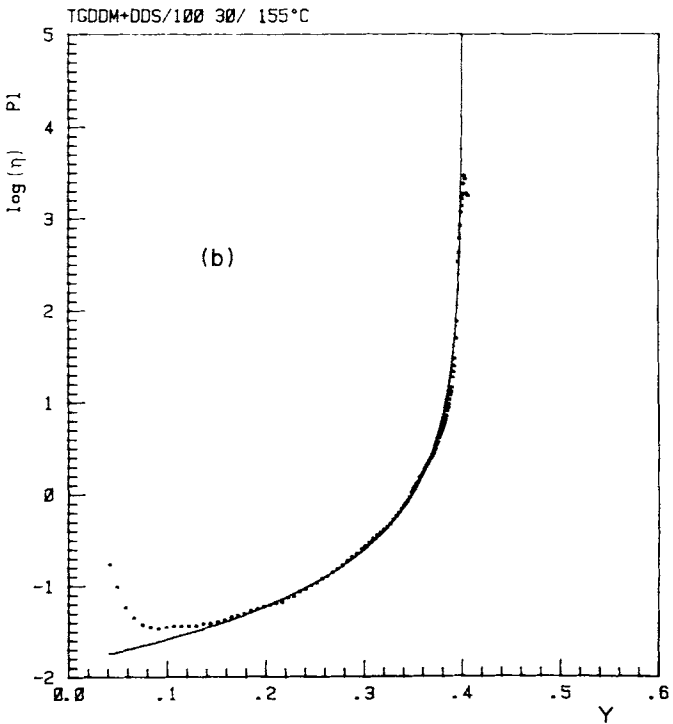
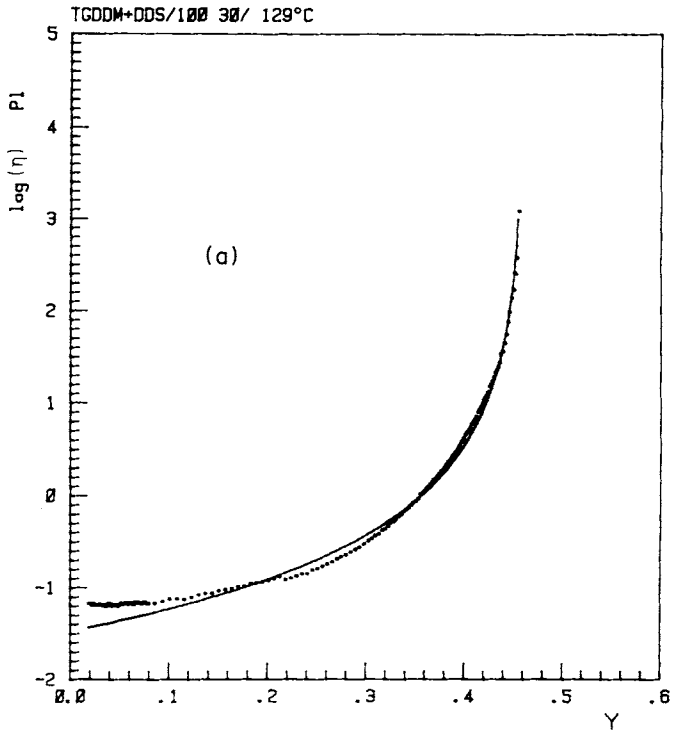


Fig. 8. Variation of viscosity vs. the rate of advancement of effective reactions $\log \eta = f(Y)$: (\cdots) curves deduced from the experimental curves $\log \eta = f(t)$ and from $Y = kt/(1 + kt)$; (—) curves deduced from the percolation law $\eta = B(1 - Y/Y_c)^{-p}$; (a) $T = 129^\circ\text{C}$; (b) $T = 155^\circ\text{C}$; (c) $T = 165^\circ\text{C}$.

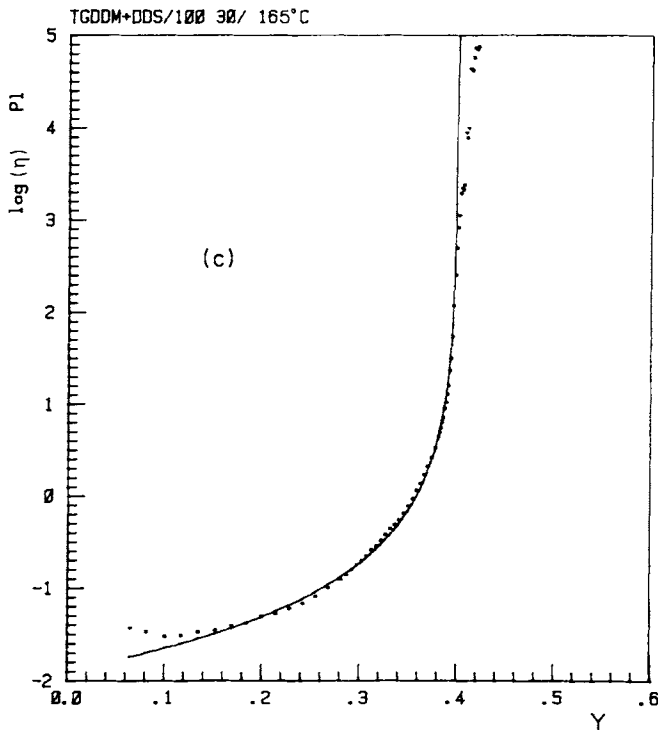


Fig. 8. (Continued from the previous page.)

from the very beginning. Values of parameter B decrease with increasing temperature, but remain well below the initial viscosity η_0 .

Values obtained for Y_c , the rate of advancement of effective chemical reactions at the critical threshold, range between 0.40 and 0.50 without exhibiting any regular variation. One can therefore give a constant mean value $Y_c = 0.45 \pm 0.05$. This relatively large degree of uncertainty can probably be explained by the fact that it accumulates the uncertainties concerning k and t_c since Y_c is determined from these two parameters.

Comparing the values of X_c (degree of advancement of all chemical reactions at the gel point) and Y_c (degree of advancement of effective reactions at that point), one arrives at the following analysis. Let $N_{(t)}$ be the total number of chemical bonds created at time t . $N_{(t)} = N_{1(t)} + N_{2(t)}$ is the sum of effective bonds (intermolecular) and ineffective bonds (intramolecular), with

$$0 \leq N_{(t)} \leq N_{\max}$$

$$0 \leq N_{1(t)} \leq N_{1\max}$$

$$0 \leq N_{2(t)} \leq N_{2\max}$$

By definition,

$$X_{(t)} = \frac{N_{(t)}}{N_{\max}} \quad \text{and} \quad Y_{(t)} = \frac{N_{1(t)}}{N_{1 \max}}$$

Hence;

$$\frac{X_c}{Y_c} = \frac{X_{(t_{\text{gel}})}}{Y_{(t_{\text{gel}})}} = \frac{1 + N_{2(t_{\text{gel}})}/N_{1(t_{\text{gel}})}}{1 + N_{2 \max}/N_{1 \max}}$$

Previous results showed that if $T = 130^\circ\text{C}$, one obtains $X_c < Y_c$, from which one concludes that $N_{2(t_{\text{gel}})}/N_{1(t_{\text{gel}})} < N_{2 \max}/N_{1 \max}$. Therefore, there are proportionally fewer intramolecular reactions at the gel point than at the end of the cure, in other words, fewer intramolecular reactions before the gel point than after it.

Conversely, for $T > 140^\circ\text{C}$, $X_c > Y_c$ shows that there are more intramolecular reactions before the gel point than afterwards. The boundary between these two patterns of behavior is located at around 140°C ($X_c = Y_c$). These conclusions are of considerable importance on a practical level because the mechanical properties of the product obtained at the end of cure depend to a significant extent on these intramolecular reactions.

The percolation exponent p varies relatively little with temperature, from 1.8 to 2.3, and one can give a mean value $p = 2.05 \pm 0.25$. This value is, however, higher than the values usually quoted in the literature: $p = 0.7$ for standard percolation (random process) and between 0.5 and 1 for the various numerical simulations.^{22,23} It can be observed in this respect that in the TGDDM–DDS system, the reactivities of the primary and secondary amines are very different (by a factor of 10 according to certain authors).²⁴ This means that the primary amines react alone with the epoxy functions in the first stage of the cure, and the secondary amine–epoxy reactions develop only in a second stage. So it is not a real random reaction as is supposed in the standard percolation model. Moreover, the small but regular decrease of p with increasing temperatures suggests that this variation is significant. It would be interesting, therefore, to verify whether this reduction of p is not accompanied by an increase in the reactivity of the secondary amines, in other words by an evolution towards the conditions of the theory.

The gel times obtained at each temperature are very much the same as those obtained using X_c in the first part of this study, and obey an Arrhenius law as a function of T , as, incidentally, does the kinetic parameter $k(t)$.

Comparison of the Rheological Gel Point and the Percolation Threshold

We have tried to compare the gel point, as defined experimentally on $\log G'' = f(t)$ curves, with the critical percolation threshold. The gel point is defined by time t_{gel} and the viscoelastic modulus G'_{gel} and G''_{gel} corresponding

to the beginning of the shoulder G'' ; the critical percolation threshold is defined on the $\log \eta = f(Y)$ [or $\log \eta = f(X)$] curves from the value of Y_c (or X_c) and the value of the viscosity η_c . However the gel time t_{gel} (under alternating shearing), with which one can associate a value X_{gel} of the degree of advancement of chemical reactions [with the kinetic law $X = f(t)$], cannot be compared with the values of Y_c or X_c (under permanent shearing; see Fig. 6). So we compared the values of viscosity at the rheological gel point and at the percolation threshold. This was not calculated using the percolation law, which is not valid at the critical threshold, but instead by intersecting the experimental $\log \eta = f(Y)$ curve with the line of coordinate Y_c . (The same operation can be carried out on $\log \eta = f(X)$ curves.) The uncertainty about Y_c leads to marked uncertainty concerning η_c since the slope of the $\log \eta = f(Y)$ curves is high in this sector. Nevertheless, the values obtained for η_c vary little with temperature, and we obtain the mean value $\log \eta_c = 3.2$ (Pa s). Allowing for uncertainties, this value is in very close agreement with the mean value measured at the shoulder on the $\log G'' = f(t)$ curves: $\eta_{\text{gel}(\text{mean})} = \sqrt{G'^2 + G''^2} / \omega = 950$ Pa s, or mean $\log \eta_{\text{gel}} = 3.0$ (Pa s).

This agreement justifies the conclusion that the point defined by the change in slope of the $\log G'' = f(t)$ curves and the shoulder on G'' which goes with it are indeed very close to the real gel point, corresponding to the formation of an infinite macromolecular network.

CONCLUSION

Experimental viscosity variation curves are very well described by a percolation-type law. When the variable used is the degree of advancement, X , of chemical reactions, the $\log \eta = f(X)$ curves are described from the beginning of cure up to the gel point. By using this method it has been possible, owing to the variations of X_c and of the exponent p , to demonstrate that the reaction mechanism evolves clearly with temperature.

Using the property of affinity of the experimental $\log \eta / \eta_0 = f(t)$ curves, we have proposed a method for defining a rate or advancement of effective reactions Y , which appears to be the only variable upon which viscosity depends in a percolation law. This effective rate Y attempts to take account of intermolecular-type bonds, which play a part in hardening the system and act on the viscosity, but not intramolecular bonds, which seem to have no effect on viscosity. So the variable Y would be the pertinent variable for studying resin hardening. But for the method, the order of the kinetics must be known. In this study it was chosen arbitrarily equal to 2.

The values obtained for Y_c , the rate of advancement of effective reactions at the critical threshold, and the percolation exponent p are constant, as an early approximation $Y_c = (0.45 \pm 0.05)$ and $p = (2.05 \pm 0.25)$. This shows that the variable Y does control viscosity variations. Comparing the values X_c and Y_c at the gel point yields information on the reaction mechanism: it would appear that, at temperatures lower than 140°C , intramolecular reactions take place especially after the gel point, whereas, for $T > 140^\circ\text{C}$, they are in the majority before the gel point. The mean value for the exponent p is higher than the values obtained in numerical simulations carried out else-

where. This means that, independently of the intramolecular reactions, the percolation mechanism associated with gelation of this resin is different from the mechanisms envisaged in the simulations, and in particular different from a random process. It is also known that the two main chemical reactions which take place in the TGDDM-DDS system are not equivalent since the primary amine is much more reactive than the secondary amine. The results show that the phenomenon of gelation could easily be described by a percolation law in the case of a simpler epoxy-amine system, for which there would be no intramolecular reaction, and in which primary and secondary amines would present comparable reactivities. In all cases, the position of the percolation threshold is in very good agreement with the point determined from the change in slope of experimental $\log G'' = f(t)$ curves and the shoulder of G'' which goes with it. As the times corresponding to this point are independent of the excitation frequency, this result shows clearly that it correctly represents the real gel point, at which the macromolecular network becomes infinite.

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