Novel Technique for Following the Rigidity Changes Accompanying the Curing of Polymers

ARMAND F. LEWIS and JOHN K. GILLHAM

Central Research Division, Chemical Research Department, American Cyanamid Company, Stamford, Connecticut

Techniques which have been used in the attempt to follow the curing cycle of a reacting polymer system include those based on refractive index,[1] electrical properties,[2,3] infrared spectroscopy,[4] dilatometry,[5] velocity of ultrasonic vibrations,[6] and reaction exotherms.[7] However, each has certain limitations with respect to general utility. Recent attempts have been made to follow curing by dynamical mechanical methods.[8] Kline[9] reported on the mechanical behavior of some epoxy resins during cure at test frequencies between 700 and 1000 cycles/sec. However, due to experimental limitations, the initial liquid–solid transition region was not included.

The present communication describes a simple technique which follows the rigidity changes which occur during the complete liquid–solid transition of a curing polymer. A modified torsion pendulum is used in which an inertial mass is supported by a fine fabric (nylon) braid which is saturated with the liquid polymer formulation to be tested. Changes in the frequency of free vibration of an inertia disk are observed as the polymer cures. These changes subsequently reflect the rigidity characteristics of the reacting polymer which inhabits the interstices of the braid.

According to classical physics, the rigidity modulus G of a shaft of uniform composition (length l and radius r) can be determined from the resonance frequency f of free torsional vibration of an inertial mass (moment of inertia $= I$) by use of the equation

$$G = 8\pi \; lf^2 I / r^4$$

Since the present experimental system is composed of a heterogeneous supporting member (nylon braid-filled polymer rod), this equation is not strictly applicable. However, it can be used to follow, qualitatively, the mechanical properties of the curing polymer. This equation was, therefore, employed in this work, but to avoid ambiguity, the rigidity term was defined as an apparent rigidity modulus and was given the symbol $\bar{G}$. In a further development, a process to normalize the data was used so as to render them somewhat more fundamental. To this end, the ratio $\bar{G}/\bar{G}_0$ was introduced, where $\bar{G}_0$ is the value of the apparent rigidity modulus extrapolated to initial behavior. This parameter, which can be referred to as the relative rigidity, may partially overcome the objections of using an absolute (classical) equation to describe an apparent rigidity modulus. Of major significance, the relative rigidity is independent of the geometry of the system (i.e., l, r, and I), and thus eliminates any problems which may arise in experimentally interpreting these quantities.

The apparatus, shown in Figure 1, consists of of cylindrical glass column constructed so as to enclose the test specimen and inertial mass under a controlled atmosphere throughout the experiment. The column is kept at a constant temperature with a circulating fluid, thermostatic jacket assembly. Torsional vibrations are manually induced at various intervals of time during curing. This is done by rapidly twisting the attached end of the specimen through an arc, via the well lubricated standard taper ground glass joint at the top of the column; and then stopping abruptly. Free vibrations are, therefore, induced into the inertia disk by reactance.

Throughout these measurements the maximum torsional strain induced into the supporting member was less than 0.5%. The time required to complete one cycle (period) was easily measured with a stop watch by averaging the time lapse for a number of swings of the pendulum. In the experiments a nylon braid (25 lb. test squidding line)
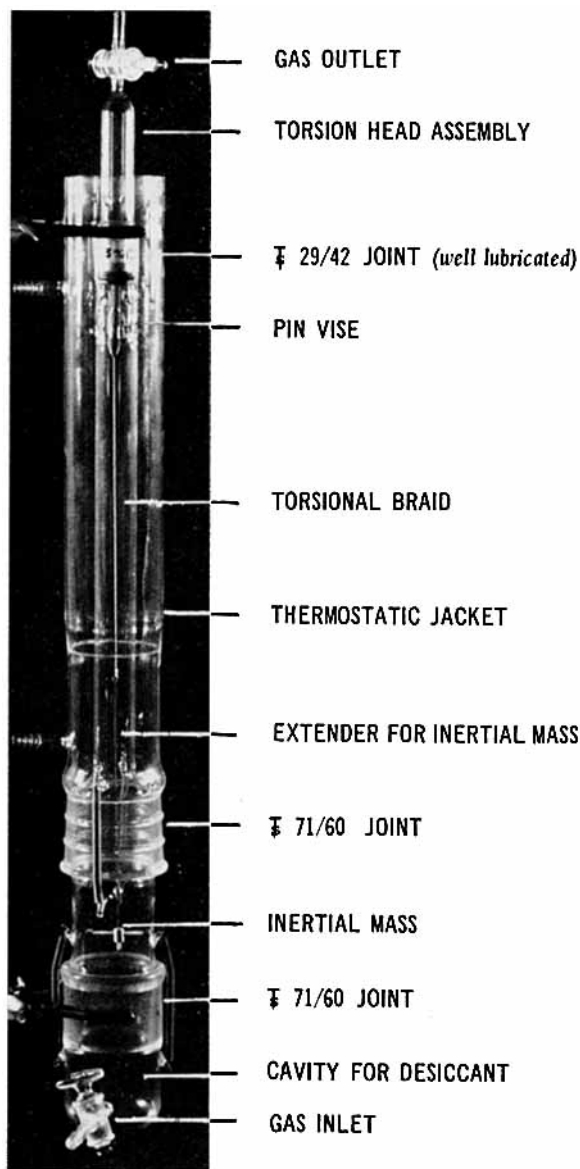
Fig. 1. Torsional braid apparatus.

gives an indication of the mechanical properties of the final product. The crosslinking reactions of the epoxy resin and linseed oil were followed without difficulty. On the other hand, during the polymerization of methyl methacrylate, evaporation from the braid during the early stages was reduced by keeping the braid in contact with catalyzed monomer. Furthermore, the braid was recoated with the reacting monomer liquid just prior to gelation. The solvent evaporation system, although not strictly a chemical curing reaction, was included for comparison. Note that in this case, no induction period is observed.
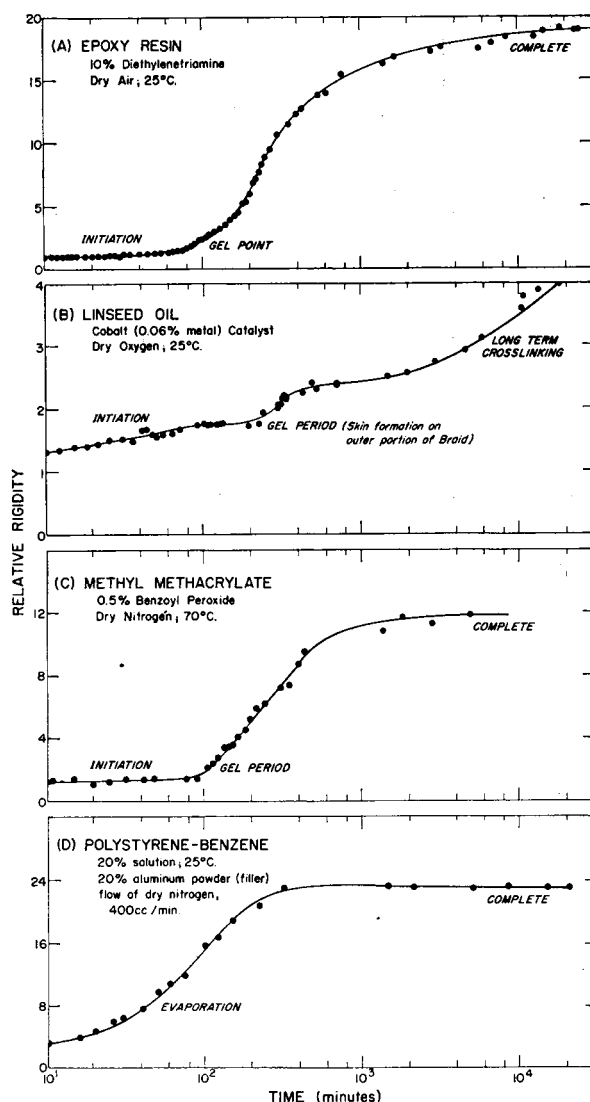

Fig. 2. Relative rigidity curves for several polymer systems: (A) epoxy resin; (B) linseed oil; (C) methyl methacrylate; (D) polystyrene–benzene.

was used as the support for the inertia disk. Its length was approximately 34 cm. for all the runs. The radius of the coated braid was not deliberately controlled and in some cases was not uniform. This was in consequence of beading, shrinkage, and uneven application of the resin. However, the influence of these inconsistencies was minimized by the introduction of the relative rigidity parameter.

Typical experimental results with several thermosetting and thermoplastic resin systems are presented in Figure 2. It is of general importance to point out that this method not only follows the kinetics of the complete curing reaction but also

From a review of the data presented, it is evident that the torsional braid rigidity apparatus has an exceptionally broad scope of utility for polymerization studies. Tests to prove a theoretical link between these physical measurements and the chemical processes influencing them are presently being conducted.

References

1. Dannenberg, H., *SPE Journal*, **15**, 875 (1959).

2. Delmonte, J., *J. Appl. Polymer Sci.*, **2**, 108 (1959).

3. Warfield, R. W., and M. C. Petree, *J. Polymer Sci.*, **37**, 305 (1959).

4. Dannenberg, H., J. W. Forbes, and A. C. Jones, *Anal. Chem.*, **32**, 365 (1960).

5. Voeks, J. F., and R. A. Crane, *Anal. Chem.*, **31**, 1906 (1959).

6. Dietz, A. G. H., E. A. Hauser, F. J. McGarry, and G. A. Sofer, *Ind. Eng. Chem.*, **47**, 75 (1956).

7. Bengough, W. I., and H. W. Melville, *Proc. Roy. Soc. (London)*, **225A**, 330 (1954).

8. VanHoorn, H., and P. Bruin, *Paint Varnish Production*, **49**, 47, August 1959.

9. Kline, D. E., *J. Appl. Polymer Sci.*, **4**, 123 (1960); *J. Polymer Sci.*, **47**, 237 (1960).

Synopsis

A method is described for measuring the rigidity of a curing polymer system throughout its complete course of reaction (liquid to solid). In this technique, a braided fiber (nylon), impregnated with the polymer system to be studied, is used as the supporting member for a free, torsionally vibrating mass. From the frequency of the vibration, the apparent rigidity modulus $\bar{G}$ of the impregnated braid is calculated. The rigidity of the reacting polymer is thus followed nondestructively during the curing period. In a further development, the term relative rigidity $\bar{G}/\bar{G}_0$ is introduced to normalize the rigidity parameter to a more experimentally adaptable quantity. The curing behavior of several types of polymer is presented to illustrate the general utility of the method.

Résumé

On décrit une méthode pour mesurer la rigidité d'un système polymérique vulcanisable pendant la réaction complète de vulcanisation (passant de l'état liquide à l'état solide). Dans cette techique, une fibre tressée (nylon), impregnée du système polymérique étudié, est utilisé comme support de la masse vibrante libre soumise à torsion. A partir de la fréquence de vibration, on calcule le module de rigidité apparent $\bar{G}$ de la fibre impregnée. La rigidité du polymère réactionnel est ainsi suivie d'une façon non-destructive pendant la période de vulcanisation. Dans un développement ultérieur on introduit le terme de rigidité relative $\bar{G}/\bar{G}_0$ afin de normaliser le paramètre de rigidité par rapport à une quantité expérimentale plus adaptable. Le comportement pendant la vulcanisation de différents types de polymères est présenté afin d'illustrer l'utilité générale de cette méthode.

Zusammenfassung

Es wird eine Methode zur Messung der Steifheit eines Polymeren während der Härtung im gesamten Reaktionsverlauf (flüssig zu fest) beschreiben. Bei dieser Technik wird eine geflochtene Faser (Nylon), die mit dem zu untersuchenden Polymersystem imprägniert ist, als Träger für eine Masse verwendet, die freie Torsionsschwingungen ausführt. Aus der Schwingungsfrequenz wird der scheinbare Starrheitsmodul $\bar{G}$ des imprägnierten Bandes berechnet. Auf diese Art wird die Starrheit des reagierenden Polymeren zerstörungsfrei während der Härtungsperiode verfolgt. In einer Weiterentwicklung wird die relative Starrheit $\bar{G}/\bar{G}_0$ zur Normalisierung des Starrheitsparameters auf eine experimentell geeignetere Grösse eingeführt. Die allgemeine Verwendbarkeit der Methode wird anhand des Härtungsverhaltens einiger Polymertypen gezeigt.