Relationship between Viscoelastic Properties and Gelation in Thermosetting Systems

CHIANG-YING M. TUNG and PAUL J. DYNES, *Rockwell International Science Center, Thousand Oaks, California 91360*

Synopsis

A method is described for determining from dynamic viscoelastic data the gel time of thermosetting resins. Gelation of nine systems including epoxies, acetylene-terminated sulfone, and silicones was correlated with the crossover of the dynamic storage G' and loss G'' moduli measured during isothermal curing. The effect of measurement frequency on gel time is discussed and related to the standard gel test. A lower temperature limit for the valid aplication of this technique was found to be at $T > T_{gg} + 30°C$, where T_{gg} is the glass transition of the system at the gel point.

INTRODUCTION

One of the most important factors influencing the processing of thermosetting resins is gelation. When gelation initiates, resin viscosity rises exponentially and thus has a marked effect on operations such as injection molding or autoclaving. A typical method for determining time to gelation is by a standard ASTM test,[1] which is based on steady-state viscosity.

A schematic representation for the cure behavior of a thermosetting system is shown in Figure 1. The entire polymerization process can be divided into two parts separated by the point of gelation. Depending on the temperature and degree of cure, four physical states can be observed.[2] They are liquid, ungelled glass, rubber, and gelled glass. Steady-state viscosity measurements only characterize the liquid state. Characterization of the rubbery and glassy states can be made with dynamic mechanical techniques. A disadvantage of the dynamic mechanical approach, however, is that gelation is not clearly observed. The objective of this study was to demonstrate the relationship between dynamic viscoelastic properties and gelation and to determine the applicability and limitations of the simple criterion for measuring the time to gelation in curing thermosetting systems.

EXPERIMENTAL

Four different types of resin were examined in this study. They were: (I) dicyandiamide (DICY)-cured, diglycidyl ether of bisphenol A (DGEBA) based, B-stage epoxy resins, (II) DICY-cured, diglycidyl ether of tetrabromobisphenol A (brominated DGEBA) based, B-stage epoxy resin, (III) acetylene terminated sulfone (ATS), and (IV) room temperature curing silicone resins. All resins were stored in a freezer to inhibit resin advancement. Resins (I) and (II) are commercially available as glass fiber reinforced prepregs used to fabricate printed wiring boards. The brittle B-stage resins were fractured mechanically and isolated from the glass fiber in powder form and pressed into pellets before use.

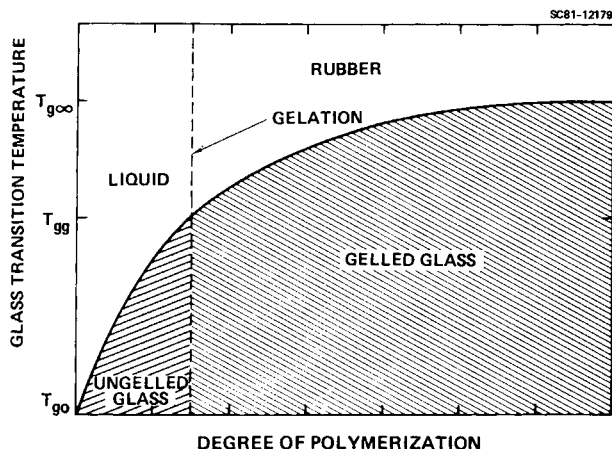CCC 0021-8995/82/020569-06$01.00

Fig. 1. Glass transition temperature vs. degree of polymerization for a thermosetting system.

Resin (III) is an experimental composite matrix resin developed by the Air Force and prepared by Gulf Research and Development Company, Pittsburgh, Pennsylvania. Resins (IV) are standard General Electric RTV silicones.

Dynamic mechanical measurements were performed on a Rheometrics, Inc. Visco-Elastic Tester. A sample thickness of 0.5 mm was used with two 25-mm diameter parallel plates. The upper plate was driven in an oscillatory motion to deform the sample sinusoidally. An initial strain amplitude of 10% at the edge of platens was reduced during cure to ensure a linear viscoelastic response. Elevated temperature experiments were conducted in a forced convection oven, using a dry nitrogen stream. The effect of frequency was studied over the range from 10 to 100 rad/s.

A modification of the standard ASTM gel time test, in which the resin sample was placed in a sample container equilibrated at the test temperature, was used. A wooden stick was used to stir the resin constantly with a slow circular motion. The gel point is the exact point at which the resin turns from a viscous liquid to an elastomer having a memory. The gel time was recorded as the elapsed time from the start of mixing to the gel point.

RESULTS AND DISCUSSION

Viscoelastic Properties and Gelation

The dynamic mechanical properties of the 171°C isothermal cure of a DICY crosslinked epoxy resin is shown in Figure 2. This cure temperature is above the maximum glass transition temperature of the fully cured resin ($T_{g\infty}$ = 132°C). Initially, the dynamic moduli increase sharply and then gradually level off as the cure approaches completion. The storage modulus, G', despite a lower initial value, attains a higher maximum at the end of the cure cycle. The two modulus curves intersect, i.e., ($G' = G''$ or tan δ = 1) at t = 1.8 min. A second example is shown in Figure 3 for the cure behavior of acetylene terminated sulfone (ATS) at 150°C. The resin remains a low-viscosity liquid below the sensitivity limits of the instrument until a rapid increase in the storage modulus G' occurs around 53 min. The two modulus curves cross at t = 59 min.
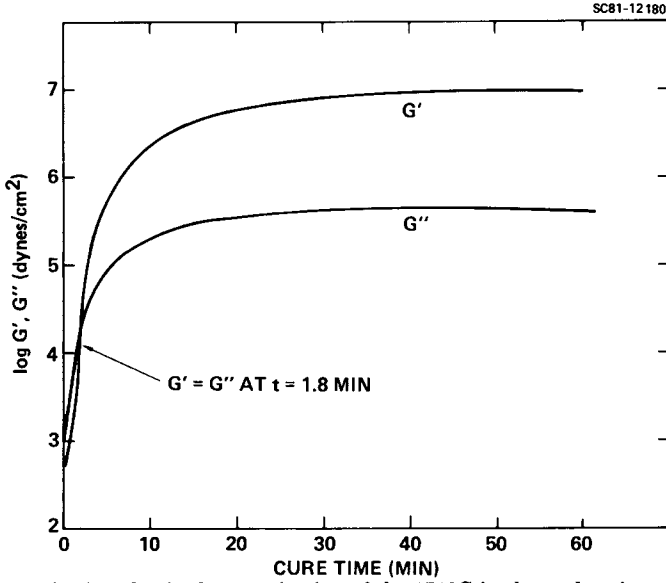
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Fig. 2. Dynamic viscoelastic characterization of the 171°C isothermal curing of a DICY cured epoxy resin at 10 rad/s and 10% strain.

The dynamic data shown here do not appear to provide a clear indication of gelation in these resins. It was found, however, that the time to reach the modulus crossover point (i.e., tan δ = 1) coincides with the gel time as measured by the standard gel time test. Further examples of this correlation are shown in Figure 4 for a variety of crosslinking systems varying widely in gel time.

This correlation suggests a loss tangent (tan δ) of unity at the gel point. Loss tangent, being the ratio of energy lost to energy stored in a cyclic deformation
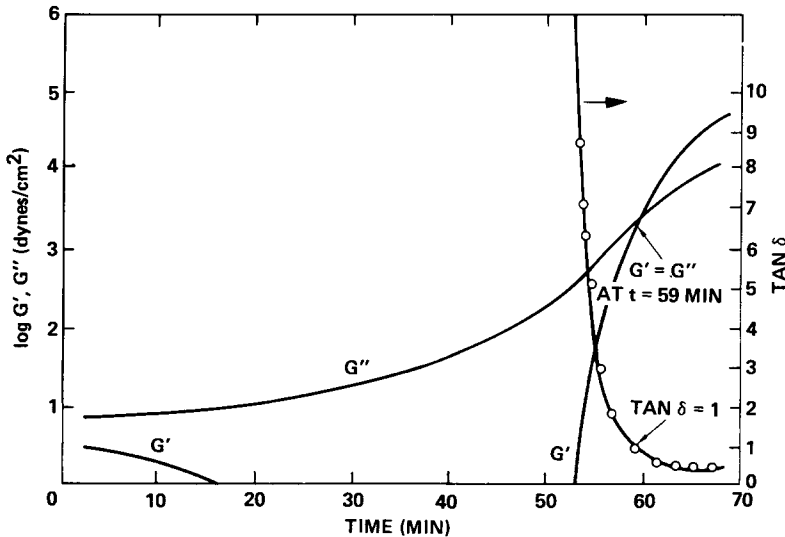

Fig. 3. Dynamic viscoelastic characterization of the 150°C isothermal curing of ATS resin at 10 rad/s and 10% strain.
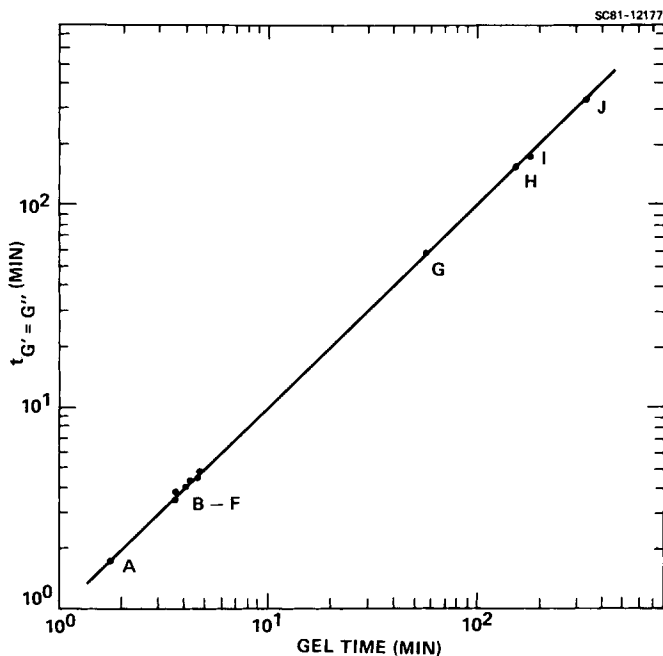
Fig. 4. Correlation of gel time and time of modulus crossover of thermosetting resins. (A) brominated epoxy, T_{cure} = 171°C; (B)–(F) epoxy, T_{cure} = 171°C; (G) ATS, T_{cure} = 150°C; (H)–(J) silicones, T_{cure} = 25°C.

(tan $\delta = G''/G'$), measures the relative contribution of elasticity and viscosity of a resin system.   Tan δ of a viscous liquid should therefore be greater than 1, while that of an elastic solid should be less than 1.   When the cure temperature is above T_{gg}, resin systems proceed from a viscous liquid through gelation to elastic solid (rubber or glass) (Fig. 1).   Under these conditions, tan δ of gelation, the transition state between viscous liquid and elastic solid, would be expected to be equal to 1.

Effect of Measurement Frequency

The frequency dependence of the time to gelation ($t_{G'=G''}$) is shown in Figure 5 for the isothermal cure of an epoxy resin.   An approximately 1-min increase in gel time is shown for each decade increase in frequency.   This result is analogous to the increase in glass transition temperature with higher frequency observed for most polymers.[3]   In an isothermal cure, increasing the frequency produces a higher T_{gg} which results in a longer time to gel.

The best agreement between the dynamic gel time test and the standard steady-state gel time test is at a frequency of 10 rad/s.   It has been established[4] that when angular frequency is expressed in rad/s and the amplitude of oscillation is small, angular frequency is the same as the steady-state shear rate expressed in s⁻¹.   A frequency of 10 rad/s (1.6 Hz) corresponds most closely to the shear rate used in the standard gel test.   This could account for the best agreement in the gel time measurement described above.
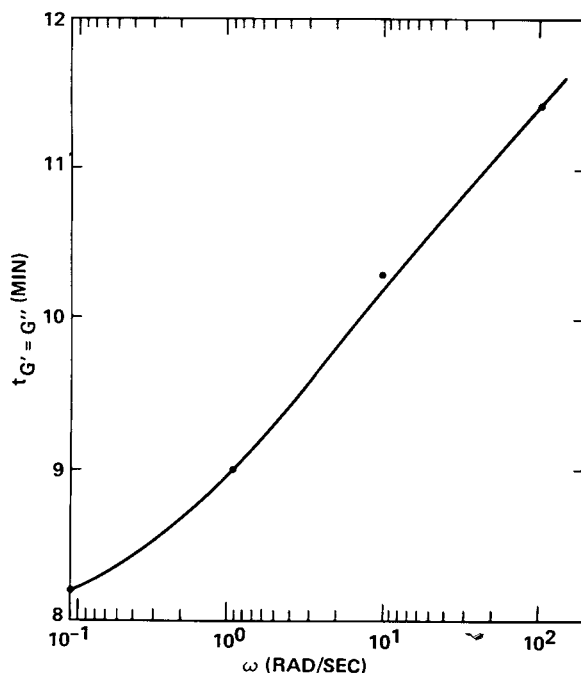
Fig. 5. Frequency dependence of time of modulus crossover of a brominated epoxy resin.

Effect of Cure Temperature

The temperature at which the measurement is performed is a second factor of importace to the validity of this criterion for gelation. In torsion braid studies of thermoset curing, Babayevsky and Gillham[5] showed that a test temperature of $T > T_{gg}$ is necessary if gelation is to be observed without the influence of vitrification which occurs at $T \simeq T_{gg}$. Because gelation represents a specific extent of reaction, the temperature dependence of the time to gel should be described by the Arrhenius equation. The gel time as determined from the time at which $G' = G''$ is plotted vs. reciprocal temperature in Figure 6. At temperatures above 120°C a linear relation is obtained, the slope of which defines the activation energy of $E_a = 18.6$ kcal/mol. This is in good agreement with that reported[6] for similar DICY-cured epoxy systems. The important feature of this curve is that below 120°C the indicated gel time decreases from the predicted by the linear portion of the curve. This is contrary to the increase in gel time expected as the cure temperature approaches T_{gg}.[2] An explanation of this behavior is that as the cure temperature approaches T_{gg} the storage modulus G' rises. This is not a result of gelation, but rather is due to onset of vitrification. The T_{gg} of this resin system was found to be 90°C, determined by differential scanning calorimetry. Therefore, the limit of validity for application of this method appears to be temperatures approximately 30°C greater than the glass transition at the gel point.
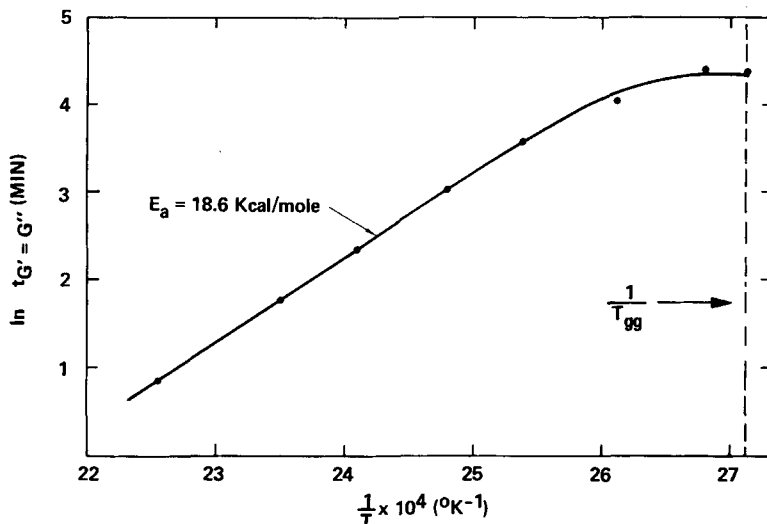
Fig. 6. Arrhenius plot: ln $t_{G'=G''}$ vs. $1/T$ (°K) for the brominated epoxy/DICY system (T_{gg} = 90°C).

CONCLUSION

A correlation between time of isothermal modulus crossover ($t_{G'=G''}$) and isothermal gel time measured by standard method is established. This correlation provides a more precise means to determine the gel point. The time of modulus crossover is frequency and cure-temperature-dependent. Best agreement between the steady state gel test and the dynamic measurement is found when frequency is near 10 rad/s and cure temperature is at least 30°C above T_{gg}.

The modulus crossover point is where the damping factor equals unity, and therefore it can be used to detect the occurrence of gelation in curing thermosetting systems. It is more precise and free of operator error than the conventional method. The modulus at the crossover point also provides an insight into the polymeric network at the onset of the crosslinking process.

References

1. ASTM D2471-71, "Gel Time and Peak Exothermic Temperature of Reacting Thermosetting Resins" (1971).

2. J. K. Gillham, "A Generalized Time-Temperature-Transformation Phase Diagram for Thermosetting Systems," TR-18, Office of Naval Research, Washington, D.C., Contract N00014-76-C-0200, 1979.

3. L. E. Neilson, in *Mechanical Properties of Polymers*, Reinhold, New York, 1962, pp. 161–162.

4. R. M. Schulken, R. H. Cox, and L. A. Minnick, *J. Appl. Polym. Sci.*, **25**, 1341 (1980).

5. P. G. Babayevsky and J. K. Gillham, *J. Appl. Polym. Sci.*, **17**, 2067 (1973).

6. T. Olcese, O. Spelta and S. Vargiu, *J. Polym. Sci. Symp.*, *No. 53*, **113**, (1975).