

Award Address

Formation and Properties of Network Polymeric Materials

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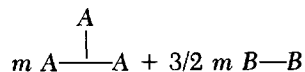
A general model for thermosetting materials which relates polymerization to properties is discussed. In particular, a phase diagram relates the four states of matter encountered (i.e., liquid, rubber, ungelled glass and gelled glass) to gelation and vitrification phenomena. The model is extended to rubber-modified thermosetting systems to show that, by control of the time to gelation, a given chemical formulation can provide different morphologies and hence different material behavior. The principal experimental approach uses a torsional braid analyzer (TBA), an automated version of which is described. Use of the technique to measure gelation and vitrification times is discussed.

GELATION AND VITRIFICATION

Polymeric materials are of two types, thermoplastics and thermosets. Unlike thermosets, thermoplastics (e.g., polyethylene, polystyrene, and polyvinyl chloride) soften and flow on heating and, when cooled, can return to their original state. The techniques of processing them (e.g., injection molding and extrusion) depend on this reversible behavior. Synthesis and processing of thermoplastic materials are distinct operations. On the other hand, thermosets are generally polymerized and processed in a single operation (e.g., compression molding), which transforms low molecular weight material to network polymer of infinite molecular weight in an irreversible process. Examples are epoxy and unsaturated polyester resins of fiber-reinforced composites used in ships.

In spite of their superior engineering properties as solid materials, thermosets have been neglected scientifically in comparison with thermoplastics. The reason lies in their intractability—which is the very characteristic that makes them so important. The present article shows how an experimental examination of the phenomena encountered in their formation leads to an unusual and yet general way of regarding both thermoplastics and thermosets. Systematic perturbation of the model should produce fuller understanding of the parameters which bear on the molecular engineering of thermosets.

The molecules of thermoplastic materials are linear and can be synthesized from bifunctional reactants (e.g., $A-B$). For example, if A in one molecule reacts with B in an adjacent molecule on a one-to-one basis, n molecules of monomer $A-B$ will polymerize to a linear molecule with a repeat unit $(-A-B-)$. Three dimensional network polymers can be synthesized from systems containing multifunctional (>2) reactants; for example,



will form a network molecule. The network structure confers macroscopic dimensional stability to the thermosets which are therefore used in applications demanding high performance. Diamond, rubber, and quartz are other examples of network molecules. In contrast, thermoplastics flow under stress, which limits their uses to those in which stability under load is not so important.

Gelation and vitrification are two macroscopic phenomena which are encountered during the reactions which convert a liquid to a solid in the thermosetting process. Gelation, like a chemical explosion, is an example of a critical condition being reached in a chemical reaction. On the molecular level, this corresponds to the incipient formation of branched molecules of mathematically infinite molecular weight and occurs at a calculable degree of reaction for the particular reactive system. Below the critical degree of reaction all of the molecules have finite size; at higher chemical conversions some are "infinite", their number and size increasing with chemical conversion. A network develops by intramolecular reactions of branched molecules (Fig. 1). Eventually the total mass can be one molecule with a molecular weight per gram-mole of more than Avogadro's number (6×10^{23}) and limited only by the amount polymerized. The mathematical theory of gelation was formulated many years ago by Paul Flory, the recipient of the Nobel Prize for Chemistry in 1974. Macroscopically, gelation is associated with a dramatic increase in viscosity and a corresponding decrease in processability. Gelation times are usually measured rheologically by the time between the beginning of the reaction and the attainment of a fixed viscosity.

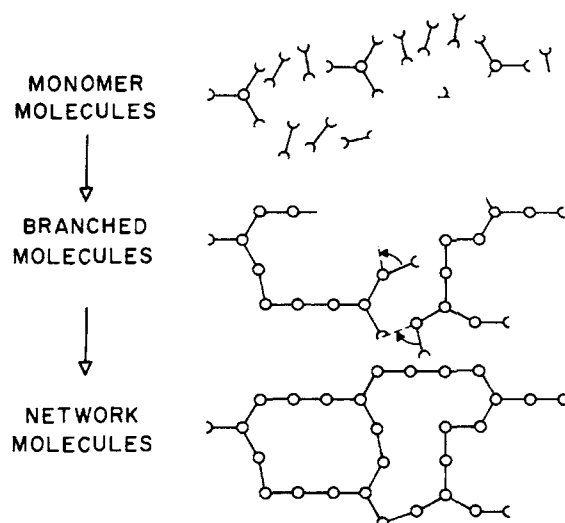


Fig. 1. Network molecules develop from branched molecules by intramolecular reactions.

Vitrification is the formation of a glassy solid. In thermosets this usually follows gelation and then occurs as a consequence of the network becoming tighter through further chemical reaction (crosslinking). A network structure will be a rubber (elastomer) at a given temperature if the segments between junction points of the network are flexible. If the segments are immobilized by further chemical reaction, or by cooling, the structure will change to a glassy (vitrified) state. Vitrification can retard further reaction. The overall transformation from liquid to gel to rubber to glass due to chemical reaction is termed "cure".

AN AUTOMATED TORSION PENDULUM (1)

An automated, free-hanging, freely decaying torsion pendulum has been developed which permits monitoring of the changes which occur throughout cure and through load-limiting transitions. There are several distinguishing characteristics of a free-hanging, freely decaying torsion pendulum. These include: (a) accurate measurement of low loss at low frequency—the state of the art of electronic data collection and analysis in forced systems has less resolution of phase angle, δ , between stress and strain than in freely decaying systems; (b) unlike forced oscillating systems a free-hanging one tends to be self-aligning (under the influence of gravity); (c) similarly, free-hanging systems maintain a constant load on the specimen without requiring adjustment for thermal expansion; and (d) the major limitation of resonance systems lies in the difficulty in obtaining the frequency dependence of relaxations. The method of Heijboer (2) provides an estimate, in many cases, of this dependence from single frequency measurements.

The specimen is made by impregnating a glass fiber braid with the reactive system. The specimen can be cured externally or in the apparatus. The pendulum is intermittently set into oscillation to generate a series of freely damped waves. The frequency of operation is about 1 Hz. The character of these waves changes throughout isothermal cure to provide a monitor of change. Similarly, the dynamic mechanical spectra of a

"cured" polymer are provided by the changing character of the waves as a function of temperature. Changes observed in the thermomechanical spectra upon further heating of a "cured" polymer can be related to cure level and/or degradation.

The two mechanical functions, rigidity and damping, are obtained from the frequency and decay constants which characterize each wave. The experiment provides plots of relative rigidity ($1/P^2$, where P is the period in seconds) and logarithmic decrement ($\Delta = \ln(A_i/A_{i+1})$, where A_i is the amplitude of the i^{th} oscillation of a freely damped wave). The relative rigidity is directly proportional to the in-phase or elastic portion of the shear modulus (G'); for example, for rod specimens of radius r and length L and for an oscillating system with moment of inertia I , $G' \approx 1/P^2(8\pi IL/r^4)$. The logarithmic decrement is directly proportional to the ratio of the out-of-phase or viscous portion of the shear modulus (G'') to G' ($\Delta \approx \pi G''/G' = \pi \tan \delta$). G' and G'' are material parameters of the specimen which characterize the storage and loss of mechanical energy on cyclic deformation; quantitative values of G' may be obtained by using dimensions of the specimen.

A schematic diagram of the automated pendulum is shown in Fig. 2. The photograph (Fig. 3) shows the pendulum (enclosed in a cabinet, top right; cabinet door open, bottom left) and the major components of the assembly. An analog computer (top center) (or digital computer—see ref. (1)) is used for automatic control of the experiment and data reduction. A printer and digital panel meter provide numerical values of the temperature (mV) or lapsed time (s), logarithmic decrement (Δ) and period (P , s) of each damped wave (top center). A monitoring strip-chart two-pen recorder provides a continuous record of the waves and temperature (mV) (below computer). A temperature controller/programmer (range -195 to 500°C ; rate of change of temperature 0°C to $\pm 5^\circ\text{C}/\text{min}$) is shown above the computer.

An XYY plotter plots, immediately after computation, the relative rigidity ($1/P^2$) and logarithmic decrement vs. temperature (mV) or log time (s) (top left). Switches permit selection of options which include ON, OFF or REVERSE of temperature programming at upper and lower set points and selection of temperature or time as the running variable (top center). Specimens, such as impregnated braid and film, are shown at bottom right. A film is shown assembled with lower and upper extension rods ready for lowering into the apparatus. The polarizer disk of the transducer is also shown (bottom right). Dimensions of specimens are selected so as to provide periods of oscillation in the range 0.25 to 15 s.

A key factor in the instrumentation was the development of a non-drag optical transducer which produces an electrical response that varies linearly with angular displacement. This was implemented by the use of a two-polarizer light attenuation system. A polarizer disc is employed as the inertial member and a second stationary polarizer is positioned, in the path of a light beam, in front of a linear-with-intensity vacuum photo tube (Fig. 2).

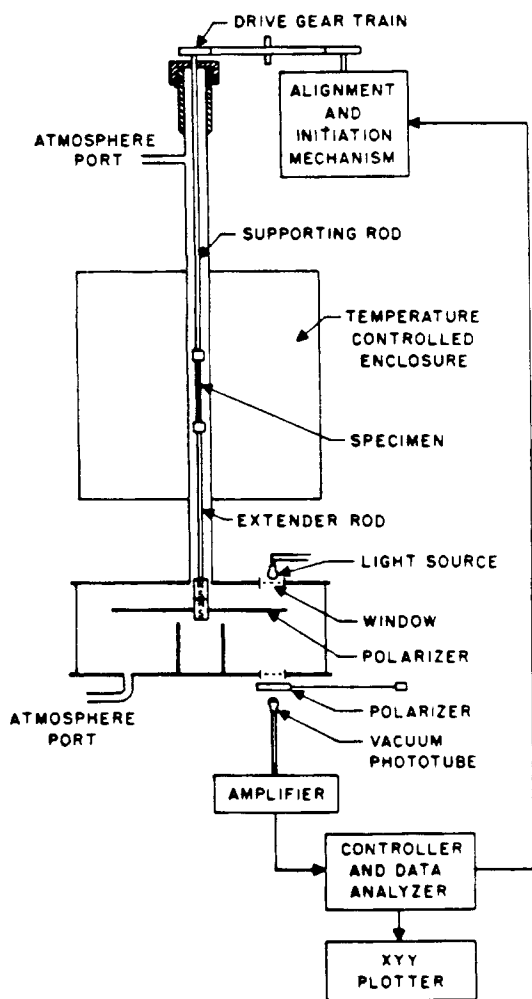


Fig. 2. Automated torsion pendulum. An analog electrical signal results from using a light beam passing through a pair of polarizers one of which oscillates with the pendulum. The pendulum is aligned for linear response and initiated by a computer that also processes the damped sine waves to provide the mechanical rigidity and mechanical damping data, which are plotted on an XYZ plotter (1).

Light transmission through two polarizers is a \cos^2 function of angular displacement. Over a useful range symmetrical about the 45° position, the transmission function approaches a straight line. The polarizer system is also insensitive to lateral oscillations. As the properties of the specimen change, twisting may cause the transducer to drift out of this linear range. The automation system described below is designed to compensate for this.

The sequence of events of the automated torsion pendulum is as follows: Strip-Chart Recorder monitor (Fig. 4, Top): (I) Previous wave decays, drift detected and correction begins. (II) Polarizers correctly positioned. (III) Wave initiating sequence begins. (IV) Free oscillations begin. (V) AB , first peak-to-peak amplitude less than initial boundary amplitude is measured. (VI) CD , first peak-to-peak amplitude $< \frac{1}{2} AB$ is measured. (VII) Time interval between peaks B and D is measured. (VIII) No drift correction required, wave initiating sequence re-starts. Controller/Data Analyzer loop (Fig. 4, Bottom): 1) Polarizers positioned. 2) Wave initiated. 3)

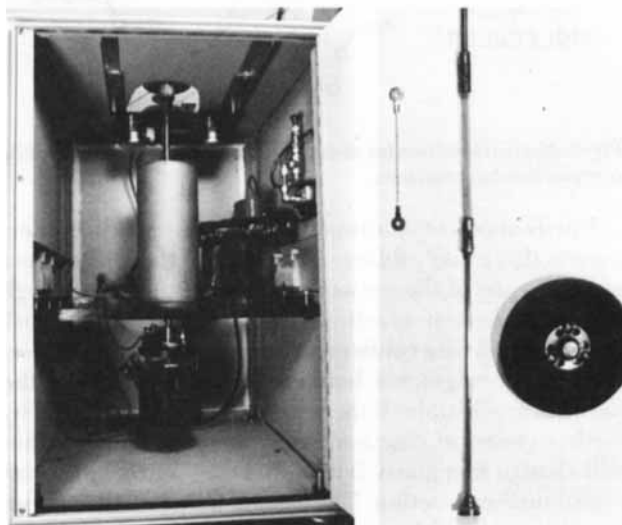
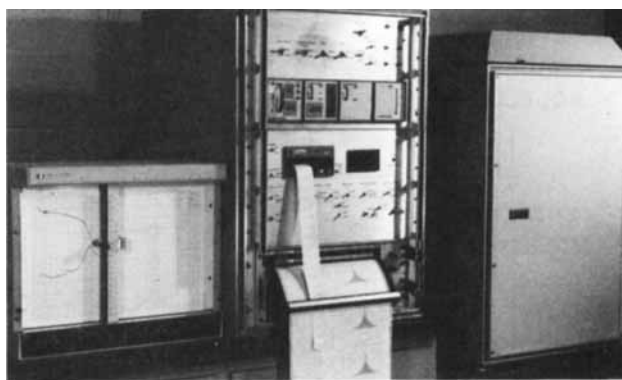


Fig. 3. Automated torsion pendulum: photograph of apparatus (see text).

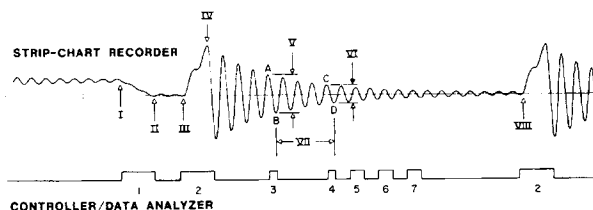


Fig. 4. Automated torsion pendulum: strip-chart recorder monitor (top); controller/data analyzer sequence (bottom) (see text).

Peak-to-peak amplitude, AB , measured. 4) Peak-to-peak amplitude, CD , measured. 5) Period (s) printed, $\log 1/P^2$ plotted. 6) Logarithmic decrement (Δ) printed and $\log \Delta$ plotted. 7) Temperature (millivolts) or time (s) printed and plotted (choice of log time or linear time).

The high quality of the data (see figures with "as plotted" data) is matched by the system's ease of operation. No alignments or adjustments of the specimen are necessary after the simple specimen preparation and mounting procedures. Other features include the control of temperature (0.2°C) and atmosphere (vacuum, inert and reactive gases, and water vapor). An on-line hygrometer can be used to continuously monitor the water vapor content of the atmosphere from <20 to $20,000$ ppm H_2O .

This adaptation of the torsion pendulum approach for characterizing small quantities of supported polymer

has been developed under the name "torsional braid analysis (TBA)" (1). An automated system is commercially available from Plastics Analysis Instruments, Inc., P.O. Box 408, Princeton, N.J.

A GENERALIZED PHASE DIAGRAM FOR THERMOSETTING SYSTEMS (3-5)

The experimental results for the cure of an epoxy system at a series of constant temperatures were used to obtain estimates of the gelation time and the vitrification time vs cure temperature. These transformation times were measured using peaks in the mechanical damping curves; they correspond to points of inflection in the rigidity curves (see Fig. 5 which results from an isothermal experiment at an intermediate temperature). Results derived from a family of isothermal plots (Fig. 6) are summarized in Fig. 7 which shows that there are three types of behavior depending on the temperature of cure. At high temperatures the liquid gels but does not vitrify. At low temperatures the liquid vitrifies, and need not gel if the chemical reactions are quenched by vitrification. At intermediate temperatures the liquid first gels and later vitrifies (Fig. 5). The time to gelation is expected to decrease exponentially with increasing temperature since the degree of reaction at the point of gelation is constant. In contrast, the time to vitrification passes through a minimum which occurs at an intermediate temperature of cure (4). This reflects competition between the increased rate constants for reaction and the increased degree of reaction required to overcome the thermal motions for vitrification at higher temperatures. The temperature at which gelation and vitrification occur together is defined as T_{gg} (3) (Fig. 7). Vitrification can occur before gelation ($T_{cure} < T_{gg}$) simply by an increase of molecular weight. Gelation occurs

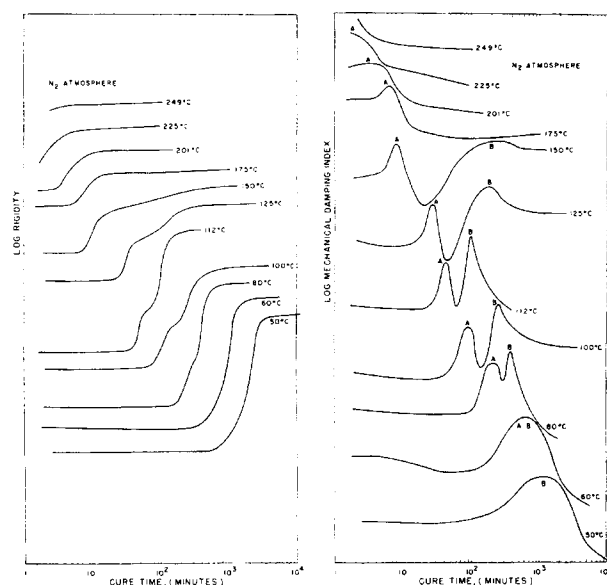


Fig. 6. Rigidity and mechanical damping vs time during isothermal cure of an epoxy system in the temperature range 50 to 249°C. For clarity the curves have been displaced vertically by arbitrary amounts.

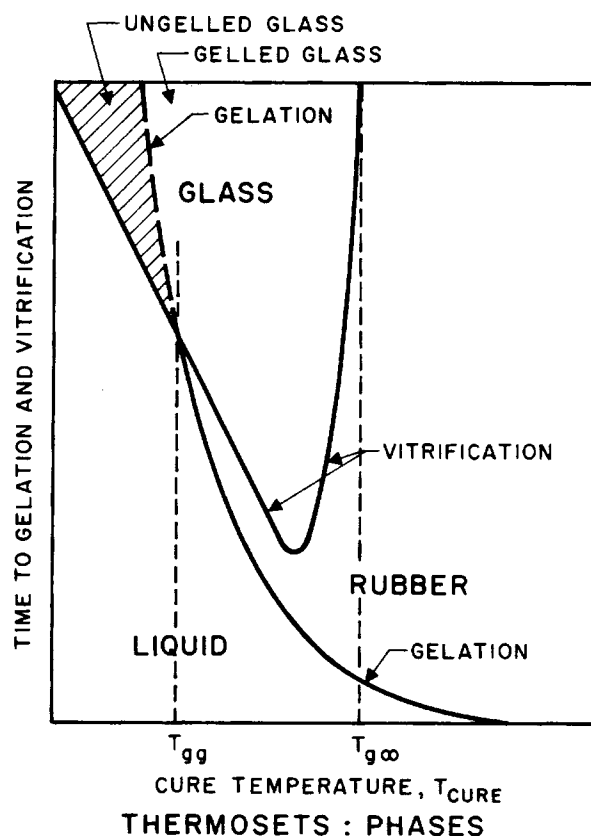


Fig. 7. Time to gel and time to vitrify vs isothermal cure temperature for an epoxy system. T_{gg} and $T_{g\infty}$ are critical temperatures in the phase diagram which shows the four states of materials encountered in the thermosetting process, i.e., liquid, rubber, ungelled glass, and gelled glass.

without vitrification when cure is performed above the maximum softening point, the maximum glass transition temperature $T_{g\infty}$ of the system (Fig. 7). It is also apparent that if reactions cease at vitrification ($T_{cure} < T_{g\infty}$), the glass transition temperature, T_g , of the system after cure

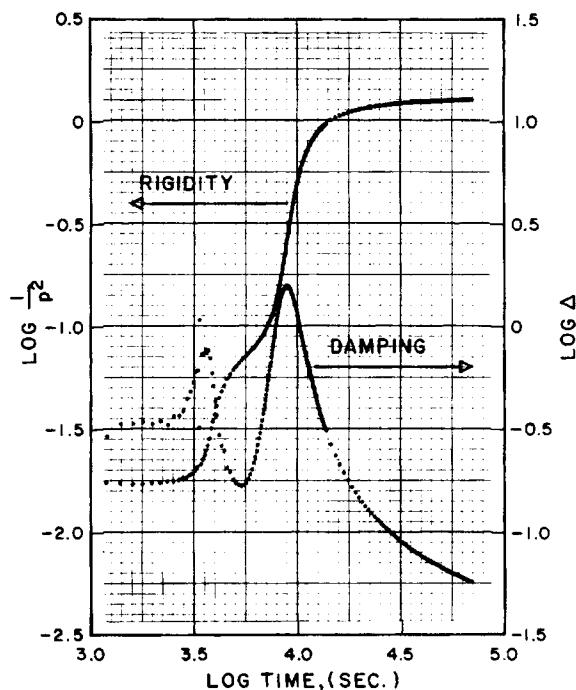


Fig. 5. Rigidity and mechanical damping vs time during cure of an epoxy at constant temperature ($T_{gg} < T_{cure} < T_{g\infty}$).

will equal the temperature of cure. The vitrification curve therefore gives the time to reach the glass transition temperature which the system can achieve by curing at T_{cure} . In particular, T_{gg} is the glass transition temperature of the reactive system at its point of gelation.

A diagram such as Fig. 7 summarizes much of the behavior of the ideal thermosetting process and in particular shows that it is characterized by two temperatures, T_{gg} and $T_{g\infty}$, which will vary from system to system. In contrast, amorphous thermoplastic materials are in principle characterized only by $T_{g\infty}$ since gelation does not occur in their formation. T_{gg} and $T_{g\infty}$ are critical temperatures of a phase diagram (Fig. 7), which shows the four types of materials encountered in the thermosetting process, i.e., liquid, rubber, ungelled glass, and gelled glass.

From the practical point of view, the diagram (Fig. 7) explains a number of practices in the field of thermosets. Examples follow.

1) Finite vs infinite shelf-life: If the storage temperature is below T_{gg} , a reactive material will convert to a vitrified solid of low molecular weight which is stable and can be later liquified by heat and processed; above T_{gg} the stored material will have a finite shelf-life since gelation will occur before vitrification. (A gelled material does not flow.) This concept lies at the basis of a widespread technology which includes thermosetting molding compounds and "prepregs" with latent reactivity.

2) Post-cure: If $T_{cure} < T_{g\infty}$, a reactive material will vitrify and full chemical conversion may be prevented; the material will then need to be postcured above $T_{g\infty}$ for development of optimum properties. For the manufacture of objects of finite size it is necessary to go through a two-step process because of the exothermic nature of the reactions. However, a more sophisticated approach for controlling highly exothermic systems is to cure the material by raising the temperature at a rate such that T_g and T_{cure} coincide.

As an example, Fig. 8 presents thermomechanical data after isothermal reaction at an arbitrary temperature for an arbitrary time and also after heating the same specimen to well above $T_{g\infty}$. Using the transitions as a measure of material properties (see Fig. 8), it is apparent that the extent of cure affects not only the value of the

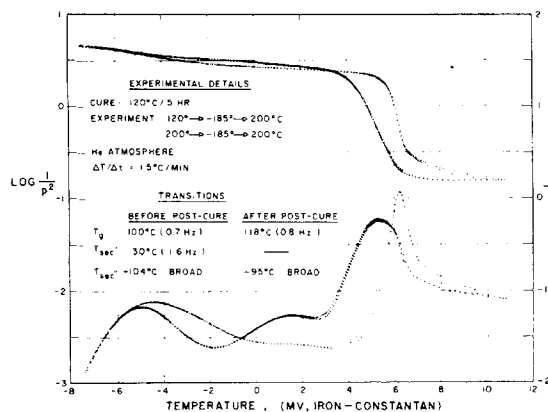


Fig. 8. Effect of cure and post-cure on the transitions of an epoxy.

glass transition but also properties at temperatures well below it. The relative rigidity at room temperature is decreased and the intensity of the $T < T_g$ relaxations (as measured by the area under the loss peaks) is increased by the post-cure. This suggests that the free volume is increased and that the density at RT is decreased by the post-cure in spite of the increase of T_g . This is presumably a result of the glassy state being further from equilibrium at RT the higher the T_g .

3) Limits of $T_{g\infty}$: For highly crosslinkable or rigid-chain polymeric materials $T_{g\infty}$ can be above the limits of thermal stability in which case the thermoset material would not have a measurable glass transition temperature and full chemical conversion could not be attained. It follows for composite materials in which a component other than the cured resin is thermally sensitive that $T_{g\infty}$ for the thermosetting resin should be below temperatures which would lead to damage of any part of the assembly.

If $T_{g\infty}$ is below room temperature, the polymer system will be used as an elastomer.

The phase diagram (Fig. 7) has been extended to two-phase systems. The following example (5) demonstrates how a given chemical system can result in different material properties. It pertains to polymeric glassy crosslinked matrices containing dispersed rubber inclusions. Rubber is incorporated in inherently brittle polymeric materials as a way of increasing toughness.

The curing of rubber-modified/epoxy systems often involves change from an initially homogeneous solution to a heterogeneous multiphase morphology. Evidence is presented to show that the process of gelation arrests the development of morphology, and therefore that the time to gelation can be used to control material properties. The gelation time can be varied by catalysts and temperature.

The effect of level of catalyst on the thermomechanical behavior (rigidity and damping vs temperature) obtained after complete cure of a single rubber-modified system is made evident by comparison of Fig. 9 (no catalyst) and Fig. 10 (with catalyst). In particular, the glass transition of the rubbery phase is more dominant for the sample cured without catalyst and therefore with

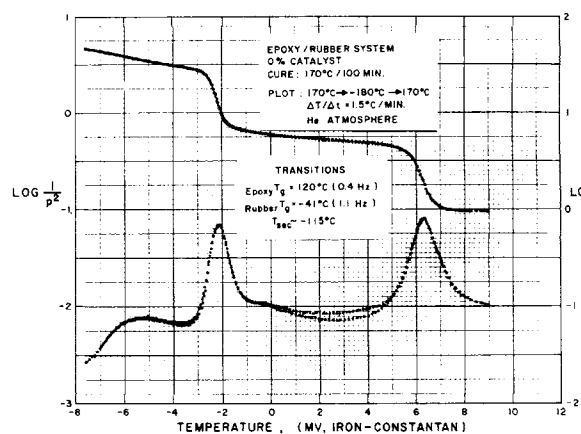


Fig. 9. Epoxy/rubber system. 0 parts per hundred catalyst. Thermomechanical behavior after cure. Experimental details and a summary of the transitions appear in the figure.

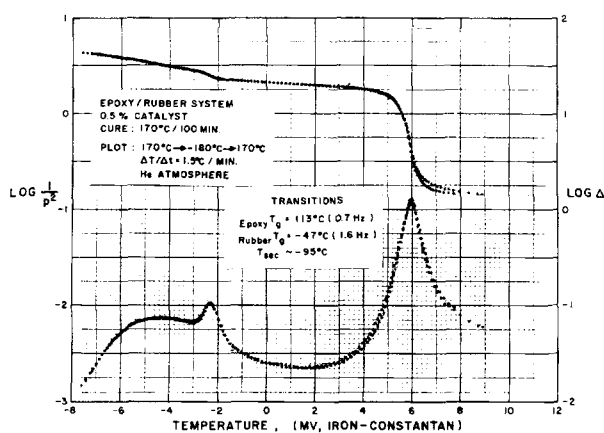


Fig. 10. Epoxy/rubber system. 0.5 parts per hundred catalyst. Thermomechanical behavior after cure. Compare the intensities and temperatures of the rubber glass transition (T_{gR}) and epoxy glass transition (T_{gE}) of the thermomechanical spectra of Figs. 9 and 10.

a longer time to gelation. This result suggests that the intensity of the rubbery transition, which directly affects macroscopic properties, depends on the time available for the development of a two-phase structure. The higher glass transition temperature of the epoxy phase for the sample cured with long gelation time also suggests more complete separation of the two phases. Optical examination of the same samples supported the conclusions in that curing without catalyst led to distinctly larger size domains of dispersed rubber than cure with catalyst. Figure 11 similarly demonstrates how, by reaction at different temperatures, a single chemical composition can produce distinctly different morphologies which in turn are responsible for distinctly different microscopic behavior.

Rubber particles nucleate and grow during the polymerization process. Generally, as in crystallization, nucleation is favored by low temperatures whereas growth is favored by high temperatures. The overall extent of phase separation can therefore be expected to be at a maximum at intermediate temperatures.

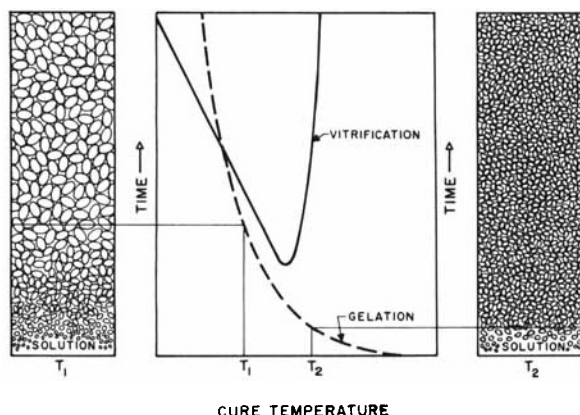


Fig. 11. Development of a two-phase rubber-modified epoxy system vs gelation temperature. As polymerization progresses rubber precipitates in domains which grow in size with time. Gelation is considered to arrest the growth process. Different morphologies therefore result from reaction at different temperatures (e.g., T_1 and T_2).

Quenching of the development of morphological changes by the phenomenon of gelation may be explained by an abrupt decrease in diffusion of rubbery material to the growing domains of rubber which occurs in the transformation from a viscous liquid to a soft gel as infinite molecules form in the process of gelation. This is a longer range and larger scale diffusion process than that which is involved in the quenching of chemical reactions which occur in the transformation from a rubbery state to a glassy state (vitrification) by restrictions on the more localized motions of chemically reactive parts of the molecules.

The phase diagram (Fig. 7) is idealized in several respects. (a) If there are competing network-forming reactions having different reaction rates then different time-temperature paths will lead to different molecular networks in the fully cured materials and so to different material behavior (6). $T_{g\infty}$ and T_{gg} will vary accordingly. (b) Vitrification times will be longer than those measured operationally from the time to the peak of the loss maximum assigned to the vitrification process since vitrification, with respect to the quenching of reactions, is better defined when the rigidity levels off. (c) As elaborated on below, the macroscopic assignment of gelation by a rheological measurement such as TBA does not necessarily correspond to its molecular definition. (d) The time to vitrify will pass through a maximum at low temperatures before being zero at the glass transition temperature of the reactants.

PROCESSABILITY—THE SIGNIFICANCE AND EQUIVALENCE OF T'_{ll} AND t_{gel}

Recent TBA work has shown the coincidence of the T'_{ll} ($>T_{ll} > T_g$) relaxation obtained as a function of temperature for low molecular weight thermoplastic material with the loss peak attributed to gelation (t_{gel} = time of gelation) observed during isothermal cure of a thermosetting system (7). Similarly it has been shown (7) that the $T_{ll}(>T_g)$ relaxation of low molecular weight thermoplastic material corresponds to a second maximum in Δ sometimes observed on isothermal cure after the "apparent" gel peak and before vitrification. The importance of these loss maxima to thermoset processing is obvious since they occur during the transformation from fluids to intractable products. It follows from the coincidence of the isothermal relaxations with the T_{ll} and T'_{ll} relaxations that these loss maxima observed in thermoplastics should bear on their processing.

Since different thermomechanical spectra have been observed after curing isothermally at different temperatures to the peak of the loss maximum which has been used to approximate gelation (7), it follows (assuming the absence of competing network-forming reactions) that this loss maximum does not correspond to the theoretical gel point which is defined as an isocompositional state. It can be demonstrated that if t_{gel} as determined by torsional braid analysis represents an isoviscous state then an Arrhenius plot of $\log t_{gel}$ vs $1/T$ ($^{\circ}\text{K}$) will give a straight line over a significant temperature range. This has been done by applying an empirical time-temperature-viscosity model that has been used to pre-

dict the change in viscosity of a curing system (8). This model, reduced to isothermal conditions, has been used by many workers (9).

The viscosity model is expressed for isothermal curing conditions as follows:

$$\ln \eta(t) = \ln \eta_{\infty} + \Delta E_{\eta}/RT + tk_{\infty} e^{-\Delta E_k/RT} \quad (1)$$

where $\eta(t)$ = viscosity at time t (s), η_{∞} = calculated viscosity of the initial material at $T = \infty$, cps, T = temperature, °K, ΔE_{η} = Arrhenius activation energy for the viscosity, cal/mole, R = gas constant = 1.987 cal/mole °K, k_{∞} = calculated kinetic constant at $T = \infty$, s⁻¹, and ΔE_k = Arrhenius "apparent" activation energy for the chemical reactions, cal/mole.

If a given isoviscosity level, η , is selected and the log of predicted time to that viscosity vs $1/T$ (°K) is plotted, the data can often be fitted with a straight line over a significant temperature range. See Fig. 12 (10). Furthermore, the fit becomes better as the viscosity range traversed (from zero time to the end point) increases. This can be accomplished by choosing a higher cure temperature (lower initial viscosity) or a higher viscosity end point. As the fit improves, the activation energy from the log t_{gel} vs $1/T$ curve approaches the "apparent" chemical activation energy in the viscosity model.

As the temperature for isothermal cure is reduced, the zero time viscosity approaches the assigned viscosity level and " t_{gel} " goes to zero. At higher temperatures, " t_{gel} " goes through a maximum and then decreases. It is in this decreasing region where the linear fit holds (Fig. 12).

From this analysis, it appears that if t_{gel} is an isoviscous state, linear Arrhenius plots can be obtained. Furthermore if the viscosity level detected for t_{gel} is sufficiently high, it is close enough to the true gel point to be representative. As with all mechanical measurements of gelation, one depends upon a viscosity measurement. Rising bubbles, tack tests and viscosity-time measurements all provide similar approximations. As a matter of fact, the SPI Prepreg Reinforced Plastics Committee Test Method: Prepreg 3—Measurement of Gel Time of Preimpregnated Inorganic Reinforcements (New York, May, 1960) was found to provide gel times corresponding to 120,000-140,000 cps (9).

It follows from the above reasoning that since, in practice, low molecular weight material is processed with thermosets and high molecular weight material is generally processed with thermoplastics that T'_u and T_u are relevant to the processing of thermosets whereas T_u is especially relevant to the processing of thermoplastics (7, 11).

GEL TIMES FROM ISOVISCOSITY DATA

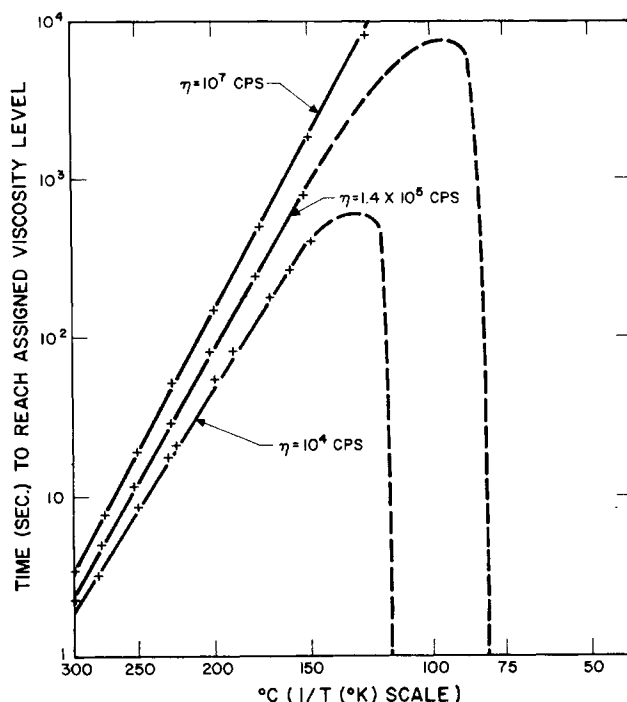


Fig. 12. Calculated times to attain specified viscosities (η) vs $1/T$ (°K) using the empirical time-temperature-viscosity relationship (see text). Activation energies calculated from the left side (higher temperatures) approach the assigned chemical activation energy (21,900 cal/mole) as the specified viscosity level increases. The points on the linear sections were used to calculate least mean square activation energies: 18,075 cal/mole for $\eta = 10,000$ cps; 19,180 cal/mole for $\eta = 140,000$ cps; and $\eta = 20,325$ cal/mole for $\eta = 10,000,000$ cps. $\eta \approx 140,000$ cps is an estimate for the viscosity at T'_u (see text), whereas $\eta \approx 10,000,000$ cps is an estimate for the viscosity at T_u (11).

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