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THE FORMATION AND PROPERTIES OF NETWORK POLYMERIC MATERIALS

by

J. K. Gillham

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Polymer Materials Program
Department of Chemical Engineering
Princeton University
Princeton, N. J. 08540

March 1978

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THE FORMATION AND PROPERTIES OF NETWORK POLYMERIC MATERIALS

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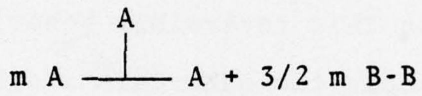
Polymeric materials are of two types, thermoplastics and thermosets. Unlike thermosets, thermoplastics (e.g., polyethylene, polystyrene, and polyvinyl chloride) soften and flow on heating and, when cooled, can return to their original state. The techniques of processing them (e.g., injection molding 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 may 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,



$$m\ \mathrm{A}\!-\!\overset{\mathrm{A}}{\overset{|}{-}}\!-\!\mathrm{A} + 3/2\ m\ \mathrm{B\text{-}B}$$

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 reaction which converts 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. It is associated with a dramatic increase in viscosity and a corresponding decrease in processibility that occur at a calculable degree of reaction for the particular reactive system. On the molecular level, this corresponds to the incipient formation of branched molecules of mathematically infinite molecular weight. 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 (Figure 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.

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 prevent further reaction. The overall transformation from liquid to gel to rubber to glass due to chemical reaction is termed "cure".

An automated torsion pendulum has been developed which permits monitoring of the changes which occur throughout cure (1). A composite specimen is made by impregnating a glass fiber braid with a solution of the reactive system and removing the volatile solvent. After mounting the specimen, the pendulum is intermittently set into oscillation to generate a series of freely damped waves. The character of each of these waves changes throughout cure. Two mechanical functions, rigidity and damping, are obtained from the frequency and damping constants which characterize each wave. A schematic diagram of the pendulum is shown in Figure 2.

The experimental results for the cure of an epoxy system at a series of constant temperatures were used to obtain the gelation time and the vitrification time versus 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 Figure 3 which results from an isothermal experiment at an intermediate temperature). Results derived from a family of isothermal plots are summarized in Figure 4 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 (Figure 3). The time to gelation decreases exponentially with temperature since the degree of reaction at the point of gelation is constant. In contrast, it is noted that the time to vitrify passes through a minimum which occurs at intermediate temperatures of cure. 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} (Figure 4). Vitrification can occur before gelation ($T_{cure} < T_{gg}$) simply by an increase of molecular weight. Gelation occurs without vitrification when cure is performed above the maximum softening point, the maximum glass transition temperature $T_{g\infty}$ of the system (Figure 4). 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 will equal the temperature of cure. The vitrification curve therefore gives the time to reach the softening 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 Figure 4 summarizes much of the behavior of the 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 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 (Figure 4), 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 (Figure 4) explains a number of practices in the field of thermosets. Examples follow.

1) Finite versus 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 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.

3) Influence of reactants: 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 need not have a measurable glass transition temperature. In contrast, if $T_{g\infty}$ is below room temperature, the polymer system will be used as an elastomer.

An understanding of the relationships between bulk properties and molecular architecture is a major goal of applied polymer science. A project is under way (2) to pursue this quest for thermosets using as manipulable parameters gelation, vitrification, T_{gg}, and $T_{g\infty}$, which depend on molecular considerations. This will involve juxtaposing the chemistry, characterization, processing, and properties of thermosetting materials.

The following example (2) 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 mechanical properties. The gelation time can be varied by catalysts and temperature.

The effect of level of catalyst on the thermomechanical behavior (rigidity and damping versus temperature) obtained after complete cure of a single rubber-modified system is made evident by comparison of Figure 5 (no catalyst) and Figure 6 (with catalyst). In particular, the glass transition of the rubbery phase is more dominant for the sample cured without catalyst and therefore with 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. Similarly, the lower the temperature of cure the longer the gelation time and the larger the size of the rubber domains. The relationship between cure temperature, gelation time, and morphology is summarized schematically in Figure 7, which demonstrates how a single chemical composition can produce distinctly different morphologies which in turn are responsible for distinctly different macroscopic behavior.

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 occurs 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.

There has been much art in industrial practice with these complex systems. The present article outlines an attempt to understand and logically exploit some of the underlying phenomena.

REFERENCES

1. "A Semimicro Thermomechanical Technique for Characterizing Polymeric Materials: Torsional Braid Analysis", J. K. Gillham, American Institute of Chemical Engineers Journal, Vol. 20, No. 6, pp. 1066-1079 (1974).

2. "Characterization of Thermosetting Epoxy Systems using a Torsional Pendulum", J. K. Gillham, C. A. Glandt, and C. A. McPherson, in Chemistry and Properties of Crosslinking Polymers (Ed. S. S. Labana), Academic Press, New York, New York, pp. 491-520, 1977.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

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

Figure 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 XYY plotter (1).

Figure 3. Mechanical rigidity and mechanical damping versus time during cure of an epoxy at a constant temperature ($T_{gg} < T_{cure} < T_{g\infty}$). The first peak in the damping curve represents gelation, the second vitrification. [Rigidity = $1/P^2$, where P is the period of oscillation in seconds. Damping = Δ = natural logarithm of the ratio of consecutive amplitudes of a freely decaying wave.]

Figure 4. Time to gel and time to vitrify versus 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.

Figure 5. Epoxy/rubber system. 0 parts per hundred catalyst. Thermomechanical behavior after cure. Experimental details and a summary of the transitions appear in the figure.

Figure 6. Epoxy/rubber system. 0.5 parts per hundred catalyst. Thermomechanical behavior after cure. Compare the intensities and temperatures of the rubber glass transition (${}_{\text{Rubber}}T_g$) and epoxy glass transition (${}_{\text{Epoxy}}T_g$) of the thermomechanical spectra of Figures 5 and 6.

Figure 7. Development of a two-phase rubber-modified epoxy system versus gelation time. 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).

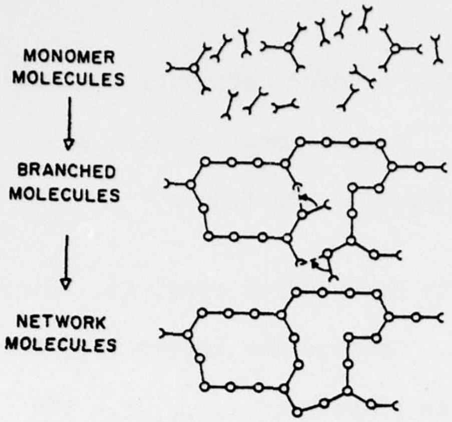

Fig. 1

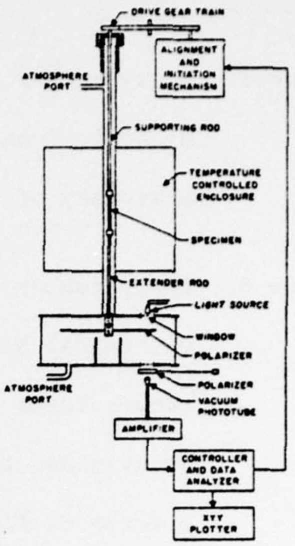

Fig. 2

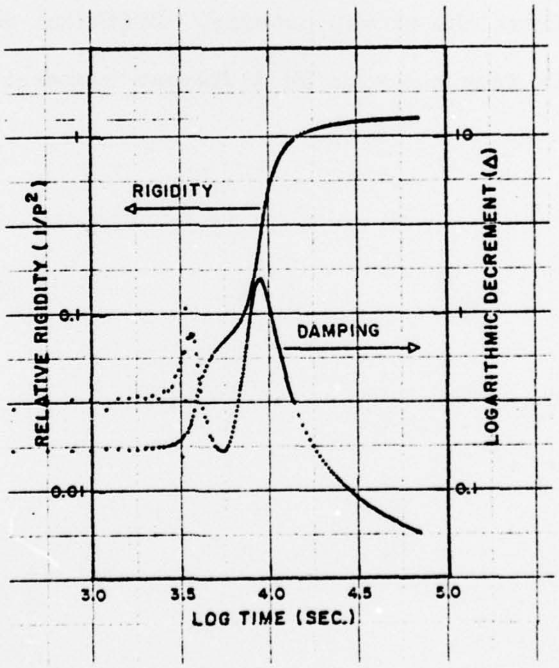

Fig. 3

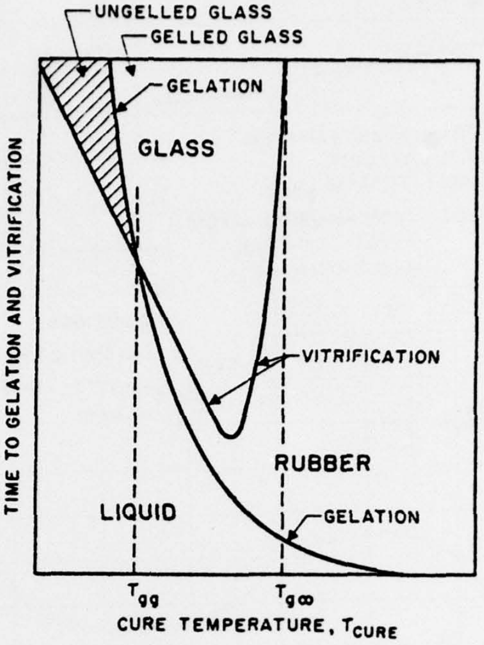
UNGELLED GLASS
GELLED GLASS
GELATION
GLASS
TIME TO GELATION AND VITRIFICATION
VITRIFICATION
RUBBER
LIQUID
GELATION
T_{gg}
$T_{g\infty}$
CURE TEMPERATURE, T_{CURE}

Fig. 4

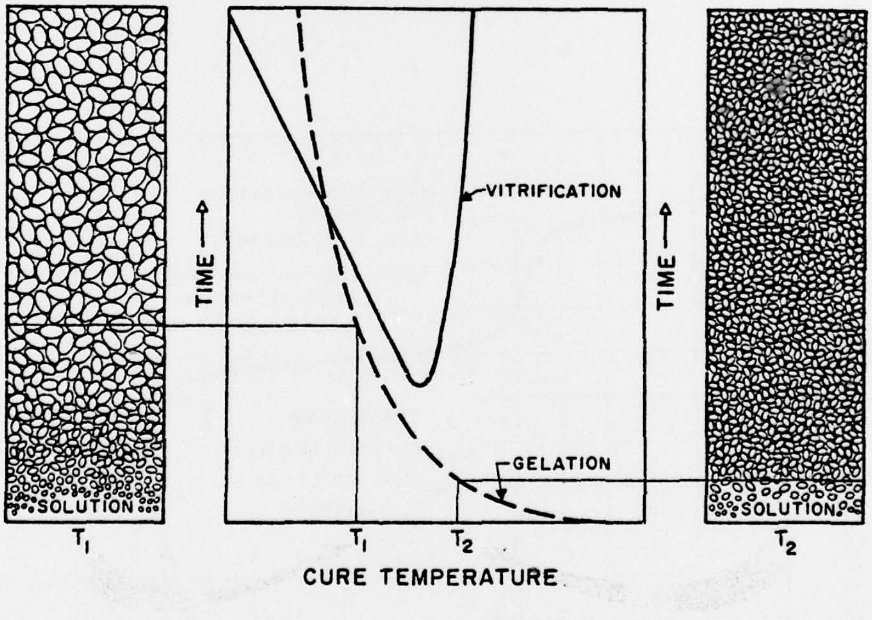
TIME
VITRIFICATION
GELATION
SOLUTION
T_1
T_1
T_2
CURE TEMPERATURE
TIME
SOLUTION
T_2

Fig. 7

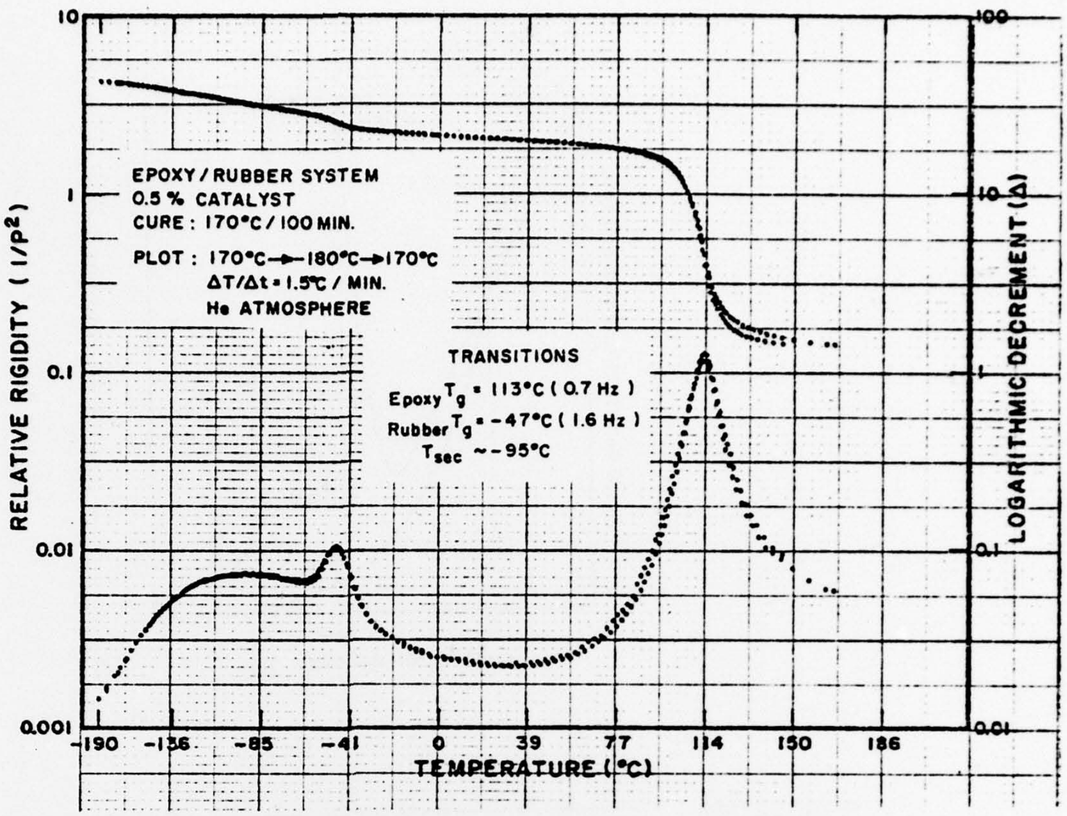
EPOXY / RUBBER SYSTEM
0.5 % CATALYST
CURE : 170°C / 100 MIN.
PLOT : 170°C → -180°C → 170°C
ΔT/Δt = 1.5°C / MIN.
He ATMOSPHERE
TRANSITIONS
Epoxy Tg = 113°C (0.7 Hz)
Rubber Tg = -47°C (1.6 Hz)
Tsec ~ -95°C
RELATIVE RIGIDITY (1/P²)
LOGARITHMIC DECREMENT (Δ)
TEMPERATURE (°C)
10
1
0.1
0.01
0.001
100
10
1
0.1
0.01
-190
-136
-85
-41
0
39
77
114
150
186

Fig. 5

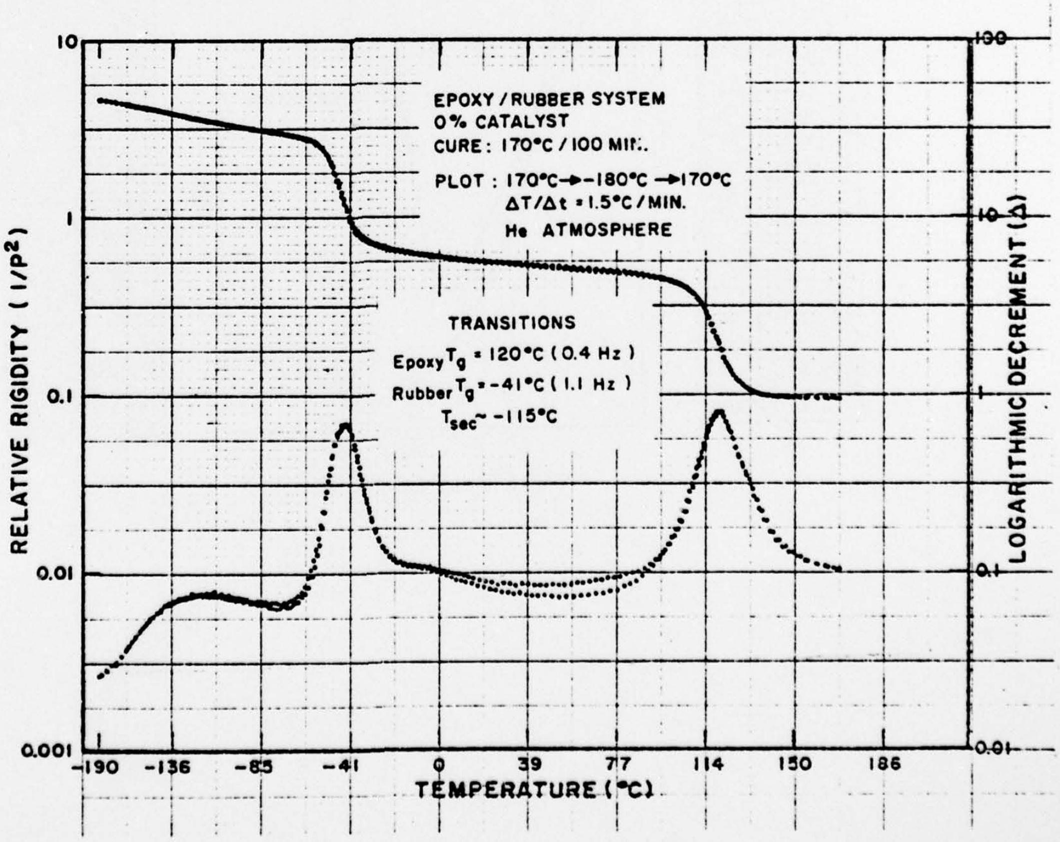
EPOXY / RUBBER SYSTEM
0% CATALYST
CURE : 170°C / 100 MIN.
PLOT : 170°C → -180°C → 170°C
ΔT/Δt = 1.5°C / MIN.
He ATMOSPHERE
TRANSITIONS
Epoxy Tg = 120°C (0.4 Hz)
Rubber Tg = -41°C (1.1 Hz)
Tsec ~ -115°C
RELATIVE RIGIDITY (1/P²)
LOGARITHMIC DECREMENT (Δ)
TEMPERATURE (°C)
10
1
0.1
0.01
0.001
100
10
1
0.1
0.01
-190
-136
-85
-41
0
39
77
114
150
186

Fig. 6

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	Torsional Braid Analysis

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A general model for thermosetting materials which relates polymerization to properties is discussed. In particular a phase diagram shows how the four states of matter encountered, (i.e. liquid, rubber, ungelled glass and gelled glass) relate to gelation and vitrification phenomena. The model is extended to rubber-modified thermosetting systems where evidence is presented to show, by control of the time to gelation, a given chemical formulation can provide different morphologies and hence different material behavior.

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