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ON-LINE MASS SPECTROMETRIC MONITORING
OF THE POLYMERIZATION OF
A PHENOLIC-RESIN-BASED MATERIAL

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ON-LINE MASS SPECTROMETRIC MONITORING OF THE POLYMERIZATION OF A PHENOLIC-RESIN-BASED MATERIAL

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SUMMARY

Polymerization of phenolic-resin-based materials requires elevated temperatures. The low thermal conductivity of these materials has led to the use of dielectric heating techniques in lieu of standard convection oven heating to obtain a satisfactory cure. The curing rate and therefore the quality of the cured material depends on the heating rate and the maximum temperature attained, parameters which are extremely difficult to measure in dielectric heating units.

The dielectric curing of these materials has been monitored by using a mass spectrometer to measure the partial pressure of phenol in the gas evolved during polymerization. The resulting plots of phenol partial pressure as a function of time have a characteristic shape, and these may be used to indicate the attainment of complete curing. The validity of the mass spectrometric technique was confirmed by chemical analysis of the polymerized samples.

INTRODUCTION

Dielectric heating offers significant advantages over conventional oven heating methods for thermally activated polymerization of materials with very low thermal conductivity (refs. 1 and 2). Such polymers have been of interest as materials for molded ablative heat shields used in reentry vehicles. Among the major advantages of dielectric heating are the possibility of achieving uniform curing throughout the mass of the polymer and a reduction in curing time relative to conventional heating methods. When a material is subjected to dielectric heating, the temperature is raised uniformly throughout the bulk of the material. As a result, the temperature distribution throughout the material is much more uniform than is possible to attain with conventional thermal methods of heating.

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A major obstacle to applying dielectric heating to polymer curing is the difficulty in measuring the temperature of the material. On the other hand, the curing rate and quality of the polymerized material are a direct function of both the heating rate and the maximum temperature encountered during the polymerization process. In conventional curing processes, temperature can be measured and controlled to achieve the desired results.

In the dielectric heating method, temperature measurement based on thermocouples is difficult because of self-heating and spurious signals arising from the electromagnetic fields. Remote temperature sensing based on pyrometry is sensitive only to the temperature of the surface, and since polymerizations are in general exothermic, measurement of the surface temperature alone may not provide an accurate indication of the reaction conditions in the bulk of the material. An alternative method for monitoring the reaction was therefore required.

The extent of chemical reactions, including polymerization processes, can be followed analytically by monitoring the disappearance of a reactant or the appearance of a product. The unique nature of monomers, or starting materials, in comparison with the products, suggested that monitoring the monomer would be the more advantageous approach.

The choice of analytical techniques is limited by the need for continuous monitoring and the difficulty of transporting gaseous samples from the material in the dielectric heating device. The mass spectrometer possesses the necessary response time, sensitivity, and selectivity needed to monitor a single component in complex mixtures of products evolved during the polymerization reaction. Mass spectrometric analysis of the volatile components evolved during the polymerization of phenol-formaldehyde resins verified that in this case the phenol monomer was the most suitable indicator of the extent of the reaction.

The present paper describes the design of an inlet system and the application of an analytical mass spectrometer to monitor the curing of a composite material based on a phenol-formaldehyde resin. The technique should be applicable to the monitoring of the polymerization of a number of materials if a reactant or product is sufficiently volatile to permit the measurement of its concentration during the polymerization process.

EXPERIMENT

Materials

The material selected for study was a composite based on a phenol-formaldehyde resin. Composition of the mixture by weight before curing was 60 percent hollow, fully cured phenolic microspheres 50 to 300 μm in diameter; 30 percent "B-stage" novolac

phenol-formaldehyde prepolymer soluble in acetone; and 10 percent fully polymerized polyamide powder (nylon 66) 150 to 400 mesh.

Apparatus

The mass spectrometer used in the experiment was a 12.7-cm radius, 180^o magnetic deflection instrument equipped with an electron multiplier detector, and the ion current was recorded on a strip chart recorder. The dielectric heating unit had a maximum output of 500 W in the range 70 to 80 MHz. Power transferred to the sample could be regulated within limits by varying the interelectrode spacing, as shown in figure 1. The effective heating area, as defined by the area of the upper electrode, was approximately 12 by 20 cm. The polymerization reaction was carried out in a molded silicone rubber bag 8 cm in length, 6 cm in width, and 1 cm in depth. The bag was closed at the bottom with a pyrex plug and the 0.95-cm-diameter neck fitted snugly around the glass inlet. A fiberglass cloth filter at the base of the neck of the bag prevented particulate matter from entering the mass spectrometer.

A major difficulty was encountered in transporting a representative sample of the evolved gas to the mass spectrometer without alteration of the gas composition through condensation. To overcome this problem the inlet system shown in figure 2 was developed to interface the mass spectrometer to the polymerization reaction.

Gases evolved during the polymerization were brought out of the dielectric heating unit through the glass manifold. The main body of the manifold was surrounded by a glass jacket through which nitrogen gas was passed. The nitrogen was heated to approximately 150^o C by passing it over a coiled Nichrome wire heater located outside the dielectric heating unit and controlled by a variable transformer. The nitrogen gas, after passing through the glass jacket, was directed at the unjacketed inlet portion of the manifold to prevent condensation in that zone. It was found that heating the unjacketed manifold inlet was necessary to prevent serious deterioration in the response time of the system due to changes in phenol partial pressure. This deterioration resulted from condensation of evolved water on the glass surface accompanied by dissolution of evolved phenol.

The outlet end of the manifold was fitted with a glass-to-metal seal sleeve which had an inside diameter of 0.95 cm and into which the mass spectrometer capillary probe fitted snugly. A sidearm on the glass manifold was connected to vacuum and was fitted with a needle valve and water manometer with a range of 63 cm of water. The stainless steel capillary connected between the manifold and the heated molecular leak of the mass spectrometer had an inside diameter of 0.015 cm and was 60 cm in length. It was heated electrically by passing current through the capillary walls.

Procedure

A 10-gram batch of the uncured composite was placed in the silicone rubber bag and the open end tightly sealed by inserting the pyrex plug. The neck of the bag was attached to the inlet manifold and the assembly placed within the dielectric heater. Electrode spacing and heating times were adjusted to the desired values.

The mass spectrometer was adjusted to monitor a mass-to-charge ratio (m/e) of 94, the most intense peak in the mass spectrum of phenol, which was absent from the mass spectra of other components of the uncured composite. The inlet vacuum was adjusted to approximately 25 cm of water and the heating cycle was initiated.

At the end of the heating cycle the sample was removed for observation and chemical analysis. This analysis consisted of a gravimetric determination of the amount of polymer precursor extracted by acetone in a Soxhlet extractor, essentially as described in reference 3. In this procedure 3-gram samples were placed in 2.2- by 8.0-cm cellulose extraction thimbles and extracted with acetone for approximately 4 hours to assure complete removal of the unreacted phenol. The extract was transferred to a Petri dish and dried at 50° C to constant weight. The amount of extractables E , in percent, was calculated from

$$E = \frac{W - D}{S} \times 100$$

where

W weight of dish and dried extract

D weight of dish

S weight of original sample

Each analysis was determined in triplicate to assure reproducibility of the results.

RESULTS AND DISCUSSION

The partial pressure of phenol in the gas evolved during the polymerization reaction varied systematically with time, as shown in figure 3 for a heating cycle of approximately 300 seconds. It was observed that the evolution of phenol increased rapidly at the onset of polymerization and reached an apparent plateau at some point during the polymerization process.

Replicate runs showed a significant scatter, as illustrated in figure 4, curve A. Each data point represents an average of 10 individual runs taken at the indicated curing time. The bars correspond to a range of twice the standard deviation of a single measurement. The phenol partial pressure in the gas initially remained low and gradually rose as the reaction rate increased with rising temperature. The signal eventually reached a reproducible plateau of sorts as a result of the opposing effects of the increasing temperature of the material and the decreasing concentration of free phenol.

Physical examination revealed that the center of the sample became visibly blackened when the sample was cured for 200 seconds and that the blackened area grew as the curing time was increased. Samples cured longer than 350 seconds became so hot at the center that charring often continued after the samples were removed from the silicone rubber bag.

The response time of the gas collection system, as judged by the time required for the signal to decrease by $1/e$ when the bag was disconnected, was approximately 12 seconds. Since the time constant of the capillary was less than 1 second, the increased response time was probably due to cooling when the bag was removed.

The time dependence of the phenol partial pressure correlates well with the concentration of unpolymerized phenol remaining in the composite. Figure 4, curve B, shows the time dependence of the acetone-extractable portion of the samples cured for various lengths of time. Each data point represents the average of three or four measurements. Initially, approximately 30 percent of the composite is the polymer precursor, indicating that the acetone-extraction technique measures the amount of phenol-formaldehyde prepolymer. The sharp drop in polymer precursor at 70 seconds corresponds closely to the onset of the polymerization reaction, as indicated by the phenol partial pressure measurements. As the samples were heated for progressively longer times, the quantity of extractable phenolic prepolymer decreased monotonically to a limiting value of 2 to 3 percent. The approach to this limiting value is seen to correspond closely to the beginning of the plateau of the phenol partial pressure curve, indicating that the achievement of the plateau corresponds to essentially complete polymerization. Unlike the partial pressure measurement, however, the acetone-extraction measurements do not give a real-time indication of the time required for the reaction to reach completion. The data do indicate that the polymerization is essentially complete after 200 seconds, and thus confirm the validity of the mass spectrometric technique for monitoring completion of cure under these conditions.

The ability to monitor the polymerization process by mass spectrometry under other conditions was demonstrated by following the behavior of samples to which 5 percent water was added. The results for samples modified in this manner are shown in figure 5. The initial rate of the polymerization reaction, as judged from the slope of the

phenol partial pressure curve, is lower than when water was not added to the sample. The lower reaction rate is also reflected in the acetone-extraction data, where it is seen that the concentration of polymer precursor decreases more slowly. This is particularly noticeable in the initial stages of the reaction where the abrupt decrease is delayed until about 100 seconds. This decrease in extractable material occurs later than that shown in figure 4 and is also less precipitous, in agreement with the mass spectrometric results.

The ability of the mass spectrometer to detect differences in polymerization rates is demonstrated by the results shown in figure 6. These data indicate the effects of varying power output of the dielectric heating unit on the phenol evolution rate. Power output variations were effected by changing the spacing of the electrodes in the oven. The maximum spacing of 10.3 cm corresponds to minimum power absorption by the sample. Each plot represents averages of five or six runs and shows that the polymerization rate increases with power input. The ability of the mass spectrometer to determine these differences demonstrates clearly the versatility of this technique in the study of polymeric reactions.

CONCLUSIONS

A mass spectrometric method to provide real-time monitoring of polymerization reactions has been developed and demonstrated by observing the dielectrically induced curing of a composite material based on a phenol-formaldehyde resin. The system sensitivity and response time are adequate to permit the determination of essentially complete polymerization. The technique should be viable in monitoring any similar reaction provided only that a volatile reactant or product exhibits a suitable mass spectral peak.

The major problem in using this technique is assuring that a representative sample is transported to the mass spectrometer ion source. This requires that the entire inlet system be maintained at temperatures sufficiently high to prevent condensation from the gas source up to and including the mass spectrometer ion source. Since electrical heating elements could not be introduced within the dielectric heater, and insufficient power could be transferred to the inlet itself from the dielectric heater, an alternative method of maintaining the elevated temperature was required. This was accomplished by the development of a pyrex inlet system heated within the dielectric region by hot, dry nitrogen gas, and outside this region by electrical resistance heating. Adequately short

response times were achieved by providing vacuum pumping at the outlet of the glass portion of the inlet system, thus facilitating gas flow to the capillary.

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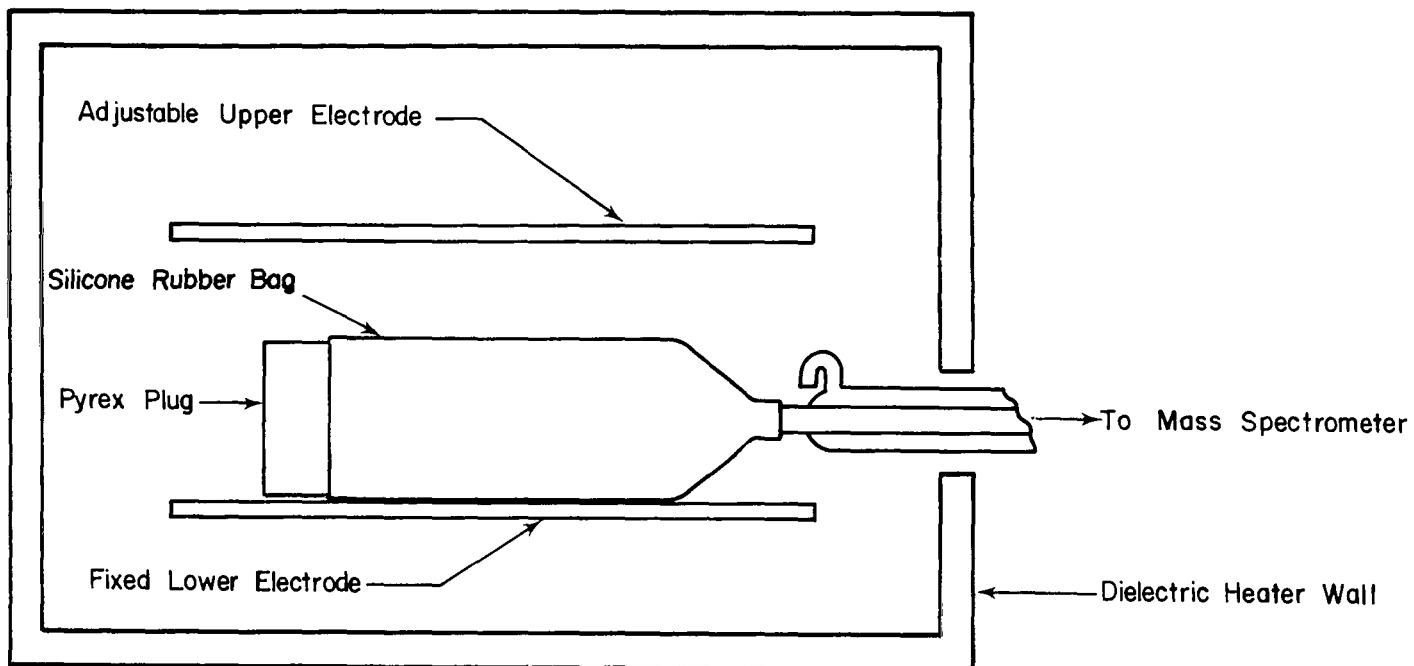


Figure 1.- Diagram of sample in heating unit.

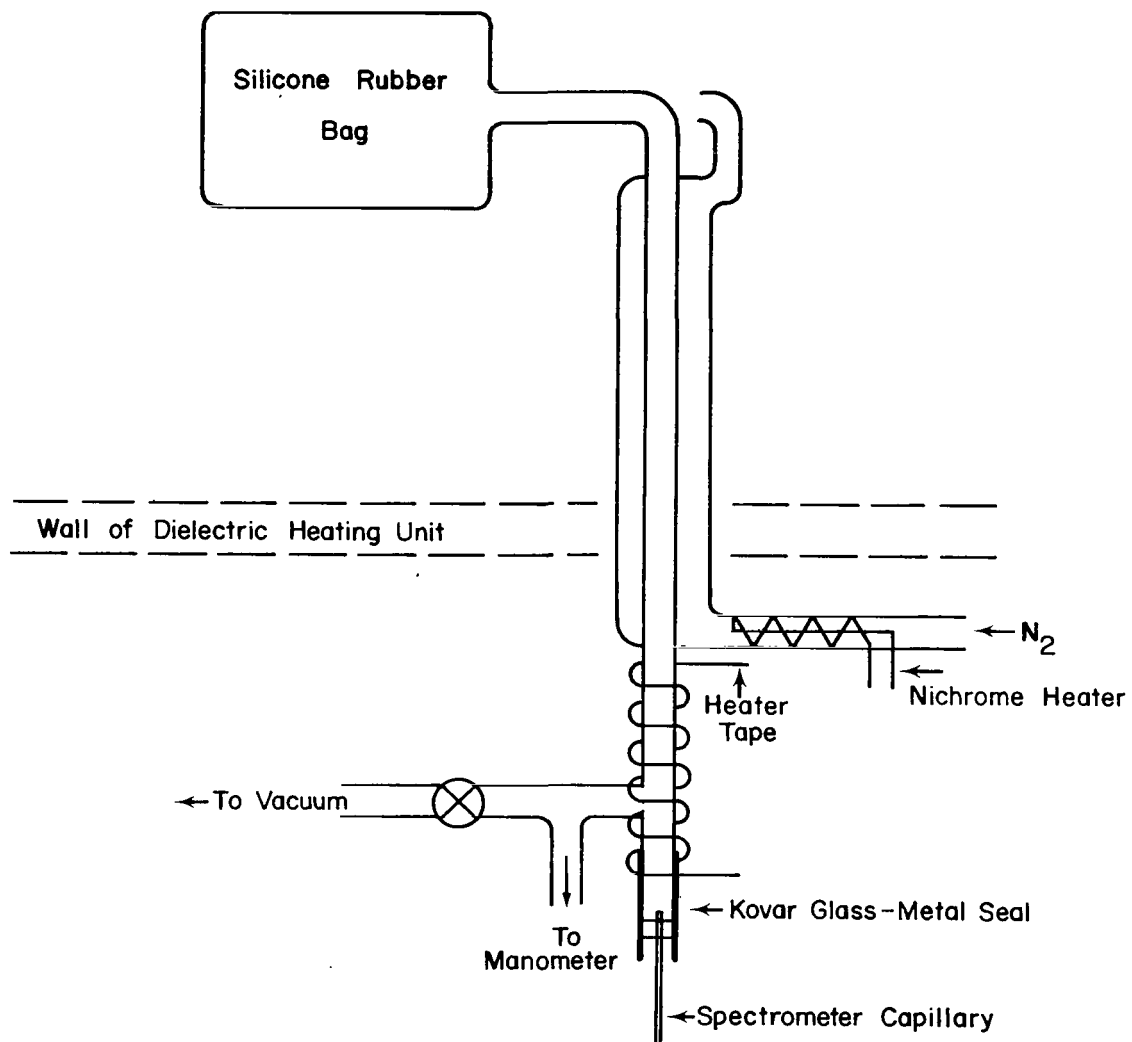


Figure 2.- Diagram of inlet system.

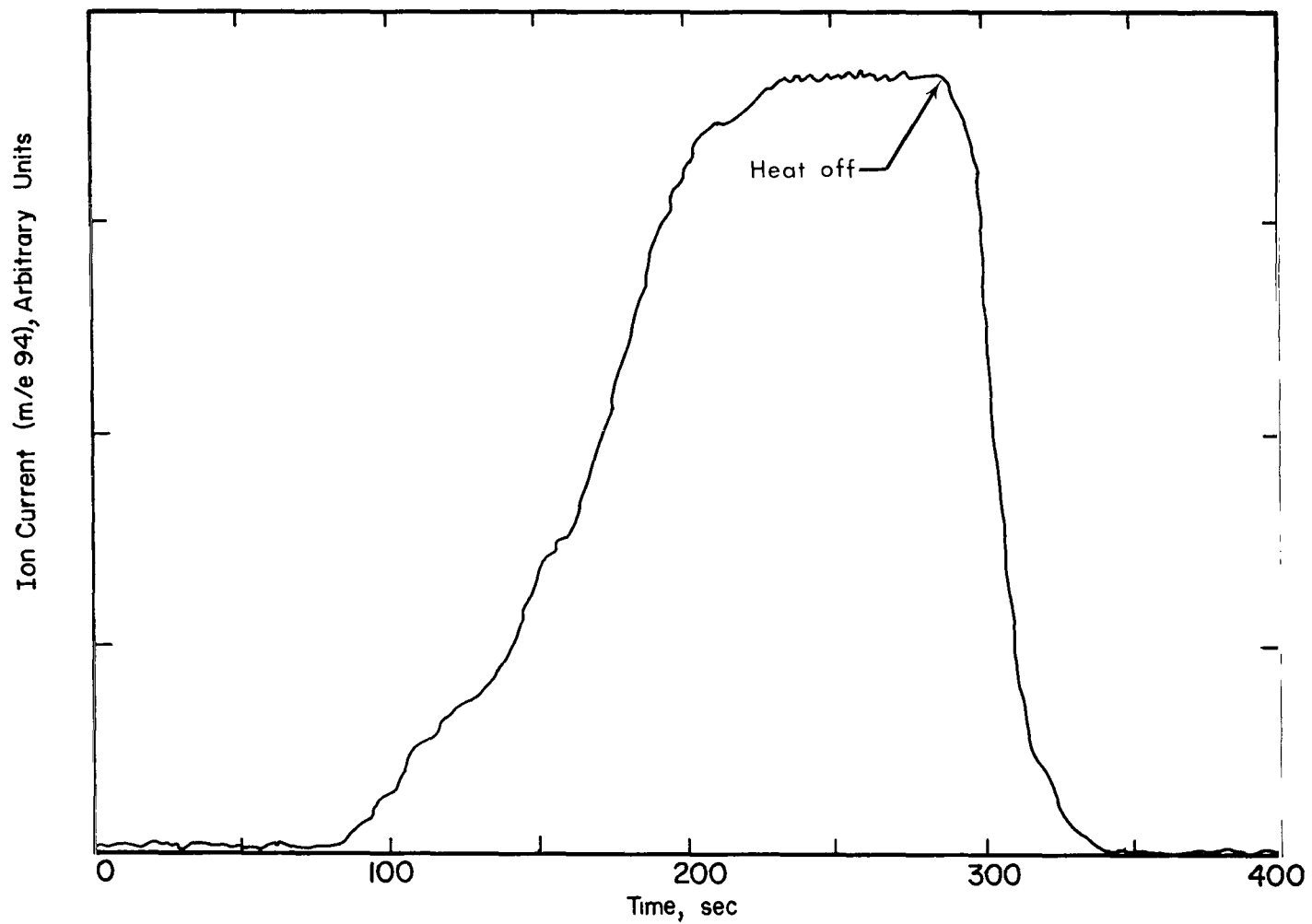


Figure 3.- Phenol evolution during polymerization.

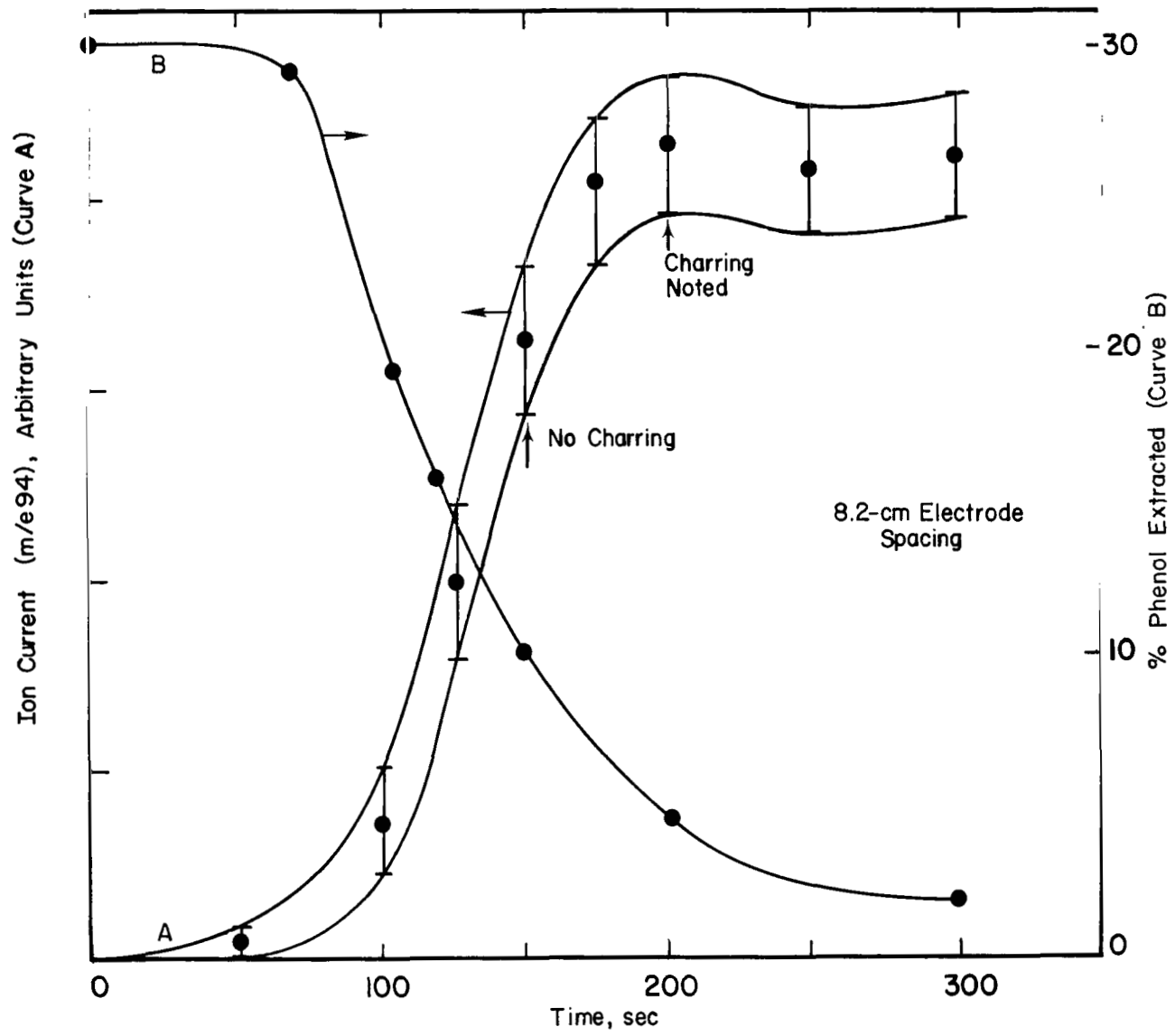


Figure 4.- Dielectric curing of dry phenolic resin.

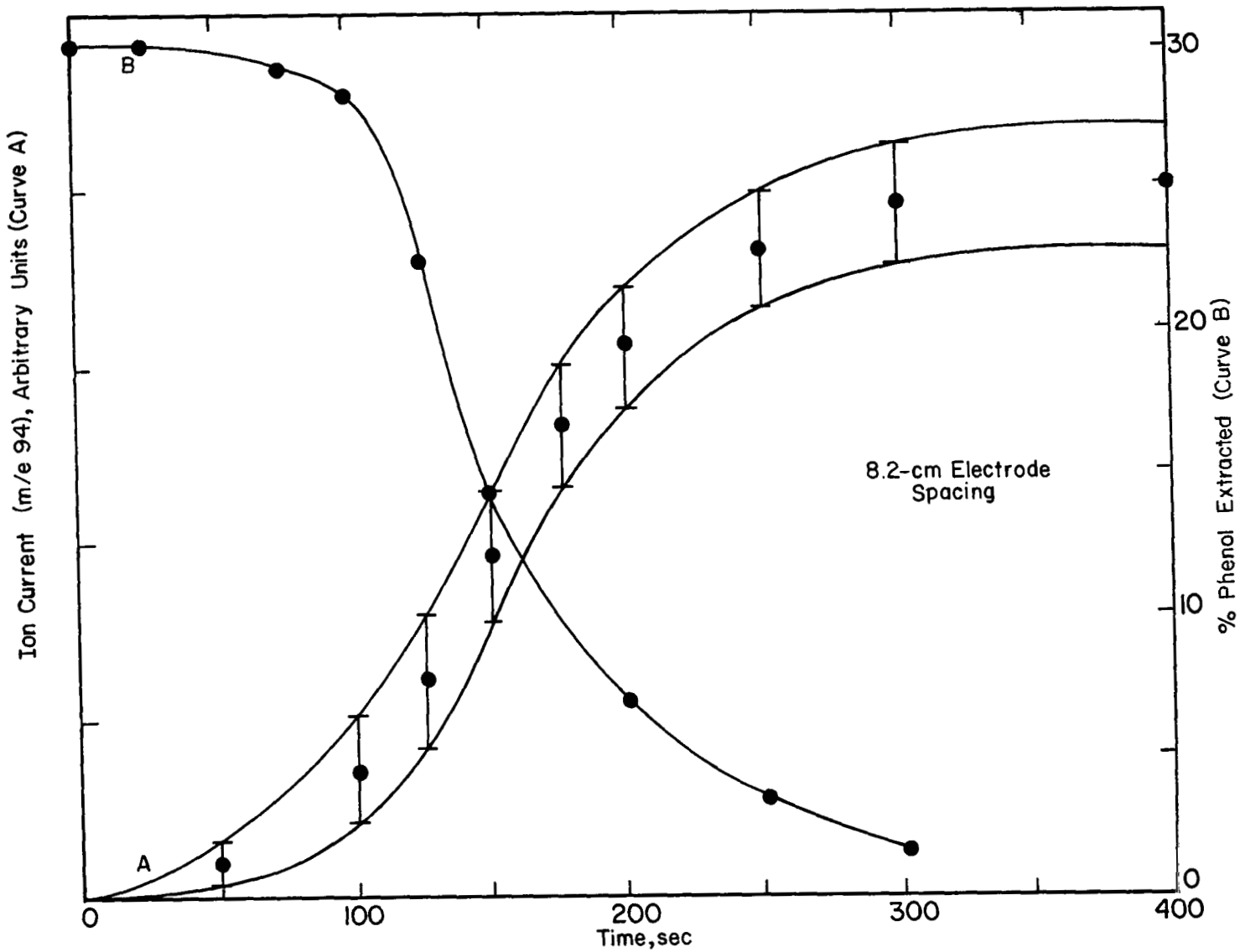


Figure 5.- Dielectric curing of phenolic resin with added moisture.

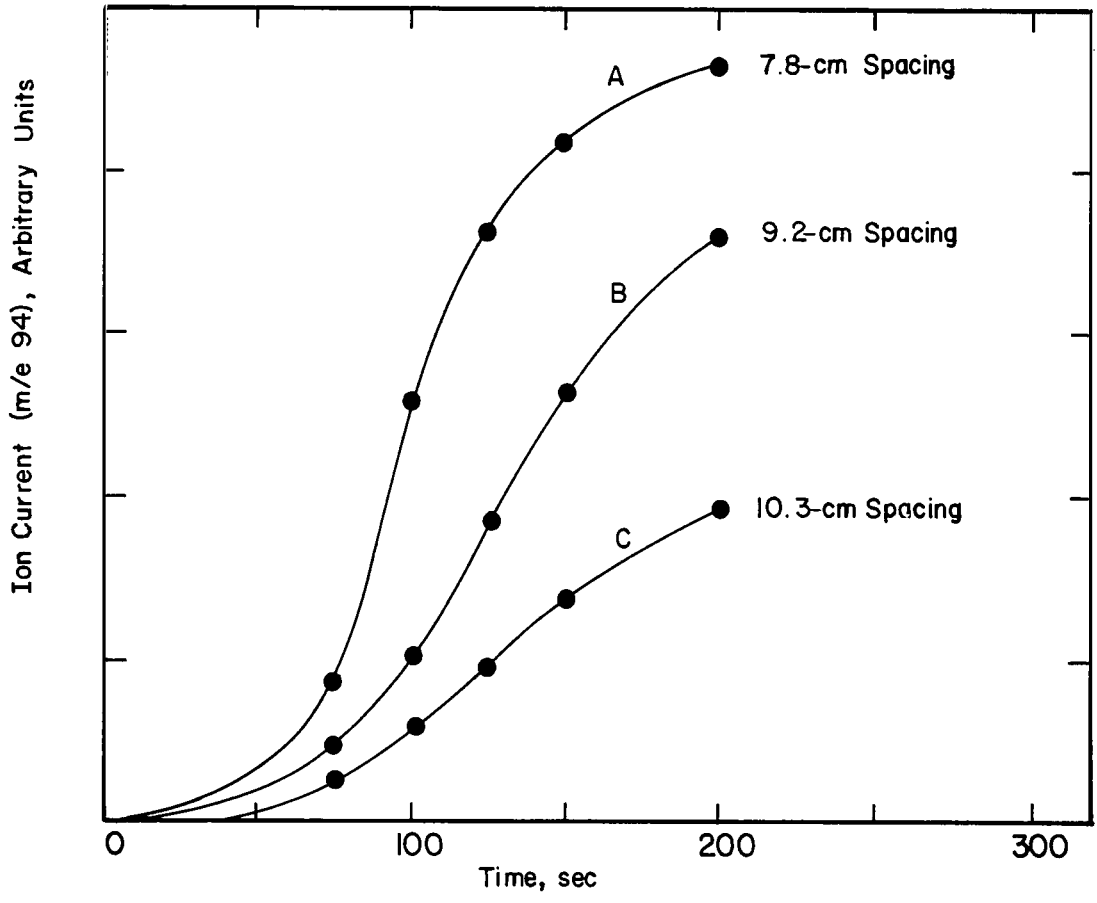


Figure 6.- Effect of electrode spacing on reaction rate.

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