

# Diluted Epoxy Adhesives II. Relationship of Shrinkage During Cure to Lap Shear Strengths

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## Synopsis

The shrinkage of a series of epoxy adhesives diluted with either phenyl glycidyl ether (PGE) or 1,4-butanediol diglycidyl ether (BDE) and cured with either diethylenetriamine (DTA) or diethylaminopropylamine (DPA) was measured and compared with the steel-to-steel lap shear strength obtained with these adhesives. It was found that the adhesives with the highest level of shrinkage also gave the highest strengths. Samples cured initially at room temperature with DPA underwent a significant expansion when postcured at elevated temperatures. The amount of shrinkage was found not to be dependent on sample size.

## INTRODUCTION

The changes in density, surface tension, and viscosity of a series of epoxy adhesives diluted with varying amounts of either phenyl glycidyl ether (PGE) or 1,4-butanediol diglycidyl ether (BDE) and cured with either diethylenetriamine (DTA) or diethylaminopropylamine (DPA) were reported previously.<sup>1</sup> When these properties of the uncured adhesives were compared with the steel-to-steel lap shear strengths of the cured adhesives, it was observed that the strengths did not correlate with their physical properties. Besides altering the physical properties of the adhesives, the addition of diluents also alters the level of shrinkage that the adhesive undergoes during cure as well as the bulk flexural and tensile properties of the cured adhesive.

It is well known that most addition polymerizations result in varying degrees of shrinkage,<sup>2</sup> from a few percent in the case of epoxy resins up to more than 50% with polyethylene. The shrinkage associated with adhesive curing is considered detrimental to its performance.<sup>3</sup> The excellent adhesion of ice to solids and the utility of some solders have been attributed partially to their expansion upon solidifying.<sup>3</sup> Conversely, the improved performance of filled epoxy adhesives has been partially attributed to a decrease in shrinkage as a result of the filler loading. The addition of diluents to an epoxy resin would be expected to alter the amount of shrinkage that these systems undergo during cure. Therefore, the shrinkage of these adhesives has been measured and these results compared with their previously reported<sup>1</sup> steel-to-steel lap shear strengths.

## EXPERIMENTAL

### Preparation of Epoxy Solutions

The description of the materials used in this research and the details concerning the preparation of the diluted adhesives were previously reported.<sup>1</sup> When diethylenetriamine (DTA) was used as the curing agent, its concentration was adjusted in order to maintain a stoichiometric balance of amine hydrogens

to epoxide groups. In the case of diethylaminopropylamine (DPA), its level was maintained at 6 parts per 100 parts epoxy solution (phr).

A coded referral numbering system for the various mixtures of epoxy resin, diluents, and curing agents will be used in this discussion. The resin (abbreviated as 330) is always assumed to be 100 parts by weight, and the level of diluent is given in conjunction with its proper designation. The third section of the referral number denotes the amount of curing agent per 100 g of the epoxy resin-diluent solution. For example, 330-50 BDE-DPA6, indicates that 100 g of a mixture initially prepared from 100 g DER 330 and 50 g BDE was catalyzed with 6 g DPA.

### Determination of Density

The densities of cured epoxy samples were determined using two methods. For samples larger than 1 g, the density was obtained by a buoyancy technique<sup>4</sup> as described below. Three glass bottles (51.4 ml) were spray coated with Frekote 44 (Frekote Inc., Boca Raton, Florida) release agent, air dried for 30 min, and heated for 15 min at 100°C. Approximately 80 g of the desired epoxy resin, diluent, and curing agent were well mixed and degassed for a minimum of 2 min. Each bottle was filled with approximately 20 g of the epoxy adhesive and then placed in a 30° ± 0.01°C constant-temperature bath. The samples were cured for 24 h when DTA was used as the curing agent and for seven days when DPA was used.

After the 30°C cure was completed, the bottles were rolled in paper towels and carefully broken with a hammer. The epoxy plug was washed with acetone to remove any small pieces of glass and release agent that were adhering to it. The samples were stored in a desiccator until the density determinations were made.

Prior to the actual measurement of density, each epoxy sample was weighed on an analytical balance. The sample was then suspended by means of a wire cage from the analytical balance into a beaker of distilled water. After ensuring that there were no air bubbles attached to the sample, the weight of the sample and wire was recorded. The density of the sample ( $d_s$ ) was determined using the following equation:

$$d_s = \frac{d_L W_0}{W_0 - (W_L - W_c)}$$

where  $d_s$  = density of the solid sample plug,  $d_L$  = density of the distilled water,  $W_0$  = weight of the epoxy sample in air,  $W_L$  = weight of the epoxy sample in water, and  $W_c$  = weight of the wire cage in water. The temperature of the distilled water was monitored during the determinations and its density was obtained by interpolation of reported values.<sup>5</sup>

When the density of small samples ( $\approx 0.02$  g) of the epoxy adhesives was required, it was obtained by a water displacement technique.<sup>6</sup> The small samples were prepared by applying, as previously discussed, a Frekote 44 release agent to a glass surface. Ten drops of the liquid epoxy, approximately 0.02 g each, were placed separately on the glass and cured at 30°C. The cure time was dependent of the type of catalyst as stated above. The ten cured drops were placed in a preweighed pycnometer bottle of known volume and the total weight of the bottle

and epoxy samples was recorded. The pycnometer, containing the cured drops, was filled with distilled water, equilibrated in a constant-temperature bath at  $30^{\circ} \pm 0.01^{\circ}\text{C}$ , dried, and weighed. In this manner the total weight of the epoxy drops and the weight of water in the pycnometer were determined. The volume of the epoxy samples was calculated as the difference between the original volume of the pycnometer and the volume of water in the pycnometer. Therefore, the density of the solid epoxy was determined from the weight and calculated volume of the epoxy samples.

### Determination of Shrinkage

The shrinkage that a liquid epoxy adhesive undergoes during its cure was measured using a dilatometer. The method used was a modification of that reported by Parry and Mackay.<sup>7</sup> A diagram of the dilatometer is shown in Figure 1. A 30-cc standard taper dropping bottle was used since it was relatively inexpensive and could be discarded after use. The dropper-stopper was modified by welding to it a 1-cc pipet with 0.01-cc scale divisions. The pipet was used to monitor the change in volume of the liquid in the dilatometer. The interior of the bottle was coated with Frekote 44 release agent as previously described.

The following general procedure was used in assembling the apparatus and obtaining the values of shrinkage. Approximately 50 g of the desired epoxy resin, diluent, and catalyst was thoroughly mixed and degassed for at least 2 min. Using a disposable syringe, approximately 20 g of the adhesive was placed carefully into the preweighed dropping bottle. An accurate sample weight was then obtained by reweighing on an analytical balance. The bottle was filled to the bottom of its ground-glass joint with lightweight mineral oil. Using a rubber bulb on the pipet, additional mineral oil was drawn up into the pipet. The pipet containing the mineral oil was placed on the bottle, avoiding the entrapment of air bubbles, and the ground-glass joint was then firmly seated in place with the aid of Halocarbon 25-5S stopcock grease. The whole assembly was then placed in a  $30^{\circ} \pm 0.01^{\circ}\text{C}$  constant-temperature bath.

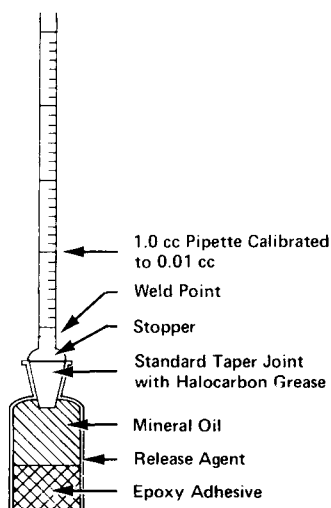


Fig. 1. Disposable dilatometer.

An initial expansion of the mineral oil was observed in the pipet as the system came to temperature equilibrium. The calculation of percent shrinkage was based on the highest point the mineral oil reached in the pipet during this initial expansion. The percent shrinkage was calculated by determining the volume decrease observed from the pipet readings and dividing this decrease by the initial volume of the adhesive sample.

The gel point of the adhesives was also determined at this time. An additional 20 g of the degassed epoxy sample was weighed into a 51.4-cc glass bottle and placed in the constant-temperature bath alongside the dilatometer. The point where the epoxy would no longer adhere to a wooden applicator stick, in the instance where the cure rate was very slow, was defined as the gel point. The interval between mixing the adhesive and its gel point was defined as its gel time.

The shrinkage of the epoxy samples was also determined from their changes in density from the liquid state to the solid state using the following equation:

$$\text{shrinkage (\%)} = \left(1 - \frac{d_0}{d_s}\right) 100$$

where  $d_0$  = initial density of the epoxy adhesive and  $d_s$  = density of the cured sample.

### Lap Shear Strengths

The steel-to-steel lap shear results were reported previously.<sup>1</sup> The same batches of materials were used to determine the shrinkage as were used in preparing the lap shear samples.

## RESULTS AND DISCUSSION

The shrinkage of the diluted epoxy solutions was determined by two methods. During the room-temperature cure, a dilatometer was used to follow the changes in volume while the measurement of density was used to follow the shrinkage of these systems during the elevated-temperature postcure cycle.

The dilatometric method has the advantage of making it possible to continuously monitor the shrinkage with respect to time. Figure 2 gives the dilatometric results for pure epoxy resin and the most highly diluted solutions cured with DTA. Intermediate amounts of diluent gave curves that fell in between the curves shown in this figure.

Samples of the epoxy solutions cured with DTA were then subjected to post-cure cycles, and additional shrinkages were measured by changes in density. These results are shown in Figure 3, and it is evident that these systems do not undergo any appreciable amount of additional shrinkage over that observed with the room-temperature cure.

The shrinkage that occurs prior to gelation of the adhesive was assumed not to have any effect on the development of internal stresses. The gel time, defined as the time from initial mixing to the gelation of the sample, was measured for each system and was indicated in Figure 2. The shrinkage prior to gelation was subtracted from the total shrinkage of each sample to yield the shrinkage after gelation (Fig. 4). When these results were compared to the lap shear strengths

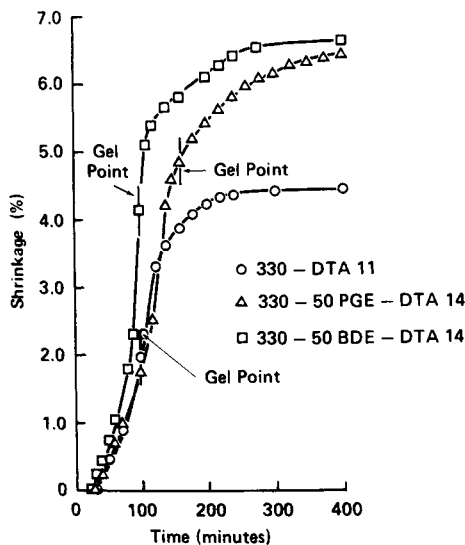


Fig. 2. Percent shrinkage vs time for epoxy solutions cured at 30°C with diethylenetriamine: (O) 330-DTA 11; ( $\Delta$ ) 330-50 PGE-DTA 14; ( $\square$ ) 330-50 BDE-DTA 14.

of room temperature-cured specimens, a reasonable correlation was found (Fig. 5). A comparison of the lap shear strengths of the adhesives cured for 4 hr at 100°C with the shrinkage after gelation for the same adhesives (Fig. 6) gave a very close correlation.

Initially, it was assumed that the greater the shrinkage, the greater the stresses that would be present in the adhesive. However, this would be expected to give an inverse correlation with the lower bond strengths for the adhesives with the highest shrinkage. With these adhesives, the higher strengths were found with systems with the highest shrinkage.

The dilatometric results for the DPA-cured adhesives were obtained (Fig. 7); as with the DTA-cured systems, the higher diluent levels gave higher shrinkages. Unlike the DTA-cured epoxy resins, however, an appreciable change in the shrinkage was found when the samples were postcured (Fig. 8). These samples were found to expand on postcuring. For example, the undiluted DPA cured

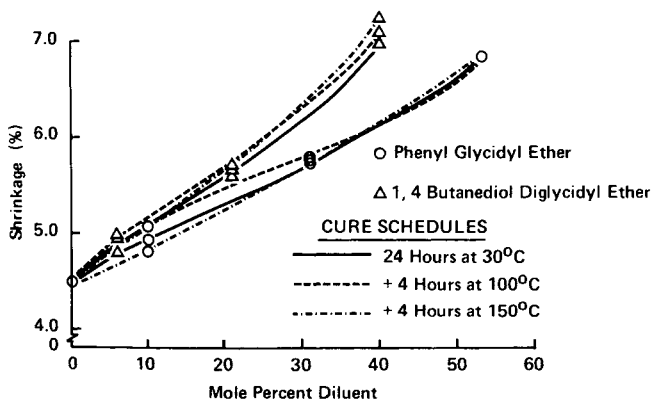


Fig. 3. Percent shrinkage vs mole percent diluent for epoxy solutions cured at various temperatures with diethylenetriamine: (O) phenyl glycidyl ether; ( $\Delta$ ) 1,4-butanediol diglycidyl ether.

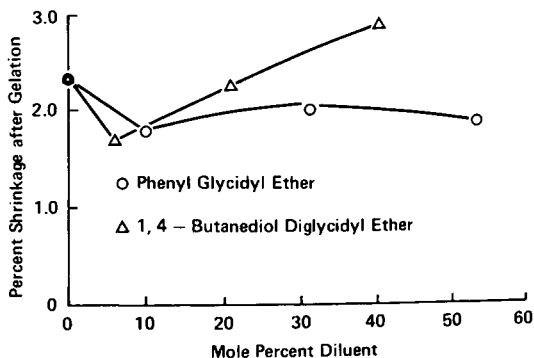


Fig. 4. Percent shrinkage after gelation for epoxy solutions cured 4 hr at 100°C with diethylenetriamine: (O) phenyl glycidyl ether; ( $\Delta$ ) 1,4-butanediol diglycidyl ether.

adhesive had a 4.2% shrinkage during the seven-day room-temperature cure but after the 4-hr 100°C cure its shrinkage was determined to be 3.0%. The reason for the expansion on postcuring with these samples is not understood. The DPA is basically a catalytic curing agent and requires a longer time than DTA to cure the epoxy resin. Since the degree of polymerization after room-temperature cure is lower for the DPA system, a greater amount of final cure will occur during the elevated-temperature postcure. If a reasonable number of short-range crosslinks are formed at this time, then the adhesive could be restrained from contracting very much during the time when it is cooling to room temperature.

The gel time was measured (Fig. 7), and the shrinkage that had occurred up to the gel time was subtracted from the total shrinkage for each DPA-cured system (Fig. 9). A comparison of the shrinkage after gelation with the lap shear results for the seven-day room-temperature-cured samples again gave a reasonable correlation of higher strengths with adhesives having higher shrinkages (Fig. 10). The correlation also held for the postcured samples (Fig. 11). The unexpected low lap shear value for the 330-50 BDE-DPA6 system was discussed previously.<sup>1</sup>

The shrinkage was determined by dilatometry or buoyancy using 20-g samples of adhesive. A lap shear test specimen, however, utilizes only 0.02–0.03 g ad-

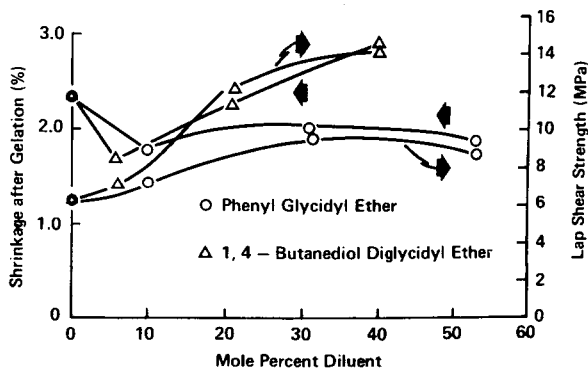


Fig. 5. Comparison of shrinkage after gelation to lap shear strengths for epoxy solutions cured seven days at room temperature with diethylenetriamine: (O) phenyl glycidyl ether; ( $\Delta$ ) 1,4-butanediol diglycidyl ether.

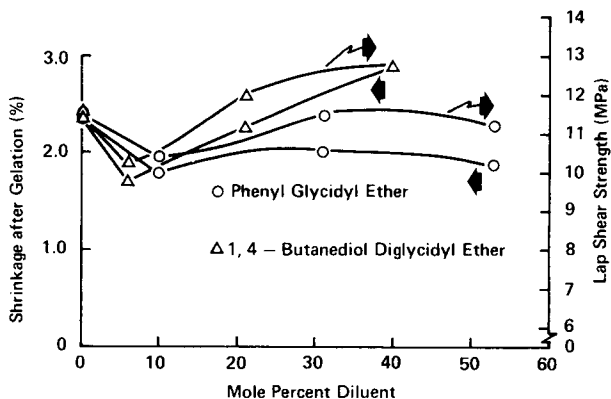


Fig. 6. Comparison for shrinkage after gelation to lap shear strength for epoxy solutions cured 4 hr at 100°C with diethylenetriamine: (O) phenyl glycidyl ether; ( $\Delta$ ) 1,4-butanediol diglycidyl ether.

hesive. Thus it was necessary to determine if the amount of shrinkage was similar for different sample sizes.

Figures 12 and 13 show the relationship of sample size to percent shrinkage for undiluted epoxy resin cured with DTA or DPA. The smallest samples measured were 0.02 g, as determined by the water displacement method. The stoichiometric curing agent (DTA, Fig. 12) produced no change in shrinkage with the small sample size. On the other hand, the catalytic curing agent (DPA, Fig. 13) produced a significant increase in shrinkage with the small sample size. There was no attempt to increase the surface area to volume ratio of the 0.02-g epoxy sample which would more closely approximate that of the adhesive bondline.

There is no obvious reason why adhesive systems that show an increase in shrinkage also yield higher lap shear strengths. As discussed earlier, it would normally be expected that lower lap shear strengths would be obtained with the higher shrinkage level. A possible explanation for these observations is that as the diluent level is increased, the bulk properties of the adhesives, such as flexural

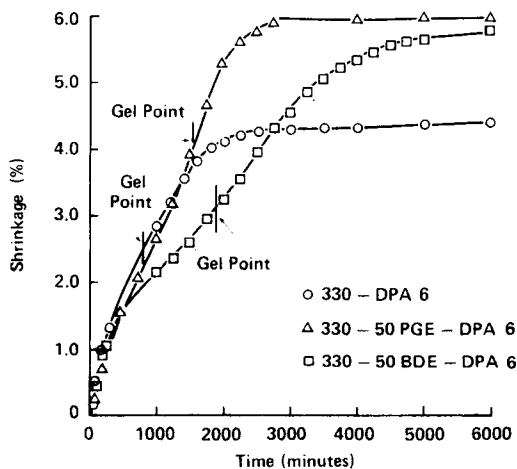


Fig. 7. Percent shrinkage vs time for epoxy solutions cured at 30°C with diethylaminopropylamine: (O) 330-DPA 6; ( $\Delta$ ) 330-50 PGE-DPA 6; ( $\square$ ) 330-50 BDE-DPA 6.

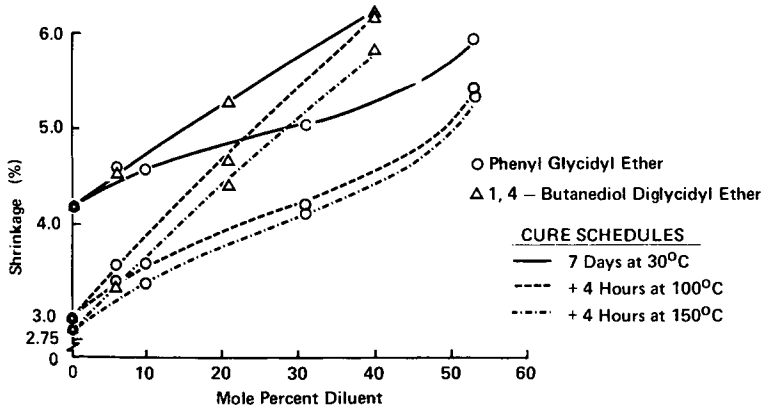


Fig. 8. Percent shrinkage vs mole percent diluent for epoxy solutions cured at various temperatures with diethylaminopropylamine: (O) phenyl glycidyl ether; ( $\Delta$ ) 1,4-butanediol diglycidyl ether.

modulus, strength, and elongation are also altered. With increasing levels of diluent, the flexural modulus, for example, would be expected to decrease. Therefore, because of the high peel forces present in a lap shear joint during its testing, the adhesives with higher diluent level could show improved strength.

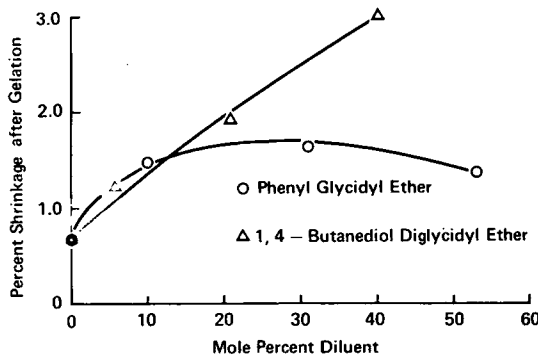


Fig. 9. Percent shrinkage after gelation for epoxy solutions cured 4 hr at 100°C with diethylaminopropylamine: (O) phenyl glycidyl ether; ( $\Delta$ ) 1,4-butanediol diglycidyl ether.

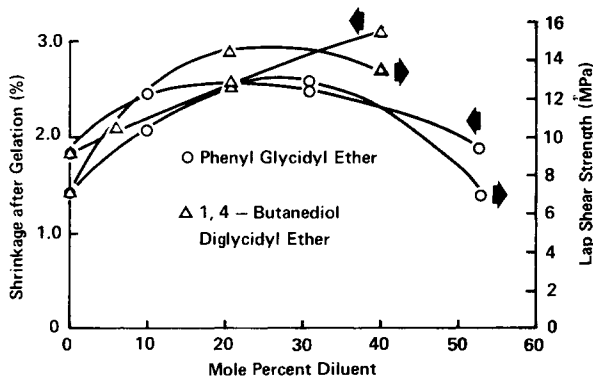


Fig. 10. Comparison of shrinkage after gelation to lap shear strength for epoxy solutions cured seven days at room temperature with diethylaminopropylamine: (O) phenyl glycidyl ether; ( $\Delta$ ) 1,4-butanediol diglycidyl ether.



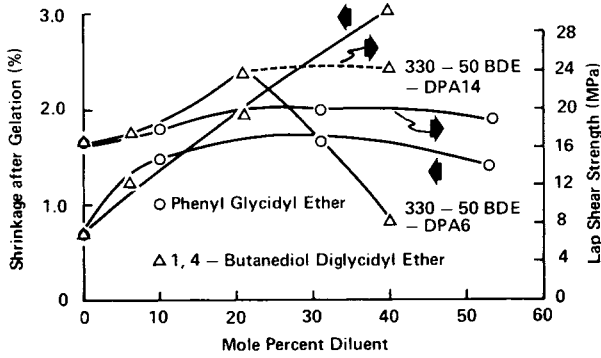


Fig. 11. Comparison of shrinkage after gelation to lap shear strength for epoxy solutions cured 4 hr at 100°C with diethylaminopropylamine: (O) phenyl glycidyl ether; ( $\Delta$ ) 1,4-butanediol diglycidyl ether.

Another possible factor is that of residual stresses present in the adhesive after cure. If the diluent lowers the residual stresses and if these stresses are indeed a factor in determining adhesive strength, then again the increased diluent level could be expected to yield improved strengths. Thus, it may well be that shrinkage of the adhesive is indeed detrimental to the lap shear strengths, but

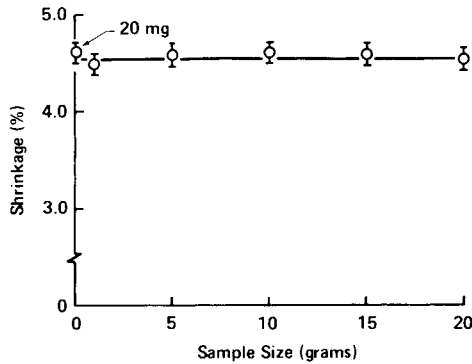


Fig. 12. Percent shrinkage vs sample size for undiluted epoxy resin cured 4 hr at 100°C with diethylenetriamine.

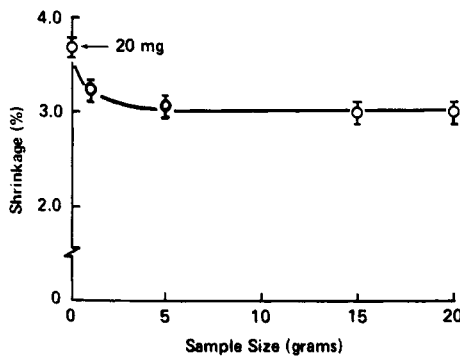


Fig. 13. Percent shrinkage vs sample size for undiluted epoxy resin cured 4 hr at 100°C with diethylaminopropylamine.

other changes in the adhesive, such as its bulk flexural or tensile strengths or the residual stresses, could have a larger positive effect on its strength. The properties in both these areas is currently being determined for the diluted epoxy adhesives.

### SUMMARY

For the diluted epoxy adhesives used in this investigation, increasing levels of shrinkage for the more highly diluted samples did not adversely affect the steel-to-steel lap shear strengths. It was shown that the sample size did not influence the percent shrinkage and that adhesives catalyzed with DPA actually expand (after an initial shrinkage) during postcure at elevated temperatures.

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