

Macrostructure and Environment-Influenced Surface Layer in Epoxy Polymers

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Synopsis

Several epoxy polymers were shown to be two-phase systems; roughly spherical floccules arranged in layers in an interstitial fluid resembling the starting materials. The size of the floccules was found to be dependent on the initial rate of cure of a given polymer. The density, hardness, glass transition temperature, etching rate, and dielectric strength were related to the floccule size. The surface layer in the epoxy polymers and in several thermoplastic polymers was found to be different from the bulk material. The properties of the surface layer are dependent on the surface energy of the mold material and on the atmospheric environment. A gradient in properties was found to extend from the polymer surface several hundred microns into the bulk.

The results obtained in a recent investigation of the physical and chemical properties of thermosetting epoxy polymers have been classed under two broad topics of general interest, the supramolecular structure, and the environment-influenced surface layer.

The epoxy polymers studied were polyol-modified, hexahydrophthalic anhydride and benzyldimethylamine-cured epichlorhydrin-bisphenol A; diethanolamine-cured epichlorhydrin-bisphenol A; *m*-phenylenediamine-cured epichlorhydrin-bisphenol A; and diethylenetriamine-cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate. These were characterized as two-phase systems; an array of roughly spherical floccules (thought to be of colloidal origin), and an interstitial fluid resembling the liquid starting materials in density, refractive index, and viscosity. The floccules were found to be ordered in layers throughout the polymer samples and were shown by five techniques.

Photomicrographs of the floccules were obtained after subjecting the polymers to one or more of several chemical etching techniques.

The floccules and the interstitial fluid are not sufficiently different in refractive index for visual observation. The former were shown photographically, after diffusing tetrahydrofuran into the interstitial regions of the polymer.¹

The floccules are harder and more rigid than the interstitial fluid and were shown by differential penetrometer measurements on a line across the polymer samples.

A layered structure, attributed to floccule layering because of size cor-

relations, was shown by sessile drop contact angle measurements and surface refractive index measurements. These measurements were made on successive sample surfaces as polymer layers were removed. The half-cycle dimensions obtained from these periodic curves were in agreement with the floccule dimensions obtained photographically.

The layered structure was shown by diamond pyramid hardness measurements. These measurements were made across a horizontal sample surface on lines parallel to a vertical mold surface. The lines were displaced 20 μ from each other. Averages of the measurements on each line were entered on a graph as a function of the perpendicular distance of the line from the mold surface. The periodic shapes of the curves were in agreement with those obtained by sessile drop contact angle and surface refractive index measurements, and the half-cycle dimension correlated with the floccule dimensions.

The average size of the floccules in a given polymer was found to be controlled by the rate of heat transfer to the sample during the initial stages of the cure. Large floccules (90 μ in diameter) were obtained with low temperature curing schedules, and small floccules (20 μ in diameter) were obtained with high-temperature curing schedules. When the sample was cured at a given oven temperature, large floccules were found near thermally insulating mold surfaces (polytetrafluoroethylene), and small floccules were found near thermally conductive mold surfaces (steel or aluminum).

The following physical or chemical characteristics are attributed to floccule formation and differences in floccule size.

Samples of the polyol-modified epoxy characterized by small floccules had a low glass transition temperature (18°C.), density (1.1825 g./cc. at 23°C.), and hardness, and were relatively easily attacked by solvents. These samples had a high pulse dielectric strength (8 kv./mil).²

Samples of this same epoxy characterized by large floccules had a high glass transition temperature (34°C.), density (1.1860 g./cc. at 23°C.), and hardness and were more resistant to solvent etching. These samples had a low pulse dielectric strength (1-2 kv./mil).²

The gel times were determined at various oven temperatures by accurately measuring the height of an epoxy sample in a cylinder as a function of time during cure. The gelation point was taken as the time at which a sharp break occurred in the shrinkage curve. For polyol-modified epoxy samples cured at high oven temperatures (200°F.), the gel times were short (70 min.) and the slope of the shrinkage curve just after the gel point was very near zero. Longer gel times (400 min.) were associated with lower cure temperatures (120°F.), and the slope of the shrinkage curve just after the gel point was appreciably different (-2.3×10^{-3} cc./min. for a 100 cc. sample). The residual strain bands (polarized light) were much more intense in the samples cured at low temperature in which it is postulated that the interfloccular spaces were sufficiently large to allow a diffusion-controlled curing process to continue after gelation. These results

are in keeping with the glass transition temperature and density measurements and may be associated with the degree of cure in the polymers.

Fracture and cleavage patterns were obtained which indicate that failure occurred in the softer interstitial region between the floccules. Milton observed phenomena similar to the stress corrosion cracking typical of metallic alloys containing grain structures.¹ Fracture patterns similar to step and line dislocations were also observed.

The formation of floccules in the epoxy materials results in a diffuse double layer and a zeta potential³ at the floccule-interstitial boundary. The electrokinetic phenomena electrophoresis and electroosmosis were observed in the polyol-modified epoxy. The electroosmotic curves indicate that the floccules are negatively charged.

The diffuse double layer (Helmholtz, Stern, or Gouy layer)³ occurs at any phase boundary in a colloidal system, and the mold-polymer interface is no exception. A gradient in properties was found from the polymer surface adjacent to the mold to a depth of several hundred microns into the polymer bulk. The surface energy of the mold was varied from that represented by a contact angle of 110° (a sessile water drop on polytetrafluoroethylene) to a contact angle of 0° (water on a clean glass or metallic oxide surface). A matching contact angle was found on the molded polymer surface. The contact angle gradient in the polymer surface layer was shown by removing successive layers from the polymer surface and successive contact angle measurements on these surfaces. The bulk polymer contact angle was 83° for the polyol-modified epoxy and 71.5° for the diethanolamine-cured epichlorhydrin-bisphenol A. Surface refractive index measurements on these surfaces showed a similar gradient in properties from a value of 1.5305 at the epoxy-polytetrafluoroethylene interface to a value of 1.5330 for the bulk polyol-modified epoxy. The periodic oscillations due to floccule layering were superimposed on these surface-to-bulk curves for both contact angle and refractive index measurements. The curves were reproduced when the polymer-mold interface was approached from the polymer bulk side and a concerted effort proved incapable of detecting a transfer of mold material to the polymer surface (multireflectance infrared analyses, concentrated solution infrared measurements of the dissolved surface layer, and neutron activation analysis at a sensitivity of 1 ppm). When epoxy samples cured in a polytetrafluoroethylene mold (110° contact angle) were aged at room temperature after removal from the mold, the surface contact angle changed over a period of 30 days toward the 65° contact angle associated with the air interface. This change was accelerated to a few hours at 71°C. and was reversed by clamping a polytetrafluoroethylene block against the polymer surface. These phenomena are thought to be due to the molecular orientation and packing of polar polymer constituents in the polymer surface layer and may correlate with the behavior observed in electrets. Preliminary measurements of the voltage generated by mechanical impact on the polymer surfaces show a correlation between the sign and magnitude of the voltage

and the surface contact angle. An additional correlation was obtained between the voltage decay times and relaxation times (molecular orientation polarization) reported by other investigators for ice⁴ and glycerol⁵ over the temperature range from -100 to 0°C .

The contact angle measurements made on mold-released epoxy surfaces showed a different time-dependent behavior. The contact angle results may be interpreted to indicate an initial diffusion of the mold release agents (silicone fluids) away from the polymer-mold interface. The silicone fluids reappeared at the surface of the epoxy a few days after removing the sample from the mold and remained at the polymer-air interface throughout the measurement time period. Zisman⁶ has shown that surface-active additives have a pronounced effect on the mechanical friction of polymeric materials.

This work was supported by the United States Atomic Energy Commission.

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Résumé

De nombreux polymères époxy forment des systèmes à deux phases, se présentant comme des floccules sphériques arrangées en couches dans un fluide interstitiel représentant les matériaux de départ. La grandeur des floccules était dépendante de la vitesse initiale de traitement du polymère déterminé. La densité, la dureté et la température de transition vitreuse, la vitesse d'attaque superficielle et la force diélectrique étaient reliées à la grandeur des flocons. La couche superficielle de ces polymères époxy et de nombreux polymères thermoplastiques était différente du matériau en masse. Les propriétés de la couche superficielle dépendaient de l'énergie de surface du matériau moulé et de l'environnement atmosphérique. Un gradient de propriétés a été trouvé depuis la surface du polymère jusque plusieurs centaines de microns à l'intérieur de la masse.

Zusammenfassung

Es wurde gezeigt, dass einige Epoxypolymere zweiphasige Systeme aus Schichten ungefähr kugelförmiger Flöckchen in einer dem Ausgangsmaterial ähnlichen Flüssigkeit bilden. Die Grösse der Flöckchen hängt von der Anfangshärtungsgeschwindigkeit eines gegebenen Polymeren ab. Dichte, Härte, Glasumwandlungstemperatur, Anätzgeschwindigkeit und Durchschlagsfestigkeit standen in Beziehung zur Flöckchengrösse. Die Oberflächenschichte unterschied sich bei den Epoxypolymeren und einigen thermoplastischen Polymeren vom Material im Inneren. Die Eigenschaften der Oberflächenschichte hängen von der Oberflächenenergie des Formmaterials und von der anwesenden Gasatmosphäre ab. Ein Eigenschaftsgradient erstreckte sich von der Polymeroberfläche einige hundert Mikron tief ins Innere.

Received June 24, 1966

Revised September 23, 1966

Prod. No. 1510