

## Electrical Properties of Epoxy Resins During Polymerization

JOHN DELMONTE

*Furane Plastics, Inc., Los Angeles, California*

Studies of the variation in electrical parameters during the polymerization of epoxy resins offer means for interpreting molecular changes occurring during the curing process, both before and after gelation. The mechanical changes which occur are numerous—an initial change of viscosity on the addition of curing agents, a rise in temperature due to exothermic reaction, and a final increase in viscosity, culminating in gelation. This pattern is well known and characteristic of many epoxy systems. Other means for observing changes in the epoxy resins during the polymerization process involve the use of infrared spectroscopy, molecular changes being indicated by changes in the spectra of infrared transmission.<sup>1</sup>

Changes of electrical properties in liquid epoxy resins, both before and after gelation, have always intrigued our research staff, and while admittedly our work is not sufficiently fundamental to interpret accurately the molecular changes taking place with the changes in electrical properties, our observations are consistent and informative. To a physical chemist equipped with clear concepts of the interdependence of electrical parameters and changes due to polymerization, observations of the behavior of the dissipation factor during cure are useful tools in reaching an understanding of these important processes.

### EXPERIMENTAL

Three liquid epoxy resins were selected for this study: a low molecular weight resin (Dow 332), a low medium molecular weight resin (Shell 828), and a medium molecular weight resin (Araldite 6020). Salient characteristics of these materials are tabulated in Table I.

In all instances, manufacturers of these resins report them as products of the reaction of bisphenol A and epichlorohydrin. The Dow product approaches most closely the theoretical structure of the diglycidyl ether of bisphenol A.

TABLE I  
Characteristics of Certain Liquid Epoxy Resins

Resin	Epoxy equivalent, g./ep. equiv.	Viscosity at 75°F., cps.
Dow 332	178	6,400
Ciba Araldite 6020	202	26,800
Shell 828	186	12,400

Test methods for the determination of the dielectric constant and dissipation factor followed ASTM D150-54T, and for volume resistivity the procedure was that of ASTM D257-57T. In order to make readings during cure, it was necessary to design special electrodes positioned within the mold in which test specimens were polymerized. Details on the electrodes and their spacing are shown in Figure 1. Thin aluminum foils were cut with projecting tabs to the necessary diameters. These were placed on  $\frac{1}{4}$  in. thick glass plates, with the use of silicone grease, and all wrinkles were carefully smoothed out so that the foils lay flat against the surface. The projecting tabs were connected to the appropriate instruments, and readings were taken during cure after calibration.

The actual thickness of test specimens during cure was  $\frac{1}{8}$  in. Data are reported for epoxy resins cured at room temperatures of 75° to 85°F. The exothermic heat rise was negligible due to the well-distributed mass and heat-dissipative characteristics of the glass plates. The temperature change during the test may have been of the order of 3-4°F., insufficient to affect the results.

Where it was necessary to conduct heat cure, the same electrode assemblies and glass plates were placed into a properly thermostated oven with forced air circulation. The elevated temperature cure and the ensuing high thermal gradients made less reliable the transient electrical measurements at higher temperatures. However, after thermal equilibrium was attained, the variables were minimized and more easily interpreted data were obtained.

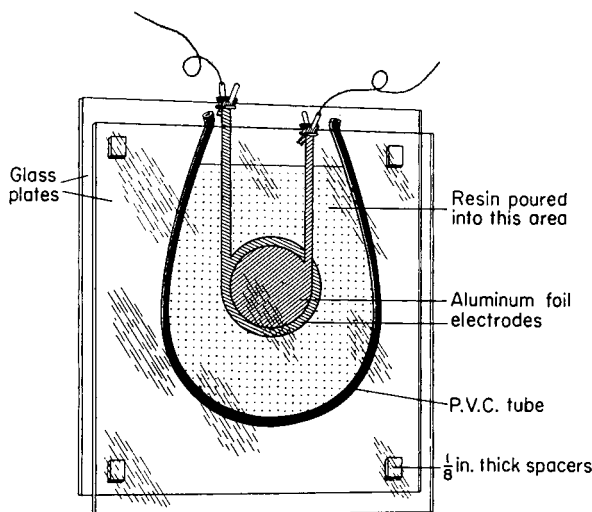


Figure 1.

### TEST RESULTS

Three curing agents were selected for reaction with the previously mentioned liquid epoxy resins: diethylenetriamine, which is representative of room temperature curing agents; *m*-phenylenediamine, high-temperature curing aromatic amine; and phthalic anhydride, a high temperature anhydride curing agent.

These were reacted in stoichiometric proportions with each of the three liquid epoxy resins, except for the phthalic anhydride, for which the molar ratio of epoxy to anhydride was slightly greater than 1.0, in accordance with accepted practices for the cure of the epoxy resins.

In Figure 2 are plotted the dissipation factors of the three resins versus cure time at room temperature when cured with the appropriate amount of diethylenetriamine. The measurements were made

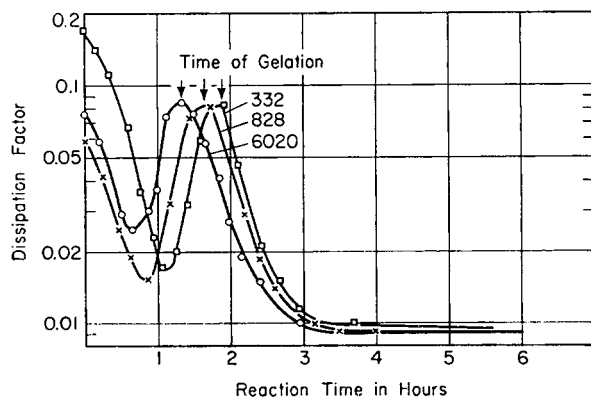


Fig. 2. Dissipation factors of epoxy resins at 10 keycycles during cure with DETA.

at 10 keycycles where electrical parameters are conveniently observed for epoxy resins.<sup>2</sup> Zero time on the curve represents the first reading immediately after mixing and pouring and is followed by the changes occurring during polymerization. Of interest is the initial wide spread of dissipation factors of the three resins, the resin of lowest molecular weight demonstrating the highest electrical losses initially, although the terminal values for all the specimens are reasonably close to one another (in the vicinity of 0.01) with a slight rise after prolonged aging. Another observation is the peak value of the dissipation factor. This was unexpected but proved to be characteristic of the epoxy resins, even with other curing agents. As indicated earlier, the change was not due to internal temperatures, although it was noted that the peak values were coincidental with the formation of an infusible and insoluble gel due to molecular crosslinking. It suggests that electrical losses as measured by the dissipation factor (which after all indicates mobility within the molecular structure) are higher as the liquid epoxy molecules are rearranging themselves through crosslinking processes into the final state of an irreversible gel structure. That the patterns for each of the epoxy resins of different molecular weight tested were identical lends support to these ideas. It is also noteworthy that peak values of dissipation factor were identical (0.083 at 10 keycycles), and the higher the molecular weight, the earlier appeared the time of gelation (maximum dissipation factor). It may also be surmised that active crosslinking commences with a rise in dissipation factor which is usually abrupt and sharp. For the  $\frac{1}{8}$ -in. thick casting this was noted as follows.

Resin	Time of start of dissipation increase, min.
Dow 332	65
Epon 828	50
Araldite 6020	40

After gelation has occurred, continued curing leads to a decrease in the dissipation factor until complete cure occurs, after which there is a slight rise on prolonged aging. Further changes in gelled structures are observed readily by changes in physical properties.

It is also of interest to observe the changes occurring in dielectric constant and volume resistivity both before and after gelation. These measurements were taken simultaneously on the same

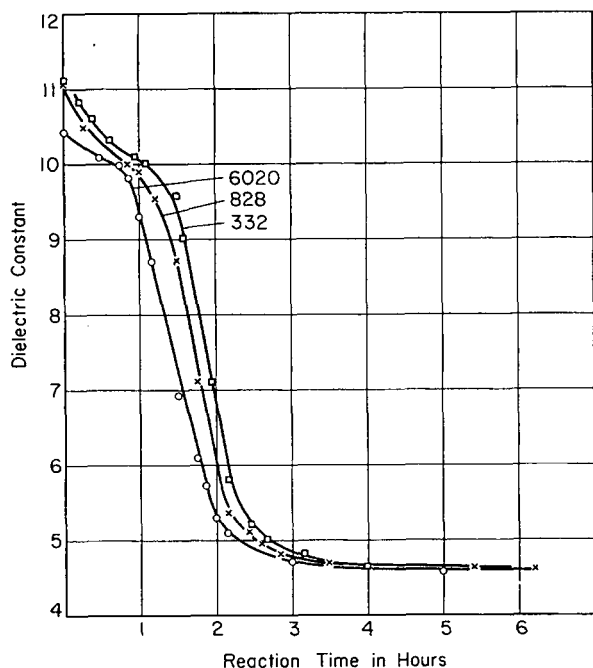


Fig. 3. Dielectric constants of epoxy resins at 10 keycles during cure with DETA.

specimens described in Figure 1. In Figure 3 are plotted dielectric constant data for curing with diethylenetriamine of the three epoxy resins. The dielectric constant data do not appear to be quite as revealing as is the dissipation factor during polymerization, although the change of dielectric

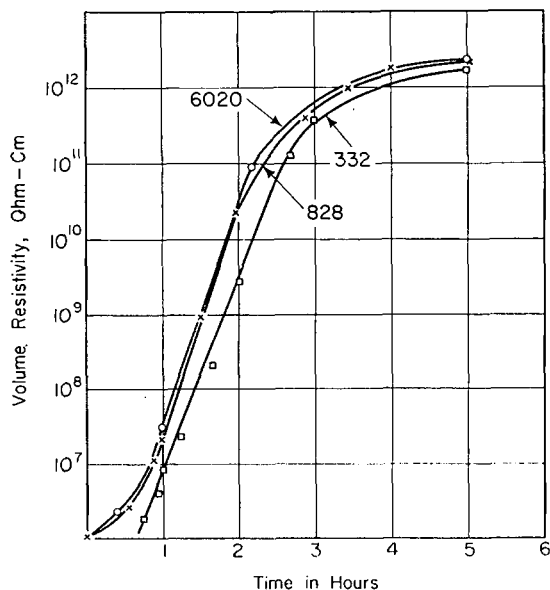


Fig. 4. Araldite 6020/DETA. Volume resistivity during cure.

constant is quite rapid during the period of gelation, the peak dissipation factor occurring at the midpoint of the maximum slope of  $dK/dt$ , where  $K$  is the dielectric constant. The dielectric constant appears to level off at 4.6 for each of the three epoxy resins of different molecular weight used in the experiment.

In Figure 4 are plotted d.c. volume resistivity versus cure or polymerization time with increasing values of resistivity occurring with increasing time. All three resins possess similar characteristics in this respect. These measurements, it should be remembered, were taken simultaneously with dissipation factor  $d$  and dielectric constant  $K$ . In view of the greater significance of  $D$  and  $K$  readings, volume resistivities were not measured throughout the other tests.

### Effect of Frequency

Tests of dielectric constant and dissipation factor were conducted at frequencies of 60 cycles, 1 keycle, 10 keycles and 1 mcycle/sec. on Epon 828 and diethylenetriamine during polymerization (see Fig. 5). The data are most revealing and difficult to interpret. The time of gelation appears within the range of 1–10 keycles/sec., closer to the 10-keycle/sec. data. However, during cure it appears that the higher the frequency of measurement, the higher the peak value of dissipation factor and the sooner it occurs. An anomalous effect occurs at 1 Mcycle/sec. in that the data reveals a peak value of dissipation factor although no minimum values

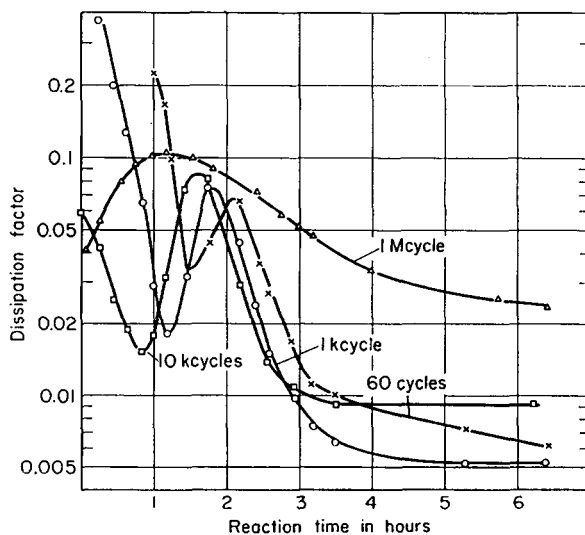


Fig. 5. 828/diethylenetriamine dissipation factor at various frequencies after mixing.

indicating the commencement of gelation. However, the peak value for the 1-Mcycle curve occurs after the minimum time for the 10-kcycle curve which was suggested as the interval indicating start of gelation. It may not be unreasonable to suggest that the oscillation of centers of charge within the molecule giving rise to electrical losses (as measured by dissipation factor) is enhanced during polymerization as the molecular groups and crosslinking are

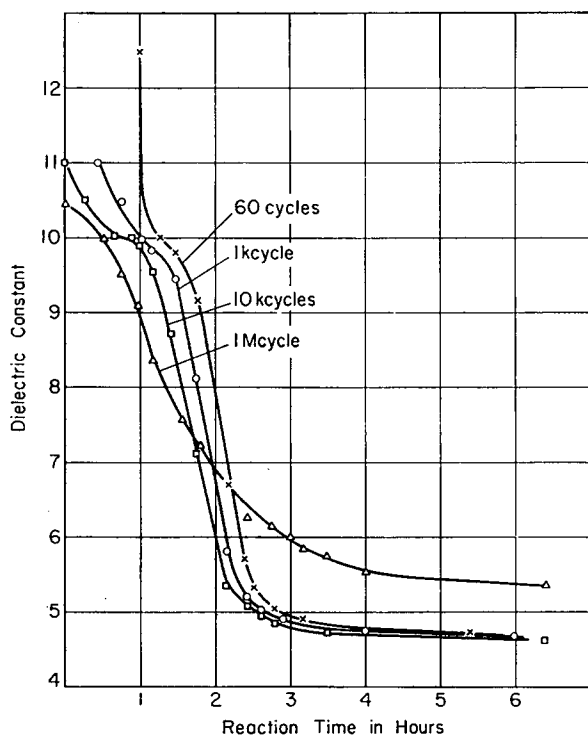


Fig. 6. 828/diethylenetriamine dielectric constant at various frequencies after mixing.

being established. Furthermore, at the higher frequencies, the tendencies are less pronounced earlier in the polymerization processes. This is borne out in part in Figure 6 which shows a more rapid fall-off in polarity at higher frequencies of oscillation, where the dielectric constant falls earlier during the time of polymerization for 1 Mcycle, followed by 10 kcycle, 1 kcycle, or 60 cycles/sec. measurements. Is this indicative of charge centers which are selective in their frequency response or of a greater reluctance of the group to change, the higher the oscillating frequency? Of course, after cure is established there is a consistent frequency-dissipation factor spectrum for the resin system (see, for example, references 3 and 4).

### Effect of Other Curing Agents

What of the effect of curing agents other than diethylenetriamine? A well-known type is *m*-phenylenediamine, an aromatic amine favored for heat cure with epoxy resin systems. In practice, the solid amine is melted into the warmed epoxy resin system. This was accomplished for stoichiometric ratios of Araldite 6020 and Epon 828. The two systems were poured and allowed to cool to room temperature, at which readings were made. Gel times were usually in the range of 6 to 10 hours. If the mixtures were heated immediately, the increases of dissipation factor due to temperature and to polymerization effects are

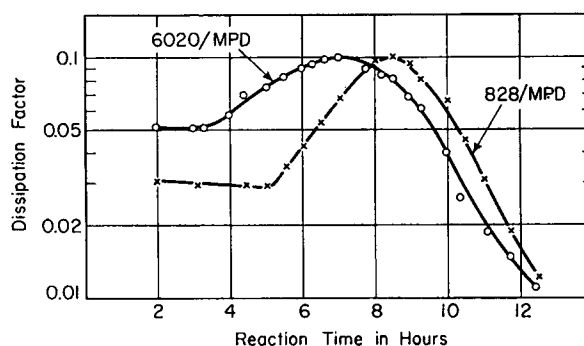


Fig. 7. Epoxy resins plus *m*-phenylenediamine dissipation factor at 10 kcycles during cure.

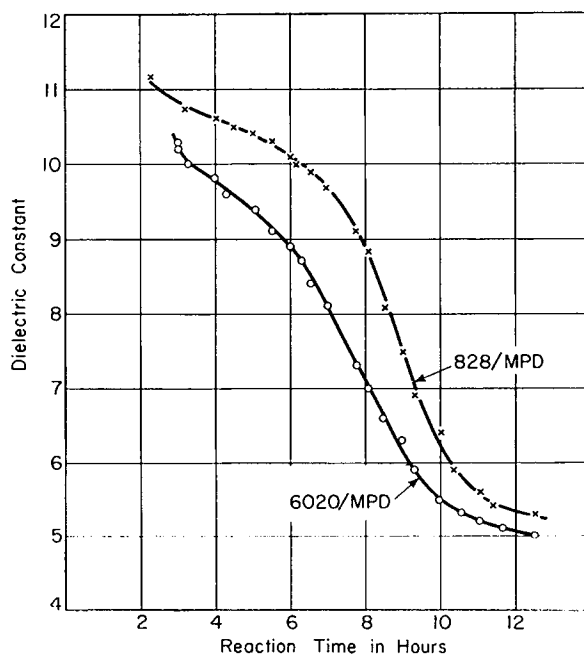


Fig. 8. Epoxy resins plus *m*-phenylenediamine dielectric constant at 10 kcycles during cure.

difficult to separate. It was decided to obtain data on room temperature values of the dissipation factor and dielectric constant (see Figs. 7 and 8) before proceeding with heat cure. Once again, peak values were observed, coincidental with molecular growth and gelation, followed by declining values after apparent completion of gelation.

Subsequent cure at 200°F., followed by cure at 300°F., completed the cure of the epoxies with *m*-phenylenediamine (MPD). At those temperatures, the steady state values of dissipation factor were as follows.

	200°F.		300°F.	
	<i>D</i>	<i>K</i>	<i>D</i>	<i>K</i>
Araldite 6020/MPD	0.0073	5.1	0.023	5.3
Epon 828/MPD	0.0073	5.3	0.015	5.5

Data on cure with phthalic anhydride was somewhat sketchy: Dow 332 cured very slowly, and the data was incomplete, although Araldite 6020 and Epon 828 gave interesting data. All polymerization and all readings were taken at 300°F. A decided minimum in the values of the dissipation factor were observed at 10 kcycles/sec. much sooner with Araldite 6020 than with Epon 828. These data are indicated in Figure 9 while Figure 10 presents the dielectric constants obtained at the same time. Values of the dielectric constant and dissipation factor were much too high for the equipment used during the early stages of polymerization with phthalic anhydride. Present in substantial

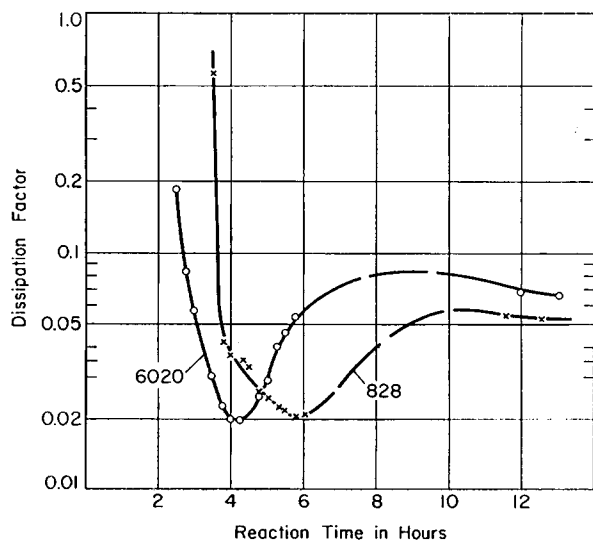


Fig. 9. Dissipation factors of epoxy resins at 10 kcycles during cure at 300°F. with PA.

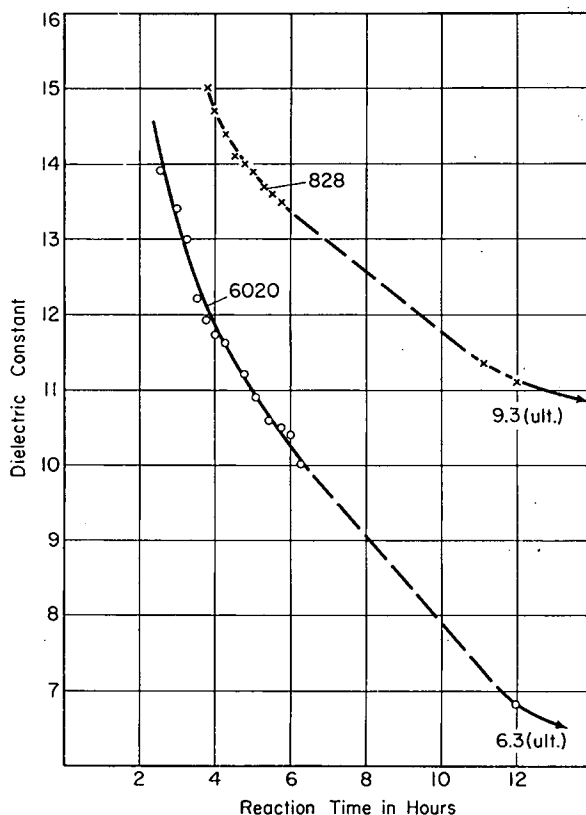


Fig. 10. Dielectric constants of epoxy resins at 10 kcycles during cure at 300°F. with PA.

quantities, phthalic anhydride, a highly polar material, may be expected to show a high dissipation factor until the anhydride groups have entered into reaction.

As nondestructive testing procedures, electrical measurements are most revealing, and yield data that may help in the interpretation of processes in the polymerization of epoxides.

Grateful recognition is accorded to assistance rendered by Ken Cressy, Research Chemist of Furane Plastics, Inc., and to the electrical measurements of Delsen Corporation, Glendale, California.

### References

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### Synopsis

Variations in electrical properties of epoxies during polymerization permit interpretation of molecular changes

occurring. Three liquid epoxy resins selected for test were of different molecular weights, varying from 6,400 to 26,800 cycles/sec. Curing agents selected included triethylene tetramine, *m*-phenylenediamine, and phthalic anhydride. Test specimens were cast between glass plates containing thin foil electrodes which permitted observations of electrical properties during cure. Test results disclose that for each of the resin systems, dissipation factors fell sharply as cure commenced and then at the onset of gelation, values rose again to a peak value, falling with continued cure and hardening of the product. These measurements were conducted over a range of frequencies, the higher the frequency the higher the peak value of dissipation factor and the sooner it occurs. The disclosures of peak values of dissipation factor during cure are unique and appeared to be correlated to the mechanical changes occurring in the polymer. Measurements of other electrical parameters were made during polymerization, such as dielectric constant and volume resistivity, and while data were carefully noted and plotted in the charts, the most revealing was dissipation factor. The influence of heat and other factors upon results is explored.

### Résumé

Les variations des propriétés électriques des résines Epoxy durant leur polymérisation, permettent d'interpréter les changements moléculaires qui surviennent. Trois résines liquides de poids moléculaires différents variant de 6.400 à 26.800 ont été choisies pour l'expérience. Les agents de traitement choisis comprenaient la triéthylène-tétramine, la métaphénylène-diamine et l'anhydride phtalique. Les échantillons furent placés entre des plaques de verre contenant des électrodes en papier d'étain, qui permettaient l'observation des propriétés électriques durant le traitement. Les expériences montrent que dans le cas de chaque résine, les facteurs de dissipation tombent fortement dès que le traitement est commencé et ensuite au début de la gélification les valeurs croissent à nouveau jusqu'à une valeur maximum, puis tombent à nouveau avec un traitement ultérieur et solidification progressive du produit. Ces mesures furent menées pour différentes valeurs de fréquences, et plus la fréquence est élevée, plus élevée est la valeur maximum du fac-

teur de dissipation et plus tôt elle se manifeste. L'occurrence de ces valeurs maximales du facteur de dissipation pendant le traitement sont exceptionnelles et semblent être en relation avec les changements mécaniques au spin du polymère. Des mesures d'autres paramètres électriques ont été faites pendant la polymérisation, telle la constante diélectrique et résistivité spécifique, mais bien que ces données fussent soigneusement notées et mises en graphiques, le plus révélateur reste néanmoins le facteur de dissipation. L'influence de la chaleur et d'autres facteurs sur les résultats sont en cours d'investigation.

### Zusammenfassung

Die Änderung der elektrischen Eigenschaften von Epoxyharzen während der Polymerisation erlaubt eine Deutung der sich abspielenden molekularen Umwandlungen. Es wurden drei flüssige Epoxyharze mit verschiedenem Molekulargewicht im Bereich von 6400 bis 26800 Cps ausgewählt. Sie wurden unter Zusatz verschiedener Stoffe, nämlich Triäthylentetramin, *m*-Phenyldiamin und Phthalsäureanhydrid, polymerisiert. Testproben wurden zwischen Glasplatten gebracht, die dünne Blattelektroden enthielten und so die Beobachtung der elektrischen Eigenschaften während des Prozesses erlaubten. Die Versuchsergebnisse zeigen, dass bei jedem Harzsystem die Verlustfaktoren vom Polymerisationsbeginn an scharf abfallen, dass dann bei Einsatz der Gelbildung die Werte wieder ein Maximum erreichen und mit fortgesetzter Polymerisation und Härtung des Produkts abfallen. Die Messungen wurden bei verschiedenen Frequenzen ausgeführt; das Maximum des Verlustfaktors liegt um so höher und es tritt um so früher ein, je höher die Frequenz ist. Das Auftreten von Maximalwerten für den Verlustfaktor während der Polymerisation ist eine Besonderheit und scheint mit den im Polymeren auftretenden mechanischen Veränderungen in Beziehung zu stehen. Andere elektrische Grössen, wie Dielektrizitätskonstante und Volumswiderstand wurden während der Polymerisation ebenfalls gemessen, sorgfältig aufgezeichnet und tabelliert, die aufschlussreichste Grösse war aber doch der Verlustfaktor. Die Abhängigkeit der Ergebnisse von der Temperatur und anderen Faktoren wird untersucht.

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