

# A Novel Method for Measuring the Uniaxial Mechanical Properties of an Epoxy Resin During Polymerization

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## Synopsis

A new sample configuration for measuring tensile mechanical properties during cure is described. The method utilizes a soft rubber membrane to physically constrain a sample in a uniaxial geometry. Using this method in combination with a Dynastat mechanical spectrometer, it was possible to follow the polymerization of an epoxy resin from the liquid to the glassy state in a single experiment. The results of a uniaxial dynamic mechanical characterization of a curing epoxy resin are presented.

## INTRODUCTION

In recent years, epoxy resins have become the matrix of choice in adhesive and high-performance composite applications. This preference for epoxies can be attributed to their mechanical integrity, ease in processing, and solvent resistance. Although many studies have concentrated on measuring the mechanical properties of cured materials, relatively few have been performed in the area of mechanical characterization during cure.

Several methods have been developed for the study of the cure process. These include calorimetric,<sup>1-3</sup> dielectric,<sup>4,5</sup> torsional braid,<sup>6-8</sup> and dynamic mechanical<sup>9-11</sup> methods. Two problems are associated with the latter two mechanical methods. The first concerns the mechanical sensitivity of these methods during the incipient stages of polymerization. Early in the polymerization, the loads required to measure the relevant mechanical properties, e.g., storage and loss moduli, are dominated by the sample support, not by the resin itself. These errors can lead to inaccuracies in the pregel data. The second problem concerns the inability to accurately measure the high loads and small deformations involved in determining the mechanical properties in the glassy state. Thus, the major obstacle to a complete study of the cure process is finding a technique capable of measuring the mechanical properties from the liquid state to the glassy state.

The objective of this study is to demonstrate a simple and novel method for measuring the mechanical properties during the polymerization of an epoxy resin that has neither of the above-mentioned problems. The technique is novel in its use of a soft rubber membrane to physically support the epoxy resin-hardener mixture during polymerization. Using this sample geometry and a Dynastat mechanical spectrometer (Imass Inc., Hingham, Massachusetts); the uniaxial dynamic mechanical properties of a curing epoxy resin

were measured over the entire polymerization history. The relationship between the conditions of cure and the dynamic mechanical properties will be discussed briefly.

### EXPERIMENTAL

Epon 828, a DGEBA (diglycidyl ether of bisphenol-A) epoxy resin, and V-40, a polyamide curing agent, were chosen as the resin system for this study. The structure of V-40 is characterized by a flexible backbone that contains both primary and secondary amine functionalities. Both Epon 828 and V-40 were provided by the Shell Chemical Company. Assuming equivalent weights of 185 g/mol for Epon 828 and 140 g/mol for V-40 (as reported in the Shell technical bulletins), samples with amine-epoxy molar ratios of 0.8, 1.0, and 1.2 were formulated. Cure temperatures of 55, 85, 115, and 165°C were investigated.

The rubber balloon, aluminum tabs, hose clamps, and epoxy mixture involved in sample preparation, as well as a complete sample assembly, are shown in Figure 1. Samples were prepared in the following manner.

1. The closed end of a  $1\frac{1}{2}$  inch long and  $\frac{1}{4}$  inch diameter rubber balloon was cut off to form a uniform rubber membrane in the shape of a tube.

2. One end of the rubber membrane was stretched over a solid  $\frac{1}{2}$  inch aluminum tab. A hose clamp was used to keep the rubber membrane in place.

3. The other end of the rubber membrane was stretched over a  $\frac{1}{2}$  inch aluminum tab that had a  $\frac{1}{4}$  inch hole drilled through its center. Similarly, a hose clamp was used to keep the rubber membrane in place.

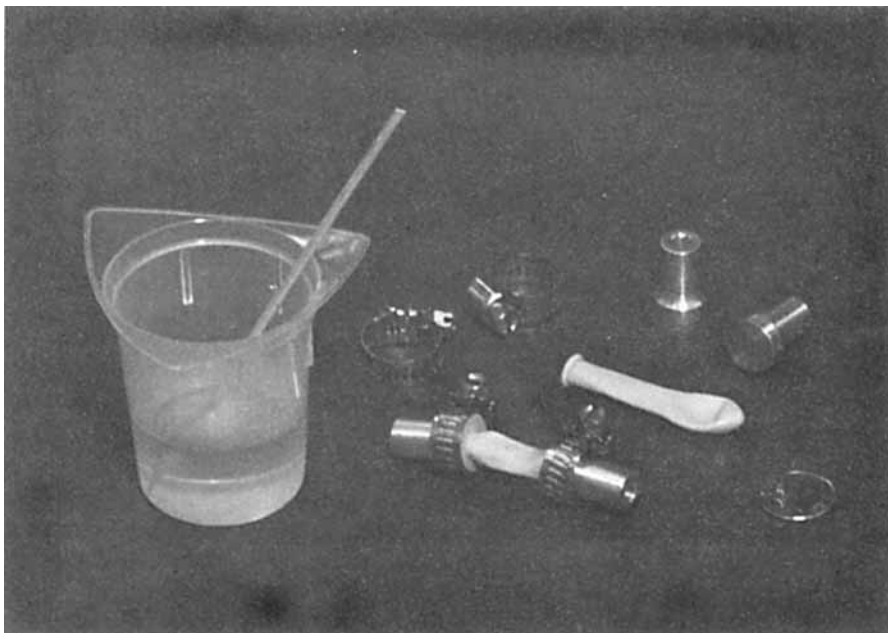


Fig. 1. Components involved in sample preparation and a complete aluminum tab-rubber membrane sample assembly.

4. The aluminum tab-rubber membrane assembly was then filled through the  $\frac{1}{4}$  inch hole with a few milliliters of the well-mixed V-40-Epon 828 mixture. The resulting sample geometry was that of a  $\frac{1}{4}$  inch slender cylinder with flared ends.

5. The sample assembly was placed inside the environmental chamber of a Dynastat mechanical spectrometer for uniaxial dynamic mechanical testing.

A  $2.3^{\circ}\text{C}/\text{min}$  temperature ramp was used to heat the samples, held at constant strain, from room temperature to the cure temperature, where it remained constant to within  $\pm 0.1^{\circ}\text{C}$  until the end of the polymerization. All samples were cured for approximately  $2\frac{1}{2}$  h.

Sinusoidal deformations at frequencies of 1.0, 3.0, and 5.0 Hz were used to characterize the curing process. The maximum strain to which the samples were subjected was initially 5% and decreased as polymerization occurred, in order to keep the applied strains in the linear viscoelastic range. Measurements of the tensile storage modulus  $E'$ , the tensile loss modulus  $E''$ , and  $\tan \delta$  were made every 100 s. At the end of the polymerization, the samples were cooled, at constant strain, at a rate of  $2.3^{\circ}\text{C}/\text{min}$ . By monitoring the change in  $E'$  with temperature, a measure of the glass transition temperature  $T_g$  was obtained.

## RESULTS

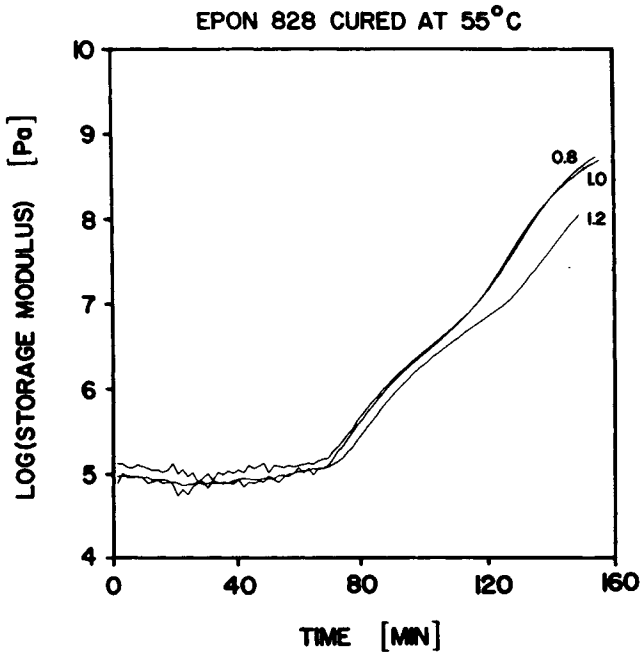
Figure 2 plots the tensile storage modulus  $E'$  at 1.0 Hz versus cure time at the three amine-epoxy ratios for the cure temperatures of 55, 85, 115, and  $165^{\circ}\text{C}$ , respectively. These curing data are replotted in Figure 3 so that the effect of cure temperature on  $E'$  for a particular amine-epoxy ratio may be viewed more clearly. Thus, Figure 3 plots  $E'$  at each cure temperature as a function of cure time for the 0.8, 1.0, and 1.2 amine-epoxy ratios. Figures 2 and 3 represent data that have not been corrected for the contribution of the rubber membrane that had an elastic modulus of 0.08 MPa over the entire temperature range studied. Such corrections were deemed unnecessary since the force required to deform the sample shortly after gelation is dominated by the sample. Since the contribution of the rubber membrane is small compared with the contributions of other sample support methods, it is possible to observe more of the cure process.

The  $E'$  data taken at 3.0 and 5.0 Hz during cure were found to occur at higher values relative to the 1.0 Hz data. This dependence of  $E'$  on frequency demonstrates the viscoelastic nature of the epoxy. Since these dynamic mechanical data were qualitatively the same as the results at 1.0 Hz, they are not presented here.

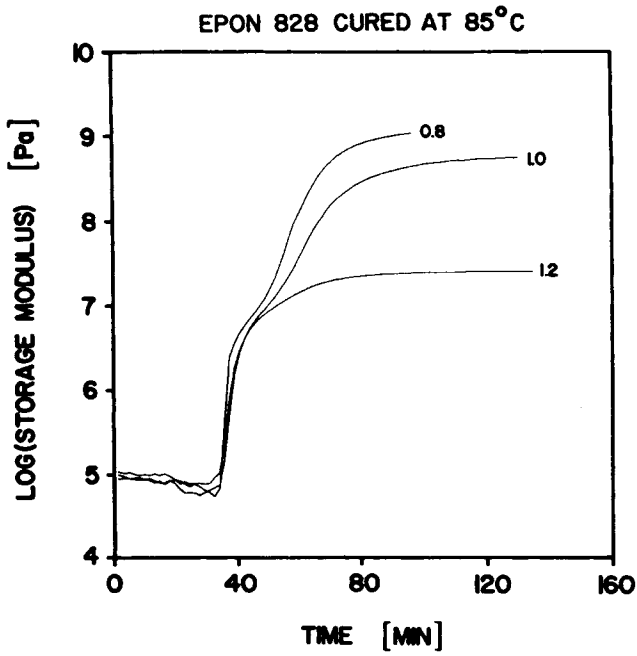
Table I summarizes the mechanical properties in terms of  $E'$  (at 1.0 Hz),  $\tan \delta$ , and  $T_g$  measured at the end of polymerization for the three amine-epoxy ratios at each of the cure temperatures.

## DISCUSSION

From Figures 2 and 3 it is clear that with the rubber membrane sample geometry and the Dynastat it was possible to measure approximately six orders of magnitude in mechanical response. This range in mechanical sensitivity appears to be sufficient to monitor the entire polymerization.



(a)



(b)

Fig. 2. Plot of the log (storage modulus  $E'$ ) at 1.0 Hz during polymerization for the 0.8, 1.0, and 1.2 V-40-Epon 828 ratios at the cure temperatures of (a) 55, (b) 85, (c) 115, and (d) 165°C.

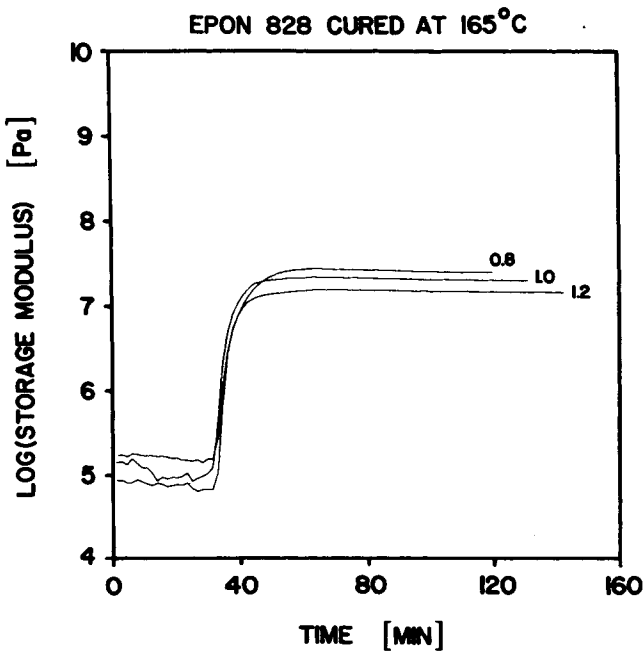
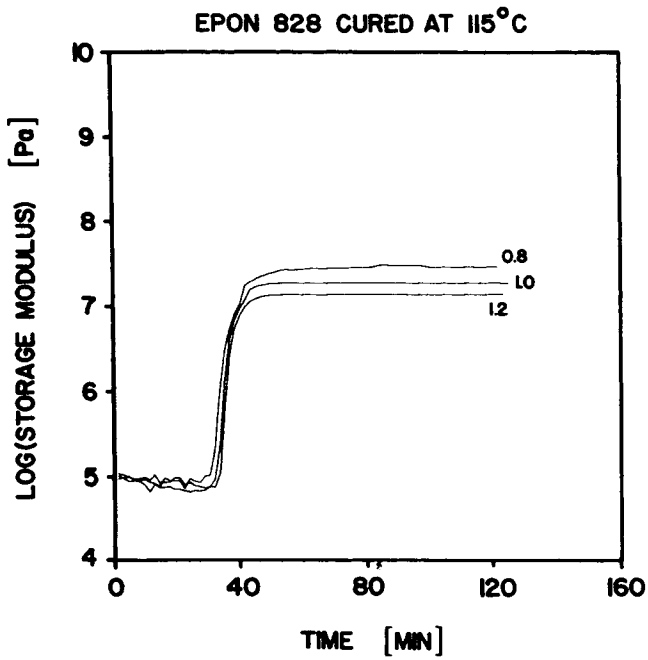
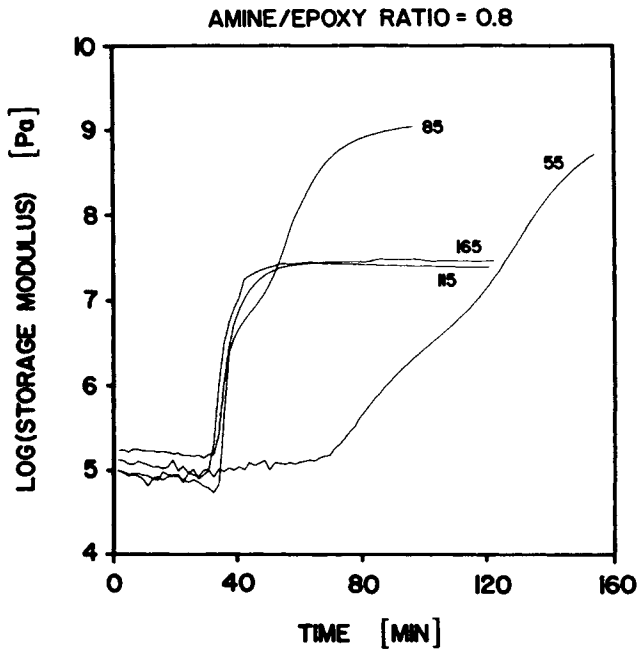
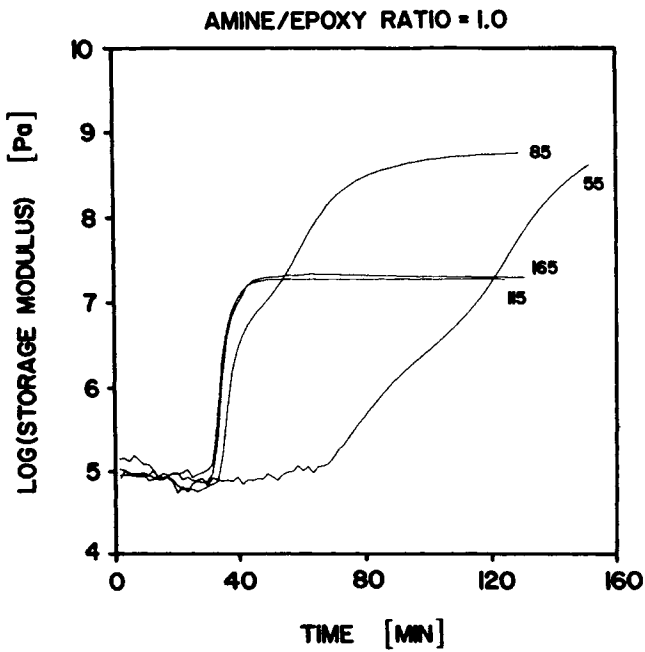


Fig. 2. (Continued from the previous page.)



(a)



(b)

Fig. 3. Plot of the log (storage modulus  $E'$ ) at 1.0 Hz during polymerization for the 55, 85, 115, and 165°C cure temperatures at the (a) 0.8, (b) 1.0, and (c) 1.2 V-40-Epon 828 ratios.

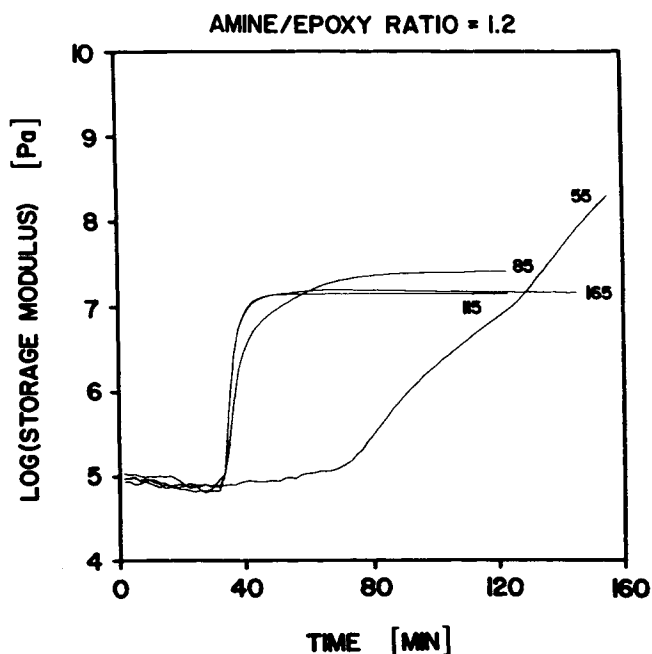


Fig. 3. (Continued from the previous page.)

TABLE I  
Summary of  $E'$  (at 1.0 Hz),  $\text{Tan } \delta$ , and  $T_g$  Data<sup>a</sup>

Cure temperature (°C)	Amine-epoxy ratio	$E'$ [MPa]	$\text{Tan } \delta$	$T_g$ (°C)
55	0.8	700	0.45	50
55	1.0	500	0.45	50
55	1.2	300	0.75	50
85	0.8	1100	0.15	75
85	1.0	600	0.35	70
85	1.2	25	0.75	65
115	0.8	30	0.30	95
115	1.0	19	0.03	80
115	1.2	14	0.006	65
165	0.8	27	0.001	90
165	1.0	22	0.0001	75
165	1.2	15	0.0001	60

<sup>a</sup> Measured at the end of polymerization for all V-40-Epon 828 ratios and cure temperatures investigated.  $T_g$  was determined from cooling experiments.

Since the objective of this paper is the description of a technique, a detailed explanation of the mechanical properties as a function of the cure conditions will not be given. A more complete study of the network formation process for the V-40-Epon 828 epoxy resins is given by Vratsanos and Farris<sup>12,13</sup> using the technique of impulse viscoelasticity and the rubber membrane sample con-

figuration. In those studies many of the properties associated with the cure process were determined as a function of the polymerization history. Among these were gel time, equilibrium tensile modulus, cure stress, cure shrinkage, elongational viscosity, mean relaxation time, and thermal expansion coefficient. These properties cannot be obtained by dynamic mechanical techniques.

As seen in Table I, the epoxies cured with the 0.8 amine-epoxy ratio had the highest storage moduli for all the cure temperatures investigated. Although the network structures resulting from the cure of epoxides with polyamides are complex,<sup>14</sup> the following explanation of the observed mechanical behavior is suggested. At the lower amine-epoxy ratios, the epoxide rings were able to react with both the primary and secondary amines. As a result, a highly crosslinked network was formed. Conversely, when an excess of amine was used, fewer epoxide-secondary amine reactions were able to take place. This resulted in a loosely crosslinked or defect-containing network. These defects could be manifested as dangling chain ends incapable of supporting an elastic stress.

The  $E'$  data for the samples cured at 115 and 165°C indicate that the polymerizations were almost complete before reaching their respective "isothermal" cure temperature. This is the result of the slow temperature ramp used in order to minimize thermal lag in the samples. At their respective cure temperatures, both sets of samples exhibited  $\tan \delta$  values that were nearly zero, suggesting that they behave elastically at these temperatures. The low  $E'$  values observed during polymerization for these samples can be explained by the fact that they were cured above the ultimate  $T_g$  of the V-40-Epon 828 system. Additionally, the samples cured at 165°C showed a slight loss in storage modulus with time and a decrease in  $T_g$  relative to the samples cured at 115°C. These phenomena can be attributed to thermo-oxidative degradation of the epoxy.

In the range of amine-epoxy ratios studied, the ultimate glass transition temperature obtained for the V-40-Epon 828 system was approximately 95°C. For the samples cured at 55°C, the competition between polymerization and vitrification limited the  $T_g$  of these samples to 50°C. Apart from these samples, the  $T_g$  of samples decreased with increasing amine-epoxy ratio. This is in agreement with the reduction in crosslink density expected with an increase in amine-epoxy ratio.

## CONCLUSIONS

A new method was developed for measuring the tensile mechanical properties during cure. The technique utilizes a soft rubber membrane to physically constrain the sample in a uniaxial geometry. The rubber membrane sample configuration offers enhanced sensitivity in the early stages of polymerization when compared with other methods used to support samples. Using this method in combination with a Dynastat mechanical spectrometer, it was possible to measure tensile moduli in the range of 0.05 MPa to 3 GPa. The curing of Epon 828 epoxy resin with V-40 as curing agent was studied as a demonstration of the usefulness of the method.

Based upon the time needed for complete cure, our findings suggest that the optimum cure temperature for the V-40-Epon 828 system is 115°C. In ad-



dition, the 0.8 amine-epoxy ratio yielded the largest storage modulus of the three ratios studied at all cure temperatures.

Future work will include the characterization of other thermosetting and thermoplastic materials using the rubber membrane sample configuration in conjunction with the impulse viscoelastic technique.

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