

# The Evolution of Thermosetting Polymers in a Conversion–Temperature Phase Diagram

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## Synopsis

A conversion–temperature phase diagram for thermosetting polymers is analyzed. The curing under different external conditions—*isothermal, at a constant heating rate, adiabatic, and in a mold at constant wall temperature*—is represented by definite trajectories in the phase diagram. Conditions related to incomplete curing or falsification of kinetic parameters are stated.

## INTRODUCTION

The transformations occurring in a thermosetting polymerization may lead to two distinct transitions: the gel point and vitrification. The first one is characterized by the appearance of a giant macromolecule—the gel—only confined by the reactor boundaries. At the glass transition, conversion and temperature levels are such that the network segments become almost immobilized and the chemical reaction is stopped for practical purposes.<sup>1,2</sup> Gillham et al.<sup>3–6</sup> have discussed different possibilities associated with both transitions, through the use of time vs. temperature diagrams.

Our aim is to analyze the behavior of thermosetting systems in a conversion–temperature phase diagram, and discuss the curing taking place under different external conditions: *isothermal, at a constant heating rate, adiabatic, and in a mold at constant wall temperature.*

## THE CONVERSION–TEMPERATURE PHASE DIAGRAM

Figure 1 shows different phases which may appear during curing, plotted in a conversion–temperature diagram. The gel conversion,  $x_{\text{gel}}$  depends on the reactants functionalities but not on temperature (note, however, that temperature might modify reactivities of functional groups or introduce substitution effects or intramolecular reactions, changing in consequence the  $x_{\text{gel}}$  value);  $x_g$  is the conversion which vitrifies the system at the glass transition temperature  $T_g$ . The reactants become a liquid phase at  $T_{g0}$ ;  $T_{g,\text{gel}}$  is the particular temperature at which both gelation and vitrification occur simultaneously, and  $T_{g\infty}$  is the maximum temperature at which the system vitrifies. The decomposition temperature  $T_d$  may be greater, equal to, or less than  $T_{g\infty}$ .

As Nielsen<sup>2</sup> states, the shift in the glass transition temperature with conversion is made up of two nearly independent effects: (1) the degree of crosslinking and

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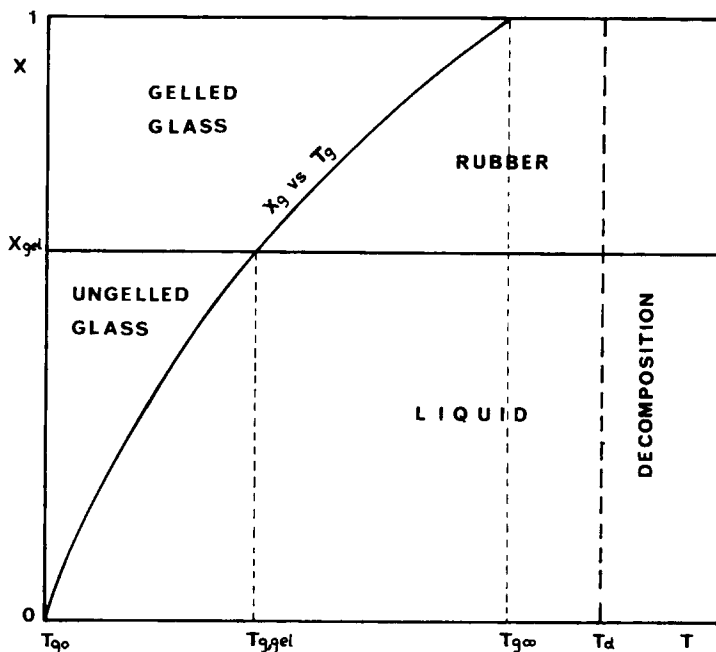


Fig. 1. Conversion-temperature phase diagram for thermosetting polymers.

(2) the copolymer effect. The crosslinking effect always increases  $T_g$  while the copolymer effect can either increase or decrease  $T_g$ , depending upon the chemical nature of the crosslinking agent. Regarding the first effect, linear<sup>2,7</sup> and logarithmic<sup>8</sup> relationships have been proposed between  $(T_g - T_{g0})$  and the crosslinking density.

Di Benedetto, as quoted by Nielsen,<sup>2</sup> proposed a theoretical equation relating the glass transition temperature with conversion:

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(\epsilon_x/\epsilon_m - F_x/F_m)x_g}{1 - (1 - F_x/F_m)x_g} \quad (1)$$

where  $\epsilon_x/\epsilon_m$  is the ratio of lattice energies for crosslinked and uncrosslinked polymer and  $F_x/F_m$  the corresponding ratio of segmental mobilities. Di Benedetto has estimated that  $\epsilon_x/\epsilon_m = 1.2$  for the styrene-divinylbenzene system, and in general it may be stated<sup>2</sup> that  $\epsilon_x/\epsilon_m \sim 1$ . So, eq. (1) reads

$$T_g^* = \frac{1}{1 - (1 - F_x/F_m)x_g} \quad (2)$$

where  $T_g^* = T_g/T_{g0}$ .

Although  $F_x/F_m$  was expected to be zero,<sup>2</sup> experimental  $T_g^* - x_g$  relationships are consistent with  $0 < F_x/F_m < 1$ . Figure 2 shows a rough agreement between Di Benedetto's equation and experimental results for epoxy resins.<sup>9-11</sup> The curve plotted for the cure of Bisphenol A diglycidyl ether (BADGE) with 4,4'-diamino-3,3'-dimethyldicyclohexylmethane<sup>11</sup> (●) overlapped with the curve reported for the cure of BADGE with ethylenediamine<sup>10</sup> (□). Increasing the separation between both amine functions in the series ethylenediamine (□),

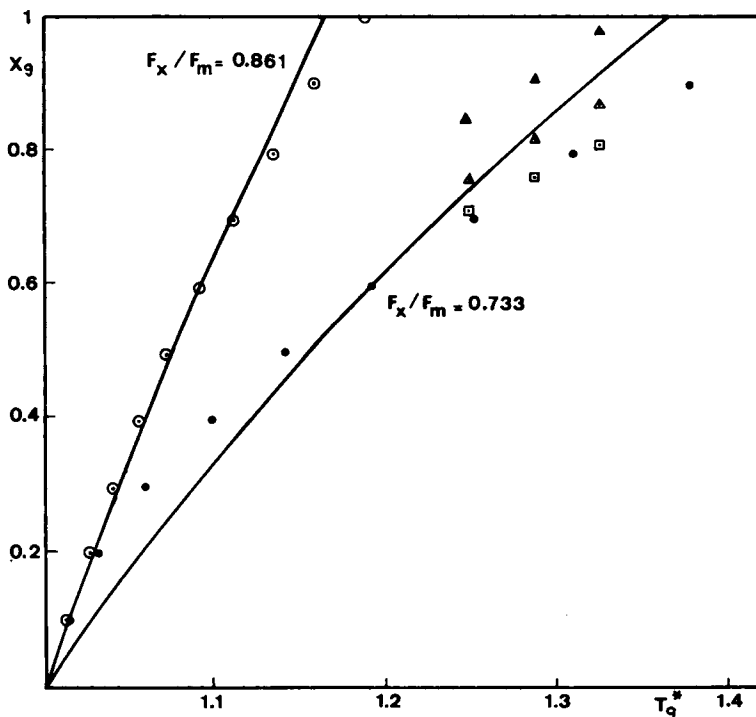


Fig. 2. Comparison of Di Benedetto's equation with experimental data for several epoxy systems: (○) Gray<sup>9</sup>; (●) Lunak et al.<sup>11</sup>; (□, Δ, ▲) Horie et al.<sup>10</sup>

trimethylenediamine (Δ), and hexamethylenediamine (▲), decreases the glass transition temperature for a given conversion.<sup>10</sup> In the same direction there is an increase in the ratio of segmental mobilities  $F_x/F_m$ . In general, the greater the crosslinking density, the lesser  $F_x/F_m$ , and the slope of Di Benedetto's equation. In these conditions, the maximum  $T_g$  might be limited by decomposition reactions rather than by complete conversion.

If the network structure consists of highly crosslinked domains embedded in a less highly crosslinked matrix, two glass transition temperatures will appear in a scanning experimental determination. This is plotted in Figure 3, where lines a and b represent, respectively, the trajectories for the highly crosslinked domains ( $x \rightarrow 1$ ) and the less highly crosslinked matrix ( $x < 1$ ). This phenomenon has been reported for particular epoxy systems.<sup>2,12</sup>

When different chemical linkages are possible, as in the cure of phenolics with hexamethylenetetramine, the  $x_g-T_g$  relationship will be a region rather than a definite curve. In this case, there will not be a sharp transition between glass and rubber. This will also be the case when a conversion distribution is present in the specimen (all the trajectories between a and b, in Fig. 3, are possible).

Other complications arise when the type of linkages changes with temperature. For example, in the copolymerization of linear polyester fumarates with styrene, the fraction of fumarate units in the crosslinked copolymer increases with temperature. This increases the crosslinking density at the same conversion level, giving an  $x_g$  vs.  $T_g$  curve passing through a maximum.<sup>13</sup> In this situation, Di Benedetto's equation is no longer valid.

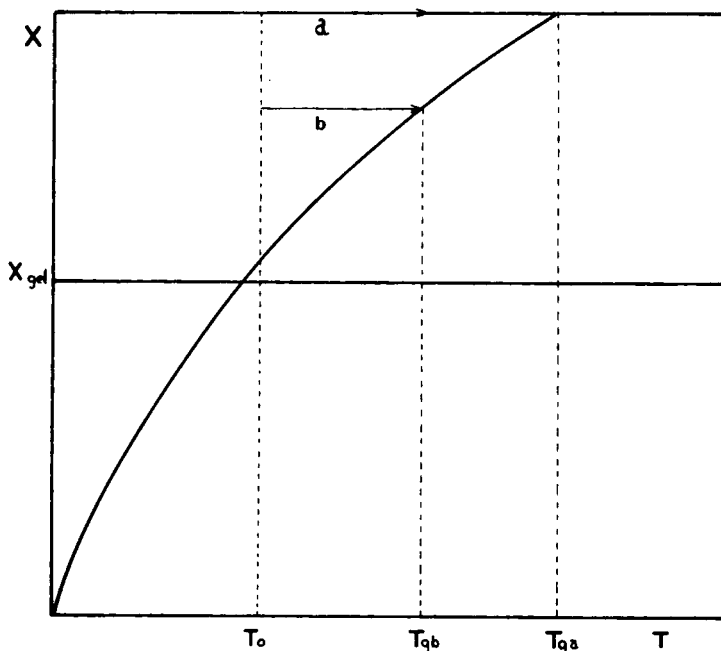


Fig. 3. Trajectories resulting from the heating of a network structure consisting of highly cross-linked domains (a) embedded in a less highly crosslinked matrix (b).

### ISOTHERMAL CURING

In this case, the system evolution in the phase diagram follows a vertical at constant temperature. The maximum attainable conversion is  $x_g$  at  $T = T_g$ , assuming the reaction is completely stopped at the glass transition.

The time to reach the glass state at constant temperature may be calculated from the phenomenological kinetic equation

$$dx/dt = Af(x) \exp(-E/RT) \quad (3)$$

If necessary, different kinetic equations for the liquid and rubber phases (before and after the gel conversion) may be used. By integration, we get

$$t_g^* = \exp(Ar/T^*) \int_0^{x_g(T^*)} dx/f(x) \quad (4)$$

where  $t_g^* = At$  is a dimensionless time,  $T^* = T/T_{g0}$  is a dimensionless temperature and  $Ar = E/RT_{g0}$  is the Arrhenius number.

For some epoxy systems,<sup>11</sup>

$$f(x) = (x + B)(1 - x) \quad (5)$$

By taking  $B = 0.5$  and  $Ar = 30$  and accepting the validity of Di Benedetto's equation with  $F_x/F_m = 0.733$ , the curve plotted in Figure 4 arises. Negative slopes indicate that the effect of increasing reaction rate by increasing temperature prevails. Positive slopes correspond to very high conversions, low reaction rates, and a dominating effect given by the increase in vitrification conversion with temperature. The location of the minimum will be shifted to the left if the reaction kinetics changes more rapidly with conversion (i.e., a second order kinetics) or if the rate is slowed down when the system approaches its glass transition. The qualitative behavior shown in Figure 4 has been experimentally reported by Gillham et al.<sup>3-6</sup>

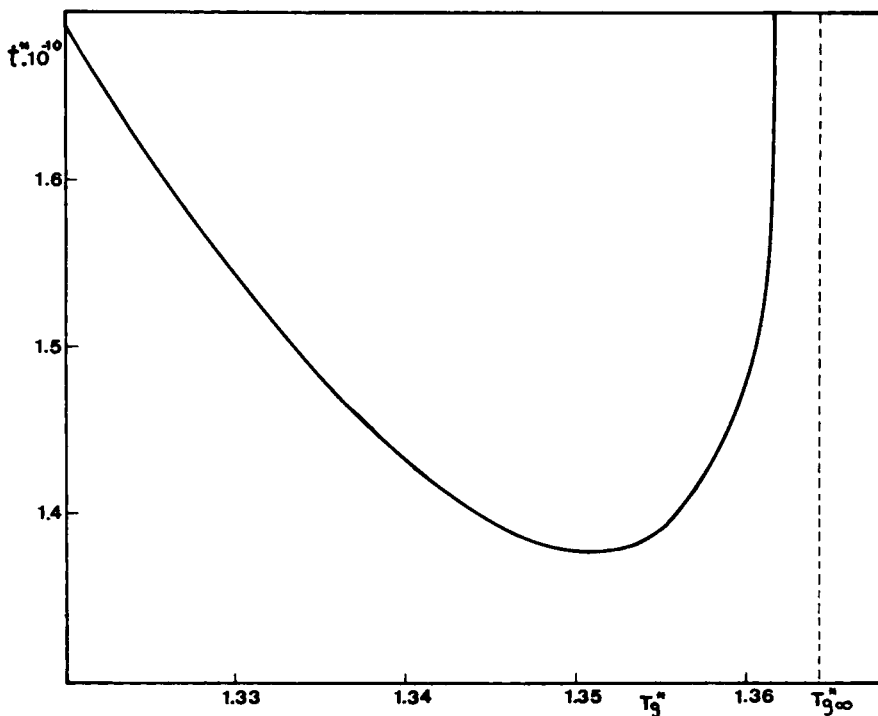


Fig. 4. Dimensionless time to reach the glass transition in isothermal curing as a function of dimensionless temperature.

**CURING AT A CONSTANT HEATING RATE**

The curing at a constant heating rate is usually performed in differential scanning calorimetry (DSC). The conversion-temperature trajectory in the phase diagram results from eq. (3), with  $q = dT/dt = \text{const}$ :

$$dx/dT = (A/q)f(x) \exp(-E/RT) \tag{6}$$

By calling  $z = E/RT$  and integrating, there results that

$$\int_0^x dx/f(x) = -(AE/qR) \int_{z_0}^z [\exp(-z)/z^2] dz \tag{7}$$

For  $z > 15$ , which is the usual range in the curing of thermosets, the integral

$$F(z) = - \int_0^z [\exp(-z)/z^2] dz \tag{8}$$

may be approximated by the following expression<sup>14</sup>:

$$\ln F(z) = -5.330 - 1.0516z \tag{9}$$

Replacing eqs. (8) and (9) into (7) and rearranging, there results that

$$\int_0^x dx/f(x) = [\exp(-5.33)/q^*] \times [\exp(-1.0516 Ar/T^*) - \exp(-1.0516 Ar/T_0^*)] \tag{10}$$

where  $q^* = qR/AE$  is a dimensionless scanning rate.

Particular solutions of eq. (10), for  $f(x)$  given by eq. (5),  $B = 0.5$ ,  $Ar = 30$ ,  $T_0^* = 1.1$ , and different  $q^*$ , are plotted in Figure 5, together with Di Benedetto's equation for  $F_x/F_m = 0.733$ . There is a range of  $q^*$  values (approximately  $q^* \leq 10^{-13}$ ) where the system vitrifies before complete conversion is attained. At this point the chemical reaction is stopped, but as heating rate is constant, temperature increases at constant conversion leaving out the glass region. Now, chemical reaction acts, again bringing the system to the vitrification curve. Thus, once the system reaches the glass state, it evolves following the vitrification curve until very high conversions are reached. When  $x$  is very close to 1, the slope  $dx/dT^*$  given by eq. (10) may be lesser than the slope arising from eq. (2), and the system will finish its evolution in the rubber region.

Then, for  $q^*$  values where vitrification takes place, there is a falsification of the chemical kinetics from the moment of the glass transition. In this range, the experimental  $dx/dT$  follows eq. (2):

$$\frac{dx}{dT} = \frac{[1 - (1 - F_x/F_m)x]^2}{T_{g0}(1 - F_x/F_m)} \quad (11)$$

By comparing eqs. (6) and (11), the apparent specific rate constant will show to be a function of the scanning rate  $q$ .

In order to avoid falsification of kinetic parameters, the range of scanning rates which may be used is limited by the minimum  $q^*$ . For example, if  $A$  is set equal to  $10^{10} \text{ min}^{-1}$  (from Fig. 4, this gives a time  $t = 1.38 \text{ min}$  to reach the glass state at  $T^* = 1.35$ ), and  $T_{g0} = 263 \text{ K}$ , the activation energy will be  $E = 15.6 \text{ kcal/mol}$  in order to give an Arrhenius number,  $Ar = 30$ . Then  $q^* > 10^{-13}$  implies  $q \geq$

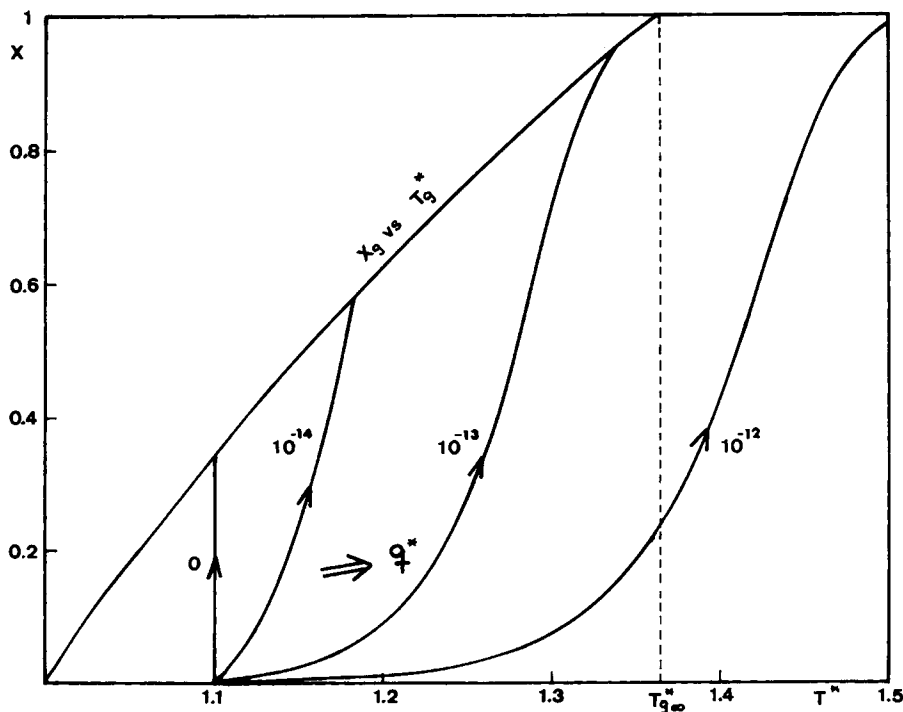


Fig. 5. Trajectories in the phase diagram for the curing at a constant heating rate.

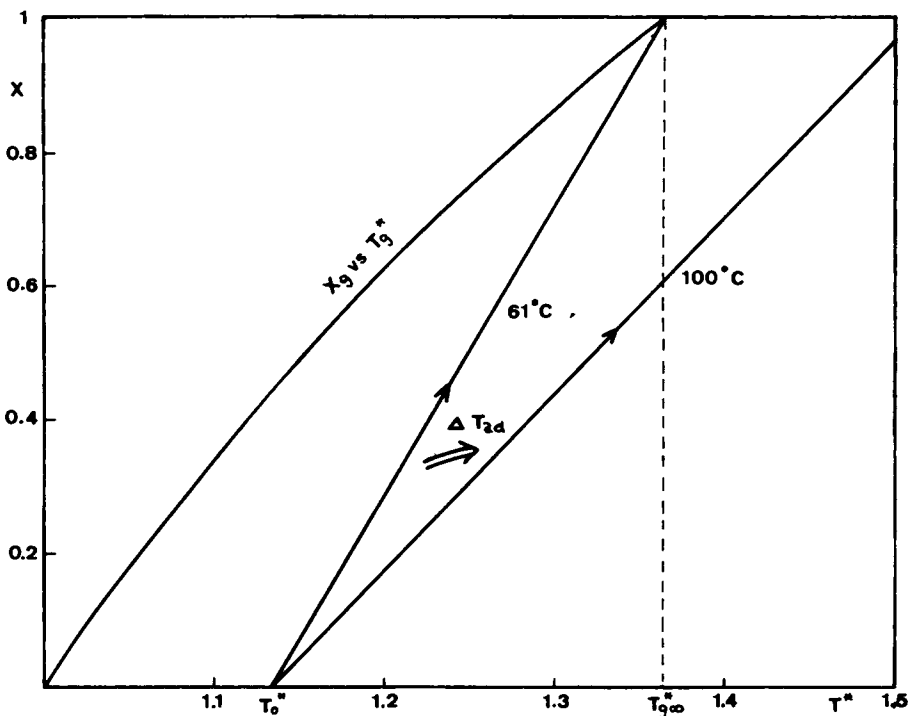


Fig. 6. Trajectories in the phase diagram for an adiabatic curing.

8°C/min, to avoid reaching the glass transition curve. This phenomenon has indeed been qualitatively observed in the copolymerization of multipurpose unsaturated polyesters with styrene at atmospheric pressure.<sup>15</sup> Working at a single scanning rate but varying the catalyst concentration, i.e., changing *A*, may lead to the same effect. Thus, if *A* increases from a certain critical value, the glass transition will be reached. All these effects should be taken into account in the thermal analysis of thermosets by DSC in the scanning mode.

### ADIABATIC CURING

For an adiabatic curing<sup>16</sup>

$$dx/dT = c_p/(-\Delta H) = 1/\Delta T_{ad} \tag{12}$$

where *c<sub>p</sub>* is the specific heat, (-Δ*H*) is the reaction heat per unit mass, both assumed constant, and Δ*T<sub>ad</sub>* is the adiabatic temperature rise. Integrating,

$$x = (T - T_0)/\Delta T_{ad} = T_{g0}(T^* - T_0^*)/\Delta T_{ad} \tag{13}$$

Figure 6 shows trajectories arising from eq. (13), for *T<sub>g0</sub>* = 263 K and *T<sub>0</sub>* = 298 K, together with Di Benedetto's equation for *F<sub>x</sub>/F<sub>m</sub>* = 0.733. Only when Δ*T<sub>ad</sub>* < 61°C, the system reaches the glass transition during its evolution. If this is the case, reaction will cease and temperature remain constant (in an experimental situation heat losses will lead to a temperature decrease at constant conversion). Thus, a limitation in the maximum attainable conversion, or in the reaction heat evolved per unit mass, will arise when Δ*T<sub>ad</sub>* < *T<sub>g∞</sub>* - *T<sub>0</sub>* (61°C in the example

plotted in Fig. 6). This condition may be achieved for thermosetting systems containing fillers, which reduce the reaction heat per unit total mass.

### CURING IN A MOLD AT CONSTANT WALL TEMPERATURE

In this case it is necessary to select a wall temperature  $T_w \geq T_{g\infty}$ . Otherwise, the material near the wall will not reach the maximum conversion, and it is precisely this material which makes the largest contribution to the elastic modulus of the cured specimen.<sup>16</sup>

The temperature and conversion evolution at every location of the sample may be predicted by solving the differential energy and mass balances.<sup>16,17</sup> This was done for  $T_w > T_{g\infty}$  and usual values of parameters characterizing thermoset curing. Results showed that no vitrification took place in these conditions.

### CONCLUSIONS

A conversion-temperature phase diagram for thermoset curing has been proposed on the basis of experimental findings reported by Gillham et al.<sup>3-6</sup> In this diagram, the evolution of the system under different curing conditions may be easily followed, and predictions regarding the possibility of incomplete curing or falsification of kinetic parameters stated.

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