EPOXY THERMOSETS AND THEIR APPLICATIONS III .
KINETIC EQUATIONS AND MODELS

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ABSTRACT

Since the curing process of an epoxy thermoset is thermally-activated and temperature-dependent, modeling the kinetics of the reaction are complex. The development of models, as well as simplified models are described. Emphasis is made on applicability of different models to different situations. Our discussion includes molecular-weight dependent viscosity changes during curing (chemoviscosity) and decomposition kinetics.

Keywords: *epoxy curing; thermoset kinetics*

1. INTRODUCTION

In the first article in this series we have listed the wide range of uses of epoxy thermosets.[1] As was noted then, epoxy-based materials have a wide range of applications but this situation is hardly reflected in Materials Science and Engineering instruction. In the second paper [2] we have reviewed methods of determination of thermophysical properties of thermosetting polymers, in equilibrium as well as reacting. We shall now discuss reactions of curing or thermosetting epoxies; kinetics of those reactions in particular. In general, *chemical kinetics* is the description of conversion of reactants to products.   In the case of cure kinetics of an epoxy + amine system, the rate of conversion will be described by the consumption of epoxide and amine functional groups and the production of aliphatic bonds. The traditional chemical method for kinetic rate determination is mechanistic: the concentrations of products or reactants are monitored throughout the reaction and the rates of change in concentrations are fitted to an equation. Once the mechanism is determined and modeled, then the reaction can be described by reactant or product concentrations in time as a function of a temperature-dependent rate constant.

However, many curing reactions are quite complex, involving multiple competing reactions with several kinetic equations superimposed at different degrees during the overall reaction, requiring very complicated models.[3-5] In addition, in many instances the exact chemistry or concentrations of reactants

may not be known, especially in industrial applications where premixed compounds or prepreg composites are supplied by an outside source. For these situations, phenomenological models are attractive and have demonstrated value and validity.[6-8]

Phenomenological models use properties, which are related to the reaction, for example the change in viscosity or shift in glass transition temperature of a growing polymer. These models describe the degree of conversion or percent of cure from uncured to fully cured as a function of time and temperature. Thus, these models do not require knowledge of the reaction mechanism, only the changes in properties.

To explain better concepts and models, we shall use a specific example. To show how complex these reactions can be, our example involves 4,4'-diaminodiphenylsulfone (DDS) cured tetraglycidyl 4,4-diaminodiphenyl methane (TGDDM) system and the application of curing commercial prepregs. Emphasis is on phenomenological modeling, with references to mechanistic models where applicable.

2.   KINETIC EQUATIONS

As any chemical reaction, the curing reaction will be described by a rate equation, which relates the rate of the reaction to the rate constant, and the consumption of reactants or production of products. In the case of thermoset curing, a generalized rate function utilizing the degree of cure α, which is the disappearance of epoxide functional groups or appearance of chemical bonds, with $(1 - \alpha)$ representing the epoxide group concentration.

$$d\alpha/dt = k (1 - \alpha)^n \tag{1}$$

We use the standard notation such that t is time, k the rate constant while n is the order parameter. Since Eq. (1) describes an n-th order equation, the reaction rate is dependent only on the concentration of epoxide (and curing agent). However, many thermosetting

materials are autocatalytic, so that the product of the reaction serves as an additional catalyst in the reaction. An example is the catalyzation of the epoxy + amine system by hydroxyl groups generated.

Kinetic modeling of autocatalytic reactions requires an additional term to account for this extra effect, namely

$$d\alpha/dt = k \alpha^m (1 - \alpha)^n \tag{2}$$

where α^m represents the catalytic effect of the products of the reaction with an order of m. It is also apparent, that an nth order reaction is a special case of the autocatalytic reaction with m = 0.

Most epoxies exhibit either nth order or autocatalytic curing reactions -although it is not always apparent which type an epoxy will follow. However, the two types are readily differentiated in experimental data. As can be easily predicted from Eq.(1), an n-th order reaction will exhibit its maximum rate at the beginning of the reaction, whereas the autocatalytic reaction described by Eq.(2), will exhibit its maximum rate at some later time during the reaction, typically between 20 and 40 % of the reaction.[9] Representing the degree of conversion as a function of time and fitting the curve generally determine the order. This can be seen using a log-log plot and is usually accomplished by fitting with the least squares[10] method. In addition to the time dependence of the rate of conversion, the rate constant k is temperature dependent, usually assumed to follow an Arrhenius relation of the form :

$$k = Ae^{-Ea/RT} \tag{3}$$

where T is the thermodynamic temperature, A is the pre-exponential function and E_a is supposed to represent the activation energy for the reaction. Thus, Eqs. (1) and (2) can be written as

$$d\alpha/dt = (Ae^{-Ea/RT}) (1 - \alpha)^n \tag{4}$$
$$d\alpha/dt = (Ae^{-Ea/RT}) \alpha^m (1 - \alpha)^n \tag{5}$$

with the incorporation of the Arrhenius temperature dependence. The initial rate of an autocatalytic reaction is not necessarily zero since the reaction can proceed via alternative paths, especially in the presence of impurities like water and catalyzing ions. Taking this into account, the autocatalytic equation is often modified to
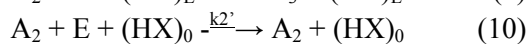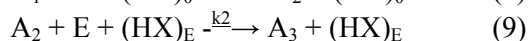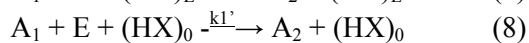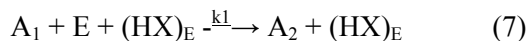
$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (6)$$

where k_1 is the reaction rate constant at zero time and k_2 is the rate constant of the reaction by traditional pathways. The initial rate constant k_1 is easily calculated from the experimental data since it equals the rate at zero conversion.

The activation energy represented by E_a in the Arrhenius formula (3) can be calculated for both mechanistic and phenomenological models and as such allows a comparison between the results. As with other chemical reactions, the activation energy can be conceptually thought of as the energy, in this case thermal energy, necessary to start the reaction. However, and as already mentioned, this interpretation should not in general be taken literally.

In mechanistic models the activation energy is the slope of the ln k *vs.* 1/T (or 1000/T) curve since ln k = ln A – E_a(1/RT). The natural logarithm of the preexponential factor, A, is the y (or ln k) intercept. The activation energies of phenomenological models are usually calculated from a time-temperature relationship computed with a shift factor or via the temperature dependence of the time to reach a certain conversion.

A mechanistic model has been developed for autocatalytic curing of epoxies with amines. To fully account for the autocatalysis by hydroxyl groups generated, the multifunctional nature of the amine curing agent, and the presence of ionic catalysts, including impurities such as water and other hydroxyl containing species, Horie[11] has proposed a rate equation which considers all reactions possible including:

$$A_1 + E + (HX)_E \xrightarrow{\ k1\ } A_2 + (HX)_E \qquad (7)$$
$$A_1 + E + (HX)_0 \xrightarrow{\ k1'\ } A_2 + (HX)_0 \qquad (8)$$
$$A_2 + E + (HX)_E \xrightarrow{\ k2\ } A_3 + (HX)_E \qquad (9)$$
$$A_2 + E + (HX)_0 \xrightarrow{\ k2'\ } A_2 + (HX)_0 \qquad (10)$$

where A_1, A_2 and A_3 are primary, secondary and tertiary amines, E is epoxide, $(HX)_0$ represents the hydroxyl groups and catalysts present in the system initially and $(HX)_E$ are hydroxyl groups generated by epoxy reactions. These reactions can be assembled into the overall kinetic equation [12] :

$$dx/dt = k_1a_1e_0x + k_1'a_1e_0c_0 + k_2a_2e_0x +$$
$$k_2a_2e_0c_0 \qquad (11)$$

where x is the epoxide consumed, c_0 and e_0 are the initial concentrations of $(HX)_0$ and epoxide, a_1 and a_2 are the concentrations of primary and secondary amines. When the primary and secondary amines are approximately equal in reactivity, the reaction rate may be simplified to

$$dx/dt = (k_1x + k_1'c_0)(e_0 - x)(\alpha_0 - x/2) \quad (12)$$

Converting the concentration of epoxide loss x to fractional conversion α transforms Eq.(12) into:

$$d\alpha/dt = (k_1\alpha + k_1')(1 - \alpha)(B - \alpha) \qquad (13)$$

where $k_1 = k_1(e_0)^2 / 2$, $k_1' = k_1'e_0c_0 / 2$ and B $= 2a_0 / e_0$. The stoichiometric ratio of amine hydrogen equivalents to epoxide equivalents, B, is unity in balanced mixtures. This model has been used successfully for certain systems, which follow the required assumptions.[13-17] However, commercial TGDDM + DDS systems cannot be adequately modeled with Eq.(13) since these systems do not follow the required assumptions.[18,19] In addition, extensive knowledge of the chemistry and stoichiometry of the mixture is essential. In the specific case where B = 1, Eq.(13) reduces to Eq.(6) with m = 1 and n = 2, as it should.

Epoxy curing reactions are further complicated by the diffusion-controlled reaction occurring at the onset of vitrification when the kinetic

reaction ends. The overall reaction is actually

$$\frac{1}{k_a(\alpha,T)} = \frac{1}{k_T(T)} + \frac{1}{k_d(\alpha,T)} \qquad (14)$$

where k_a is the overall reaction rate constant, k_T is the Arrhenius rate constant for the kinetically controlled reaction and k_d is the diffusion rate constant.

3. KINETIC METHODS

3.1 Isothermal DSC

Fitting isothermal DSC data to autocatalytic phenomenological Eq.(6) is difficult due to the number of variables including two different exponents. Several numerical methods including rate analysis and linear regression have been used. However, many methods rely on a combined order - that limits the generality. A differential method has been proposed which does not rely on a combined order.

Several methods assume a combined or overall reaction order where the sum of exponents m and n is assumed to be constant. In the simplest method, the overall reaction order assumption allows the calculation of the rate constant k_2 which can be substituted back into Eq.(6) and the values of m and n calculated. This method is based on several assumptions : the primary and secondary amines are of similar reactivities and the hydroxyl groups function only as catalysts for the amine reactions. This has been verified for some amine-catalyzed epoxy systems,[20-22] especially in amine-rich systems. However, Dušek [23,24] found that the assumption of equal reactivities of amines is only true for aliphatic amines, not for aromatic amines. The combined reaction order has been shown to be invalid for multifunctional aromatic amines [25-29] and epoxy-rich systems [30,31] specifically for the epoxy-rich commercial TGDDM + DDS systems. [32-36]

A method, proposed by Ryan and Dutta,[37] uses the time at the maximum rate. It was successfully used to model an epoxy-amine system. However, this model also relies on the combined order assumption limiting its applications. A nonlinear regression analysis method was used by Moroni, *et al.*[38] for an epoxy; however, this method also relies on the combined order assumption limiting its use.

Kenny proposed one method which does not rely on a combined order.[39] The method involves taking the natural logarithm of both sides of Eq.(6); this yields

$$\ln(d\alpha/dt) = \ln(k_1 + k_2\alpha^m) + n\ln(1-\alpha) \qquad (15)$$

A plot of $\ln(d\alpha/dt)$ as a function of $\ln(1 - \alpha)$ generates a line with slope n. Rearranging Eq.(6) in a different form yields

$$\ln\{[(d\alpha/dt)/(1 - \alpha)^n] - k_1\} = \ln k_2 + m \ln\alpha \qquad (16)$$

Substituting n and k_1, m can be calculated by the slope and k_2 from the intercept.

3.2 Single Scan DSC

Although isothermal DSC evaluation produces accurate quantitative results, it is very time-consuming stimulating a desire for a fast method to characterize cure kinetics even at the cost of accuracy. The desire for a method to quickly characterize a curing reaction in a single DSC scan led to several methods.

Borchardt and Daniels proposed the first single scan DSC method.[40] The method is somewhat similar to the isothermal method in that the degree of conversion throughout the scan is a function of the fractional enthalpy change in time. Thus

$$\ln[(d\alpha/dt)/(1 - \alpha)^n] = \ln k = \ln A - E/RT \qquad (17)$$

with the temperature T as a function of time. Using Eq.(17), the variables ln A, E and n can be calculated from a single DSC scan. Such an

nth order equation, as well as the autocatalytic equation, are generally written as

$$k_n = (d\alpha/dt) / (1 - \alpha)^n \qquad (18)$$

$$k_a = (d\alpha/dt) / \alpha(1 - \alpha)(B - \alpha) \qquad (19)$$

For the n-th order equation Barrett[41] proposed representing $\ln [(d\alpha/dt) / (1 - \alpha)^n]$ as a function of T^{-1} that gives ln A and E from the slope and intercept providing that n is chosen to produce a linear plot. Alternative evaluation techniques that have been proposed use the incremental form[42] and a second derivative [43] of Eq.(15). While this technique has given adequate approximations for some nth order reactions,[44-47] it generally gives much higher activation energy values[48-52] in some cases completely invalid results.[53-55]

3.3 Multiple Scanning Rate DSC

Multiple heating rate dynamic DSC scans are isoconversion measurements. That is the time-dependent temperature to reach a certain degree of conversion is measured as a function of the heating rate.   Several models have been proposed to relate the isoconversion temperatures to scanning rate. Most models use the peak in the curing exotherm in the scan as an isoconversion point.

One of the first successful models to relate the temperature of the exotherm peak to the scanning rate was proposed by Kissinger.[56,57] His model, based on Differential Thermal Analysis (DTA) experiments, provides

$$\frac{d[\ln(\varphi/T_p^2)]}{d[1/T_p]} = \frac{-E}{R} \qquad (20)$$

where $\varphi = dT/dt$ is the heating rate and T_p is the peak temperature. Eq.(20) may also be written as

$$A = \frac{\varphi E \exp[E/RT_p]}{RT_p^2[n(1 - \alpha_p)^{n-1}]}$$
$$\cong \frac{\varphi E \exp[E/RT_p]}{RT_p^2} \qquad (21)$$

where α_p is the conversion at the peak and the approximation is based on Kissinger's assumption that $[n(1 - \alpha_p)^{n-1}] = 1$. This is the model for an n-th order reaction. However, an autocatalytic equation based on this relationship has been developed [58] as follows:

$$A \cong \frac{\varphi E \exp[E/RT]}{RT_p^2[2\alpha_p + 2B\alpha_p - 3\alpha_p^2 - B]} \qquad (22)$$

The most common method is based on work by Ozawa [59,60] and Flynn and Wall.[61,62] Integration of the general rate equation and rearrangement produces

$$\int_0^{\alpha i} \frac{d\alpha}{dt} \cong \frac{AE}{\varphi R} p(E/RT_i) \qquad (23)$$

where α_i is a specified conversion and T_i is the temperature to reach that conversion, φ is the scanning rate and p(E/RT) is an approximate solution to the exponential integral. Using values tabulated by Doyle [63] the exponential can be approximated as

$$\log p(E/RT_i) \cong - 2.315 - 0.4567 \, E/RT_i \quad (24)$$

Using this value, the equation can be rewritten as:

$$E \cong \frac{- R \, \Delta(\log \varphi)}{0.4567 \, \Delta(1/T_i)} = \frac{- R \, \Delta(\ln \varphi)}{1.052 \, \Delta(1/T_i)} \qquad (25)$$

A similar model proposed by Fava[64] employs a rigorous approach based on Ozawa's model. Values for $(d\alpha/dt)_p$ at various scanning rates are plotted against $1/T_p$ and parameters calculated.

Barton [65] used a model relating conversion and conversion rate to the activation energy:

$$\ln \frac{(d\alpha/dt)_i}{(1 - \alpha_i)^n} = \frac{-E}{RT_i} + \ln A \qquad (26)$$

where i = 1 or 2, represents the two different scanning rate values. Setting $\alpha_1 = \alpha_2$ for the isoconversion peak temperatures, T_1 and T_2,

and combining the equations yields

$$\ln \frac{(d\alpha/dt)_1}{(d\alpha/dt)_2} = \frac{-E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad (27)$$

This model allows calculation of the activation energy from two different rate scans, independent of rates. However, this equation gives no indication of the reaction order or the pre-exponential factor A. Hernández-Sánchez and Vera-Graziano [66] set $(d\alpha/dt)_1 = (d\alpha/dt)_2$, yielding

$$\ln \frac{1 - \alpha_1}{1 - \alpha_2} = \frac{-E}{nR} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad (28)$$

Eq.(25) can also be solved for a nonisoconversion situation where $T_1 = T_2$,

$$\ln \frac{(d\alpha/dt)_1}{(d\alpha/dt)_2} = n \ln \frac{1 - \alpha_1}{1 - \alpha_2} \qquad (29)$$

These equations, particularly Ozawa's and Barton's, have been used successfully for both simple [67-70] and complex [71,72] thermosetting systems, including the TGDDM + DDS [73] system which was not successfully modeled by the single rate method. In addition, in situations where multiple curing reactions [74-77] can be resolved separately, e.g. primary and secondary amine reactions, the parameters can be calculated for each reaction.[78]

3.4 Time-Temperature Superposition

The viscoelastic nature of polymers is the basis for the principle of time-temperature superposition[79] - the time of an event is related to the temperature at which it takes place. This is apparent in polymers which have large viscous and elastic characteristics - although it can be detected in viscous liquids and elastic solids also. The principle is well accepted in the field of polymers, as demonstrated by predicted ambient temperature lifetime studies conducted in short times at elevated temperatures [80] and the velocity dependence of impact tests,[81] which can lead to low velocity

predictions of ballistic impact property predictions conducted at low temperatures. The relationship has been demonstrated for many characteristics by Ferry [82] and Goldman.[83] While a qualitative understanding of the relationship between time and temperature has been known for a long time, creating a quantitative formula which would describe the behavior has proven difficult.

The most common relationship used for polymers above the glass transition is the Williams-Landel-Ferry[84] (WLF) model which can be represented as

$$\log a_T = -[C_1 (T - T_r)]/[C_2 + (T - T_r)] \quad (30)$$

where a_T is defined as the shift factor, or the degree to which the property curve will be shifted vertically or horizontally in relation to the reference curve by the temperature difference, and C_1 and C_2 are constants. However, this model only works for temperatures higher than the glass transition temperature T_g. For temperatures below the glass transition temperature, i.e. in the glassy state, the most common model is based on an Arrhenius relationship given as [85]

$$\ln a_T = \frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \qquad (31)$$

A model based on free volume derived by one of us,[86,87] which works for all temperatures is

$$\ln a_T = A + [B/(\breve{v} - 1)] \qquad (32)$$

where A and B are constants and $\breve{v}$ is the reduced volume, defined as the ratio of the specific volume to incompressible or hard-core volume. The WLF equation is a special case of Eq. (32) which relies on the assumption of linear proportionality of reduced volume and temperature, which is only a good approximation from the T_g to around 50 K above the T_g. However, the simplicity of the formula and the lack of complex intrinsic material behavior combined with the fact that

most studies are performed within a limited range of reliability provide the popularity of the equation.

These models have been applied to thermosets, usually in the form of time to reach a specific conversion as a function of temperature. Prime [88] proposed an isoconversion Arrhenius relationship between the times (t_1 and t_2) to reach a certain conversion at two temperatures (T_1 and T_2) :

$$\ln a_T = \frac{E (T_1 - T_2)}{R \, T_1 \, T_2} \qquad (33)$$

Wisanrakkit and Gillham[89,90] proposed a similar isoconversion relationship, namely

$$\ln a_T = \ln (t_2) - \ln (t_1) \qquad (34)$$

where t_1 and t_2 are the times to reach a specified conversion.

4. PHYSICAL MODELS

4.1 Glass Transition Temperature Shift

During the polymerization part of the reaction, before gelation and crosslinking, the increase in T_g associated with the linear chain growth is proportional to the concentration of monomers, using the decrease in concentration α in the form

$$1/T_g = 1/T_{g0} + k\alpha \qquad (35)$$

where T_{g0} is the glass transition temperature at zero conversion.   Eq.(35) is only valid for values up to gelation, since it assumes that no crosslinking takes place - a good approximation at low degrees of conversion.

In the region between gelation and vitrification where crosslinking is the dominant reaction, two primary models have been used. Fox and Loshaek [91] proposed a model which predicts a linear increase in T_g with crosslink density whereas DiMarzio [92] proposed a model which

predicts linearity of $1/T_g$ with crosslink density.

Later modeling approaches combined both effects, polymerization and crosslinking, into one model. The first of these T_g as a function of conversion models was proposed by DiBenedetto.[93] He established a relationship to predict the shift in T_g based on lattice energies and segmental mobilities of the cured and uncured materials,

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{[(\varepsilon_\infty/\varepsilon_0) - (C_\infty/C_0)] \, x}{1 - [1 - (C_\infty/C_0)] \, x} \qquad (36)$$

where x is the crosslink density or fraction of segments crosslinked, ε is the lattice energy, and c is the segmental mobility. This equation has been used successfully for many cross-linking systems,[94-98] except in cases of very highly cross-linking.[99] The equation was modified by Couchman[100] to combine the lattice energy and segmental mobility into the heat capacity value, namely

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda) \, \alpha} \qquad (37)$$

where λ is a structure dependent parameter defined as $\Delta C_{p\infty}/\Delta C_{p0}$. This equation was found to model some systems [101] with λ calculations ranging from 0.43 [102,103] to between 0.46 and 0.58.[104] However, the equation does not adequately model epoxy-rich systems, due to the complexity of the reactions.[105,106] Venditti and Gillham [107] further modified Eq.(36) to the following form:

$$\ln(T_g) = \frac{(1 - \alpha) \ln(T_{g0}) (\Delta C_{p\infty}/\Delta C_{p0}) \, \alpha\ln(T_{g\infty})}{(1 - \alpha) + (\Delta C_{p\infty}/\Delta C_{p0}) \, \alpha} \qquad (38)$$

This equation was found to model the epoxy-rich systems, which the previous models could not in addition to the systems which were modeled by the other equations.

The diffusion-controlled part of the reaction after vitrification has been evaluated by

phenomenological models, and Wisanrakkit and Gillham proposed a separate conversion-T_g model to cover this part of the overall reaction :

$$\ln[k_d(T)] = \ln[k_d(T_g)] + \frac{2.303\, C_1\, (T - T_g)}{C_2 + |T - T_g|} \qquad (39)$$

where C_1 and C_2 are WLF parameters. Assuming $k_d(T_g)$ is constant and setting $r = 2.303 C_1$, Equation 25 becomes

$$\ln(k_d) = \ln(k_{d0}) + \frac{r\,(T - T_g)}{C_2 + |T - T_g|} \qquad (40)$$

which may be used to calculate the activation energy and preexponential factor. Needless to say, Eq.(40) can be used only in narrow temperature ranges since it relies on the WLF formula.

4.2 Viscoelastic Relaxation Time Shift

The glass transition temperature shift described above can also be described using a different viscoelastic model. The T_g shift can be described as resulting from changes in the frequency-dependent relaxation time $\tau(\omega)$ due to the change in mobility of the growing chains and network.[108]

The relaxation time is taken to be a thermally activated process, hence it can be modeled by an Arrhenius relationship

$$\tau(T, \alpha) = \tau_\alpha \exp(E_a/RT) = 1/\omega \qquad (41)$$

where E_a is now the activation energy of the glass transition, τ is the relaxation time, τ_α is the relaxation time at the conversion at the transition and ω is the frequency. The T_g can be defined as

$$T_g = -E_a / [R \ln(\omega \tau_\alpha)]. \qquad (42)$$

The last equations, this can be written as

$$T_g = \frac{E_a}{R\, \ln[D_1\, (1 - \alpha)^\Phi + D_2]} \qquad (43)$$

where

$$D_1 = \exp(E_a/RT_{g0}) - \exp(E_a/RT_{g\infty}) \qquad (44)$$

$$D_2 = \exp(E_a/RT_{g\infty}) \qquad (45)$$

and Φ is a parameter accounting for chain entanglements. The activation energy of the transition may be determined by multiple frequency experiments using the relationship[109,110]

$$E_a = \frac{d(\ln \omega)}{d(1/T_{max})} \qquad (46)$$

This model has been successfully used for a multifunctional epoxy through the complete curing reaction.[111]

4.3 Gelation

The degree of conversion at the microscopic gel point can be calculated if the chemistry of the reactants is known. The first formula for calculating the microscopic gel point proposed by Flory [112] in 1941 is

$$(\alpha_1 \alpha_2)_{gel} = \frac{1}{(f_1 - 1)(f_2 - 1)} \qquad (47)$$

where α_1 is the conversion of reactant 1, α_2 is the conversion of reactant 2, f_1 is the functionality of reactant 1, f_2 is the functionality of reactant 2, and

$$\alpha_2 = B\, \alpha_1 \qquad (48)$$

where B is the stoichiometric ratio. For an epoxy + amine reaction, where the amine is reactant 1 and the epoxy is reactant 2, B is the ratio of the number of amino hydrogens to the number of epoxide groups, so Equation (16) reduces to

$$\alpha_{2gel} = \left(\frac{B}{(f_1 - 1)(f_2 - 1)} \right)^{1/2} \qquad (49)$$

5. CHEMOVISCOSITY

The molecular-weight dependent viscosity change during the reaction has been modeled using a semi-empirical model

$$\eta(t) = \eta_0 \exp(kt) \qquad (50)$$

where η_0 represents the minimum viscosity at very low conversion.[113-115] An Arrhenius temperature dependence for both η_0 and k was introduced by Roller [116,117] resulting in

$$\ln \eta(t) =$$
$$\ln \eta_\infty + \Delta E_\eta/RT + tk_\infty \exp(\Delta E_k/RT) \qquad (51)$$

where η_∞ is the viscosity at infinite temperature or T_∞, ΔE_η is the activation energy for viscosity, k_∞ is the rate constant at infinite temperature and ΔE_k is the activation energy for the reaction kinetics. In the early stage of cure, the viscosity is assumed to be Newtonian. Analogous to models using other techniques, this isothermal model can be modified to a dynamic model by integration of the kinetic term [118]; then

$$\ln \eta(t,T) =$$
$$\ln \eta_\infty + E_\eta/RT + {}_0\!\int^t [k_\infty \exp(\Delta E_k/RT)]dt \qquad (52)$$

Since the model was developed in 1975, the change in viscosity during the curing reaction has also been modeled[119] using a WLF equation, namely

$$\log \eta(T) = \log \eta(T_S) + \frac{a(T - T_S)}{b + (T - T_S)} \qquad (53)$$

where T_S is a reference temperature which will depend on the degree of cure while a and b are constants. The shift factor a_T between the isothermal viscosity functions is defined by

$$a_T = \eta(T)/\eta(T_S). \qquad (54)$$

Tajima and Crozier [120] found T_S to be a linear function of α^2 and log $\eta(T_S)$ to be a linear function of α by regression analysis of epoxy viscosity data. Lee and Han [121] modified Eq.(35) to

$$\log \eta(T,\alpha) =$$
$$(a_1 + b_1\alpha) - \frac{a_2(b_2 + T - c_2\alpha)}{a_3 + T - c_2\alpha} \qquad (55)$$

where a_1, a_2, a_3, b_1, b_2 and c_2 are parameters. A simple equation, which is used often was developed by Castro [122] and Wang, *et al.*[123]

$$\eta/\eta_0 = \left(\frac{\alpha_g}{\alpha - \alpha_g} \right)^{f(\alpha,T)} \qquad (56)$$

where α_g is the conversion at the gel point and η_0 is the initial viscosity at zero conversion at the isothermal temperature which is described by the equation

$$\eta_0 = A_\eta \exp(E_\eta/RT) \qquad (57)$$

where A_η and E_η are defined similarly as above the viscosity dependent pre-exponential factor and activation energy. This equation has been used successfully for fast curing resins.[124]

A similar relationship introduced by Stolin, et al [125] relates η to the degree of cure, namely

$$\eta = \eta_\infty \exp(E_\eta/RT) - K\alpha \qquad (58)$$

where η_∞ is the viscosity at maximum cure, a constant, E_η is the activation energy of the viscosity change, and K is a constant. Using this data a good estimate of η has been found for a TGDDM + DDS system.[126] We have reviewed methods of experimental determination of viscosity and other pertinent properties in an earlier paper.[2]

6. DECOMPOSITION KINETICS

Thermal degradative stability has been related

to the degree of cure.[127] Activation energy of the degradation process increases with increasing cure temperature. Apparently increasing the cross-link density raises the amount of thermal energy required to degrade the structure to volatiles. Prime[128] has verified this for a cross-linking magnetic tape coating. The degree of cure of many thermosets has been investigated in terms of TGA thermal stability[129-131]; (TGA has also been described in our earlier paper[2]).

Degradation of cured epoxies is a multistep process, which includes chain scission, char formation or carbonization, and char stabilization.[132] Since both TGDDM and DDS contain aromatic ring structures and the network contains cyclic structures, degradation begins at these points.[133-135]

TGA degradation kinetics may be performed by either isothermal or by varied heating rate methods. The derivation of the equations from differentiation and integration of formulas relating the degree of cure to activation energy and temperature are described by Dickens and Flynn,[136] Flynn and Wall,[137,138] and in the ASTM standard.[139]

Although a series of isotherms of different samples at different temperatures can be performed and the curves analyzed by classical curve fitting and the parameters determined, the technique is very time consuming and tedious and other techniques give similar results. A technique called "factor-jump" simulates the series of isotherms by using temperature jumps between isotherms with one sample. This is similar to the temperature-jump and pressure-jump methods common in chemical rate measurements.[140] In the factor-jump method, the sample is subjected to a series of isotherms, with rapid jumps between the isotherms, while the weight and temperature are monitored. The activation energy is estimated from the relationship,[141]

$$E_a = \frac{RT_1T_2}{T_2 - T_1} \ln\frac{r_2}{r_1} \qquad (59)$$

where r and T are the rates and temperatures of the two isotherms. These isotherms are assumed to occur at the same degree of conversion which is not a variable.[142]

A common method in TGA degradation stabilty is the use of multiple scanning rates. The scanning rate and temperature of degradation can be related by

$$\ln \beta = 1.05(E_a/RT) \qquad (60)$$

where β is the scanning rate and E_a is the activation energy associated with the degradation process occurring at temperature T.[143,144] The activation energy can be calculated by representing $\ln \beta$ versus 1/T for a series of different heating rate scans.

7. TTT DIAGRAM

Adjusting parameters during thermoset curing was a tricky situation in industry until the introduction of the TTT diagram. A 10 % decrease in temperature did not usually correspond to a 10 % increase in curing time; in fact, a 10 % decrease in temperature might produce uncured parts regardless of the time given. The TTT diagrams have been used extensively to describe time and temperature dependent transformations in metals[145] for many years especially in nonequilibrium states. The adaptation of the TTT diagram to thermosetting polymers by Gillham and Enns[146] gave a fast understanding of the relationship between processing parameters and an understanding of the physical state of the material in response to the conditions it had been exposed to. The TTT diagram tells processors at which temperature to store their materials to ensure no precuring, how much they can precure material and still ensure adhesion between components, how much they have to precure to ensure dimensional stability, what the optimum processing conditions should be, the lowest temperature that ensures full cure or a certain degree of cure and the maximum cure temperature to avoid degradation. A TTT
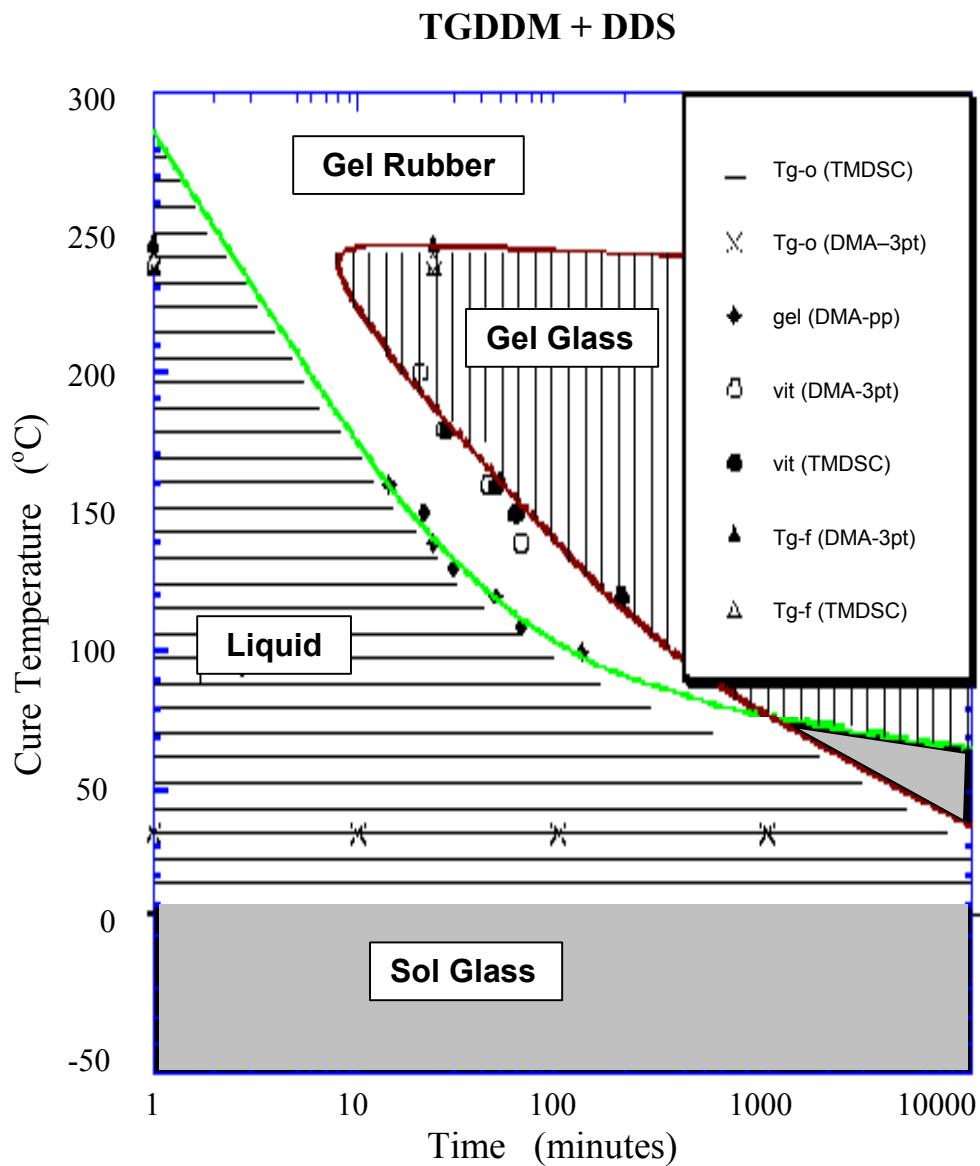
TGDDM + DDS

Figure 1. A TTT diagram from the work of the present authors[149] for tetraglicydyl 4,4-diaminodiphenyl methane (TGDDM, a tetrafunctional epoxy) + 4,4¹-diaminodiphenyl sulfone (DDS, a tetrafunctional amine).

diagram is usually presented with T_g plotted as as a function of the natural logarithm of curing time in isoconversion curves.[147,148] The primary curves shown are gelation and vitrification as a function of time and temperature. An example is given in Figure 1.

Actually, separation of gel formation from vitrification (glass formation) is not as simple as it sounds. In Figure 1 we provide a TTT diagram from the work of the present authors[149] for tetraglicydyl 4,4-diaminodiphenyl methane (TGDDM, a tetrafunctional epoxy) + 4,4¹-diaminodiphenyl sulfone (DDS, a tetrafunctional amine). Basically, temperature-modulated differential scanning calorimetry (TMDSC) was used to determine glass transition temperatures, degrees of conversion (Section 2 above) and vitrification. The gelation data were created using results from the dynamic mechanical analysis (DMA). The DMA method has been described in some detail by one of us.[150, 151] We recommend a combination of these two methods for reliable determination of the TTT diagram.[149] If one technique is to be used, then DMA is preferred over other methods.

Finally, we return to the issue of cure progress as a function of temperature T and time t. A single equation describing the progress of cure as a function of both T and t has been developed[152]. It works well for curing curves with an initial (bottom) plateau as well as for those which do not exhibit such a plateau. The complex viscosity or else the storage modulus[150, 151] have been used as measures of curing[152].

8. ABBREVIATIONS / ACRONYMS

DDS	4,4'-diaminodiphenylsulfone
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
TGA	Thermogravimetric Analysis
TGDDM	tetraglycidyl 4,4-diaminodiphenyl methane
TTT	Time-Temperature-Transformation

| WLF | Williams-Landel-Ferry |

9. SYMBOLS

a	amine concentration.
a_T	shift factor in time-temperature superposition.
A	preexponential term or frequency factor.
B	stoichiometric ratio of amine hydrogen to epoxide equivalents.
c	segment mobility
C_p	specific heat capacity at constant pressure.
e	epoxide concentration.
E_a	activation energy of reaction or transformation.
f	functionality of components, i.e. number of functional groups on reactant.
HX	abbreviation for hydroxyl groups
k	rate constant.
K	constant
m	order of catalytic term in autocatalytic reaction.
n	order (power function) of non-autocatalytic or nth order reaction.
r	rate
R	gas constant.
t	time.
$t_{i,g,p}$	time to reach specific point i, gel point or peak rate.
T	temperature.
$T_{0,i,g,p}$	temperature at beginning of reaction, point i, gel point or peak rate.
α	degree of conversion or cure representing the % aliphatic bonds formed.
$\alpha_{i,p,g}$	degree of conversion at a specific value i, peak rate or gel point.
$d\alpha/dt$	rate of conversion in time.
β	heating rate.
δ	phase angle (usually expressed as tan delta or phase lag)
ε	lattice energy
φ	heating rate.
Φ	chain entanglement factor.

η viscosity

$\eta_{0,\infty}$ viscosity at beginning of reaction or end of reaction.

λ structural parameter

τ relaxation time

ω angular frequency

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