

# Epoxy Resins: Effect of Extent of Mixing on Properties

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## Synopsis

Inhomogeneities observed in cured epoxy resins by several workers appear to be related to the effectiveness of mixing the reactants. This mixing effectiveness also has an effect on the softening temperature  $T_g$ , of DETA cured resins, of as much as 10°C. Improved mixing of both DETA and Versamid 140 cured systems resulted in substantial ultimate strength improvement, in agreement with other recent results. Samples were mixed by hand, by a concentric cylinder mechanical mixer, and by application of an electrical field between the cylinders of the mechanical mixer while mechanical mixing was in progress.

## INTRODUCTION

Several workers have reported regions in cured epoxy resins which have different optical and thermal properties relative to the surrounding material.<sup>1-4</sup> Erath and Robinson<sup>1</sup> found fracture surfaces of certain molded and cured resins to have a 800–900-Å diameter “micellar” structure. Racich and Koutsky<sup>2</sup> also used electron microscopy and reported inhomogeneities in the form of nodules, 100–600 Å in size; the nodules seemed to form networks. Cuthrell<sup>3</sup> reported much larger spherical floccular aggregates, ranging from 20 to 90 μm in diameter. Kreibich and Schmid<sup>4</sup> found that, by annealing below  $T_g$ , a phase separation of higher and lower crosslink density occurred; they found two glass transition temperatures by differential scanning calorimetry. Kenyon and Nielsen<sup>5</sup> varied the resin/amine ratio in a system of Epon 815 and a flexibilizer, and a broad double peak was found in the dynamic mechanical loss behavior as a function of temperature. This was interpreted as higher modulus particles imbedded in a lower modulus matrix. Matyi, Uhlman, and Koutsky<sup>6</sup> found evidence for inhomogeneities in the size range of 100–1000 Å, with the most frequent size being 100–200 Å, by small-angle X-ray scattering. On the other hand, Dusek et al.<sup>7</sup> argue, primarily on the basis of small-angle X-ray measurements, that cured epoxy resins are homogeneous.

The rationale behind the present research is that inhomogeneities arise, at least in part, from problems inherent in short-time hand mixing of relatively viscous fluids. If true, this would explain the differences in size and degree of inhomogeneities observed by prior authors. The mixing must be done rapidly, before the reaction proceeds so far that the resin cannot be poured or cast. Vigorous mixing often introduces bubbles which interfere with the intended use; lower shear during mixing is often used to avoid bubbles. As best we can determine, no one has previously reported a study of the effect of intimacy of mixing on homogeneity. A recent presentation by Tateosian and Royer<sup>8</sup> on January 7, 1981 at the American Chemical Society Middle Atlantic Regional Meeting in Washington, D.C., reported an improvement in impact strength by as much as

58% by use of dynamic mixing. Striations observed under polarized light were used as a measure of the effectiveness of mixing.

In the present paper we compare results from electron microscopy, dynamic mechanical, and mechanical (stress-strain) measurements on epoxy samples mixed by hand, by hand followed by a concentric cylinder mixer, and by hand followed by the cylindrical mixer with a high voltage electrical field.

The use of an electrical field to induce mixing of viscous fluids of different conductivity is an interesting new technique with a literature of its own.<sup>9-11</sup> The method appears effective for intimate mixing of certain viscous systems, concurrent with bulk mechanical mixing, of viscous fluids of different conductivity. The electrical method has provided improved mixing in the preparation of polyurethanes,<sup>9</sup> and has been briefly examined in a few other polymer systems.

## EXPERIMENTAL

### Mixing

A photograph is shown in Figure 1. It consists of two concentric cylinders. The outer is fixed, and the inner is rotated at a controlled speed. The outer and inner cylinders are electrically insulated from one another and the frame, such that it is possible to apply a potential across the gap between them of up to a few thousand volts.

The epoxy resin used was a standard commercial material, Epon 828 (trade name of Shell Chemical Co.), chemically very similar to the diglycidyl ether of bisphenol A. Two amine curing agents were used: (1) diethylene triamine (DETA), obtained from Aldrich Chemical Co., and (2) a room-temperature-cure polyamide, marketed as Versamid 140 (trade mark of General Mills Chemical Co.). Both of these resin-curing agent combinations are commonly used room temperature cure systems.

TABLE I  
Sample Preparation and Curing

Curing agent	Mixing ratio	Test	Preparation and curing conditions
Versamid 140	0.8 g/1.0 g	1	Samples were mixed and the highly viscous fluid was poured onto a glass plate coated with mold release agent; the plate was then introduced into a pump vacuum; after about 0.5 h in the vacuum, a second plate was clamped onto the first, and the epoxy resin was allowed to cure for 48 h at 37°C
		2	Same as above except that the plate remained in the vacuum for 1 h before covering with the second glass plate
DETA	0.11 g/1.0 g	1	The Epon 828 and DETA were mixed, and the viscous fluid was then poured into a glass mold, consisting of two prepared glass plates clamped together; the epoxy resin was then cured for 24 h at 110°C
		2	As for sample.1 except the viscous fluid was put into a beaker and introduced into a vacuum for a maximum of 5 min before being poured into the prepared glass plates

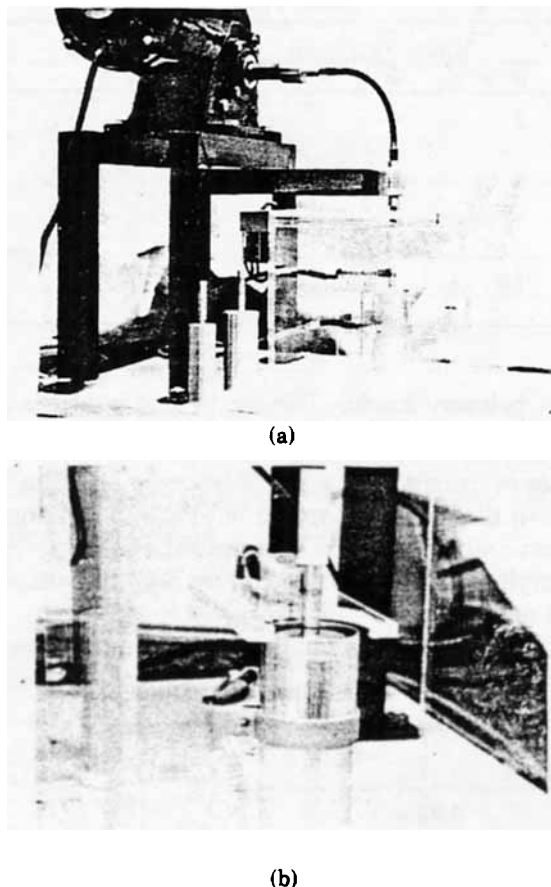


Fig. 1. Concentric cylinder mixer: (a) side view; (b) front view.

At room temperature, the Epon 828 epoxy has a viscosity of 10,000–16,000 cP, DETA has a viscosity of 0.9 cP, and Vesamide 140 has a viscosity of 8000–12,000 cP. In the first case we are mixing low- and high-viscosity fluids, and in the second case, both viscosities are high. Stoichiometric amounts of resin and curing agent were used in both cases. Details of the curing conditions are given in Table I. Since the cured specimens were to be used in dynamic mechanical and tensile measurements, care was taken to minimize bubbles.

The epoxy resins were mixed by three different methods, including (1) hand mixing in a beaker for 5 min, (2) hand mixing for 1.5 min followed by mixing for 5 min mechanically in the mixer at a predetermined speed (See Table II), or (3) hand-mixed for 1.5 min and then mechanically mixed for 5.5 min while an electrical potential was applied for 5 min.

### Characterization of Cured Resins

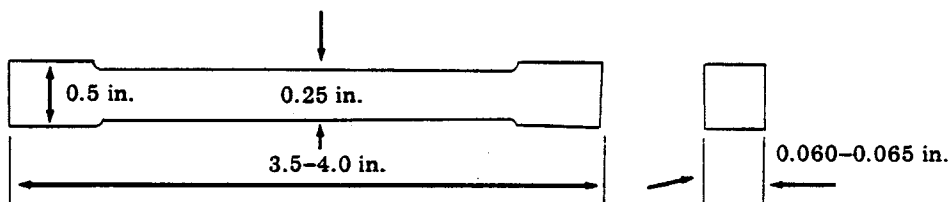
Glass transition temperatures and dynamic mechanical properties were obtained from a Rheovibron Dynamic Viscoelastometer (Toyo Measuring Instruments, Ltd.), at 11 Hz and 110 Hz. Samples were about 5 cm long  $\times$  0.3 cm  $\times$  0.05 cm thick, and were measured from room temperature to 150°C, in 3°C intervals. For transmission electron microscopy, cured 2 mm thick, cast samples were frozen in liquid N<sub>2</sub> and fractured, blown dry with canned air, and coated

TABLE II  
 Mixing Procedures

Sample	Mixing Time (min)			Mixer speed (rpm)	EMF (V)	Spacing (cm)
	Hand	Mech.	Elec.			
Hand mixed	5.0	—	—	—	—	—
Mech. mixed	1.5	5.0	—	125	—	0.8
				180	—	0.8
				125	—	0.4
Elec. mixed	1.5	5.5	5.0	125	300	0.8
					600	
					900	
					1200	

with 250,000 MW polyacrylic acid. Polyacrylic acid is soluble in water, and water has little effect on the epoxy in comparison with other possible solvents, such as acetone. After overnight drying, the polyacrylic acid film was peeled off and a platinum-carbon film was evaporated onto it at a 20° angle. The film was supported by evaporating a carbon base onto the sample. After mounting on a grid, the polyacrylic acid was removed and the replica examined under a Hitachi 200-kV electron microscope.

Samples for tensile strength measurements were machined to the following dimensions from cast plates:



The measurements were made according to ASTM test method D638 using a 0.2 in./min Instron® crosshead speed. Five samples were broken for each test condition, and the average was taken.

## RESULTS AND DISCUSSION

### Electron Microscopy

Figure 2 shows a fracture surface from an Epon 828-DETA sample that was hand mixed for 5 min. Close inspection reveals many small nodular regions of approximately the same size as that reported by Racich and Koutsky (100-1000 Å). We found a variation in size of the inhomogeneous regions which depended upon the vigor of the 5-min mixing, with less vigor resulting in larger nodules. An effect of the viscosity of the two fluids would also be expected, although only DETA was used for this part of the work.

The 1.5-min hand-mixed, 5-min mechanically mixed sample, in Figure 3, appears to contain larger particles with an interstitial fluid. The variations in composition appear on a larger size scale. We do not know the relative effectiveness of the spatula-beaker hand-mixing procedure as compared with the

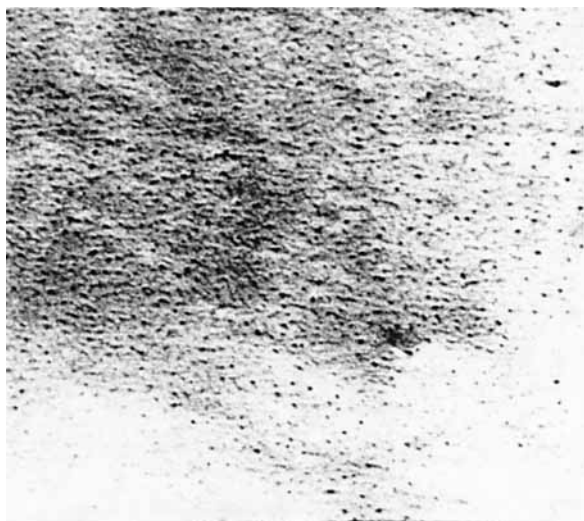


Fig. 2. Hand-mixed stoichiometric sample of cured Epon 828-DETA, fractured in liquid  $N_2$ . The magnification is 30,000 $\times$ .

cylindrical mixer, and, indeed, it may vary greatly depending on who is doing the hand mixing. The concentric cylinder mixer was by no means designed to be an optimum mixer.

The combination of 1.5-min hand mixing and 5.5-min electro-mechanical mixing (1200 V) shows the most homogeneous appearance (Fig. 4). Little indication of inhomogeneity remains relative to the other two mixing procedures. We conclude that increased mixing results in a more homogeneous product, with the electrical mixing being a new and apparently effective technique. The nodules and inhomogeneities previously reported may well be associated with the problem of intimately and rapidly mixing these viscous materials.

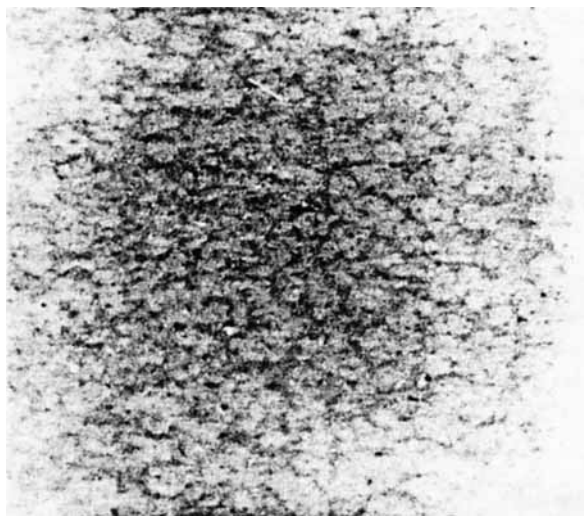


Fig. 3. Concentric cylinder-mixed sample of Epon 828-DETA; liquid  $N_2$  fracture surface. The magnification is 30,000 $\times$ .

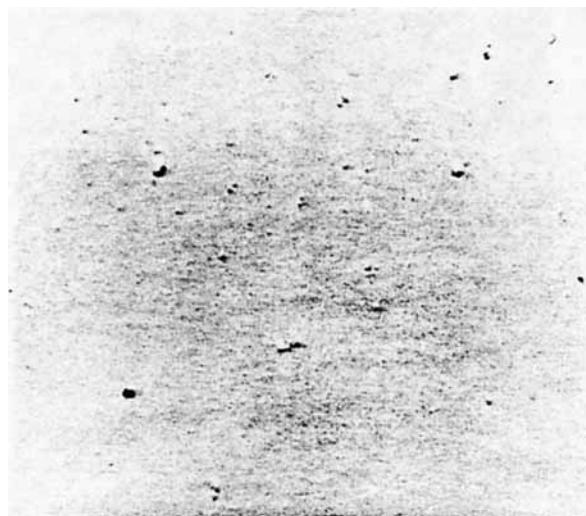


Fig. 4. Concentric cylinder with imposed 1200-V electrical field; Epon 828-DETA liquid N<sub>2</sub> fracture surface. The magnification is 30,000 $\times$ .

### Glass Transition Temperature

While the particular samples we have investigated were not so disparate as to show two transition temperatures, such as were observed by Kenyon and Nielsen, we do find some differences which appear related to the mixing procedure. Since  $T_g$  is closely related to the heat distortion temperature (HDT), a lowering of  $T_g$  owing to a mixing problem will also mean a lowering of HDT, which is of considerable practical importance. The data are shown in Table III for Versamid 140 curing agent and Table IV for DETA. The Versamid 140 data indicate that hand mixing and brief hand mixing followed by the cylindrical mixer are somewhat better than when the voltage is applied. No clear trend is observed with changing voltage. It may be that an electrochemical side reaction is taking place; one would not expect the voltage to have a *lowering* effect on  $T_g$ .

TABLE III  
Glass Transition Temperatures, Epon 828-Versamid 140 System

Method of mixing		$T_g$ ( $^{\circ}$ C)	
		From: $E''$	$E'$ Inflection
		<u>11 Hz</u>	
Hand		75	84
Mechanical		76	83
Electro-mechanical	300 V	72	78
	600 V	74	78
	900 V	72	76
	1200 V	72	80
		<u>110 Hz</u>	
Hand		82	92
Mechanical		83	91
Electro-mechanical	300 V	80	87
	600 V	80	90
	900 V	78	88
	1200 V	78	91

TABLE IV  
Glass Transition Temperatures Epon 828-Versamid 140 System

Method of mixing		Glass transition temp $T_g$ ( $^{\circ}\text{C}$ )
	<u>11 Hz</u>	
Hand		134
Mechanical		134
Electro-mechanical	300 V	136
	600 V	141
	900 V	141
	1200 V	146
	<u>110 Hz</u>	
Hand		137
Mechanical		137
Electro-mechanical	300 V	139
	600 V	145
	900 V	144
	1200 V	149

The less-viscous DETA curing agent exhibits the opposite effect (Table IV). While there is still little difference between hand and mechanical mixing, all samples with the imposed voltage have higher  $T_g$ 's, and the higher the voltage, the higher the  $T_g$ . The average increase was about  $7^{\circ}\text{C}$ , and the maximum (1200 V) over  $10^{\circ}\text{C}$ . We believe that a more homogeneous product, consistent with the microscopy results, was obtained from the electromechanical mixing. The continuous phase or matrix will have a higher degree of crosslinking in a homogeneously mixed sample. The continuous phase crosslink density will have a strong effect on both the onset of the glass transition and on mechanical properties.

Voltages over 1200 V may be even more effective, based on work with polyurethanes; our equipment at that time was limited to 1200 V.

### Tensile Strength Measurements

The tensile strength results are shown in Table V. Each strength reported is taken from the average of five breaks. The two vacuum treatments were used to minimize bubbles; specimens exposed to vacuum for 1 h were almost bubble-free, whereas those exposed for 0.5 h still contained enough voids to act as stress concentrators and reduce the strength. The vacuum could also have removed volatile lower molecular weight materials from the curing agent and resin, although we believe this was a lesser effect. The longer time of exposure to vacuum clearly resulted in a strength improvement in all cases.

From the  $T_g$  results, we would expect little difference between hand-mixed and machine-mixed Versamide 140 samples, and no major difference is observed. It is surprising, however, that the electro-mechanically mixed Versamide samples improve significantly in strength as the voltage is increased, and are generally stronger than the hand or machine mixed samples. The 1200-V sample is low for an unexplained reason.

Reduction of the spindle spacing in the mixer from 0.8 cm to 0.4 cm resulted in an increase from 8500 psi to 9000 psi in strength, as might be expected. In-

TABLE V  
 Tensile Strength Results

Curing agent	Mixing method	Run 1	Run 2
		Tensile strength (lb/in. <sup>2</sup> )	Tensile strength (lb/in. <sup>2</sup> )
V-140	Hand	<u>0.5-h vacuum</u>	<u>1-h vacuum</u>
		7040	8320
	Mechanical	7360	8512
		Electrical-mechanical	300 V
	600 V		8960
	900 V		9280
	1200 V		8640
	Reduced spacing		—
	Increased spindle speed	—	8670
	DETA	Hand	<u>No vacuum</u>
4800			6400
Mechanical		5440	—
		Electric-mechanical	300 V
600 V			—
900 V			8320
1200 V			9665

creasing the spindle speed, with the wide spacing of 0.8 cm, from 125 rpm to 180 rpm had only a small effect, if any. These effects of the gap change and speed change seem, at least qualitatively, consistent with their effects on the shear rate at the cylinder wall.

As might be expected from the  $T_g$  results, the electrico-mechanical mixing results for the DETA cured samples are considerably higher than the controls. The results for 900 V and 1200 V without vacuum pretreatment may be low because of bubbles; the samples given 5 min of vacuum exposure at these voltages were much stronger. Data have not yet been obtained for DETA with 5-min-vacuum pretreatment. The improvements in strength we have observed appear consistent with the recent results of Tateosian and Royer.<sup>8</sup>

In overview, increased mixing effectiveness decreased the observed nodules in DETA cured resins, raised the glass transition temperature, and significantly increased the ultimate tensile strength. No  $T_g$  increase was observed when the more-viscous Versamide 140 curing agent was used, although strength improved with electro-mechanical mixing and with increased shear (decreased gap) in the mixer.

No effort has yet been made to optimize mixer design or to determine necessary shear rates, times, etc. The electro-mechanical system reportedly provides shear on the Angstrom size scale,<sup>9-11</sup> which seems desirable to diminish the size and number of nodules we and others have found. Equivalent mechanical means may be possible, however. The effect of the electrical and viscous properties of various curing agents on mixing should be methodically investigated, and minimum criteria set up to guide the many fabrication processes that use epoxy resins.

The experimental work was conducted by a series of three University of Connecticut Chemical Engineering undergraduates: Michael Cantor, apparatus and early work; Warren Volles, microscopy; and Jonathan Rowe,  $T_g$  and strength measurements.



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