Epoxy Polymers. II. Macrostructure

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Synopsis

A variety of measurements indicate that thermosetting epoxy polymers contain closely packed floccules and an interstitial liquid similar to the starting materials. The floccules are thought to be of colloidal origin and appear to be ordered with respect to each other in a three-dimensional array.

INTRODUCTION

For many years a certain degree of ordering has been postulated in liquids and in emulsions.[1] Although these treatments have been primarily concerned with molecular dimensions, it is not inconceivable that molecular forces (besides gravitational forces and shrinkage stresses in polymeric systems) could give rise to ordering on a macroscopic scale in colloids. Several epoxy polymers exhibit the electrokinetic phenomena associated with colloids[2] and have been shown to be two-phase systems containing roughly spherical floccules in a low-density liquid medium resembling the uncured starting materials.[3] Several different measurements indicate that the floccules are packed in a regular arrangement.

EXPERIMENTAL

Casting compound C 13-009 (in Parts A and B), a polyol-modified, anhydride-cured epichlorohydrin–bisphenol A epoxy resin, was obtained from the Shell Chemical Company. The polyol structure is

$$H_2C—[O—CH_2—CH(CH_3)—]_xOH$$
$$HC—[O—CH_2—CH(CH_3)—]_xOH$$
$$H_2C—[O—CH_2—CH(CH_3)—]_xOH$$
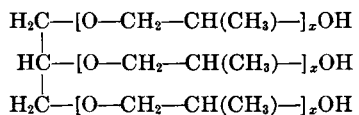
The average value of x is 3.6. The curing agents used were hexahydrophthalic anhydride and benzyldimethylamine. Parts A and B were heated to 54°C., mixed in equal quantities by weight, and placed in an evacuated chamber to remove air bubbles. The curing conditions were varied to give different properties.

The compositions of the starting materials for the polyol-modified epoxy are shown in Table I.

TABLE I
The Polyol-Modified Epoxy Materials[a]

Material	Part A, wt.-%	Part B, wt.-%
Bisphenol–epichlorhydrin resin	82	—
Hexahydrophthalic anhydride	—	62.3
Polyol (P-1180)	18	36.1
Benzyldimethylamine	—	1.6

Table II lists material sources. The chemicals were used as obtained without further purification.

TABLE II
Chemicals and Sources

Chemical	Source
Epichlorhydrin–bisphenol A (Epon 828)	Shell Chemical Company
Curing agent: diethanolamine (DEA)	Fisher Scientific Company
Curing agent: triethylenetetramine (TETA)	Furane Plastics, Inc.
Curing agent: m-phenylenediamine (MPDA)	E. V. Roberts & Associates, Inc.
Unox Epoxide 221[a]	Union Carbide Corporation
Curing agent: diethylenetriamine (DETA)	Hysol Corporation

[a] 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate.

The gross polymer structure was differentiated by etching techniques with one or more of the solvents ethyl alcohol, acetone, benzene, tetrahydrofuran, and dimethylformamide. These techniques involve differential rates of dissolution or diffusion in the heterogeneous polymer medium, in order to show the structures present. The contrast necessary to differentiate between structures of similar refractive index and structural moieties (but widely different molecular weights) was obtained, in many cases, by the change in refractive index associated with the more rapid diffusion of a particular solvent or solution in the lower molecular weight polymer constituents.

The polyol-modified epoxy polymer is thought to contain a large number of hydroxyl groups per molecule regardless of its molecular weight. These were oxidized to carboxyl groups by immersing the polymer in aqueous chromic acid solutions at about 100°C. This treatment rendered the lower molecular weight polymer constituents more soluble in water without appreciably affecting the solubility of the floccular constituents of high molecular weight. By rinsing the oxidized polymers with distilled water the more soluble constituents were removed, leaving the floccule phase, which could then be detected easily by microscopic examination.

Photomicrographs of the polymer surfaces were made by reflected light microscopy with a Bausch and Lomb research metallograph. Photographs were also obtained by transmitted-light microscopy by Milton (Sandia Corporation, Albuquerque, New Mexico). Both microscopes were equipped with polarizers and light filters.

Fracture patterns on the sample surfaces were photographed after breaking the polymers at liquid-nitrogen temperatures.

The electric fatigue measurements made by Milton[5] resulted in a breakdown path through the bulk epoxy polymers, from which cleavage leaves radiated. These presumably occurred as a result of the intense local heating and high gas pressures generated upon the decomposition of the polymer during the breakdown. The rapidity of the tests assured a brittle failure at room temperature.

Sessile-drop (water) contact-angle measurements were made on the polymer surfaces with an instrument previously described.[3] The standard deviation of the mean of eight measurements (one measurement on each side of four drops placed randomly across the surface) was between $\pm 1.0°$ and $\pm 0.2°$. The contact angle measurements were made as a function of the depth of the measurement plane from the original surface of the polymer. The surfaces were sanded by hand with No. 600 grit silicon carbide paper and finished with No. 600 soft microcut paper. A slow figure-eight motion was used, to avoid heating the sample and to produce a random scratch pattern. The sample thickness was determined with a micrometer to the nearest 1/10,000 in. Deviations from coplanarity of the measurement planes were determined to be less than $\pm 0.09°$ for samples 0.5 in. in diameter.

Relative-hardness measurements were made as a function of position across the polymer surfaces with a Kentron Micro-hardness Tester. The load applied with the diamond pyramid point was varied as required, to produce an indentation about 20 μ wide in each of the polymers tested (1 g. load for the polyol-modified epoxy, a 25 g. load for the 221-DETA system, and a 200 g. load for the m-phenylenediamine–828 system). The precision of the hardness measurements was $\pm 1.5\%$ of the average value.

The densities of the polymer samples were measured with a precision of ± 0.2 mg./cm.[3] by the buoyancy method with a Chainomatic balance (the samples were weighed in air and in distilled water at a constant temperature.)[6]

The strain bands in the polymers were observed under crossed polaroids, and layering during polymerization was shown by curing the polymer on the end of a heated copper rod.

RESULTS

Photomicrographs of the polyol-modified epoxy are shown in Figure 1. These were obtained by reflected light after etching of the samples in chromic acid.

Figure 2 shows a similar pattern obtained by Milton for the polyol-modified epoxy after diffusing tetrahydrofuran into the interstitial regions of the sample. This photomicrograph was obtained by transmitted-light microscopy.

The two types of fracture pattern are shown in Figure 3 and in Figures 4–6, respectively. The two views in Figure 3 were obtained by reflected light from
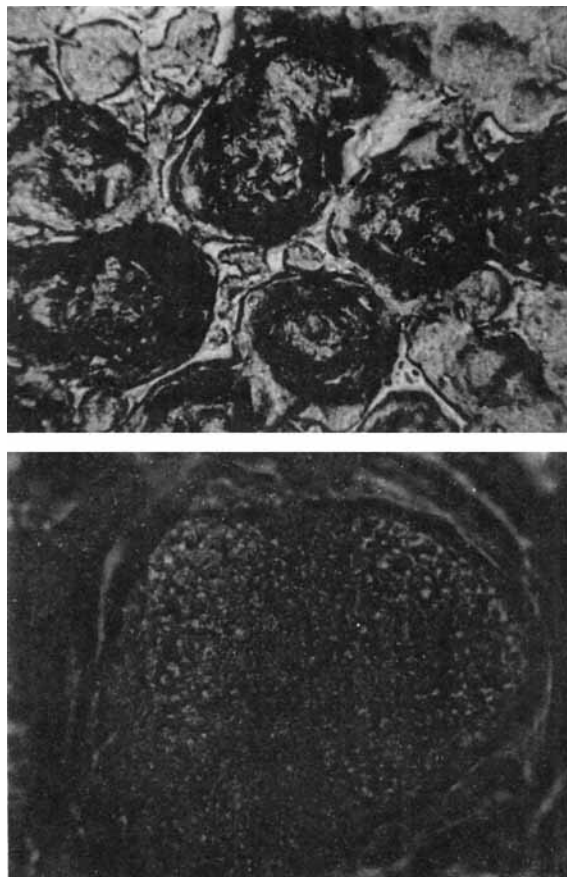
Fig. 1. Floccules in polyol-modified epoxy shown after etching the sample with aqueous chromic acid (upper, 400×; lower, 1167×).
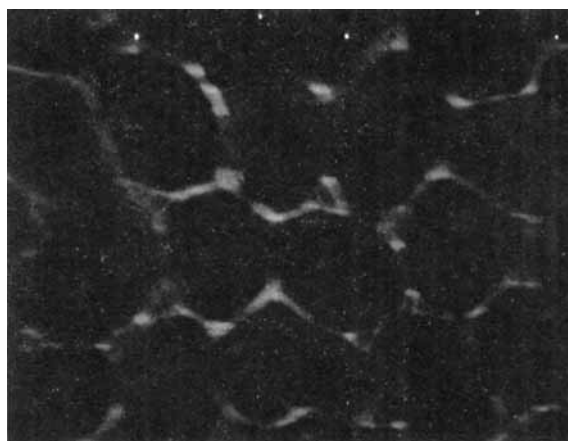

Fig. 2. Floccules in polyol-modified epoxy shown after diffusing tetrahydrofuran into sample (100×) (Courtesy of O. Milton).

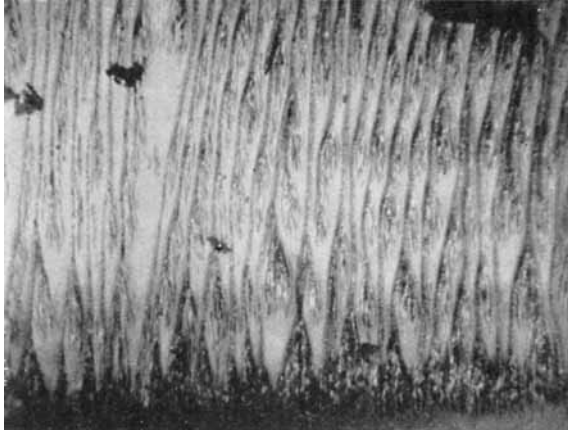Fig. 3. Fracture patterns in polyol-modified epoxy surface (upper, 110×; lower, 400×)
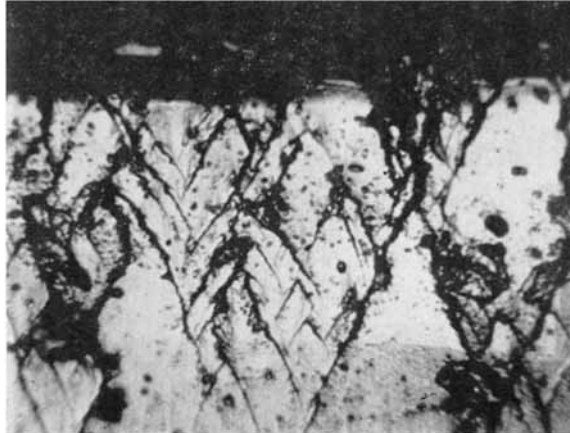

Fig. 4. Fracture patterns on polyol-modified epoxy surface (upper, 110×; lower, 270×).

the surfaces exposed by impact fracture at low temperature.   Figures 4 and 5 show patterns obtained by reflected light from the surfaces exposed by bending fracture at room temperature after diffusing ethanol into the polyol-modified epoxy sample.   In an effort to define more clearly the floccules in
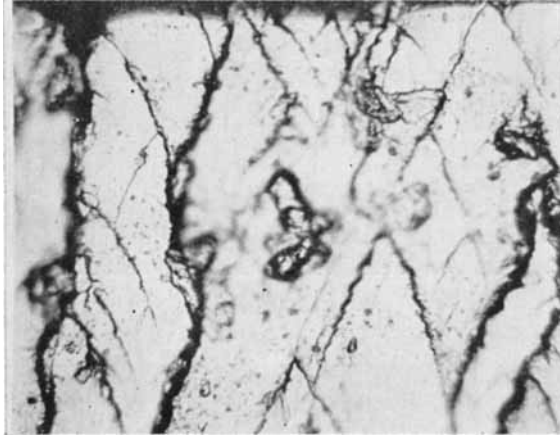

Fig. 5. Fracture patterns on polyol-modified epoxy surface (400×).
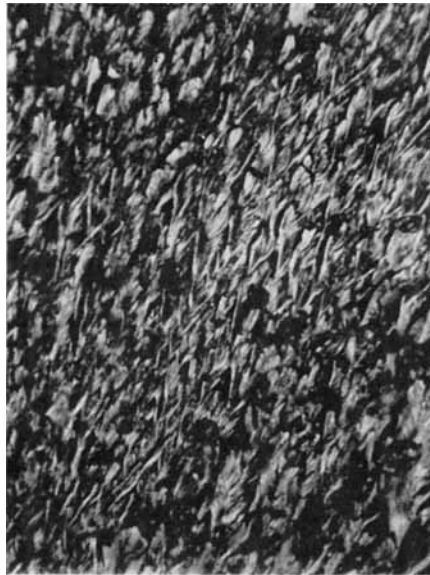

Fig. 6. Fracture patterns on surface of polyol-modified epoxy sample doped with benzene (10% by weight). (110×).

this polymer, a sample was cured with about 10% benzene (by weight). This experiment was not successful in showing the floccules but did show fracture patterns in the diamond shape more clearly.   The sample was cut and then photographed by reflected light (Fig. 6).

A typical example of the electrical cleavage patterns obtained by Milton is shown in Figure 7.

The contact angle-depth measurements, when taken on successive planes parallel to a vertically mounted mold surface, show a characteristic periodicity (Figure 8). The initial measurement surface was a polyol-modified epoxy–steel interface. A piece of smooth, flat sheet steel was mounted
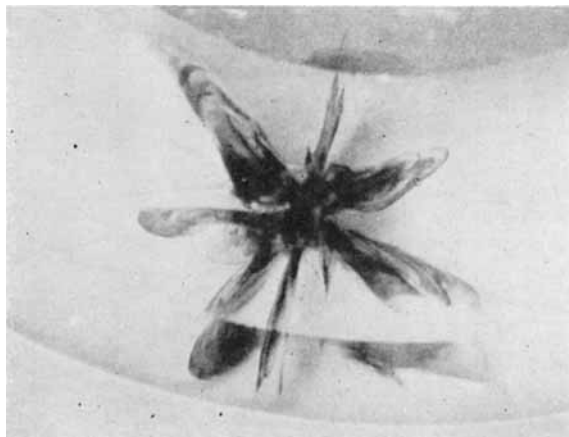

Fig. 7. Electrical breakdown cleavage patterns in polyol-modified epoxy sample (4×) (Courtesy of O. Milton).
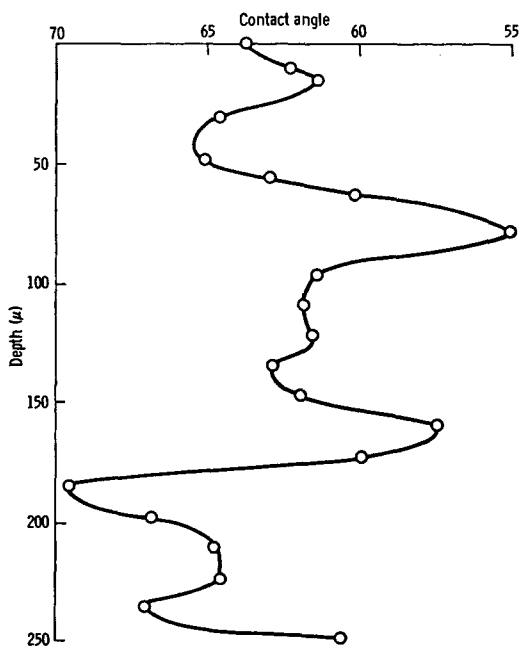

Fig. 8. Water contact angle on polyol-modified epoxy as a function of depth from a polymer–steel interface oriented perpendicular to polymer–air interface.
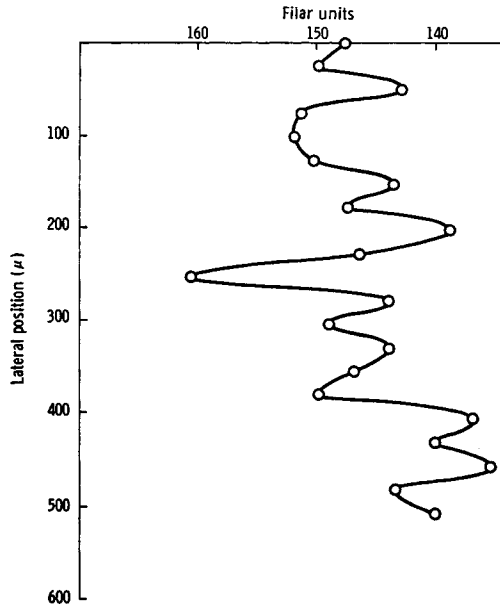
Fig. 9. Relative hardness of polyol-modified epoxy as a function of position from polymer–steel interface.
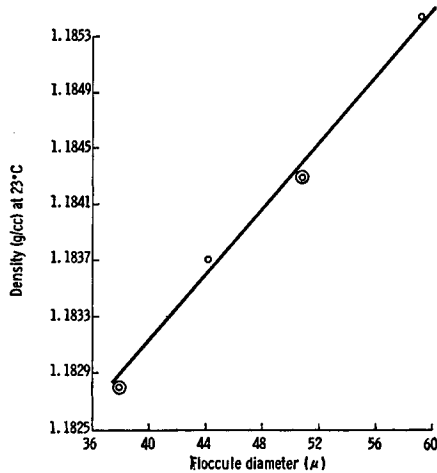

Fig. 10. Polyol-modified epoxy polymer density as a function of average floccule size.

vertically in the center of a large-diameter shallow potting container. The container was filled with the polyol-modified epoxy and cured on a hot plate from the bottom. A sheet of copper $1/4$ in. thick, at the bottom of the container, served to smooth the isotherms parallel to the bottom and the air interface. Figure 9 shows data obtained by hardness measurements. The periodic pattern is similar to that shown in Figure 8. A series of measurements on the polymer surface perpendicular to the steel sheet were
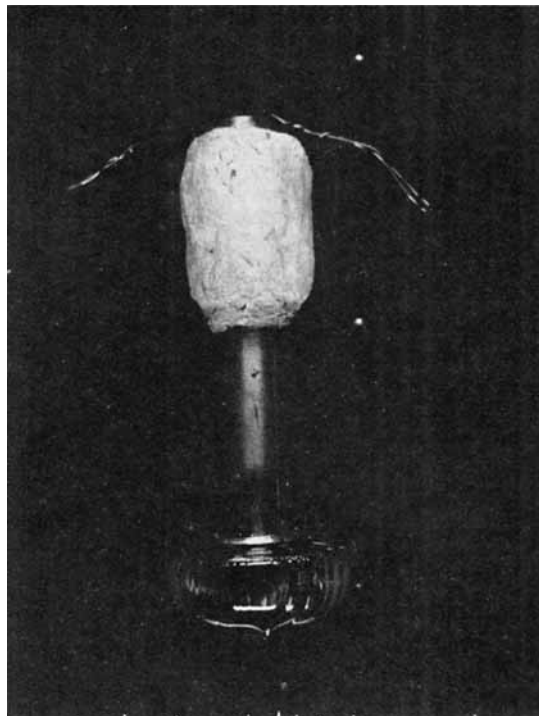
Fig. 11. Layered curing process in polyol-modified epoxy. The polymer surface is conformal with the isotherm.

made in a line parallel to, and about 25 μ from, the polymer–steel interface. These data were averaged and entered as the initial point in Figure 9. Measurements were repeated at 25 μ increments from the initial series. The perpendicular distance of each series of measurements from the initial line is shown on the vertical axis in Figure 9. The averaging technique gives a measure of the hardness in planes comparable to those upon which contact angle measurements were made (Fig. 8).

The density of the polyol-modified epoxy is shown as a function of the floccule diameter in Figure 10. The floccule size was varied by curing the polymer at different oven temperatures. The floccule diameter determinations were made by penetrometer measurements; they are described elsewhere.[7]

Strain bands visible in the epoxy samples with the use of polarized light were found to be parallel to the isotherms. The shape and location of the isotherms was varied by varying the shape of the potting container and the location of the heat source during cure.

Figure 11 shows a heater constructed by wrapping the upper portion of a copper rod with a nichrome wire (a resistance heater). The lower surface of the cylindrical copper rod was placed in contact with the air interface of the uncured polymer mixture. The rod was heated to 160°F. and removed

after a 24 hr. curing period.   The cured portion of the epoxy adhered to the rod and, as shown in Figure 11, was conformal with the isotherms which would be calculated for the rod geometry.

DISCUSSION

Floccular Nature of Epoxy Polymers

Several epoxy polymers appear to be two-phase systems: floccular aggregates and an interstitial fluid.   Photographic evidence of the presence of floccules is presented in Figures 1 and 2 for the polyol-modified epoxy. Physical evidence of the presence of floccules in this polymer was obtained by mapping the sample surface with a micropenetrometer; it is presented elsewhere.[7]   A diffusion-controlled curing process in an interfloccular capillary matrix has been postulated.   The presence of an uncured or partially cured liquid allows electrolytic conduction, and the capillary constraint appears to affect the dielectric strength of the polymer.   Data supporting the postulated cure and dielectric breakdown mechanisms will be presented in subsequent papers.   The floccule size and, therefore, the interfloccular capillary size, appears to be an important factor in both.

Evidence of an Ordered Floccule Structure

The photomicrographs showing the floccules in the polyol-modified epoxy (Figs. 1 and 2) indicate that the floccules are approximately spherical in shape and are about the same size in a given region.   Some variation can be seen about an average size.   An overall order is shown in the floccule arrangement, such that adjacent floccules may be connected with the floccule centers at the apices of an equilateral triangle.   This is most clearly shown in Figure. 2.   Occasionally two small floccules or an oddly shaped floccule are found at the site where one large floccule should be, if this type of ordering were perfect.

The fracture patterns shown in Figure 3 indicate a fairly uniform arrangement of material in horizontal layers.   The tree-like patterns are approximately equidistant, center-to-center, measured horizontally.   This dimension is about 30 μ (the floccule sizes range from about 20 to about 90 μ in this material and are dependent upon the curing temperature).   Here, again, the arrangement of the visible pattern is such that triangles may be drawn with apices at tree centers.

Another type of fracture pattern, shown in Figures 4–6, occurs in this same material and is characterized by a series of parallelograms containing angles averaging about 60° and 120°.

When the epoxy materials are broken down by an electric discharge, fracture in leaf-like planes occurs around the central breakdown path. These planes intersect at about 60° or 120° angles (there is some variation in this angle of intersection).   Figure 7 shows a typical example.

Contact angle-depth and hardness-position measurements (Figs. 8 and 9,

respectively) indicate that the epoxy material is arranged in layers. A periodic pattern was shown for the three orthogonal sample orientations.

Figure 10 shows the variation in material density as a function of the average floccule size. This trend would be expected in any nucleating two-phase solid–liquid system. When there is a finite separation between solid particles, there would be a greater volume fraction of low-density interstitial fluid in samples containing small solid particles than in samples containing large particles. The relation between these measurements and a specific type of ordering will be shown later.

The epoxy polymers change from a liquid to a solid during cure, and this phenomenon was observed to occur in layers parallel to the isotherms, the cured polymer increasing in thickness in a direction perpendicular to the isotherms, away from the heat source (Fig. 11). Strain bands observed under crossed polaroids were also conformal with the isotherms.

A Theoretical Model

Figure 2 shows that the floccules in this sample are arranged in an order approximating a hexagonal close-packed layer. If all layers are similarly arranged and exhibit a similar degree of ordering, then it should be possible to find a theoretical model which most nearly describes the system mathematically. There are two three-dimensional geometric arrangements of hexagonal close-packed layers, the face-centered cubic (FCC) and the three-dimensional hexagonal close-packed (HCP) structures. These are often found to coexist in the same material, and a change from one to the other accompanying a change in the sample temperature is not uncommon. There is no evidence presented here that clearly distinguishes between these
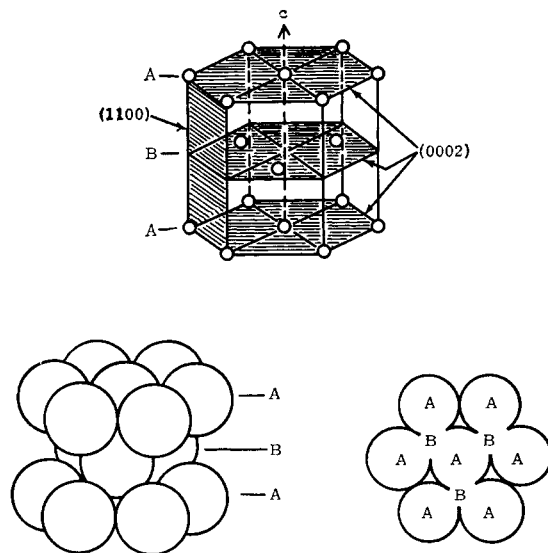

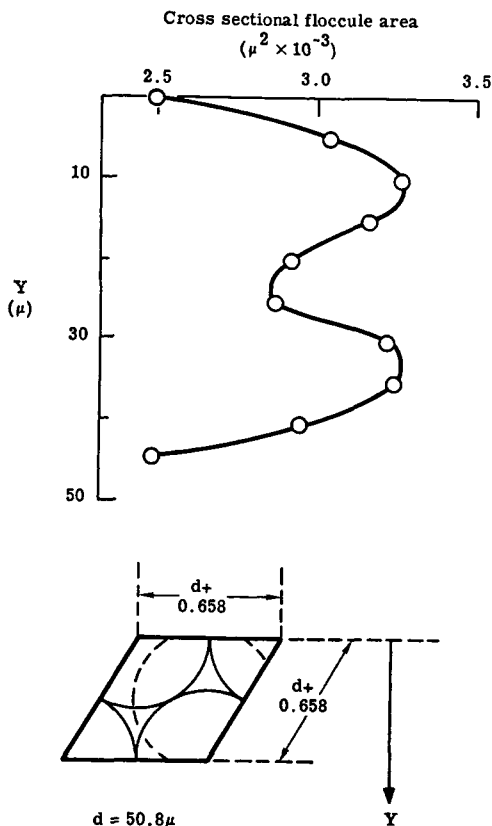Fig. 12. Hexagonal close-packed structure.

Fig. 13. Theoretical floccule cross-sectional area as a function of position of measurement plane as it is moved through unit cell.

two arrangements, but it is the author's opinion that these two structures are far more likely than any other of the fourteen space lattices.

Assuming the HCP structure shown in Figure 12, a periodic shape can be calculated for the floccule cross-sectional area curve as the measurement plane is moved through the unit cell. This curve is shown in Figure 13 and bears a close resemblance to that obtained by contact angle-depth and hardness-position measurements (Figs. 8 and 9, respectively). The average hardness and the contact angle would be a function of the relative amounts of floccule and interstitial material characterizing the plane of measurement. The amount of floccular material in the plane would be proportional to the cross-sectional area.

Samples of the polyol-modified epoxy were ground to a fine powder and extracted with ethyl alcohol (and in other experiments with toluene followed by ethyl alcohol). The liquid phase was separated in this way from the solid phase. The density, molecular weight, viscosity, refractive index, dielectric constant, and phase-transition temperatures were obtained for the liquid after removal of the alcohol under vacuum. The density and phase-
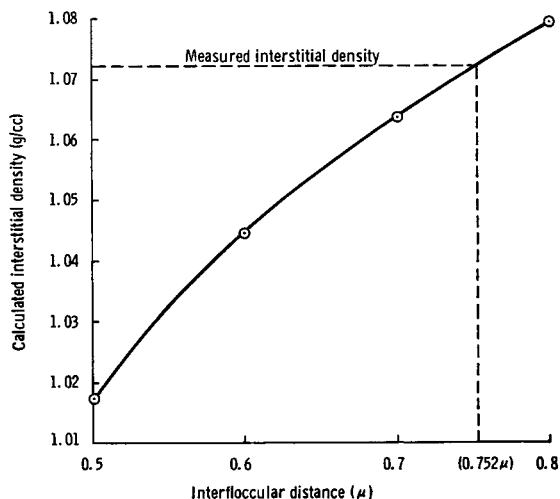
Fig. 14. Calculations based on HCP model.

transition temperatures of the solid residue were measured. These results are reported elsewhere,[3] and a summary of the density data is given in Table III.

In the following theoretical treatment involving the floccule cross-sectional area curves and the density approximations these assumptions were made:

(*1*) All the floccules in a given sample are perfect spheres, the same size, and symmetrically arranged.

(*2*) The density of the interstitial fluid and that of the floccule are constant and independent of size or cure schedule (the floccule size could be made large or small by curing at low or high oven temperatures).

(*3*) The variation in polymer density with floccule size (Fig. 10) is assumed to occur because of a variation in volume fraction of interstitial
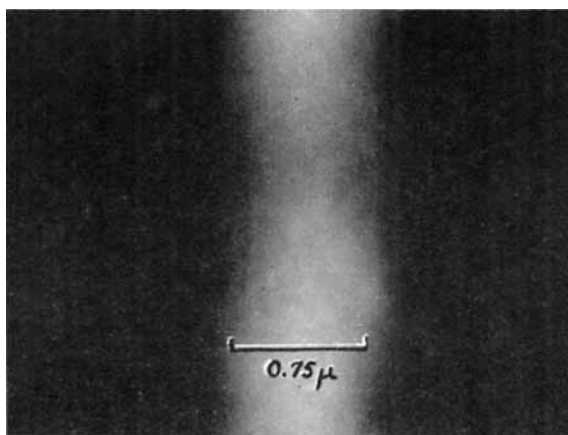

Fig. 15. Interfloccular space at point of closest approach (31,478×).

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TABLE III
Density of Polyol-Modified Epoxy Constituents

Material	Density, g./cm.[3]
Polyol (P-1180)	1.0290
Interstitial fluid	1.0724
Part A	1.1390
Part B	1.1466
Solid residue (experimental)	1.2273
Floccule (theoretical)	1.2300

fluid. This can occur under the conditions described above if there is a finite separation between floccules.

(4) The separation between floccules (controlled by the electrokinetic zeta potential in colloidal systems) is assumed to be a constant.

(5) The HCP model was assumed for the floccule arrangement.

With these assumptions, the density and volume fraction of interstitial fluid can be calculated for systems containing floccules of various sizes and various interfloccular distances (the polymer density–floccule size relationship shown in Figure 10 was also used in these calculations). The calculated interstitial density as a function of interfloccular distance (surface-to-surface) is shown in Figure 14. This graph was entered with the measured interstitial fluid density, and a value for the interfloccular distance was obtained. This theoretical surface-to-surface spacing is compared in an en-
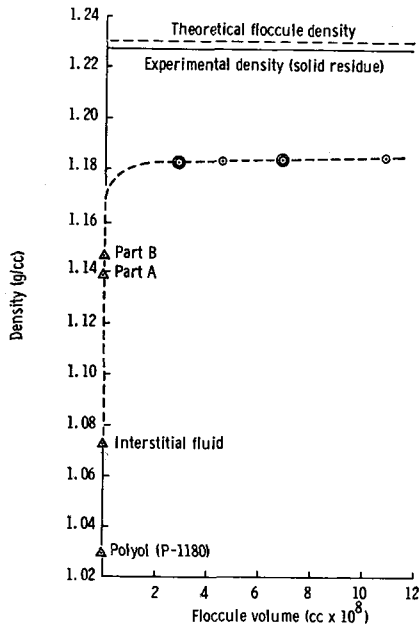

Fig. 16. Polyol-modified epoxy polymer density as a function of calculated floccule volume.

larged photograph of an interfloccular region in Figure 15. The 0.75 μ figure is a fairly good estimate, as shown by the photograph, though high precision is lacking because of the difficulty in photographically defining the floccules.

The theoretical floccule density obtained in this calculation is shown by the upper dashed line in Figure 16 and is compared with the experimentally determined density of the solid residue after solvent extraction (solid line). The difference between the two (0.0027 g./cm.^{3}) is less than the experimental error (±0.0088 g./cm.^{3}) in the solid residue density determination. This difference is 0.22% of the theoretical value. The lower dashed line is the polymer density–floccule volume curve obtained by fitting the measured polymer density points (Figs. 10 and 16) and the measured interstitial fluid density (Table III) with the HCP model.

Postulated Mechanism of Ordering

The epoxy materials were shown to be layered by several different techniques. There is a correlation between the layer dimensions and the floccule size (as obtained by photographic and penetrometer measurements). If the layering in a sample is due to the arrangement of the floccules, then it follows that the floccules are three-dimensionally ordered. One type of ordering (the HCP model) appears to fit the data under the assumptions made. An extended investigation would be necessary to show that all other types do not fit. The data presented indicate an ordered arrangement of floccules. It is of interest to consider how this might come about. A very simple experiment, which results in a hexagonal arrangement of spheres under gravitational forces alone, is performed by shaking small balls in a large container; an analogy may be drawn in the epoxy systems, where thermal agitation replaces the mechanical shaking. This may be sufficient to obtain the degree of ordering described in the preceding sections.

There are other factors, however, which must be considered. The layering along the isotherms appears to be a result of forces stronger than gravity. All of the materials studied are of high viscosity, and the fluidity decreases rapidly as cure continues. It is difficult to believe that any large amount of floccule motion occurs after gelation (though some motion or deformation certainly does occur in the relief of strain and in cure shrinkage). The geometrical arrangement of floccules is probably essentially complete prior to gelation. The floccules have been postulated to be of colloidal origin.[3] The effects of repulsive forces arising from the diffuse double layer of charged species at phase boundaries have been extensively studied by macromolecular phenomenologists[2] in both organic and inorganic polymer systems. These forces would result in a certain interfloccular separation and, if the forces are spherically symmetric, could give rise to an ordered arrangement as shrinkage occurs during cure. The floccule shape of least surface energy would be that of a sphere, and the

closest packing that could occur due to shrinkage would be the HCP or the FCC arrangement.

CONCLUSIONS

The data indicate that the epoxy polymers studied are floccular in nature and that the floccules are ordered in a symmetrical array. The hexagonal close-packed theoretical model appears to fit the density data, the periodic layering data, and the fracture patterns. A diffraction experiment and a crystallographic analysis would be of considerable interest. The long-wavelength lasers (40–90 μ) would be necessary because of the large size of the floccules and the low-energy characteristics of conventional light sources.

The ordering mechanism probably involves a combination of the forces characteristic of colloidal material, the shrinkage during cure, and gravitational forces.

References

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