Dielectric Properties of an Epoxy Resin During Polymerization

E. N. HARAN,* H. GRINGRAS,* and D. KATZ, *Scientific Department,
Israel Ministry of Defence, Tel Aviv, Israel*

Synopsis

Dielectric measurements were utilized in the investigation of the polymerization of
epoxy resin Epon 826 with diethylenetriamine (DETA) as the crosslinking agent. The
time variation of the dissipation factor and of the dielectric constant were measured
continuously, while the epoxy system was held at a constant temperature. A range of
11 frequencies (330 cycles/sec.–10 Mcycles/sec.) at three different polymerization
temperatures (30, 45, 60°C.) was covered. The test results are given as a set of curves
for the dissipation factor and the dielectric constant versus time. Nearly all the dissi-
pation factor curves have the same characteristic shape, with a well-defined minimum
(valley) followed by a maximum (peak). The dielectric constant falls monotonously
from a high initial value to a small final one that is specific for the fully cured resin.
If the time at which the dissipation factor reaches the valley t_v and the peak t_p are
plotted versus the logarithm of the frequency, two straight lines will be obtained.
Such a plot can be utilized as an aid in controlling the curing process of cast resins.

INTRODUCTION

The use of dielectric measurements in the investigation of polymeriza-
tion processes is relatively new and has been described in several recent
studies.[1-8]   Such measurements appear to be especially suitable for this
purpose because they are nondestructive, do not interfere with the process
itself, and are easily adaptable to continuous monitoring.   They could thus
be very useful for quality control during production processes requiring the
extraction of inserts (that will form internal cavities in the final product)
before the material is fully polymerized.   Of special importance would be
the application of this kind of measurements for the determination of the
gelation point of thermosetting resins or the end of the polymerization
process.

The change of the electrical properties during the polymerization has
been studied by a number of workers.[3-5]   It has, however, been indicated
by Warfield and Petree[5] that the slope of the resistivity versus time does
not change at the observed gelation point in the case of diallyl phthalate,
several epoxides, and polyesters.   Furthermore, resistivity measurements
in the range of 10^6–10^{15} ohms are not easily adapted to production tech-
niques which have to be simple, straightforward, and should not require
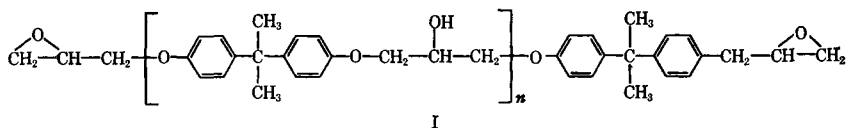
* Present address: Technion, Israel Institute of Technology, Haifa, Israel.

elaborate cleaning procedures. On the other hand, continuous measurements of the dissipation factor (or loss tangent) tan δ and of the dielectric constant ϵ appeared to be a worthwhile field of investigation, especially in the light of the work of Delmonte,[8] who suggested that the peak values of tan δ curves coincided with the formation of an infusible and insoluble gel due to molecular crosslinking.

EXPERIMENTAL

Materials

In all our investigations we used the same type of epichlorhydrin–bisphenol A epoxy resin, Shell's Epon 826, with diethylenetriamine (DETA) as the crosslinking agent. A 10% excess of reactive hydrogen above the quantity theoretically required to open all epoxy rings was added to ensure complete reaction. Epon 826 was chosen because its chemical structure is simple[4] and contains the largest amount of molecules represented by $n = 0$ in the general formula (I):

$$
\underset{\text{I}}{\text{CH}_2\text{—CH—CH}_2\left[\text{O—}\bigcirc\text{—}\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{—}\bigcirc\text{—O—CH}_2\text{—}\underset{\text{OH}}{\text{CH}}\text{—CH}_2\right]_n \text{O—}\bigcirc\text{—}\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{—}\bigcirc\text{—CH}_2\text{—CH—CH}_2}
$$

Thus the influence of the hydroxyl groups within the resin chain on the crosslinking mechanism of Epon 826 may be neglected, and the curing reaction can be represented solely by an interaction between the amine and the epoxy groups.

Measuring Cells

All experiments were carried out in glass cells specially prepared for the purpose. The cells described in the literature were either expensive to
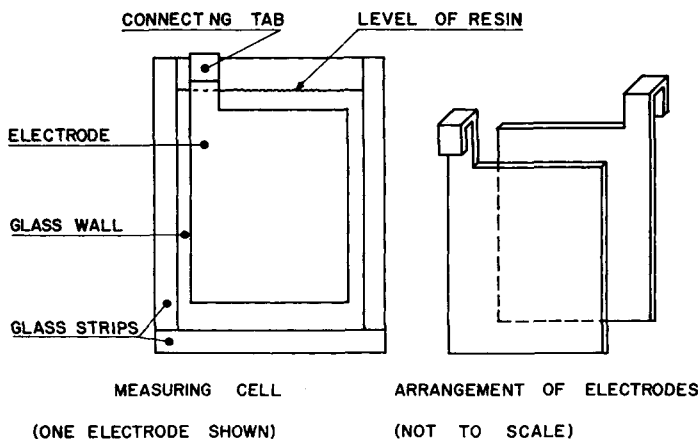

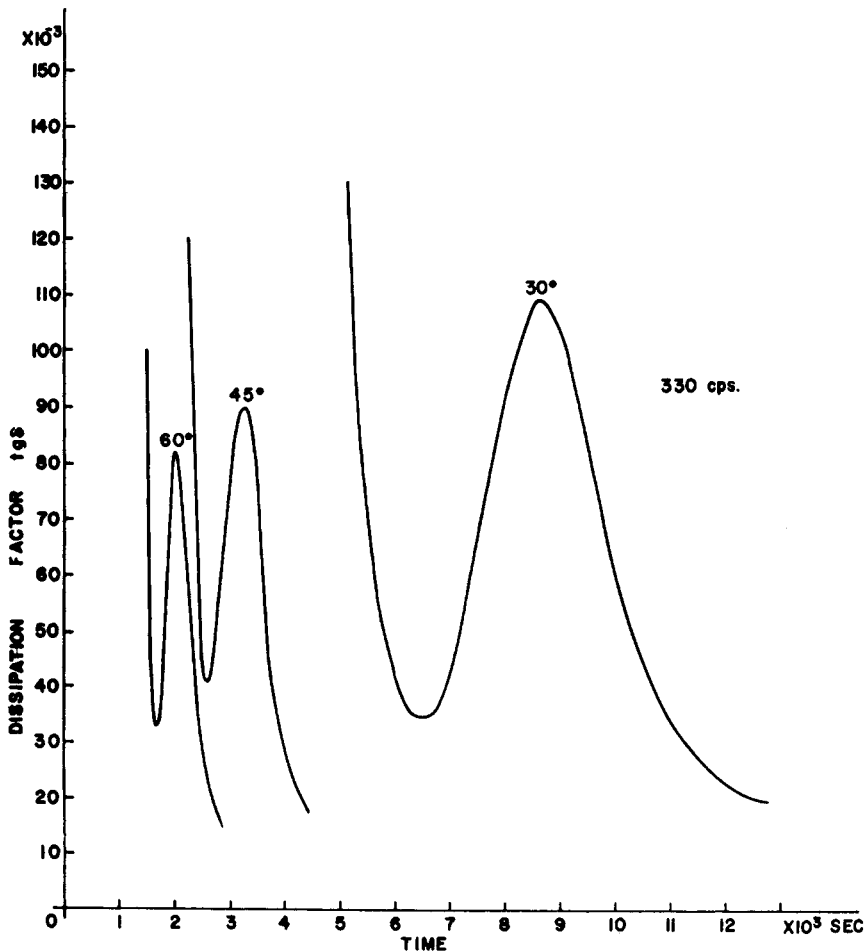Fig. 1. Construction of a measuring cell for isothermal polymerization.

Fig. 2a. See caption p. 3511.

construct[1] or had too low a capacitance.[8] The final design, which was adopted after some experiments with vacuum-deposited electrodes, is shown in Figure 1. Both electrodes, made of 0.1 mm. thick aluminum foil, were cemented to the inner surface of two glass plates; the connecting strips were bent around the upper edge and bonded to the outer surfaces of the glass plates. The cells for measurements up to 330 kcycles were made of used and cleaned 81 × 107 mm. photographic plates; cells for higher frequencies were half that size. The distance between the glass plates was fixed to 1.3 mm. by glass strips cut from the same material. Careful assembly with Eastman 910 adhesive ensured complete tightness of the cells.

Electrical Connections to the Cells

The capacity of the wires connecting the cell and the measuring instrument should be much smaller than that of the cell and their inductivity
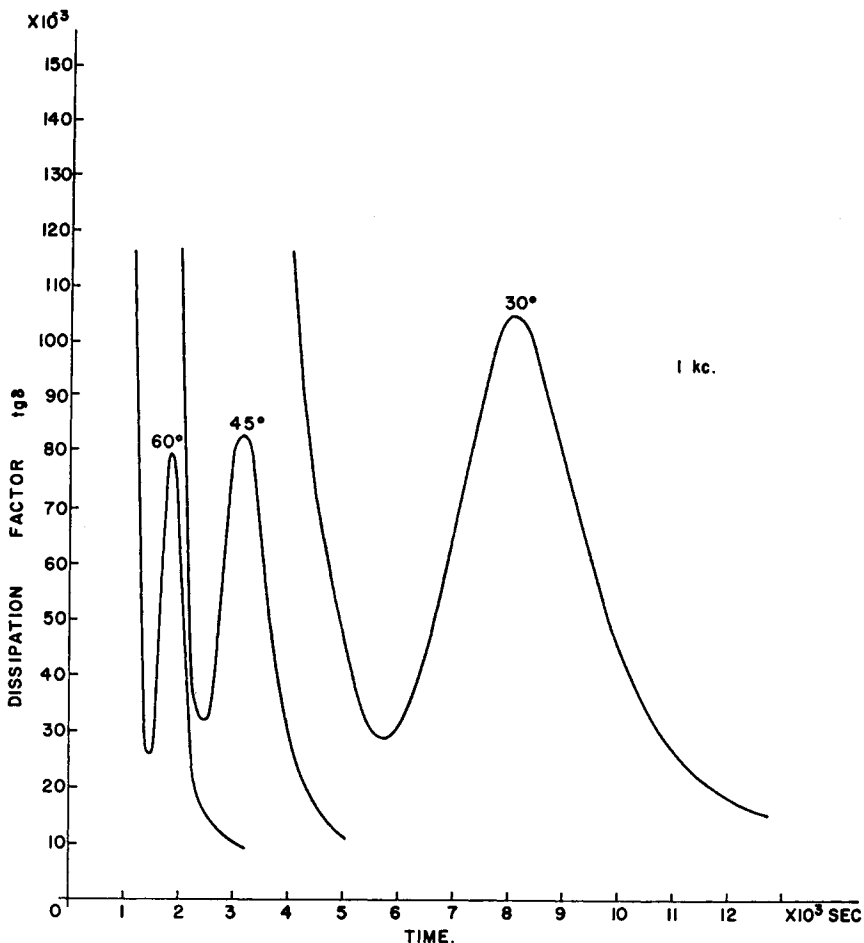
Fig. 2b. See caption p. 3511.

must be kept small for measurements at higher frequencies. Coaxial cables used in such setups were found to be unsuitable because their capacitance (20–90 pF./m.) was much too large as compared with that of an empty small (12 pF.) and an empty large cell (45 pF.). Very low capacitance with good electromechanical stability was achieved by means of a locally made twin-conductor open wire line (commercially available twin lines had too large a capacitance). The data for the line were: 80 cm. total length, 0.5 mm. conductor diameter, 16 mm. conductor spacing, 4.5 pF. capacitance, and 1.4 μhy. inductance. The line was connected to the cell by means of two standard alligator clips.

Range of Variables and Instrumentation

It was intended to cover as wide a range of variables as possible. The two main parameters, which were changed from one experiment to another,
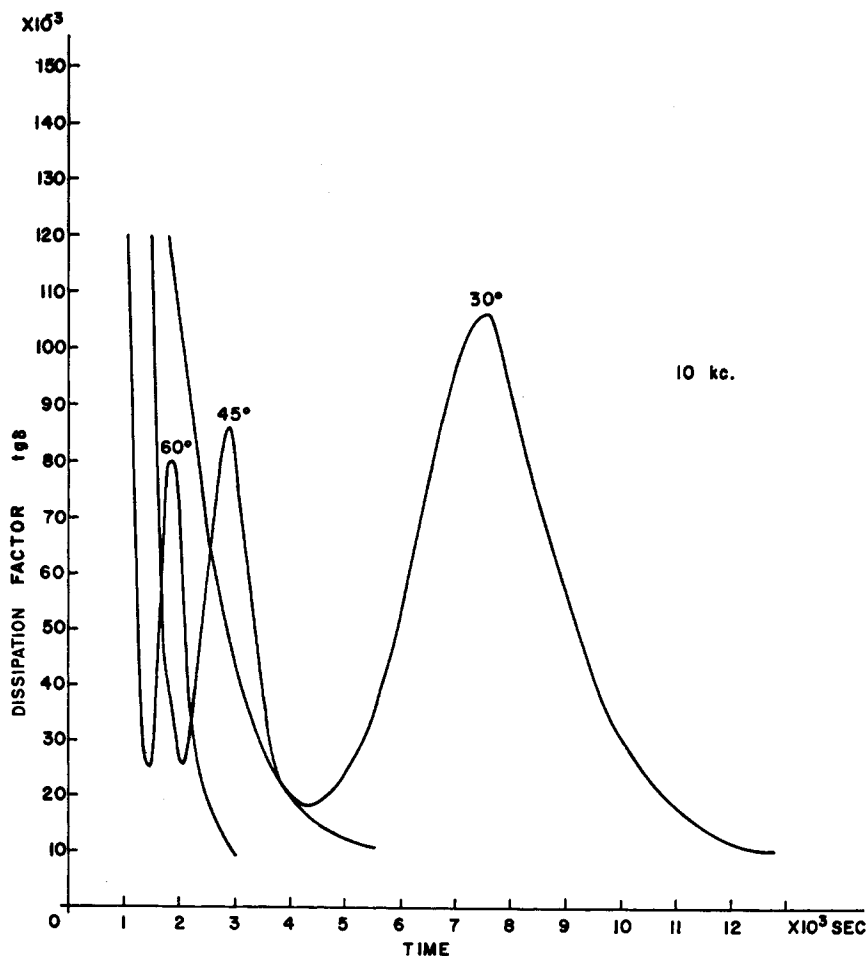
Fig. 2c. See caption p. 3511.

but held constant during each run, were the temperature and the frequency. It was not possible to perform tests at widely different temperatures, since the upper and lower limits of the practical range are fixed for any material and formula. At low temperatures, the speed of reaction is very low, and a complete test would take too long. On the other hand, a high temperature will induce a very fast reaction which cannot be monitored and controlled thermally with adequate accuracy. Pilot experiments showed that the preferred range for Epon 826 + DETA lies between 30 and 60°C. The range of frequencies was limited mainly by the instruments selected and the cell capacitance. Since the frequencies of interest extend over many decades, no single instrument and setup was adequate to cover the whole range of all tan δ and ϵ measurements. Two of the commercial instruments at hand were found suitable: the GR type 1608 impedance bridge for the lower range of 330 cycles/sec.–20 kcycles/sec. and the Marconi
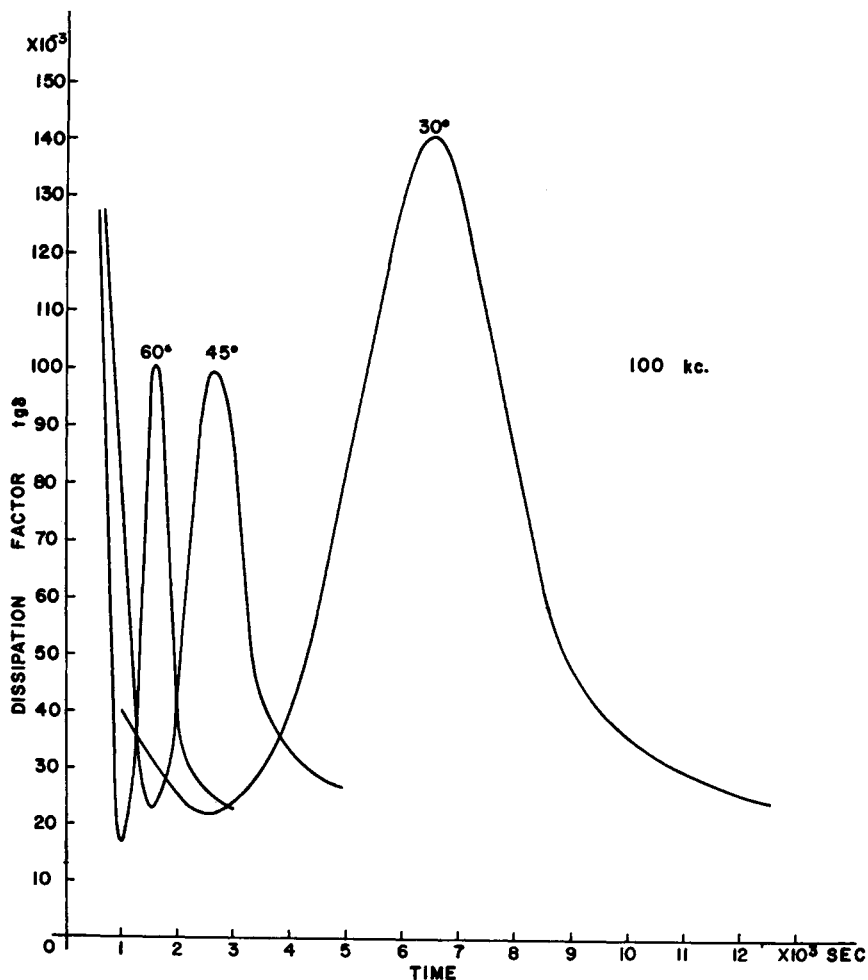
Fig. 2d. See caption p. 3511.

type TF 329G circuit magnification meter for the upper range of 50 kcycles/sec.–10 Mcycles/sec.

Measurements made at 3.3 Mcycles/sec., and even more so at 10 Mcycles/sec., were only partially valid, since the capacity of the epoxy-filled cell and the inductivity of the line resonate near these frequencies. As the resonant frequency changes with cell capacity—and hence with the dielectric constant of the resin that varies during the experiment—no definite test frequency limit could be estimated. Tests at higher frequencies, in the VHF band or even in the microwave region, would require different experimental setups and cells. Measurements below 330 cycles/sec. were difficult to perform with the type of bridge used.

The voltages applied to the test cell by both measuring instruments were usually 4–8 v. and never exceeded 13 v. This means that the electrical
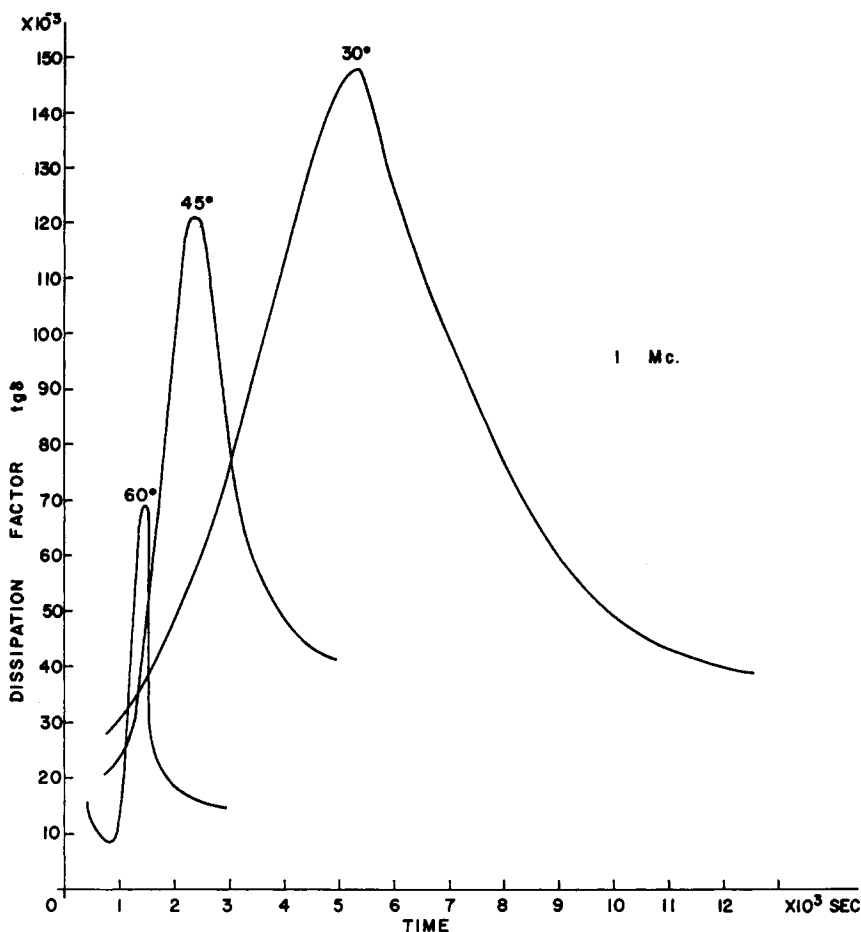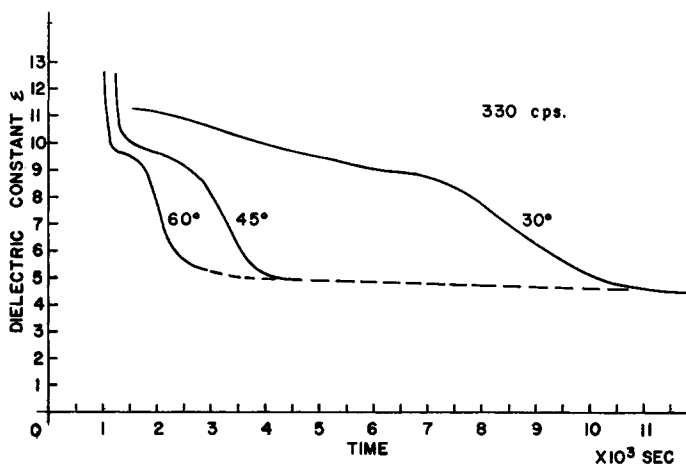
(e)

Fig. 2. Loss tangent as a function of curing time at various test frequencies: (a) 330 cycles/sec.; (b) 1 kcycle/sec.; (c) 10 kcycles/sec.; (d) 100 kcycles/sec.; (e) 1 mcycle/sec.

field in the dielectricum tested was about 100 v./cm. or $1/3$ esu. No appreciable influence on the dielectric constant was exerted, as the induced molecular orientation is very small.[10]

Heat Transfer Medium

Since the polymerization process is highly temperature-dependent, special care was taken to ensure isothermic conditions. All cells used in the tests had large, closely spaced electrodes which guaranteed good thermal contact between the sample and the glass walls. The heat transfer medium that kept the cell at a constant temperature had a high temperature conductivity, a low dielectric constant, and a high electrical resistance. A well-stirred 4-liter paraffin bath, held constant by a Fenwall Type 318H
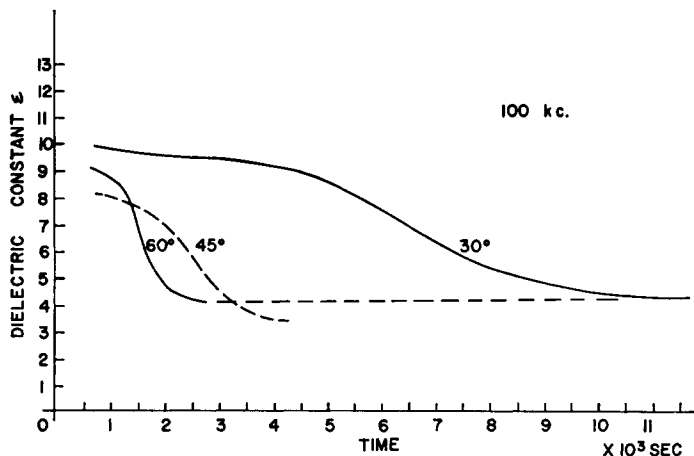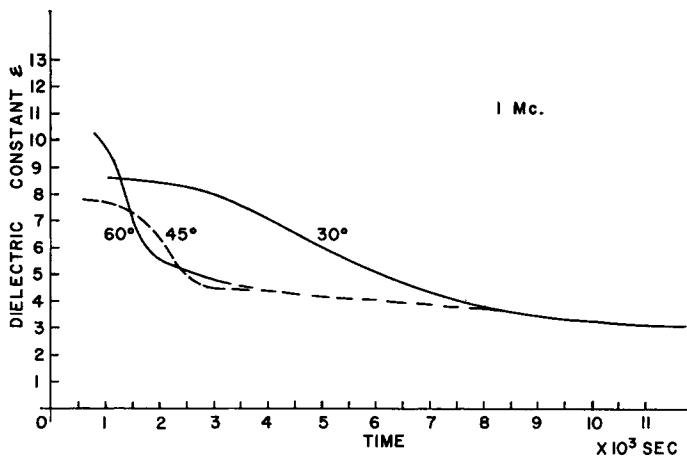
(a)
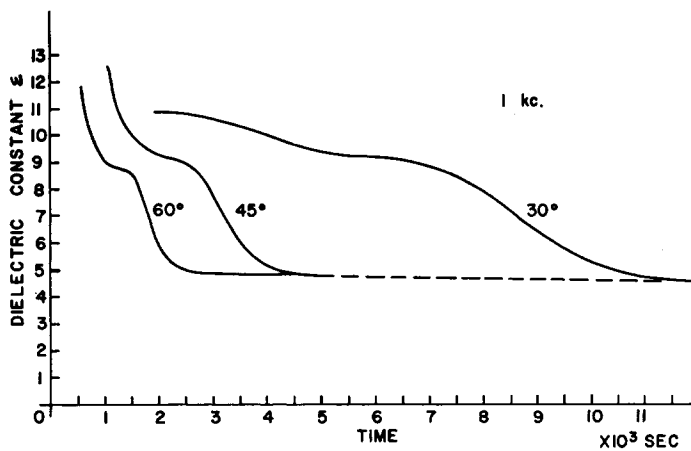
(b)
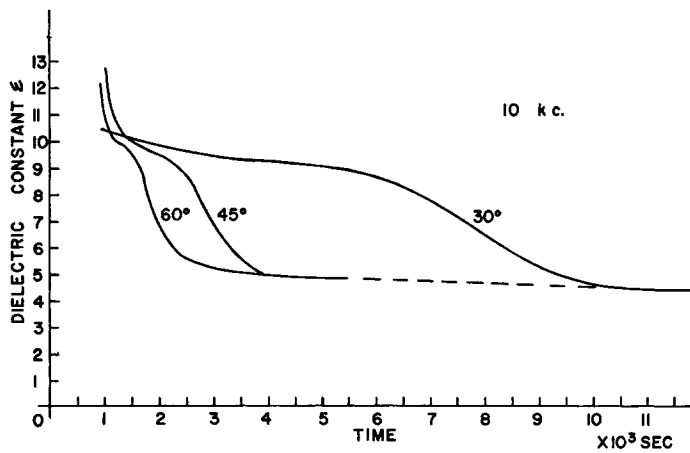
(c)

(d)

(e)

Fig. 3. Dielectric constant as a function of curing at various test frequencies: (a) 330 cycles/sec.; (b) 1 kcycle/sec.; (c) 10 kcycles/sec.; (d) 100 kcycles/sec.; (e) 1 mcycle/sec.

thermostat to within ±0.5°C., was found adequate. Special care was taken that the cells, hung by their connecting wires, were immersed in the paraffin well above the active electrode area, leaving free only the upper folded parts of the connecting strips. It was demonstrated by a simple test that the heat transfer through the glass walls was in effect very rapid and that the resin reached the bath temperature 30–45 sec. after inserting the cell into the paraffin.

Sample Preparation and Test Procedure

Sample preparation was standardized in order to minimize variation between different test runs. All measurements were carried out at three tem-

peratures: 30, 45, 60°C. and at all frequencies: 330 cycles/sec., 1, 3.3, 10, 20, 50, 100, and 330 kcycles/sec., and 1, 3.3, and 10 Mcycles/sec.

The mixture of Epon 826 and DETA in the proportion mentioned previously was preheated to 40°C. in order to decrease its viscosity and ensure a homogeneous mixture which could be poured into the cells without much difficulty. Only very few air bubbles remained in the sample after it had settled for a few moments. No significant error was caused by these bubbles, as their total volume was negligible compared with the volume of the material between the electrodes. It took 2–3 min. from zero time, i.e., the instant of DETA addition, until any readings were taken. Furthermore, measurements made during the first few hundred seconds were rather unreliable, since both the dielectric constant and the loss tangent were high and out of range for the instruments used. Sample preparation time varied to a certain extent, and absolute time correspondence between different test runs could not be maintained. It is nevertheless safe to suppose that this falsifies the time quoted in the results to a negligible degree only, as the preparation procedure itself was constant for all tests and was very short compared with the time required for a complete test run. The initial high and uncontrolled rate of polymerization which was caused by preheating of the Epon led to an additional time base error. This, too, was negligible for tests at 45 and 60°C., as the rate of polymerization during the test proper was much higher than during the preparation period.

A complete test, run until a stable polymer is obtained, may take an inconveniently long time, especially at low temperature. The measurements can be stopped after an experimentally determined period, as the most significant changes occur long before the final equilibrium has been reached. The information lost by this truncation of the experiment does not seem to be very important and may be determined from measurements performed on some aged samples. Several tests were continued for longer periods in order to ascertain the properties of a nearly finished product. The electrical properties after 6 hr. did not differ from those obtained after prolonged aging (12, 16, or 40 hr.) at the test temperature by more than ±10%, which is less than the experimental error for small loss angles.

RESULTS

The results of nearly one hundred complete test runs carried out at different temperatures and frequencies are summarized in Figures 2 and 3. If one compares the plots tan δ and ϵ for different temperatures but for the same frequency, one finds that their general shape remains the same. The most important phenomenon is the drastic change in the time scale, the amplitudes varying only to a small degree.

Most dielectric dissipation factor curves go through a well-defined minimum and maximum before they approach asymptotically a final constant value. At any particular temperature the character of the curves changes gradually while the frequency is raised, until the minimum disappears and the maximum gets flatter and flatter.
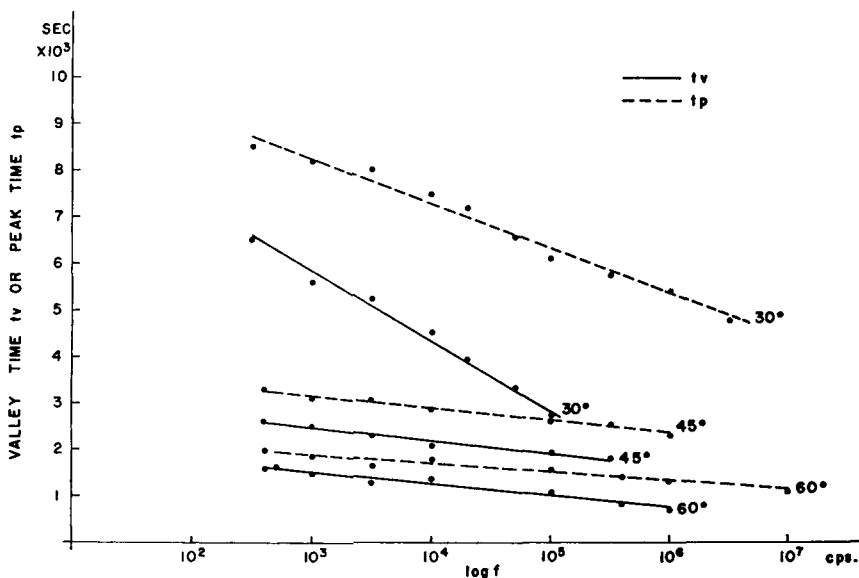
Fig. 4. Variation of peak time t_p and valley time t_v with frequency at different test temperatures.

Variations of the dielectric constant with time are not as spectacular as those of the loss tangent. All curves have a similar form, beginning at a high initial value (9–12) and falling after an inflection to the final constant of about 4 (for 30°C.).

The experimental values of tan δ and ϵ differ from test to test by about 5–10%, which may be due to a slight unnoticed variation of any test parameter such as composition, temperature, homogeneity, or recording of meter deflection.

A positive result was noted only if several curves coincided over appreciable percentages of their range.

The times at which the loss tangent reaches the minimum (valley time t_v), and then the maximum (peak time t_p) decrease with increasing frequency f. The plots of t_v and t_p versus log f turn out to be straight lines. This semilogarithmic behavior holds for all three test temperatures and is shown in Figure 4. Most points fit a straight line very well. The system chosen is known to have a low curing temperature and may reach its final state even at 30°C. This was proved to be the case by comparing the results for 30°C. after 6 hr. with those obtained at 45 or 60°C., which were indeed identical.

POSSIBLE APPLICATION

The dielectric measurements which could be used as a production aid might be compared with other suitable parameters, such as the viscosity, indicative of the state of polymerization attained. The determination of
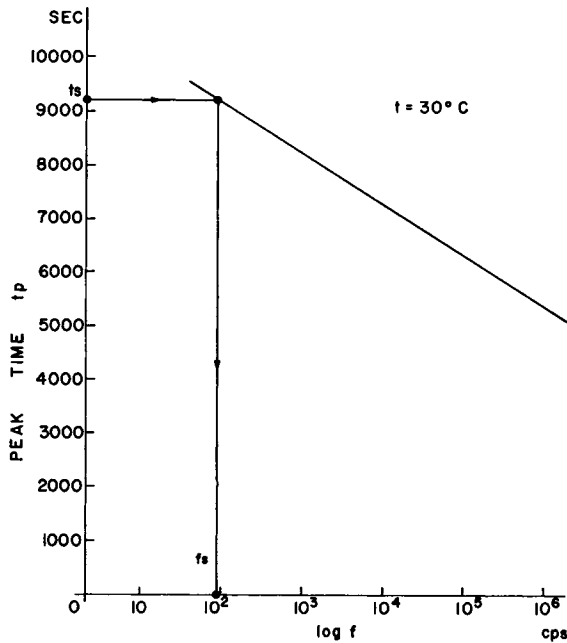
Fig. 5. Method to obtain the process supervision frequency f_s from the time t_s necessary to reach a required state of polymerization.

the viscosity or gel time of a near-solid is awkward, as the instruments jam easily and are cleaned only with difficulty; the measurement may also interfere with the process itself. It is easier and sometimes more reasonable to determine the consistency of a resin by simple penetration tests. By inserting the time necessary to reach the required consistency into the plot of t_p versus $\log f$ as shown in Figure 5, the value f_s can be found. Only at the particular frequency f_s, specific for all subsequent production tests to be made with the composition and curing conditions selected, will the peak time t_p coincide with t_s.

This method is a little laborious, but nevertheless seems to be quite well suited for monitoring the polymerization of epoxy resins in large castings.

The penetration test is suitable only for small castings or for the surface of larger ones, but not for the deeper layers of the latter. Since the rate of polymerization is temperature-dependent, it may not be constant over the whole cross section, and may vary from batch to batch, no simple time measurement will provide an adequate quality control. On the other hand, dielectric measurements are not restricted by size and can be performed between any two convenient conducting surfaces whose dimensions and relative positions remain fixed during the polymerization. A good arrangement for these measurements is a mold with an insert that is insulated from it (fixed or extractable), because such a setup provides an electrically shielded system. Its capacity must, however, be larger than that of the connecting cable; otherwise, measurement errors are unavoidable.

DISCUSSION

The proposed solution for a production problem should not be regarded as a theoretically based approach that leads to a fixed, well-defined relationship between gel time and peak time. On the contrary, the very fact that the experimentally determined peak time varies from one test frequency to the other seems to indicate that it is not a material constant and not directly related to the gel time. Gel times vary only with composition, experimental procedure, or size of casting, but their values should not change if different frequencies are used for the same test. This contradicts the conclusion of Delmonte[8] that there is a correlation between the peak time of the dielectric dissipation factor and the gel time; this author did not fully realize that the peak time shifts with test frequency.

A more fundamental explanation of the tan δ and ϵ versus time relation is rather complicated. It is probable that the peak of the tan δ curves may be due to molecular absorption phenomena. This possibility and the correlation between the tan δ and ϵ curves are presently under investigation.

References

1. Warfield, R. W., *SPE J.*, **14**, 39 (1958).
2. Knudsen, J., paper presented to Society of Plastics Engineers Reinforced Plastics Meeting, Feb. 1958; Section 2B p. 1.
3. C. F. Chadwick, paper presented at 145th Meeting, American Chemical Society, New York, Sept. 1963.
4. Warfield, R. W., and M. C. Petree, *J. Polymer Sci.*, **37**, 305 (1959).
5. Warfield, R. W., and M. C. Petree, *Makromol. Chem.*, **58**, 139 (1962).
6. Ishiola, Y., *Kolloid-Z.*, **168**, 29 (1960).
7. Mikhailov, G. P., *J. Polymer Sci.*, **30**, 605 (1958).
8. Delmonte, J., *J. Appl. Polymer Sci.*, **2**, 108 (1959).
9. Shell Chemical Company, *Technical Bulletin* SO: 61-8.
10. Smyth, C. P., *Dielectric Behavior and Structure*, McGraw-Hill, New York, 1955, p. 15.

Résumé

On a utilisé des mesures diélectriques pour l'étude du processus de polymérisation de la résine époxy. Epon 826 avec la diéthylenetriamine (DETA) comme agent de pontage. Les variations en fonction du temps du facteur de dissipation et de la constante diélectrique sont mesurées continuellement, tandis que la système époxy est maintenu à température constante. On a couvert un domaine de 11 fréquences (330 cpc à 10 Mc) à trois températures de polymérisation différentes (30, 45 et 60°C). Les résultats témoins sont donnés en un ensemble de courbes pour le facteur de dissipation et pour la constante diélectrique en fonction du temps. De façon précise, toute les courbes de facteurs de dissipation ont la même allure caractéristique avec un minimum bien défini (vallée) suivie par un maximum (pic). La constante diélectrique diminue régulièrement d'une grande valeur initiale à une faible valeur finale, qui est caractéristique pour des résines entièrement traitées. Si on porte en graphique le temps mis par le facteur de dissipation pour atteindre une vallée t_v et un pré t_p en fonction du logarithme de la fréquence, on peut obtenir deux lignes droites. Un tel graphique peut être utile pour le controle du processus de traitement des résines coulées.

Zusammenfassung

Dielektrische Messungen wurden bei der Untersuchung des Polymerisationsprozesses des Epoxyharzes Epon 826 mit Diäthylentriamin (DETA) als Vernetzungsmittel verwendet. Die Zeitabhängigkeit des Dissipationsfaktors und der Dielektrizitätskonstanten des Epoxysystems wurde bei konstanter Temperatur kontinuierlich gemessen. Ein Bereich von 11 Frequenzen (330 Hz–10 MHz) wurde bei drei verschiedenen Polymerisationstemperaturen (30, 45 und 60°C) erfasst. Die Versuchsergebnisse werden als Kurvenschar für den Dissipationsfaktor und die Dielektrizitätskonstante gegen die Zeit dargestellt. Nahezu alle Dissipationsfaktorkurven haben die gleiche charakteristische Gestalt mit einem gut definierten Minimum, gefolgt von einem Maximum. Die Dielektrizitätskonstante fällt monoton von einem hohen Anfangswert auf einen kleinen Endwert ab, welcher für das voll ausgehärtete Harz spezifisch ist. Bei der Auftragung der Zeit, bei welcher der Dissipationsfaktor das Minimum erreicht t_v und derjenigen für das Maximum t_p gegen den Logarithmus der Frequenz werden zwei gerade Linien erhalten. Ein solches Diagramm kann zur Kontrolle des Härtungsprozesses der Harze verwendet werden.