

five good points are needed on either side of the equivalence point. These should extend at least 1.5 ml. on either side; points closer than 0.1 ml. should be avoided.) Correct the observed current readings,  $G$ , for dilution by the titrant through the relation

$$G_{\text{corr.}} = G \frac{V_o + V_z}{V_o}$$

where  $V_o$  is the initial volume of the vanadium solution being titrated and  $V_z$  is the volume of titrant at current reading  $G$ . A plot of  $G_{\text{corr.}}$  vs. volume in milliliters of ferrous sulfate defines the equivalence point as the intersection of two straight lines. The data from a typical run are shown in Figure 2.

Check runs are readily made on the same sample by taking fresh aliquots for titration.

**Table IV. Determination of Vanadium in Titanium Samples by Amperometric Titration**

| Designation<br>Wt.,<br>G. | Solvent   | Iron(II)<br>Soln. Required |              | Vanadium Content,<br>% |       |
|---------------------------|---|----------------------------|--------------|------------------------|-------|
|                           |   | Concn.,<br>N               | Vol.,<br>ml. | Reported               | Found |
| WA-15 1.005               | 50% H <sub>2</sub> SO <sub>4</sub>              | 0.0493                     | 2.48         | 2.53                   | 2.50  |
| WA-15 1.008               | HF + H <sub>2</sub> SO <sub>4</sub><br>to fumes | 0.0493                     | 2.50         | 2.53                   | 2.49  |
| WA-14 1.016               | 50% H <sub>2</sub> SO <sub>4</sub>              | 0.1005                     | 1.30         | 2.64                   | 2.62  |
| WA-14 1.003               | HF + H <sub>2</sub> SO <sub>4</sub><br>to fumes | 0.0503                     | 2.53         | 2.64                   | 2.64  |

#### RESULTS

The data shown in Table IV are representative of the results obtained on the two available titanium-base alloys.

The results on a variety of alloys, containing significant amounts of chromium, manganese, tungsten, titanium, molybdenum, cobalt, and other constituents, are shown in Table V.

**Table V. Amperometric Determination of Vanadium in Ferrous Alloys**

| Sample Designation         | Vanadium Content, % |                         |
|----------------------------|---------------------|-------------------------|
|                            | Reported            | Found                   |
| NBS No. 111 steel          | 0.003               | 0.005                   |
| NBS No. 116a ferrotitanium | 0.33                | 0.343                   |
| Brit. Chem. Std. "V" steel | 0.273               | 0.274, 0.269            |
| NBS No. 134 steel          | 1.13                | 1.12, 1.11 <sup>a</sup> |
| NBS No. 153 steel          | 2.04                | 2.00 <sup>a</sup>       |

<sup>a</sup> Separated WO<sub>3</sub> filtered off and acid-washed.

It is evident that the method, which is rapid and direct, is capable of giving good results over a wide range of vanadium concentrations, and in the presence of any of the common alloying constituents. The amperometric end-point determination is more objective in character than are comparable indicator techniques, and is especially advantageous at low concentrations where indicator blanks are significant. Its success in the presence of equal amounts of tungsten is especially noteworthy, but it should be anticipated that low results would certainly follow the removal (by filtration of separated tungstic oxide) of tungsten in excess of about 2%.

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## Determination of Cure and Analysis of Cured Epoxy Resins

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The degree of cure of thermosetting epoxy resins is determined from the extent of the chemical conversion and the extent of cross linking. The chemical conversion is calculated from the residual epoxy content. Two methods for determination of epoxy groups in insoluble resins are presented, one based on infrared spectroscopy, the other on chemical reaction of a suspension of the resin in a swelling agent. The estimation of the cross linking of cured resins is based on their resistance to deformation at elevated temperatures and to swelling in organic solvents. In the first case, a hot-point hardness tester is used; in the second, the finely powdered resin is exposed to the vapors of a swelling agent until equilibrium has been reached. Data obtained on experimental and commercial epoxy resins are presented.

THE advent of the epoxy resins has brought with it a number of analytical problems, relating not so much to the epoxides in the esterified form—i.e., after combination with drying fatty acids—as to the epoxides that are converted into a hard, insoluble, and infusible form by the effect of chemical curing agents and by a reaction commonly called "cure."

The physical and mechanical properties of a cured epoxy resin are to a large degree dependent on the type and amount of curing

agent as well as on the cure time and temperature of cure. A systematic study of these factors appeared desirable, especially an evaluation of the degree of cure as a function of the cure conditions. The term "cure" is a rather loose description of the reaction that converts a thermosetting resin from the soluble, fusible into the insoluble, infusible state and does not lend itself to numerical evaluation. It was necessary to define this term more precisely for the purpose of quantitative studies.

Cure may be subdivided into two components. One, called conversion, describes the chemical reaction during the cure and expresses it as disappearance of reactive groups. In the case of epoxy resins, these are the epoxy groups, and when, for example, 80% of the initially present epoxy groups have been used up to form a polymer, the conversion would amount to 80%. The other component is related to the three-dimensional structure or network that appears during the cure, called cross linking. The degree of cross linking is dependent on the progress of the chemical reaction—i.e., the conversion—but it is also related (11) to the functionality of the chemical compounds entering the reaction.

The knowledge of both conversion and cross linking appears to give a complete description of the cure of a thermosetting resin and one that lends itself to quantitative evaluation. The experimental material in this article is confined to one type of epoxy resins—namely, the condensation polymers of epichloro-

Table I. Determination of Conversion of Cured Epon 828

| Curing Agent,<br>Parts/100 Parts<br>Epon       | Cure Conditions    |               | Spectroscopic Method             |                       | Chemical Method                  |                       |
|--|--------------------|---------------|----------------------------------|-----------------------|----------------------------------|-----------------------|
|  | Time,<br>hours     | Temp.,<br>°C. | Epoxy value,<br>equiv./100<br>g. | Conver-<br>sion,<br>% | Epoxy value,<br>equiv./100<br>g. | Conver-<br>sion,<br>% |
| Piperidine <sup>a</sup> , 5                    | 24                 | 65            | 0.103                            | 78.8                  | 0.096                            | 80.3                  |
|  | + 4 <sup>b</sup>   | 100           | 0.085                            | 82.5                  | 0.087                            | 82.1                  |
|  | + 1 <sup>b</sup>   | 150           | 0.074                            | 84.8                  | 0.074                            | 84.8                  |
|  | + 0.5 <sup>b</sup> | 200           | 0.067                            | 86.2                  | 0.059                            | 87.9                  |
| Tris(dimethylaminomethyl)phenol,<br>‡          | 24                 | 65            | 0.099                            | 79.8                  | 0.106                            | 78.4                  |
|  | + 4 <sup>b</sup>   | 100           | 0.072                            | 85.3                  | 0.072                            | 85.3                  |
|  | + 1 <sup>b</sup>   | 150           | 0.049                            | 90.0                  | 0.024                            | 95.1                  |
|  | + 0.5 <sup>b</sup> | 200           | 0.045                            | 90.8                  | 0.016                            | 96.7                  |
| <i>m</i> -Phenylenediamine <sup>a</sup> , 12.5 | 24                 | 65            | 0.124 <sup>c</sup>               | 69.8                  | 0.12                             | 70.6                  |
|  | + 4 <sup>b</sup>   | 100           | 0.117                            | 71.5                  | 0.108                            | 73.5                  |
|  | + 1 <sup>b</sup>   | 150           | 0.090                            | 78.0                  | 0.105                            | 74.3                  |
|  | + 0.5 <sup>b</sup> | 200           | 0.083                            | 79.7                  | 0.095                            | 76.8                  |

<sup>a</sup> Pure compound.<sup>b</sup> Cures in addition to cures indicated in line or lines above.<sup>c</sup> Value determined by rock salt cell method and used as calibration standard.

hydrin and bisphenol A that are known commercially as Epon (Shell Chemical Corp.) resins—and to one class of curing agents, the organic amines.

#### DETERMINATION OF CONVERSION

The conversion, in per cent, of a cured epoxy resin is calculated as

$$100 \times \frac{(\text{epoxy value of uncured resin} - \text{epoxy value of cured resin})}{\text{epoxy value of uncured resin}}$$

The epoxy value of the uncured resin is easily determined by known methods (10, 12). However, the determination of epoxy values in cured epoxy resins presented problems in view of the insolubility of these materials. No similar material of precisely known composition was available to serve as a standard in the development of a new method. Under these circumstances, efforts to develop a suitable method were carried out in two different directions, hoping that it would be possible to corroborate the results of one method by those of the other. The same resins were used for each method.

**Determination of Epoxy Content of Cured Epon Resins.** By INFRARED SPECTROSCOPY. The infrared analytical method for the determination of epoxy groups in cured Epon resins uses the absorption band at 10.92 microns which the authors assigned, in agreement with findings by Herzberg (8) and Patterson (14), to a fundamental vibration of the oxirane ring  $\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—}\text{C—}$ . When

the epoxy resin is cured, the ring is opened and the 10.92 band disappears (Figure 1). The absorption of the uncured resin is represented by the heavy line. When a curing agent is added and the mixture is heated, cure takes place and the absorption spectrum changes progressively, as indicated, until, at 100% conversion, it assumes the shape indicated by the broken line of Figure 1.

Samples used for recording spectra such as those shown in Figure 1 were prepared as thin films about 0.025 mm. thick between rock salt plates. The curing took place in the rock salt cell, and the spectrum was recorded at various time intervals. Because the film thickness decreased slightly during the first part of the cure, through cell leakage, relative film thicknesses were obtained by measuring the intensity of a band at 6.325 microns due to phenyl group absorption and, accordingly, all 10.92 absorbances were corrected to correspond to a single thickness. To calculate from these spectra the epoxy values of the resins, the absorptivity per epoxy group was determined for the 10.92 band from the spectrum of the uncured resin using the chemically determined epoxy value. The epoxy value of each sample was

determined from the absorbance at 10.92 microns divided by the absorptivity. A correction was applied for the film thickness as indicated and a second correction for the presence, at 10.92 microns, of some absorption not caused by epoxides (see Figure 1, broken line).

A cure curve obtained by this method is shown in Figure 2. The method includes the assumption that the absorbance at 10.92 microns per epoxy group is constant regardless of the degree of cure and that there is no deviation from

Beer's law. Though these assumptions are reasonable, they could not be confirmed experimentally in view of the unavailability of suitable calibration standards.

The described method is not practical for routine testing, partly because a rock salt cell is sacrificed in each run, and partly because samples are usually submitted in the cured state. For such samples spectroscopic examination was made possible by the use of the pressed plate technique—i.e., by embedding the finely powdered substance in potassium bromide. This tech-

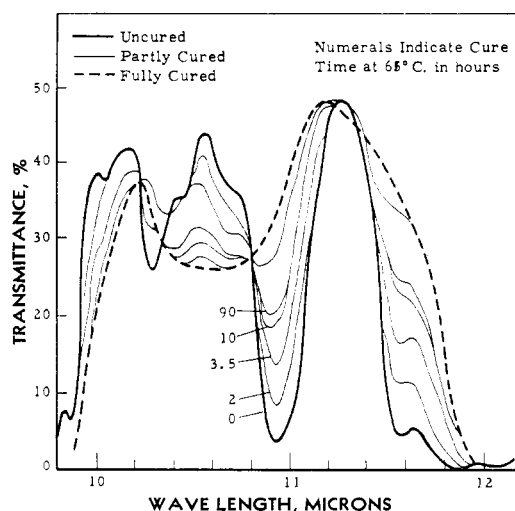


Figure 1. Infrared absorption of epoxy group in Epon resin

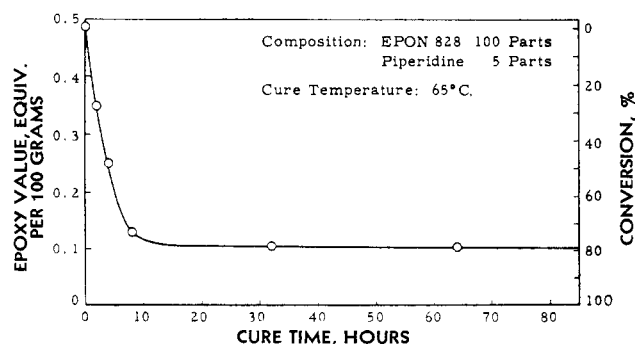


Figure 2. Epoxy value and conversion as function of cure time

nique and its theoretical background have been described (7, 15, 19, 20). The comminution of the cured resin to the required particle size of a few microns was carried out by means of a vibratory ball mill (6). Potassium bromide proved to be a very suitable carrier for cured Epon resins; the obtained spectra had the same resolution as those obtained on homogeneous samples in rock salt cells.

In the evaluation of the spectra obtained by the pressed plate method, corrections were applied similar to those described for homogeneous samples. In addition, the pressed plate method was calibrated by comparison with the rock salt cell method—i.e., samples of the same composition, cure time, and cure temperature were analyzed by both methods, and the epoxy value obtained by the rock salt cell method was used to calculate the absorptivity to be used in the evaluation of pressed plate data.

Epoxy values and conversions obtained by the pressed plate method on Epon resins of different composition and cure are presented in Table I. The samples were selected to describe the influence of the curing agent as well as the effect of increased cure temperature. The curing agents were: piperidine, a secondary amine, relatively slow; tris(dimethylaminomethyl) phenol, a tertiary amine, fast and effective; and *m*-phenylenediamine, a diprimary amine, fast and very effective, especially at higher temperatures. The cure schedules were 24 hours at 65° C., 4 hours at 100° C., 1 hour at 150° C., and 0.5 hour at 200° C.; samples cured at the higher temperatures had been subjected to the cure schedules at the lower temperatures. The conversions found for these samples vary from 70 to 91%, and the influence of the cure temperature is pronounced.

BY CHEMICAL ANALYSIS. The infrared-spectroscopic method is based on two assumptions: the validity of Beer's law and constant absorbance at 10.92 microns per epoxy group irrespective of the change-over from the liquid to the solid state. Since the correctness of the latter assumption is difficult to prove, an independent method was desired for the determination of residual epoxides in cured epoxy resins. Moreover, there appeared to be a general need for a method for determining functional groups in cured thermosetting resins.

The development of such a method was based on the following considerations. If the resin sample is reduced to a very small particle size and suspended in a liquid which acts as a swelling agent, the molecules of the resin should be accessible by diffusion. More specifically, a solution of an analytical reagent should diffuse into the swollen particle and perform the analytical reaction, and the reaction products should diffuse out of the particle. The time needed for such a reaction decreases with decreasing particle size—i.e., extremely fine particles are required for a rapid reaction.

Chemical reactions in swollen solids are not novel—e.g., the acetylation of cellulose can be carried out in the swollen state without destruction of the fiber structure (9), and the acid number of paint films has been determined in a swollen condition (13).

PREPARATION OF SAMPLES. As shown by preliminary experiments, the contemplated method is not practical unless the particle size is in the order of a few microns. Thus, the pulverization of the hard resins to micron size is a major part of the problem. A suitable procedure was developed using a Wiley laboratory mill for coarse grinding (to 20-mesh size) and a vibratory ball mill (6) for the final pulverizing. This mill reduces coarse powders to very fine powders without formation of much material of intermediate size. A charge of 10 grams and a grinding time of 1 hour are used in most cases. Handling and separation of the fine Epon powders are handicapped by electric charges; however, the difficulties are overcome by using a wet method consisting of the steps of: suspending the ground material in anhydrous alcohol; separating the fine portion from the unchanged coarse material by screening the suspension through a 325-mesh screen; collecting the fine fraction on a Büchner funnel on Whatman No. 50 paper; and vacuum drying the powder at 65° C.

ANALYTICAL PROCEDURE. For the determination of epoxy values on the fine powders, a modification of the method of King (10, 12) was employed. The substance was suspended in a solution of hydrochloric acid in dioxane and the unused acid titrated after 15 minutes. The reaction appeared to be complete after this time.

RESULTS. The results appear in the last two columns of Table I. Figure 3 serves to compare the spectroscopically obtained values with those determined by chemical analysis. The agreement is fairly good; in some cases identical values were obtained, but in others some discrepancy appears, especially when the epoxy values are very small.

The curves connecting the experimental points obtained for each curing agent are plausible; they show clearly the influence of the cure temperature on the conversion as well as the differences in the activity of the three curing agents. Thus, the presented methods for the determination of the conversion, though still somewhat lacking in precision, are believed to give essentially correct values and can serve as guides for evaluation and comparison of epoxy resins, curing agents, and cure conditions.

ESTIMATION OF CROSS LINKING

The determination of the degree of cure from the amount of chemical conversion is not satisfactory as the sole means of evaluation of thermosetting resins, because the values obtained in this

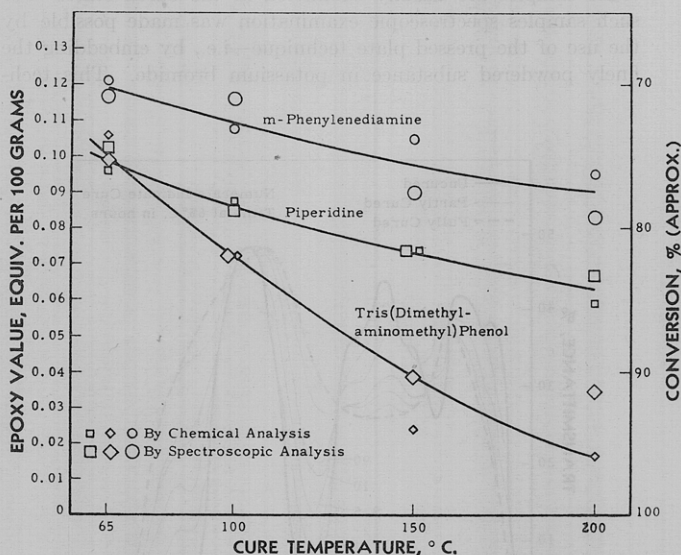


Figure 3. Conversion of Epon 828 upon curing with different curing agents and at different cure temperatures

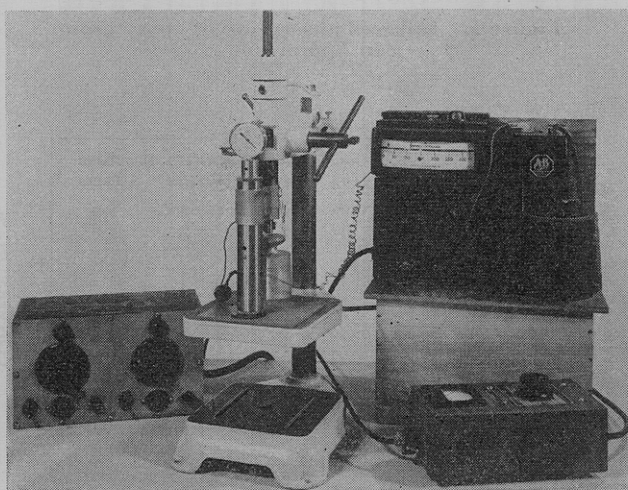


Figure 4. Hot-point hardness tester

way do not necessarily agree with the performance of the cured resins. An additional factor to be considered is the extent and character of the three-dimensional network formed during the cure. Though all cured thermosetting resins are three-dimensionally linked, various ways of linking are possible. The molecular weight and functionality of the reacting compounds are likely to have a great influence on the structure formed.

The determination of the degree of cross linking in highly cured thermosetting resins is a problem that has not been fully solved. However, the theoretical treatment by Huggins, Flory, Rehner, and others (5), based on methods of statistical thermodynamics, gives a lead on how to correlate the cross linking of polymeric substances with other more easily measurable properties. Two such possibilities have been established; one relates the cross linking to the deformation under load at elevated temperatures, the other to the amount of swelling when immersed in a solvent. Both principles have been utilized to estimate the degree of cross linking in cured epoxy resins.

**Determination of Softening Temperature.** Known methods for the determination of deformation under load at elevated temperatures include heat distortion tests (1), plasticity tests (2), and hardness tests with conventional hardness testers on preheated specimens. In the case of cured epoxy resins the situation was complicated by the fact that the temperatures needed to obtain a well measurable deformation are frequently higher than the customary cure temperatures. Thus, an undesirable continuation of the cure may result while the specimen is heated for the test. To avoid this source of error, a testing method was desirable in which the major part of the specimen is kept at room temperature, and heat is applied over a small area and during a limited time only. An arrangement in which a preheated, pointed tool is used to make a measurable indentation into a resin sample appeared to be the ideal solution.

An elaborate instrument of this type has been described (16), but is not available commercially; thus, the hot-point in-

dentation tester was developed independently. A photograph of the tester with accessories is given in Figure 4, a drawing of the essential parts in Figure 5. The major features of the instrument are:

The indentation tool is a small steel tip with an included angle of 90°, inserted in a cylindrical copper block.

The copper block is heated electrically to temperatures up to 300° C.

Temperature control is obtained through a copper-constantan thermocouple located very close to the steel tip.

The indenter—i.e., copper block with tip—is loaded by dead weight. The total load is 700 grams.

The hot indenter is lowered smoothly and in precisely perpendicular direction onto the specimen, which must have a plane surface.

After a contact time of 20 seconds, the penetration of the indenter—i.e., the depth of the indentation—is read directly from a dial gage. The range is 0 to 0.025 inch.

The measurements reported were made on 1-mm. thick sheets of cured epoxy resins at temperatures of 25°, 50°, 100°, 150° C., etc., until the depth of indentation reached the limit of the gage. The depth values found were plotted against the temperature at the indentation point. Figure 6 shows a family of curves of the type. From these curves, the temperature at which the indentation reached a depth of 0.0075 inch was determined. This value, called arbitrary softening temperature, is highly typical for a cured resin and was selected as a relative measure for the degree of cross linking.

The choice of the curing agent, as well as the cure temperature, has a strong influence on the softening temperature (Table II, column 4); under favorable circumstances—i.e., when an efficient curing agent and a high cure temperature were employed—values up to 229° C. were obtained.

**Determination of Swelling Value.** The second of the two principles that are thermodynamically related to the degree of cross linking is the swelling of the cross-linked materials in solvents. To utilize this principle, a method of measuring the swelling of cured resins was developed.

The theory relates the degree of cross linking to the amount of swelling at the swelling equilibrium; thus, one cannot be satisfied with swelling rates, but must continue the swelling procedure until a stationary condition has been established.

**Swelling in Liquid Solvents.** The conventional method for swelling measurements on cross-linked polymers consists in immersing weighed or measured specimens into suitable solvents and observing the gain of weight or volume over a period of time. This method, tried extensively on samples of cured Epon resins, gave disappointing results. Difficulties were caused by cracking of the specimens or even disintegration into small fragments

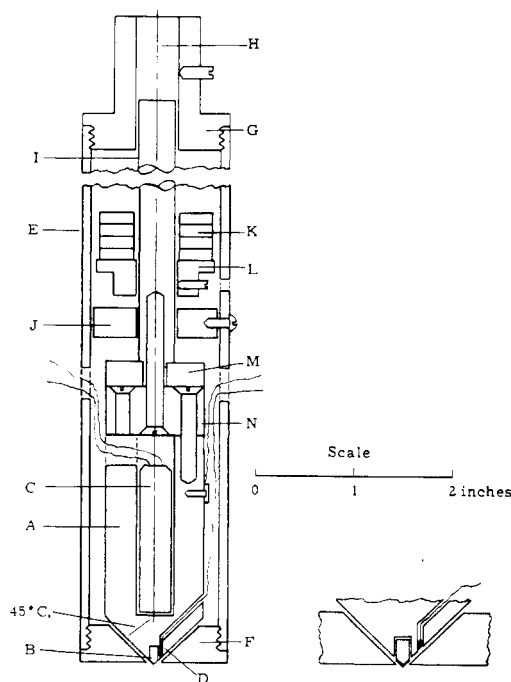


Figure 5. Hot-point hardness tester, indenter assembly

- |                                   |                                    |
|-----------------------------------|------------------------------------|
| A. Copper cylinder, chrome plated | H. Insert dial gage (Ames No. 212) |
| B. Steel tip                      | I. Connecting rod                  |
| C. Cartridge heater (50 watt)     | J. Brass bushing                   |
| D. Thermocouple                   | K. Lead disk                       |
| E. Housing                        | L. Loading platform                |
| F. Foot plate                     | M, N. Transite blocks              |
| G. Upper bushing and gage holder  |                                    |

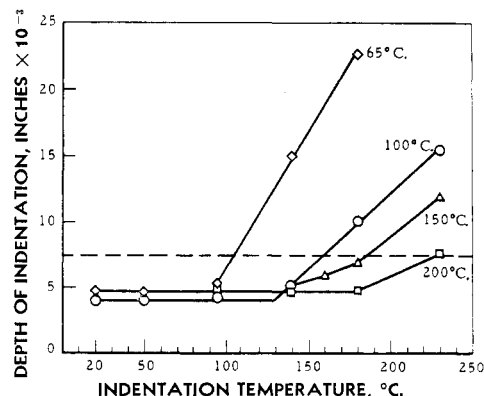


Figure 6. Hot hardness curves of cured Epon 828

Curing agent, *m*-phenylenediamine  
Maximum cure temperatures as indicated

while the swelling was in progress (17, 18). Even where the cracking was not very obvious, the swelling went through a maximum instead of approaching an equilibrium. Similar observations have been reported and discussed (3, 4). Since the method did not give equilibrium values on cured Epon resins, it was considered unsuitable for the present purposes.

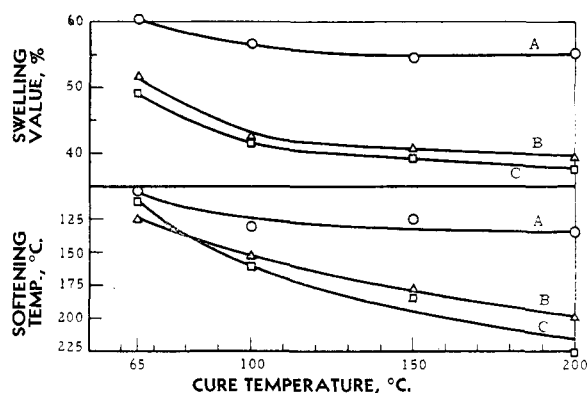


Figure 7. Comparison of swelling values and softening temperatures of cured Epon 828

- A. Curing agent, piperidine  
B. Curing agent, tris(dimethylaminomethyl)phenol  
C. Curing agent, *m*-phenylenediamine

**Swelling in Solvent Vapors.** In order to avoid the difficulties described, a different method was developed in which the swelling is carried out on finely divided powders of the substance by contact with the vapors of a solvent. This method offers three advantages: No disturbance by crazing, cracking, or leaching occurs; the swelling equilibrium is established rapidly; and precise, gravimetric determination of the amount of swelling is possible.

The samples are ground to micron size, vacuum-dried, and conditioned at 25° C. and 50% relative humidity. Samples of 0.5 gram are weighed into glass jars and placed in a desiccator containing a mixture of 1,2-dichloroethane and cetane (hexadecane) in the molar ratio of 95 to 5. The desiccator is evacuated and kept at constant temperature (25.0° ± 0.3° C.) for 24 hours, and the gain of weight of the samples is determined. The experiment is continued for another 24 hours to ascertain that equilibrium has been established. Condensation of solvent, a potential source of error, was avoided by keeping the temperature constant, by diluting the solvent (dichloroethane) with a non-solvent (cetane), and by releasing the vacuum slowly.

The results obtained by this method were very satisfactory. The final value was always obtained within 24 hours and the reproducibility of the results was within a few tenths of 1%. The last column of Table II shows swelling values obtained by this method; they are expressed as per cent gain of weight and vary from 60.5% for an inadequately cured resin to 37.6% for a very well cured resin.

**Discussion.** It would be valuable to convert these swelling values to another value more directly representative of the degree of cross linking, such as the average molecular weight between cross links. However, this has not been possible as yet, partly because the available theoretical treatment applies primarily to slightly cross-linked resins, partly because the conversion requires the knowledge of an interaction constant which is difficult to determine.

Since the swelling values are considered to be a measure for the degree of cross linking (within groups of similar chemical composition), the results were compared with the softening temperatures obtained by the indentation method, a method also believed to furnish a measure for the degree of cross linking. In Figure 7 the upper part illustrates swelling values, the lower

Table II. Softening Temperatures and Swelling Values of Cured Epon 828

| Curing Agent,<br>Parts/100 Parts<br>Epon            | Cure<br>Time,<br>Hours | Cure<br>Temp.,<br>° C. | Arbitrary<br>Softening<br>Temp., ° C. <sup>a</sup> | Swelling<br>Value,<br>% |
|---|------------------------|------------------------|--|-------------------------|
| Piperidine <sup>b</sup> , 5                         | 24                     | 65                     | 103  | 60.5                    |
|   | + 4 <sup>c</sup>       | 100                    | 131.5  | 56.5                    |
|   | + 1 <sup>c</sup>       | 150                    | 125.5  | 54.6                    |
|   | + 0.5 <sup>c</sup>     | 200                    | 135  | 55.2                    |
| Tris(dimethyl-<br>aminomethyl)<br>phenol, 4         | 24                     | 65                     | 125  | 51.8                    |
|   | + 4 <sup>c</sup>       | 100                    | 153  | 42.5                    |
|   | + 1 <sup>c</sup>       | 150                    | 178  | 40.5                    |
|   | + 0.5 <sup>c</sup>     | 200                    | 199  | 39.3                    |
| <i>m</i> -Phenylene-<br>diamine <sup>b</sup> , 12.5 | 24                     | 65                     | 113  | 49.2                    |
|   | + 4 <sup>c</sup>       | 100                    | 161  | 41.6                    |
|   | + 1 <sup>c</sup>       | 150                    | 185  | 39.2                    |
|   | + 0.5 <sup>c</sup>     | 200                    | 229  | 37.6                    |

<sup>a</sup> For indentation of 0.0075 inch within 20 seconds.

<sup>b</sup> Pure compound.

<sup>c</sup> Cures in addition to cures indicated in line or lines above.

part softening temperatures obtained on the same samples. Though a perfect agreement of the two sets of curves does not exist (and cannot be expected), the similarity is unmistakable. This appears to strengthen the opinion that either method gives results that can be considered, in a relative way, to be estimates of the degree of cross linking and can be used, within groups of similar chemical composition, for a comparison and evaluation of cured thermosetting resins.

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