INTRODUCTION

This article pertains principally to the formation and properties of high $T_g$ polymeric glasses that are made by the transformation of liquid to amorphous solid by chemical reaction. The area is of particular importance in the making of composites, coatings, and adhesives by thermosetting "cure" reactions in which molecules of low molecular weight are converted into network macromolecules. An attempt has been made to produce a generalized model for the formation and properties of thermosetting systems which also incorporates linear systems: an example of the former is the cure of a neat epoxy resin; an example of the latter is the polymerization of neat styrene monomer below the glass transition of polystyrene. This article will, therefore, emphasize thermosetting systems with some reference to linear systems. The simplest model for chemical setting assumes a single reaction mechanism and no phase separation.

THE TIME-TEMPERATURE-
TRANSFORMATION (TTT) ISOTHERMAL
CURE DIAGRAM

A TTT isothermal cure diagram (Fig. 1) may be used to provide an intellectual framework for understanding and comparing the cure and physical properties of thermosetting systems (1, 2). The main features of such a diagram can be obtained by measuring the times to events that occur during isothermal cure at different temperatures, $T_{\text{cure}}$. These events include the onset of phase separation, gelation, vitrification, full cure, and devitrification. Phase separation may occur, for example, by precipitation of rubber from solution in rubber-modified formulations, or by the formation of monomer-insoluble oligomeric species, by the formation of gel particles, and by crystallization in crystallizable systems. Gelation corresponds to the incipient formation of an infinite molecular network, which gives rise to long range elastic behavior in the macroscopic fluid. It occurs at a definite conversion for a given system according to Flory's theory of gelation (3). After gelation the material consists of normally miscible sol(s) (solvent-soluble) and gel(s) (solvent-insoluble) fractions, the ratio of the former to the latter decreasing with conversion. Vitrification occurs when the glass-transition temperature, $T_g$, rises to the isothermal temperature of cure. The material is liquid or rubbery when $T_{\text{cure}} < T_g$; it is glassy when $T_{\text{cure}} > T_g$. Devitrification occurs when the $T_g$ decreases through the isothermal temperature, as in degradation. The diagram displays the distinct states encountered on cure due to chemical reactions. These states include liquid, sol/gel rubber, gel rubber (elastomer), ungelled (sol) glass, gelled glass, and char. The gelled glass region in the TTT cure diagram is divided into two parts by the full-cure line; in the absence of degradation (Fig. 1, devitrification and char), the top and lower parts can be designated fully cured gel glass and undercured sol/gel glass regions, respectively. The technological terms, A-, B- and C-stage resins correspond to sol glass, sol/gel glass, and fully cured gel glass, respectively. The illustration also displays the critical temperatures $T_{gel}$, $T_{gel}$, and $T_{gel}$, which are the glass-transition temperature of the fully cured system, the temperature at which gelation and vitrification occur simultaneously, and the glass-transition temperature of the reactants, respectively.

Figure 1 includes a series of zero shear-rate isoviscous contours in the liquid region; successive contours differ by a factor of ten (4). The vitrification process below $T_{gel}$ has been constructed to be an isoviscous one.

Much of the behavior of thermosetting materials can be understood in terms of the TTT cure diagram through the influence of gelation,
vitrification, and devitrification upon properties. Gelation retards macroscopic flow, and growth of a dispersed phase (e.g., in rubber-modified systems). Vitrification retards chemical conversion. Devitrification, due to thermal degradation, marks the lifetime for the material to support a substantial load.

The isothermal TTT cure diagram is more limited for the curing of linear rubber systems than for thermosetting systems because in practice only the region above $T_g$ is relevant for the former. Gelation in the vulcanization of rubbers occurs at low conversions in comparison with typical thermosetting systems.

The ungelled glassy state is the basis of commercial molding materials since, upon heating, the ungelled (sol) material flows before gelling through further reaction. Formulations can be processed as solids (e.g., molding compositions) when $T_{go} >$ ambient temperature; they can be processed as liquids (e.g., as casting fluids) when $T_{go} <$ ambient temperature.

The $T_g$ of the material at the composition corresponding to gelation is $\omega_TT_g$. Since gelation occurs as the material vitrifies when the temperature of cure is $\omega_TT_g$ (5). The gelation curve [Fig. 1], therefore, corresponds to $T_g = \omega_TT_a$. Temperature $\omega_TT_g$ is critical in determining the upper temperature for storing reactive materials to avoid gelation (which relates to "pot life"). However, cure below $\omega_TT_g$ eventually leads to gelation.

The morphology developed in two-phase systems, for example, those in which rubber-rich domains nucleate and grow as a dispersed phase, depends on the temperature of cure. The reaction temperature determines the competition between thermodynamic and kinetic (i.e., transport) factors that affect the amount, the composition, and the distribution of dimensions of the dispersed phase. As an example, reaction at intermediate temperatures can result in a maximum in the amount of precipitated phase which may give rise to a minimum in the time to the onset of phase separation (Fig. 1). For optimum mechanical properties, a two-phase system is cured first at one temperature to provide a particular morphology, and subsequently...
at a higher temperature to complete the reactions of the matrix (6, 7). The $T_{gm}$ of the matrix will be determined by the extent of phase separation.

In composite systems, shrinkage stresses due to volume contraction of the resin on isothermal cure begin to develop with adhesion of the curing resin to a rigid inclusion. This occurs after gelation above $T_g$ and before vitrification below $T_g$. The tensile stresses in the resin and the corresponding compressive stresses on an inclusion affect composite behavior. One consequence is fiber-buckling in resin/fiber composites. A related consequence of the shrinkage due to cure and the different coefficients of expansion and contraction of the constituents in brittle resin/fiber composites is the formation of spiral and helical cracks in the resin around isolated filaments and yarns (8, 9). Their large surface areas per unit volume of matrix may contribute to the toughening of fiber/resin composites.

Prolonged isothermal cure at $T_{cure}$ below $T_{gm}$ would lead to $T_g = T_{cure}$ if the reactions were quenched by the process of vitrification. In practice, $T_g$ is higher than $T_{cure}$ because it can increase during the heating scan employed for measurement. Although vitrification has been defined to occur when $T_g = T_{cure}$, $T_g$ as usually measured, does not correspond to the glassy state, but rather to a state approximately halfway between the rubbery and glassy states: therefore reactions at $T_{cure}$ continue beyond the assigned time to vitrification, which also results in $T_g > T_{cure}$. Furthermore, the extent to which reactions proceed in the glassy state depend on the influence of the glassy state on the reaction mechanism. However, even the intramolecular reactions involved in the imidization of polyamic acids to polyimides are restricted by the vitrification process, leading again to $T_g$ being controlled by the temperature and the time of cure. In practice, for epoxies and polyimides, $T_g$ is greater than $T_{cure}$ by about 30° to 50°C after “normal” isothermal cure below $T_{gm}$ (10 to 13). This corresponds approximately to the half-width of the glass transition temperature region since $T_g$ (as measured) increases through the isothermal temperature $T_{cure}$ to about $T_{cure} + 40°C$, after which the reaction rate is controlled by the low physical relaxation rates of the glassy state.

Correlations between macroscopic behavior and molecular structure of the reactants are most clearly defined in fully cured materials. Full cure is attained most readily by reaction above $T_{gm}$, and more slowly by curing below $T_{gm}$ to the full-cure line of the TTT cure diagram (11). The full cure line corresponds to $T_g = T_{gm}$.

In practice, full cure is in general not a unique state because the state depends upon the time-temperature reaction path. In commonly used systems, this is a consequence of competing chemical reactions with different activation energies. Furthermore, material properties also depend on the reaction path for physical reasons, such as the density of the polymerizing system depending on the temperature of reaction. Similarly, the time-temperature path of cooling after cure affects, for example, density and behavior at room temperature.

At high temperatures, non-curing chemical reactions result in degradation. Thermal degradation can result in devitrification as the $T_g$ decreases through the isothermal temperature due to a reduction in cross-linking or formation of plasticizing material. Degradation can also result in vitrification, e.g., char formation (Fig. 1), as the $T_g$ increases through the isothermal temperature because of an increase in cross-linking or volatilization of low molecular weight plasticizing materials (13). In high $T_g$ systems, cure and thermal degradation reactions compete. There is a need to obtain high temperature polymers from low temperature processing.

The limiting viscosity in the fluid state is controlled by gelation above $T_g$ and by vitrification below $T_g$. At gelation, the weight-average molecular weight and zero shear-rate viscosity become infinite, although the number-average molecular weight is very low. Viscosity in the vicinity of vitrification below $T_g$ is described by the Williams-Landel-Ferry (WLF) equation (4, 14).

The time to reach a specified viscosity (Fig. 1) is often used as a practical method for measuring gelation times. Although this isoviscosity approach is inconsistent with the isoconversion theory of gelation, above temperature $T_g$, the apparent activation energies obtained from the temperature dependence of the time to reach a specified viscosity approach the true activation energy for the chemical reactions leading to gelation with increase of the specified viscosity [1].

The time to gelation can be computed from the reaction kinetics and the conversion at gelation, which is constant according to Flory’s theory of gelation. The time to vitrification can be computed from the reaction kinetics and the conversion at vitrification (4, 15, 16), which increases with $T_{cure}$. Since vitrification occurs when the $T_g$ reaches the temperature of cure, computation of the time to vitrify requires knowledge of the relationship between $T_g$ and conversion. Figure 2 shows that $T_g$ increases with conversion at an increasing rate. In the absence of diffusion control, the general kinetic equation describing the reaction is

$$\frac{dX}{dt} = A\exp(-E_a/RT)f(X)$$

where $X$ is the extent of reaction, $E_a$ the activation energy, and the other characters have their usual significance. The times to gelation and to vitrification can be computed versus temperature when $X_{gel}$ (for gelation), a relationship between $X$ and $T_g$ (for vitrification) (Fig. 2), and the reaction kinetics are known. The
influence of diffusion control on the reaction rate can be deduced in principle from the differences between the experimentally measured and the computed gelation and vitrification curves.

The S-shaped vitrification curve obtained experimentally in the absence of thermal degradation has been matched by computation for one epoxy system from temperature \( T_{go} \) to temperature \( T_{gw} \) (4).

The vitrification curve is generally S-shaped (16). At temperatures immediately above \( T_{go} \), the time to vitrification passes through a maximum because of the opposing influences of the temperature dependencies of the viscosity and the reaction rate constant. Immediately below \( T_{gw} \), the time to vitrification passes through a minimum (17) because of the opposing influences of the temperature dependence of the reaction rate constant and the decreasing concentration of reactive sites at vitrification as \( T_{gw} \) is approached. Knowledge of the minimum time and the corresponding temperature is useful in molding technology.

Cure of finite specimens at temperatures below that for the minimum time for vitrification (Fig. 1) will lead to the hotter inside vitrifying before the outside when the reaction is exothermic. Conversely, cure at higher temperatures would lead in principle to the outside vitrifying before the inside; in this case internal stresses develop as the inside contracts relative to the vitrified outside due to the volume contraction of polymerization. Similarly, cooling cured material from above \( T_{gw} \) will lead to the outside vitrifying before the inside; internal stresses in this case will be minimized by cooling very slowly (i.e., annealing). These stresses, which are due to nonisothermal conditions in neat systems, are supplemented in composites by the differential shrinkage stresses that were referred to earlier in the article.

The conversion at vitrification can be computed in principle by relating the \( T_g \) to contributions from the molecular weight and the cross-linking density, both of which vary with conversion (16). For polymerization prior to gelation (and for linear polymerization), the computation is simplified by the absence of cross-linking.

The fractional extent of reaction at vitrification and the time to vitrify, like gelation, decrease with increasing functionality of the reactants (13). The effect of increasing functionality on gelation, vitrification, and the temperatures \( \varphi, T_g, T_{go}, \) and \( T_{gw} \) can be understood by considering the X-vs-\( T_g \) and the \( X \rightarrow T_g \) relationships, such as those in Fig. 2. For example, the figure shows how temperature \( \varphi \rightarrow T_g \) for the material of lower functionality can be higher than that of higher functionality.

Increasing reaction time at any temperature leads to increasing conversion, \( T_g \), and cross-linking density. The modulus and density at the curing temperature also increase. However, upon cooling intermittently from the curing temperature to a temperature well below \( T_g \), e.g., room temperature for high \( T_g \) materials, the modulus and density can decrease, whereas equilibrium absorption of water can increase with increasing extent of cure. A common basis for these phenomena is the increasing free volume at \( RT \) with increasing extent of cure (18). This may simply be a result of free cooling through \( T_g \) at increasing cooling rates (as \( T_g \) increases with conversion), thereby giving less time for physical aging. It could be a result of more subtle factors (18, 19).

The concept of the TTT cure diagram can be extended to nonisothermal conditions for forming and annealing polymeric materials. For example, a continuous heating time-temperature-transformation (CHT) diagram results from heating a reactive system from (say) 25°C to 300°C at a series of different rates of increasing temperature. The vitrification curve will be joined to a devitrification curve to form an envelope (20). This devitrification is a consequence of the rising \( T_g \) eventually not increasing at the same rate as the rate of rise of temperature. Such a diagram is useful in molding technology for defining time-temperature cure paths in which vitrification does not occur, for example, so as to obtain full cure. Conversely, vitrification can be an essential part of a cure.
cycle so as to control reaction rates that could run out of control because of the exothermic nature of a reaction. The polymerization of 250 gallons of epoxy to encapsulate a magnetic coil in Princeton University's experimental Tokomak nuclear fusion reactor is accomplished by heating at a very low rate of temperature increase; the reaction rate is controlled in the process by the $T_g$ increasing in concert with the temperature until $T_g$, i.e., full cure, is attained.

**LINEAR POLYMERIZATION AND THE TTT DIAGRAM**

This section attempts, in a general manner, to incorporate linear polymerization of neat systems into the concept of the TTT diagram.

Difunctional liquid monomers can be transformed into glassy linear polymeric materials by reaction below the maximum $T_g$ of the polymer, $T_{g(x)}$. The time to vitrification curve for the isothermal free radical polymerization of neat styrene versus the isothermal temperature of reaction, $T_{r(x)}$, has been computed in the absence of diffusion control [21]. The calculation involved using the well established chemical kinetics from zero conversion to the conversion corresponding to $T_g = T_{r(x)}$. Since the neat mixture at any time consists of mostly monomer and polymer (neglecting initiator and active chain radicals), the proportion of polymer to monomer (i.e., the conversion) was calculated from the glass transition temperatures of the monomer and polymer and $T_g = T_{cure}$. The computed vitrification curves for the free-radical polymerization of styrene and for a linear-forming step-growth polymerization were S-shaped.

Phase separation can occur in neat linear polymerization as a consequence of insolubility of oligomer or polymer. This has been a particularly important consideration in the synthesis by step-growth polymerization of high $T_g$ linear polymers, which of necessity have relatively inflexible chain structures. Precipitation often effectively removes the growing species from the reaction medium, thereby limiting the molecular weight. In the same type of polymerization, the reaction temperature must be such that vitrification also does not occur (i.e., $T_{r(x)} > T_{g(x)}$). Phase separation can be analogous to vitrification in limiting molecular weight and $T_g$. (Use of exotic solvents overcomes the problems of insolubility and vitrification in the synthesis of high $T_g$ rigid molecules; however, these solvents must be subsequently removed, often by ingenious methods.)

Although chemical gelation does not occur in linear polymerization, long range elasticity can develop in the polymerizing fluid as the consequence of entanglements between polymer molecules. These will occur at lower conversions for chain reactions where high molecular weight polymer forms throughout the reaction, than for step-growth polymerizations where high molecular weight polymer develops only late in polymerization.

The situation is more complex for the conversion of liquid monomers into polymers that can crystallize. Polymerization of neat monomer above $T_{m(x)}$ can lead to solidification because of crystallization. (The maximum melting temperature, $T_{m(x)}$, is greater than the maximum glass transition temperature, $T_{g(x)}$.) Polymerization below $T_g$ can lead to solidification as the result of vitrification or crystallization. The melting temperature range, as well as the $T_g$ should be directly related to the temperature of reaction; it is well known that $T_m$ of a linear polymer is directly related to the isothermal temperature of crystallization [22].

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**REFERENCES**