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CURE SHRINKAGE IN CASTING RESINS

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ABSTRACT

A method is described whereby the shrinkage of a casting resin can be determined. Values for the shrinkage of several resin systems in frequent use by Sandia have been measured. A discussion of possible methods for determining the stresses generated by cure shrinkage and thermal contraction is also included.

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CURE SHRINKAGE IN CASTING RESINS

Introduction

Two related problems of constant concern in the development and evaluation of encapsulating resins are failures of encapsulated components due to stress imposed upon them by the resin and cracking of the resin itself during cure and thermal testing. In addition to acknowledge the physical, electrical, and thermal properties of casting resins it would be useful to know the actual stresses existing within a resin and the cure shrinkage which gives rise, at least in part, to those stresses.

Theoretical Considerations

The process by which an epoxy resin is transformed from a liquid to a useful solid is primarily one of cross linking a number of units of the epoxy resin through the action of a hardener. Such a change of state gives rise to changes in the physical properties of the system. In particular, there is usually an increase in density which may cause stresses to be set up within the curing resin which, in turn, may impose stresses on embedded objects if the resin has sufficient rigidity.

Consider, for example, an idealized system in which the temperature remains constant throughout the resin mass during the curing process. In such a case all portions of the resin would be undergoing reaction at the same rate and, therefore, any shrinkage would occur evenly throughout the casting and would give rise to an even distribution of stress within the resin mass.

The reaction of unfilled epoxy resins with hardeners, amines in particular, is usually exothermic and often highly so. Since the plastic itself is a poor thermal conductor there should be a more rapid transfer of heat from the resin near the surfaces of a mold to the mold than from the interior of the resin mass to its edges. When the heat in the center of a resin mass cannot be rapidly dissipated there is a rise in temperature which tends to speed up the reaction rate, which increases the amount of heat liberated, and so on. In this manner a thermal gradient is set up throughout the resin with the hottest portions being in the center of resin masses distant from heat sinks. Because of this difference in temperature, different portions of the reactants will be at different energy levels causing reaction at different rates. Generally, the exterior portions of a casting will cure more slowly than those portions in the interior of the resin mass.

As a resin cures it remains a fluid of increasing viscosity for a period of time. During this time it may undergo shrinkage from the cross-linking process, but no stresses can be set up within the mobile resin or exerted on any encapsulated objects. Because of the thermal gradients existing in the curing resin, the transition from fluid to solid, called gelation, occurs at different times in different portions of the resin mass. It is this process which sets up stress patterns within the resin mass which may lead to cracking of the resin during cure or thermal cycling. In addition, as the reaction tapers off and the semicured plastic cools to the curing temperature, stresses are again imposed due to differences in the rate of cooling within the mass. The absolute level of such stresses will depend on the flexibility of the system, the more flexible systems being able to relieve such stresses.

If an object were embedded in the curing resin under isothermal conditions, the only stress imposed upon it would be from postgelation shrinkage of the resin and would be uniformly applied to all surfaces, the magnitude of which would depend both on the amount of shrinkage and the flexibility of the resin. Should the ambient temperature be changed at any time after some rigidity has been obtained in the system, any difference in the thermal coefficients of expansion of the resin and the insert would cause compressive or tensile stresses on the insert (depending on the relationship of the coefficients and the direction of the temperature change) and, if the insert were bonded to the resin, shear stresses would develop at the points of contact.

The situation is further complicated if the polymerization process is no longer isothermal but includes temperature gradients and changing temperatures during the course of the reaction. So long as the resin has not obtained any rigidity, stresses will not be set up within the resin. As soon as any rigidity is established in the resin, however, further shrinkage or temperature change will cause stresses to be set up within the resin and imposed on the insert.

It is with these processes and effects that the present study is concerned: pregelation and postgelation shrinkages, stresses within a curing resin, stresses upon an embedded object and the variables controlling these factors.

Discussion of the Literature

Most of the research in this area has appeared in the literature since 1957. With regard to stress measurements, the method developed by Bush[1] has been successfully applied to a variety of systems. This method makes use of a tubular stainless-steel transducer with strain gages bonded to the inner surface. From temperature- and hydrostatic- pressure calibration curves for the transducer it was possible to arrive at stress values during cure and thermal cycling from strain gage and temperature readings.

It should be noted that the values for stresses thus obtained are not true indications of the actual stress within the resin itself, but are composite values including shear stresses developed between the plastic and metal due to differences in their thermal coefficients of expansion. Such data, then, are useful for distinguishing between rigid and flexible systems and provide a relative scale for the magnitude of stresses experienced by components encapsulated in various plastics, but indicate neither the absolute stress imposed upon any transducer other than the one used in the experiments nor the absolute magnitude of the stress within the plastic itself which may lead to crack formation.

Sampson and Lesnick[2,3] have used the method developed by Bush to study flexible and rigid systems and the effects of reactive diluents, hardener, cure cycle, filler type and content, and rate of thermal shock on the stresses experienced. Of particular interest is the rather sharp transition point found on cooling flexible resins. As a flexible resin is cooled little stress is exerted on the encapsulated transducer until a characteristic temperature is reached. At that temperature the plastic assumes the stress-imposing characteristics of a rigid system. Presumably, most systems would show similar behavior if a large enough temperature range were considered, with systems normally thought to be rigid becoming flexible at sufficiently elevated temperatures. Further study of this behavior and the variables affecting the transition temperature could be potentially useful in developing resin-hardener systems with reduced stress levels.

In an attempt to minimize stresses due to the resin-transducer bond and more closely approximate the absolute stress level within the resin, Scheid[4] employed spherical plastic transducers with externally mounted strain gages. Although the thermal coefficient of expansion of the resin changes as cure progresses, the more closely matched coefficients of expansion for the resin and transducer should, in principle, provide information of a more basic nature. The drawback to this method, however, lies in creep of the plastic in the transducer at the points of bonding to the strain gage. In spite of this difficulty Scheid was able to show that the stress imposed on the insert at room temperature was highly dependent on the peak exotherm of the polymerization reaction, that temperature being an indication of both the temperature at which the resin-transducer bonds were formed (the temperature at which gelation occurred) and the size of the thermal gradients existing in the resin during gelation.

In substantiating previous work with polyester resins[5,6] Scheid showed the applicability of using insulated molds to minimize cracking of resins during cure. Molds were insulated with chopped fiber glass which retained the exothermic heat, reducing thermal gradients in the resin mass which caused stress patterns responsible for cracking of the resin. If the higher peak exotherms resulting from this procedure can be accommodated by the encapsulated components, this would appear to offer a method for reducing cracks in unfilled resin systems.

Dewey and Outwater[7] employed a different approach in showing that the variation of pressure with temperature on an embedded object in a fully cured rigid resin could be calculated from the differences in the thermal coefficients of expansion of the resin and the embedded object and other physical properties of the materials. The transducer used was a mercury thermometer modified so that hydraulic pressure could be exerted on the column of mercury to cause the thermometer to read the same as the temperature indicated by a thermocouple embedded next to the thermometer bulb. The magnitude of the pressure exerted by the oil on the mercury was considered to be equal to the pressure exerted on the glass bulb by the resin surrounding it. As was the case with a metal transducer, this method can provide estimates of the stress exerted on a specific transducer (in this instance glass) and the variation of that stress with temperature, but it cannot provide absolute values of stresses within the resin itself.

In the related area of shrinkage measurements Lascoe[8] studied the volumetric and linear shrinkage of an unfilled epoxy resin cured with diethylenetriamine (DTA). For the volumetric measurements of interest here he employed a closed metal mold and followed the shrinkage during cure by changes in the level of mineral oil in the pipette tube above the resin. Even though a metal mold was used, the resin mass used for the measurements (approximately 65 grams) probably resulted in appreciable exothermic expansion, curing part of the cure giving average values including expansion and shrinkage. No attempt was made to distinguish between shrinkage before and after gelation.

Parry and Mackay[9] refined the general method of Lascoe to reduce the contribution of exothermic expansion and introduced modifications to determine the point at which gelation occurred. By using a smaller resin mass (about 20 grams) they limited peak exotherms to less than 2°C for systems cured at 25°C and less than 10°C for those cured at 65°C. The gelation point was determined by checking a comparable mass of resin in a beaker at the same temperature with an applicator stick. Both the total and postgelation shrinkages determined in this manner were highly repeatable for a given system, but gave only fair agreement with values for total shrinkage obtained from measured density changes of the same samples. From comparison of the data for different hardeners with the same epoxy resin they were able to make some generalizations concerning size and structure of the hardener molecule and the type and amount of shrinkage encountered.

One system using Epon 828 cured with metaphenylenediamine (MPD) cured at 65°C was given a postcure of 2 hours at 150°C and a decrease in density was noted when the resin was returned to 65°C. It was suggested that the semicured resin had a higher thermal coefficient of expansion than the postcured resin, causing the expansion on heating to be greater than the subsequent contraction on cooling. It should be noted that this decrease in density may be a net effect of the behavior just described combined with further shrinkage due to additional cross linking during the postcure.

For the casting of parts from unfilled epoxy systems Nelson, Morrisey, and Marcey[10] found that by reducing the peak exotherm during cure, and thus reducing the thermal gradients in the resin mass, they were able to obtain castings which followed closely the contours of the mold. The explanation for such behavior is that with large thermal gradients the portions of the resin next to mold surfaces are the last to solidify and thus are more easily distorted by stresses in the curing resin, while a reduction of thermal gradients evens out the shrinkage in the resin and reduces the stresses developed. This is a second approach to the thermal gradient problem mentioned previously in connection with the cracking of unfilled resins during cure.

In summary, there would appear to be two fundamentally different approaches to the study of stresses during cure and thermal cycling and of shrinkage during cure. The first is to choose an admittedly arbitrary resin mass and configuration (and transducer in the case of stress measurements) which is somewhat representative of the actual encapsulation and casting conditions under which the systems will be used. Data obtained in this manner would represent the net effect of a number of contributing variables, but should provide information as to the relative behavior of different systems in a given application. Closely connected with this type of work would be, for example, the development of methods for reducing resin cracking.

The second approach, although of less immediate value, would probably be of greater ultimate value. This would center in attempts to eliminate as many variables as possible and compare one specific property among a variety of systems. If this could be done for enough of the contributing variables, a more basic understanding of the physical and chemical processes occurring would result which could lead not only to the explanation of observed behavior, but also to at least semiquantitative predictions of behavior on the basis of structures of the reactants.

Shrinkage studies carried out in this laboratory have been for the evaluation of epoxy casting resins already in use and for the testing of a method for determining pregelation and postgelation shrinkages. For these reasons some of the systems studied are proprietary formulations and the curing schedules are usually those specified for actual encapsulation processes.

Procedure

The method used in these shrinkage studies was suggested by A. J. Quant, Organization 1111-1, Sandia Corporation. Calibrated 100-milliliter volumetric flasks were employed as molds for the shrinkage determinations. The initial density of the system being studied was taken to be the weighted average of the densities of its individual components at the prescribed mixing temperature. The mixed and evacuated resin-hardener system was poured into preweighed, mold-released flasks, the flasks and their preheated contents brought to the prescribed temperature as indicated by a thermocouple placed in the center of the resin mass in one flask, the level of the resin in the other flasks adjusted to the calibration mark, then the weight of the flasks determined for calculating the density at the time the levels were adjusted. After the prescribed cure was completed the volumetric shrinkage in the neck of the flask was measured and was assumed to have occurred while the resin was in the fluid state. This shrinkage could then be combined with any shrinkage noted between the time of mixing and the time at which the level of the resin in the flask was adjusted to give the pregelation shrinkage. Samples of the cured plastic were then cut from the resin mass and their densities determined both at the last temperature of the cure schedule and at room temperature. In this way, values for the total shrinkage from time of mixing to the cured state at room temperature could be calculated, as well as postgelation shrinkage and contraction of the cured plastic upon cooling.

Preparation of Materials

All but the neck of each flask was mold released with Garan 225 Mold Release and the empty flask weighed to the nearest 0.001 gram. Densities of the individual components at the mixing temperature were determined from the weight of a known volume at that temperature. The epoxy resin and curing agent (or components if kits were used) were preheated to the mixing temperature as were the flasks to be used.

Mixing and Pouring

The components were added by weight to the nearest 0.1 gram, then mixed by hand for 3 to 5 minutes with a wooden spatula, taking care that no unmixed material remained on the sides or bottom of the container. Following mixing the resin was evacuated to remove all air bubbles. The pressure was decreased until the foam broke, then was held at less than 3 mm Hg for at least 3 minutes. The evacuated mix was then poured down the side of the flask to avoid entrapment of any air. A thermocouple was positioned in the center of one flask of each group and the flasks and their contents brought to the specified mixing temperature as indicated by the thermocouple. When the correct temperature had been reached the level of the resin in each flask was adjusted by adding or removing resin until the bottom of the meniscus coincided with the calibration mark. The flasks were then weighed to the nearest 0.001 gram and returned to a forced-draft oven for curing.

Cure

The oven temperature was controlled to within 2°F of the cure temperature specified. During cure the flasks were placed in one-quart paper cups with 1/2 inch of plastic foam insulation in the bottom to reduce localized surface cooling of the flasks during exotherm. This was done in an attempt to reduce void formation near the mold surfaces without providing insulation sufficient to appreciably raise the exothermic temperatures, and proved relatively successful. The exothermic temperature as experienced by the thermocouple in one flask was recorded throughout the cure.

Shrinkage and Density Measurements

After the cure was completed the volumetric change of the resin in the neck of the flask was determined. If the level of the resin was below the calibration mark the weight of water at that temperature needed to fill the neck to the mark was determined by weighing by difference. From the weight and temperature of the water added its volume could be calculated. If the level of the resin was above the mark on the flask due to gelation of the resin in an expanded state during exotherm or cure temperature change, the height of the plastic above the mark and the diameter of the neck of the flask were measured and the volume expanded (negative shrinkage) calculated. After completion of the volumetric measurements the flasks were broken and four samples of the cured resin cut from each resin mass for density determinations.

At room temperature (75-78°F) the specific gravity of each sample was determined using a specific gravity balance. From the specific gravity and the density of distilled water at the measured temperature the density of the sample could be calculated. For determining the density of the same samples at cure temperatures less than the boiling point of water (about 200°F at this altitude), the specific gravity of the sample was determined, as before, but using water kept at the desired temperature with an insulated heating cloth controlled by a Variac and wrapped around a 1000-milliliter beaker. Again, the density was calculated from the specific gravity and the known density of water at that temperature.

In two cases it was necessary to measure densities near or above the boiling point of water. A mixture of water with ethylene glycol was used whose density was found by determining the specific gravity of a sample of copper metal immersed in it. From the density of the copper measured at room temperature and its thermal coefficient of expansion it was possible to calculate the density of the copper, and thus of the water-ethylene glycol mixture, at the elevated temperatures. From the calculated density of the mixture and the measured specific gravity of a sample relative to the mixture it was possible to obtain the density of the sample at the elevated temperature.

Results

Method of Calculation

In the calculation of volumetric shrinkages the following symbols will be used:

D_1 = Initial density in grams/cc of the mixed resin at the mixing temperature--weighted average of the components at the mixing temperature

D_2 = Density in grams/cc of the resin at the mixing temperature when level of the resin adjusted

D_3 = Density in grams/cc of the cured plastic at the last cure temperature

D_4 = Density in grams/cc of the cured plastic at room temperature (74-78°F)

ΔV = Measured volumetric shrinkage in neck of flask in cc

m = Mass of resin in the flask in grams

The following shrinkages can then be calculated relative to the initial volume of the resin at time of mixing at the mixing temperature by assuming that the mass of the resin remains constant:

Total shrinkage, percent from initial density at time of mixing to the density of the cured plastic at room temperature

$$= \frac{D_4 - D_1}{D_4} \times 100$$

Cure shrinkage, percent
from initial density at
time of mixing to the density
of the cured plastic at the
final cure temperature

$$= \frac{D_3 - D_1}{D_3} \times 100$$

Mix-pour shrinkage, percent
from time of mixing to
time level is adjusted

$$= \frac{D_2 - D_1}{D_2} \times 100$$

Pregelation shrinkage, percent
from time of mixing to
gelation point

Mix-pour shrinkage, percent

$$+ \frac{D_1(\Delta V)}{m} \times 100$$

Postgelation shrinkage, percent
from gelation point to the
density of the cured plastic at
final cure temperature

Cure shrinkage - Pregelation shrinkage

Cooling shrinkage, percent
from density of the cured
plastic at the final cure
temperature to its density at
room temperature

$$\frac{D_1(D_4 - D_3)}{D_3 D_4} \times 100$$

As can be readily seen the total shrinkage should be the sum of the pregelation, postgelation, and cooling shrinkages. Since each of these values was computed for every flask and then the average value taken for all the flasks with a given system, the results were not always strictly additive due to experimental variation. As an indication of the spread in the data averaged to obtain the values presented, the following statistical analysis based on standard deviations was used:

$$\sigma = \left(\frac{\sum x^2 - n\bar{x}^2}{n - 2}\right)^{1/2}$$

where

x = an individual value
n = the number of values of x considered
$\bar{x}$ = the average value of x

and

1σ should include 68.2 percent of the data
2σ should include 95.45 percent of the data
3σ should include 99.73 percent of the data

All tolerances presented with the data will be $\pm 2\sigma$ of the average value, that is to say that 95.45 percent of the determinations for that value would be expected, on the basis of standard deviations, to fall within the indicated limits.

Tabulation of Data

In the following tabulation of data, n, is the number of determinations included in the average as used to calculate tolerances of $\pm 2\sigma$, PBW stands for "parts by weight" and negative shrinkage values indicate net expansion.

TABLE I

Formulation	Epon 828	100 PBW
	Diethanolamine (DEA)	12 PBW
Mixing temperature	165°F	
Cure	15 hours at 165°F	
n	6	
D_1	1.1114 grams/cc	
D_3	1.1733±0.0068 grams/cc	
D_4	1.1973±0.0024 grams/cc	
Total shrinkage	7.17±1.4 percent	
Pregelation shrinkage	2.82±0.68 percent	
Postgelation shrinkage	2.46±1.0 percent	
Cooling shrinkage	1.90±0.49 percent	
Peak exotherm	191°F	

TABLE II

Formulation	Epocast 867-B	100 PBW
	(Epon 828 - 50 PBW	
	4X Mica = 50 PBW)	
	DEA	6 PBW
Mixing temperature	165°F	
Cure	15 hours at 165°F	
n	4	
D_1	1.5727 grams/cc	
D_3	1.6419±0.0072 grams/cc	
D_4	1.6528±0.0062 grams/cc	
Total shrinkage	4.85±0.34 percent	
Pregelation shrinkage	2.12±0.20 percent	
Postgelation shrinkage	2.10±0.42 percent	
Cooling shrinkage	0.63±0.44 percent	
Peak exotherm	184°F	

TABLE III

Formulation	Epon 828	100 PBW
	N-hydroxyethylpiperazine (N-HEP)	6 PBW
Mixing temperature	Room temperature	
Cure	15 hours at room temperature	
	5 hours at 115°F	
	15 hours at 165°F	
n	6	
D_1	1.1501 grams/cc	
D_3	1.1731±0.0020 grams/cc	
D_4	1.1873±0.0012 grams/cc	
Total shrinkage	3.13±0.10 percent	
Pregelation shrinkage	-2.05 ±2.0 percent	
Postgelation shrinkage	4.01±2.0 percent	
Cooling shrinkage	1.20±0.18 percent	
Peak exotherm	199°F	

TABLE IV

Formulation	Epon 828	100 PBW
	Diethylaminopropylamine (DEAPA)	6 PBW
Mixing temperature	Room temperature	
Cure	15 hours at room temperature 5 hours at 115°F 15 hours at 165°F	
n	4	
D_1	1.1305 grams/cc	
D_3	1.1609±0.0010 grams/cc	
D_4	1.1745±0.0010 grams/cc	
Total shrinkage	3.75±0.09 percent	
Pregelation shrinkage	2.87±0.84 percent	
Postgelation shrinkage	-0.25 ±0.54 percent	
Cooling shrinkage	1.12±0.09 percent	
Peak exotherm	219°F	

TABLE V

Formulation	Epon 828	100 PBW
	Piperidine (PIP)	6 PBW
Mixing temperature	Room temperature	
Cure	15 hours at room temperature 5 hours at 115°F 15 hours at 165°F	
n	4	
D_1	1.1345 grams/cc	
D_3	1.1646±0.0014 grams/cc	
D_4	1.1796±0.0020 grams/cc	
Total shrinkage	3.82±0.16 percent	
Pregelation shrinkage	1.20±1.1 percent	
Postgelation shrinkage	1.39±1.2 percent	
Cooling shrinkage	1.24±0.18 percent	
Peak exotherm	190°F	

TABLE VI

Formulation	Epon 828	100 PBW
	Polyglycolamine (PGA) (Dow X-3483.1)	40 PBW
Mixing temperature	Room temperature.	
Cure	15 hours at room temperature 5 hours at 115°F 15 hours at 165°F	
n	4	
D_1	1.1027 grams/cc	
D_3	1.1250±0.0014 grams/cc	
D_4	1.1580±0.0012 grams/cc	
Total shrinkage	4.78±0.09 percent	
Pregelation shrinkage	3.18±0.42 percent	
Postgelation shrinkage	-1.21 ±0.41 percent	
Cooling shrinkage	2.80±0.09 percent	
Peak exotherm	168°F	

TABLE VII

Formulation Semirigid inspection Resin (SRIR)	Hysol 13-009 A	50 PBW
	Hysol 13-009 B	50 PBW
Mixing temperature	130°F	
Cure	15 hours at 130°F 24 hours at 160°F	
n	4	
D_1	1.1223 grams/cc	
D_3	1.1497±0.0022 grams/cc	
D_4	1.1814±0.0006 grams/cc	
Total shrinkage	5.00±0.05 percent	
Pregelation shrinkage	3.00±0.16 percent	
Postgelation shrinkage	-0.62 ±0.11 percent	
Cooling shrinkage	2.62±0.20 percent	
Peak exotherm	166°F	

TABLE VIII

Formulation Transformer impregnating Resin (TIR)	Hysol 6366-A Hysol 6366-B	70 PBW 30 PBW
Mixing temperature	140°F	
Cure	15 hours at 140°F 2 hours at 170°F 24 hours at 200°F	
n	4	
D_1	1.1067 grams/cc	
D_3	1.1156±0.0011 grams/cc	
D_4	1.1820±0.0024 grams/cc	
Total shrinkage	6.37±0.20 percent	
Pregelation shrinkage	3.62±0.46 percent	
Postgelation shrinkage	-2.82 ±0.40 percent	
Cooling shrinkage	5.58±0.12 percent	
Peak exotherm	No exotherm	

TABLE IX

Formulation	Epon 828 Shell Curing Agent "Z"	100 PBW 20 PBW
Mixing temperature	Room temperature	
Cure	8 hours at room temperature 15 hours at 120°F 8 hours at 212°F	
n	3	
D_1	1.1537 grams/cc	
D_3	1.1703±0.0008 grams/cc	
D_4	1.2019±0.0032 grams/cc	
Total shrinkage	4.01±0.26 percent	
Pregelation shrinkage	2.43±0.48 percent	
Postgelation shrinkage	-1.01 ±0.55 percent	
Cooling shrinkage	2.59±0.22 percent	
Peak exotherm	Greater than 250°F	

Discussion

Results

AND THE THERMAL COEFFICIENT OF EXPANSION OF THE FILLED SYSTEM.

The one filled system tested was included to see whether shrinkage for a filled system could be predicted from that of the corresponding unfilled system on the basis of a ~~simple~~ "loading factor". In the case of the mica-filled system it was calculated from the densities of the components that the resin and hardener together comprise ~~approximately~~ 72.3 ~~75~~ percent and the mica ~~25~~ 27.7 percent of the total volume. On this basis one would expect to find a corresponding decrease in shrinkages for the mica-filled system of about one-fourth. THE LINEAR THERMAL COEFFICIENT OF EXPANSION OF THE FILLED SYSTEM IS 36.8×10^{-6} IN/IN/°C.

TABLE X

VOLUMETRIC Shrinkage in Unfilled and Mica-Filled 828-DEA Systems

Type of Shrinkage	Shrinkage in Unfilled System (percent)	Shrinkage Predicted for Filled System (percent)	Shrinkage Found in Filled System (percent)
Total	7.2±1.4	~~5.4~~ 4.4	4.8±0.3
Pregelation	2.8±0.7	~~2.1~~ 2.0	2.1±0.2
Postgelation	2.5±1.0	~~1.9~~ 1.8	2.1±0.4
Cooling	1.9±0.5	~~1.4~~ 0.6	0,6±0.4

POSTGELATION

As can be seen from Table X the predicted values for pregelation and COOLING ~~postgelation~~ shrinkage agree quite well with those found, while the disagreement in values for ~~cooling~~ shrinkage is largely responsible for the discrepancy in the total shrinkage. ~~Since data are not presently available for these two systems showing the variation in their respective thermal coefficients of expansion over the temperature range of interest, it is not clear whether a straight "loading factor" should be expected to apply to thermal shrinkage.~~

Considering the unfilled systems the total shrinkages found correspond roughly with the temperatures of mixing as shown in Table XI.

TABLE XI

Total Shrinkage and Mix Temperature
(Unfilled Systems)

System	Mixing Temperature	Total Shrinkage (percent)
828 and N-HEP	Room	3.1
828 and DEAPA	Room	3.8
828 and PIP	Room	3.8
828 and "Z"	Room	4.0
828 and PGA	Room	4.8
SRIR	130°F	5.0
TIR	140°F	6.4
828 and DEA	165°F	7.2

Such a trend would be expected since, other factors being held constant, at a higher temperature the initial density of a system will be decreased so that there is, in effect, an added thermal shrinkage included for systems mixed at elevated temperatures. For example, had the Epon 828 and DEA system been mixed at room temperature the total shrinkage would have been around 4 percent instead of the 7 percent total shrinkage found when mixing was accomplished at 165°F.

Of much greater interest than the total shrinkage, however, is a consideration of its component parts. Pregelation shrinkage, although not stress imposing, is responsible for the initial change of the vertical dimension in castings. It must be remembered, however, that the gelation point is rather ill defined in many cases and that the process of gelation occurs at different times throughout a casting that has developed thermal gradients in the resin mass.

In the present method for determining pregelation shrinkage the interaction of reaction exotherm and gel time with the actual shrinkage before gelation complicates interpretation of the data. As may be seen in Table XII the two similar hardeners, N-HEP and PIP, show a small and a negative pregelation shrinkage, respectively. Both of these systems exhibited a small initial exotherm at room temperature followed by a temperature rise close to 200°F shortly after the reaction was "kicked off" by raising the cure temperature to 115°F. Other systems also showed this characteristic, but only in these two systems did gelation occur while the resin was still in the expanded state. For example, the Epon 828 and PGA formulation showed a higher exotherm but did not assume any rigidity until after it had been cured at 165°F. For Epon 828 and N-HEP the expansion before gelation was greater than any shrinkage which did occur, while for Epon 828 and PIP the expansion was not sufficient to obscure completely the previous or concurrent shrinkage. The difference in pregelation shrinkage values for these two similar hardeners was probably due to the interaction between exotherm and gelation time.

TABLE XII

Pregelation Shrinkage

System	Pregelation Shrinkage (percent)
828 and N-HEP	-2.0
828 and PIP	1.2
828 and "Z"	2.4
828 and DEA	2.8
828 and DEAPA	2.9
SRIR	3.0
PGA	3.2
TIR	3.6

For the remaining unfilled systems the pregelation shrinkages found were within about 1 percent of each other with the only detectable trend being for greater pregelation shrinkage in the more flexible polyol and anhydride formulations. In order to sort out the specific effect due to each polyol and anhydride it would be necessary to make determinations of shrinkages in systems using each separately and run at the same temperatures.

Considering postgelation shrinkages (Table XIII), negative values indicating net expansion were found for five of the unfilled systems. In each of these cases there was an increase in the cure temperature after gelation had occurred.

TABLE XIII

Postgelation Shrinkage
(Unfilled Systems)

System	Postgelation Shrinkage (percent)
TIR	-2.8
828 and PGA	-1.2
828 and "Z"	-1.0
SRIR	-0.6
828 and DEAPA	-0.2
828 and PIP	1.4
828 and DEA	2.5
828 and N-HEP	4.0

The probable explanation is that the increase in cure temperature caused an expansion of the resin which more than offset any further postgelation shrinkage.

The PIP and N-HEP systems apparently underwent relatively more postgelation shrinkage since they had gelled in an expanded state and at a higher temperature than any subsequent cure temperature, while the DEA system was held at a constant temperature throughout its entire cure.

The values obtained for cooling shrinkage, when reduced to percent shrinkage per °F, fall in the same order as do available thermal coefficients of linear expansion[11]. By assuming that the volumetric coefficient of expansion is three times the corresponding linear coefficient of expansion, calculations from the cooling shrinkage data show agreement to within an order of magnitude with the corresponding linear coefficients even though somewhat different temperature ranges are used.

Test Method

In evaluating the test method used there are three primary considerations: the type of data obtained and its usefulness, the reproducibility of the results, and the correspondence of results from this method with those reported in the literature.

The total shrinkage data reported here, being based on initial and final densities of the materials, are relatively reproducible and depend largely on the temperature of mixing. Such data, however, are of limited use and provide little or no information about stresses generated.

Values for pregelation and postgelation shrinkages, being relatively more difficult to determine accurately, show wider variability. With this method the gelation time depends heavily on the exotherm generated, often obscuring actual shrinkage which may be occurring. It does, however, more closely approximate gelation conditions encountered in actual casting applications than do other methods put forward for distinguishing between pregelation and postgelation shrinkage. Use of several-step cures also colors the results, particularly the postgelation shrinkage. Since there is great variety in the resin mass and mold configuration with which a resin may be used, it is likely that the pregelation and postgelation shrinkages for a particular formulation will vary with the conditions of the individual casting situation. Even though such variability exists, one should be able to predict some aspects of the relative behavior expected from several resins under identical conditions.

Attempts to compare shrinkage data obtained by different methods have thus far met with little success. In the work by Parry and Mackay, mentioned previously, there were inconsistencies between total shrinkage values obtained from densities and dilatometer measurements. Their data, too, gave only fair agreement with that of Lascoe. The values obtained by Parry and Mackay for Epon 828 and "Z" at 65°C were 5.6-percent total and 2.3 percent after gelation shrinkage as compared with 4.0 percent and -1.0 percent for the same shrinkages by the present method. Their values for Epon 828 and DEAPA at 65°C were 6.1-percent total and 2.9 percent after gelation shrinkage as compared with 3.8 percent and -0.2 percent again by the present method. From this it can be seen that the test method used can entirely change the complexion of the results obtained.

Recommendations

With regard to shrinkage measurements, it is apparent that there is a need to establish a single method applicable to a wide variety of systems. Such a method should include a means for determining pregelation and post-gelation shrinkage and for following the entire course of the shrinkage if possible. It should be adaptable for use at several cure temperatures and should at least minimize exotherms. The use of averages for initial densities and taking the time of mixing as time zero seem to be adequate.

In the light of these considerations, the method of Parry and Mackay seems to be the most profitable point of departure. In order to further reduce exotherms while possibly allowing the use of a larger resin mass to increase accuracy, further work could investigate metal molds which would provide a larger surface-to-volume ratio for the resin mass. If exotherms could be successfully eliminated from the shrinkage studies, extensive work should then be done with exotherms themselves, studying the effects of resin mass and configuration, cure temperature, filler type and content, hardener concentration, and thermal conductivity. Such data relating exotherms, gelation time, and cure shrinkage would be useful in gaining a fuller understanding of the relationship between chemical structure and cure phenomena, including the many reaction mechanisms already elucidated in the literature.

For stress studies the metal transducer developed by Bush would seem to offer the best method available at this time. Although actual measurements of stress within the resin cannot be made by that method, it would give useful relative information which could be correlated with other physical properties of the casting resins. Effors should be made, as in the shrinkage studies, to develop a method that would approach isothermal curing conditions. If such conditions were obtained, correlation between postgelation shrinkage and any residual stress in the resin after cure should be possible by taking into consideration the elastic properties of the resin. For flexible systems the temperature at which the resin makes a transition to rigidity should be studied as a function of cure temperature and other variables to find if it is a physical characteristic which should be catalogued. Its usefulness in predicting the ability of systems to withstand cold shock, should also be investigated.

One other area of interest in stress measurements is the temperature at which a rigid resin exerts no stress on a transducer. That temperature depends on the temperature at which gelation occurs, and probably to a lesser extent on the amount of postgelation shrinkage. For thermal cycling over a particular temperature range a change in the "zero stress" temperature should cause a corresponding shift in the distribution of tensile and compressive stresses. By changing the gelation temperature, the total stress change over a given temperature range would remain the same, but the maximum stress experienced by an embedded object during a thermal cycle could be reduced.

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