Environment-Influenced Surface Layer in Polymers

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Synopsis

Several epoxy polymers, poly(methyl methacrylate), a highly plasticized polyethylene, and a polyethylene of molecular weight 2500 were found to be influenced to a considerable depth from the surface by the mold material or the atmospheric environment. The results presented are interpreted in terms of a diffuse double layer induced by the mold in the polymer surface region. These environmental effects appear to be greatest for the epoxy systems and are evident to a lesser extent, progressively, as the molded polymer is changed to materials of higher purity or narrower molecular weight range.

INTRODUCTION

Diffuse double-layer formation at solid–liquid phase boundaries has been studied in connection with electrokinetic and electrode phenomena.[1] High molecular weight polymers, which may exist as colloidal dispersions, exhibit the electrokinetic phenomena arising from the diffuse double-layer adsorption of ions at the surfaces of the colloidal particles. When a fluid phase containing ions, dipoles, or polarizable molecules is present in the polymer, a double layer could be expected to form at the polymer–mold interfaces. The data presented here characterize this surface region for several thermosetting epoxy polymers and some thermoplastic materials.

EXPERIMENTAL

Materials

Casting compound C 13-009 (in parts A and B), a polyol-modified, anhydride-cured epichlorhydrin–bisphenol A epoxy resin, was obtained from the Hysol Corporation, Olean, New York. The polyol structure is

$$H_2C—[O—CH_2—CH(CH_3)—]_xOH$$
$$HC—[O—CH_2—CH(CH_3)—]_xOH$$
$$H_2C—[O—CH_2—CH(CH_3)—]_xOH$$
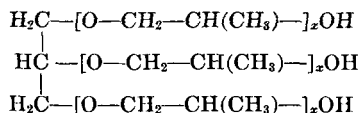
where the average value of x is 3.6.[2] The curing agents used were hexahydrophthalic anhydride and benzyldimethylamine. After heating parts A and B to 54°C., they were mixed in equal quantities by weight and placed in an evacuated chamber to remove air bubbles. The curing conditions

were varied to obtain different properties. Table I lists sources of other materials. These were used as obtained without further purification.

TABLE I
Materials and Sources

Material	Source
Epichlorhydrin–bisphenol A (Epon 828)	Hysol Corporation
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
Poly(methyl methacrylate)	
As 1/4-in. sheets	Rohm and Haas Co., Inc.
In powder form	Adolph I. Buehler, Inc.
Epolene E-10 polyethylene	
(2500 molecular weight)	Texas Eastman Company

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

Measurements of Contact Angle

The contact angle exhibited by a sessile liquid drop on a surface is defined by the interior angle made by a line tangent to the curve of the image of the drop at the surface of the solid and a line defining the base of the drop (Fig. 1).[3]
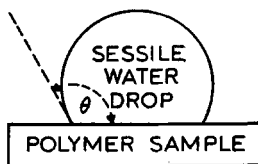

Fig. 1. Contact angle exhibited by a sessile liquid drop.

An apparatus for measuring the contact angle exhibited by a sessile drop is shown in Figure 2. A high-intensity tungsten light source was focused on the surface of the solid where the liquid drop was placed. A stand capable of vertical and lateral adjustments was used to support the sample and was constructed by mounting the sample stage from a simple microscope on a solid brass cylinder. (The cylinder afforded a rigid base relatively free from vibration.) The base from a micromanipulator served as an alternate sample support. The solid sample was placed on a metal plate in an inert atmosphere chamber fixed on the stand.

When the sessile drop is a very volatile liquid the inert atmosphere chamber may be flushed with nitrogen saturated with the liquid. The chamber was made from a flat-ended Pyrex tube bearing two side arms (for the flushing gas) and a ground-glass tapered joint. A short Pyrex standard taper joint closed by a flat glass plate served as a front cover for the inert
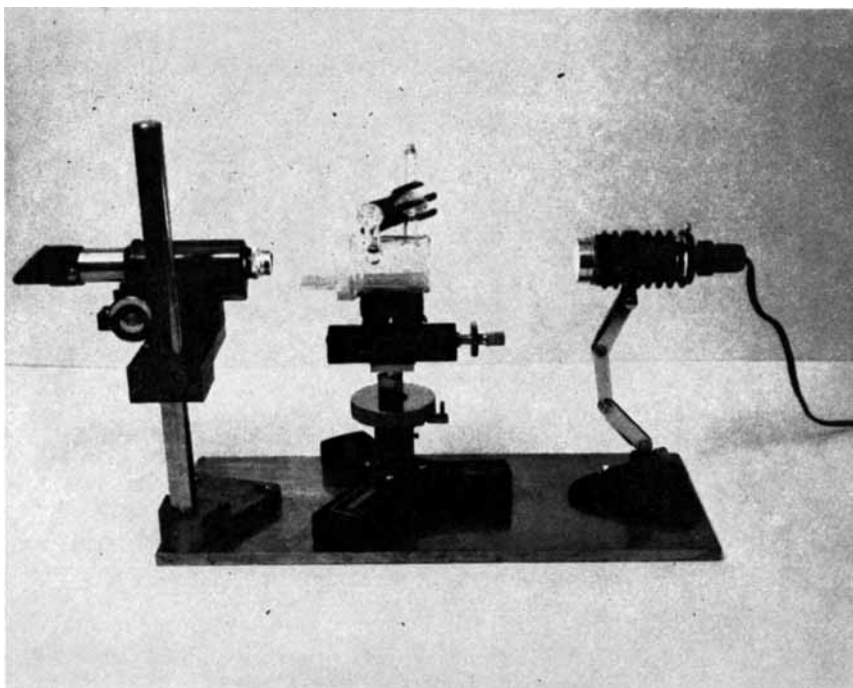
Fig. 2. Apparatus for measurements of contact angle.

atmosphere chamber. A short side arm in which a syringe cap could be inserted was sealed to the upper surface of the cover. The sessile drop liquid was placed on the surface of the solid by inserting a syringe needle through the syringe cap or by the use of a capillary pipet when the syringe cap was removed. A microscope body was mounted horizontally to focus on the sessile drop at the surface of the solid sample. The microscope was equipped with a $4\times$ (32 mm.) objective and a $12.5\times$ eyepiece. A reflecting prism was mounted over the eyepiece so that the image of the sessile drop was produced on the table surface below the prism. The contact angle made by the liquid drop with the surface of the solid was then measured with a 6-in. protractor. 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 $\pm 0.2°$.

Figure 3 indicates that measurements of water contact angle made within 3 min. of the time the drop is placed on the surface were not appreciably affected by the evaporation of the liquid. The average time required to measure the contact angle on both sides of a sessile drop was about 1 min., well within the period in which the greatest precision could be obtained for advancing contact angles.

Measurements of the contact angle of water drops on the surfaces of the polymers were made with twice-distilled water boiled in a quartz beaker to expell carbon dioxide and stored in covered quartz containers. The drops
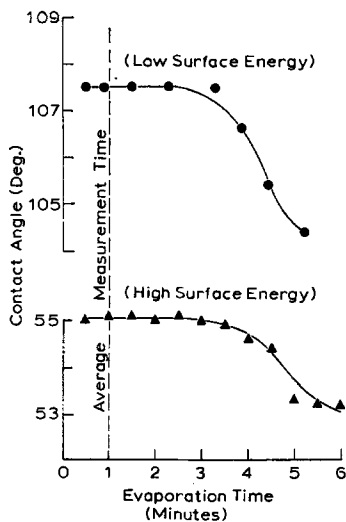
Fig. 3. Change in contact angle of a sessile water drop as a function of the evaporation of the drop.

were placed on the sample surface with a quartz capillary tube. The polymer samples were cured or solidified and allowed to cool to room temperature (23°C.) in molds of various materials. The measurements of contact angle were made on the polymer surface as a function of time after removing the sample from the mold. Contact angle measurements were made also as a function of 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 thickness of the samples was determined with a micrometer to the nearest 10^{-5} in. The deviations from coplanarity of the measurement planes were determined to be less than ±0.09° for samples 0.5 in. in diameter.

Measurements of Refractive Index

Refractive index measurements were made in conjunction with the contact angle measurements with a precision of ±0.0001 refractive index unit. The refractometer illuminator was so positioned that the light was directed along the polymer–prism interface. The refractive index of the polymer near the surface rather than that of the bulk material was obtained by this technique. Extremely flat, smooth polymer surfaces were required in order to make satisfactory contact with the refractometer prism; such surfaces could not be obtained by hand-sanding. Additional heating produced by machine-sanding the sample was unavoidable, and its effect will be discussed below.

RESULTS

Contact Angle at Polymer–Mold Interfaces

The water drop contact angle was measured on the mold materials (polytetrafluoroethylene, steel with various mold-release agents, cleaned steel, and glass) prior to potting the polymers. The resins were cured against these surfaces and allowed to cool to room temperature (23°C.) in the mold. Contact angle measurements were made on the molded polymer surface and mold surface immediately after separation from the mold and are shown in Table II.

TABLE II
Contact Angle of Water at Polymer–Mold Interfaces

Polymer	Mold[a]	Mold–water contact angle, degree	Polymer–water contact angle, deg.	Bulk polymer–water contact angle, deg.
Polyol-modified epoxy	PTFE	110.0 ± 0.6	110.0 ± 0.7	83
	S + MR	100.6 ± 0.5	100.2 ± 0.5	—
	S + SiOil	77.3 ± 0.6	78.6 ± 0.9	—
	Air	—	64.8 ± 0.8	—
	Nitrogen	—	66.1 ± 1.0	—
	Argon	—	68.7 ± 0.6	—
	Carbon dioxide	—	68.7 ± 0.6	—
	Steel	46.0 ± 1.0	About 46	—
	Glass	About 0	About 0	—
DEA–828	PTFE	110.0 ± 0.6	112.2 ± 0.5	71.5
	S + MR(CFP)[b]	90.7 ± 0.4	90.0 ± 0.2	—
	S + SiOil(CFP)[b]	91.2 ± 0.7	90.7 ± 0.3	—
	Air	—	67.2 ± 1.6	—
TETA–828	Air	—	65.2 ± 0.5	—
Poly(methyl methacrylate)	Air	—	64.2 ± 0.9	—
Polyethylene film	Steel	46.0 ± 1.0	42.8 ± 1.0	94.0 ± 1.0
	Air	—	83.2 ± 1.0	—
	Glass	About 0	About 0	—
Polyethylene (2500 molecular weight)	PTFE	110.0 ± 0.6	104.4 ± 0.9	—
	Air	—	91.9 ± 1.0	—
	Glass	About 0	About 0	—

[a] PTFE = polytetrafluoroethylene; S + MR = steel coated with mold-release agent RAM-225 (proprietary silicone oil); S + SiOil = steel coated with a chlorophenylsilicone oil.

[b] CFP denotes cohesive failure occurred in the polymer on separation from the mold. In these cases, the mold–water contact angle reported was measured on the film adhering to the steel surface after separation of the polymer.
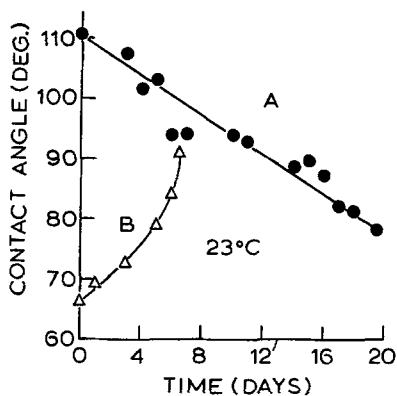
Fig. 4. Contact angle measurements on the surface of the polyol-modified epoxy as a function of sample aging time at 23°C.: (A) sample cured in a polytetrafluoroethylene mold; (B) sample–air interface clamped against polytetrafluoroethylene after curing.

The contact angle measurements were made at room temperature in all cases. Curve A of Figure 4 shows the contact angle as a function of time (polymer age) from the removal of the polyol-modified epoxy sample from a polytetrafluoroethylene mold (the initial contact angle was 110° on both the epoxy and the mold surfaces). The epoxy–air interface (a stable surface exhibiting a contact angle of about 65°), when clamped against a polytetrafluoroethylene surface, shows the reverse process, an increase in contact angle toward that of water on polytetrafluoroethylene. Figure 5 indicates that the change in contact angle was accelerated from several days to a few hours by aging the polymer at an elevated temperature (71°C.). Figures 6 and 7 show compilations of these data obtained for the polyol-modified epoxy, DEA–828, and polyethylene cured or solidified in a polytetrafluoroethylene mold and aged at 23 and 71°C., respectively.
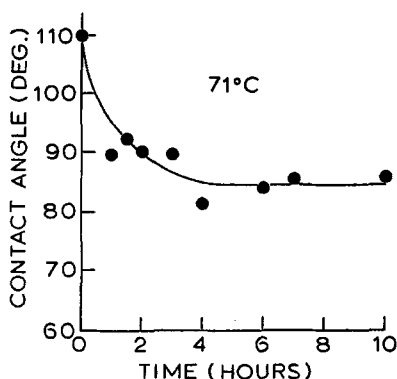

Fig. 5. Contact angle measurements on the surface of the polyol-modified epoxy as a function of sample aging time at 71°C. The sample was cured in a polytetrafluoroethylene mold.
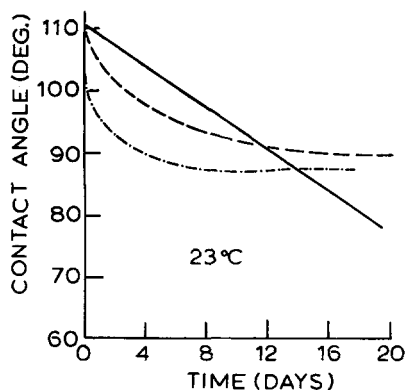
Fig. 6. Contact angle measurements on several polymers removed from a polytetra-fluoroethylene mold and aged at 23°C.: (——) polyol-modified epoxy; (— —) DEA–828; (—·—) polyethylene.
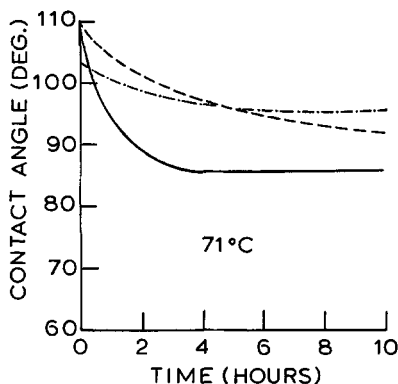

Fig. 7. Contact angle measurements on several polymers removed from a poly-tetrafluoroethylene mold and aged at 71°C.: (——) polyol-modified epoxy; (— —) DEA–828; (—·—) polyethylene.
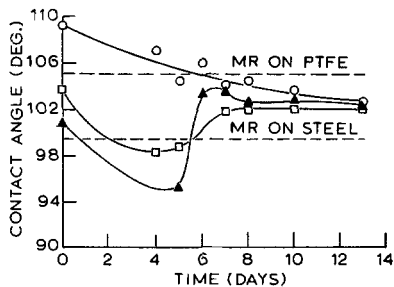

Fig. 8. Contact angle measurements on the polyol-modified epoxy as a function of time after removing the samples from: (O) a polytetrafluoroethylene (PTFE) mold, (□) a glass mold, and (▲) a steel mold. The mold surfaces were coated with a silicone mold-release agent (MR). The two dashed lines represent water contact angle measurements on the indicated mold surfaces.
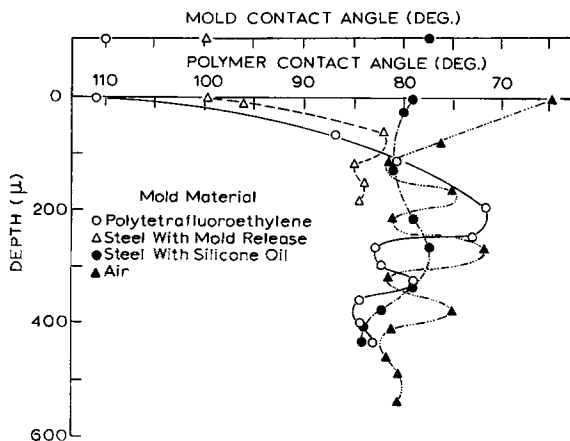
Fig. 9. Water contact angle on mold surfaces and on the molded polymer surface (polyol-modified epoxy) as a function of the mold material and the depth of the measurement plane from the original surface.

When the polyol-modified epoxy was cured in molds of various materials which had been coated with RAM-225 (RAM Chemicals silicone fluid mold release agent) the water contact angle on the molded epoxy surfaces exhibited the time-dependent behavior shown in Figure 8.

Surface Layer and Polymer Bulk

The contact angles on the surfaces of the polyol-modified epoxy cured in molds of various materials are shown as the initial points in Figure 9. The curves indicate the changes in contact angle values that were obtained as successive layers were removed from the polymer surfaces. Similar curves were obtained for DEA–828, TETA–828, poly(methyl methacrylate), a plasticized polyethylene film, and a 2500 molecular weight polyethylene.

The results obtained for a poly(methyl methacrylate) sample are shown in Figure 10.

A 0.004-in. sheet of a plasticized polyethylene material was melted on a polished steel surface and allowed to cool slowly to 23°C. Contact angle measurements were made on the polymer–air interface and as a function of depth through the polymer to the polymer–steel interface; results are shown in Figure 11.

The surface refractive index of the polyol-modified epoxy and of the TETA–828 epoxy polymers was measured in conjunction with water contact angle measurements as a function of depth from the polymer–polytetrafluoroethylene interface for the former and the polymer–air interface for the latter. These data are shown in Figures 12 and 13.
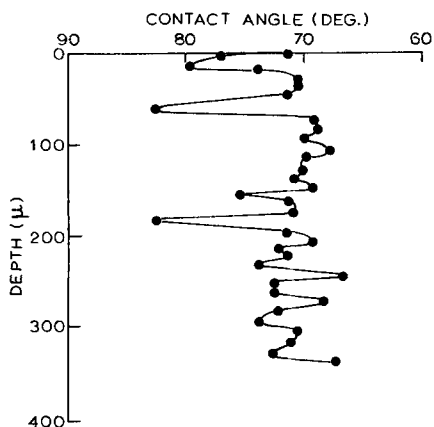
Fig. 10. Contact angle on a poly(methyl methacrylate) sample as a function of the depth of the measurement plane from the polymer–air interface.
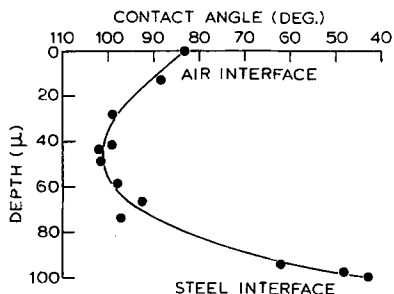

Fig. 11. Contact angle on a polyethylene film as a function of the depth of the measurement plane from the polymer–air interface to the steel substrate.
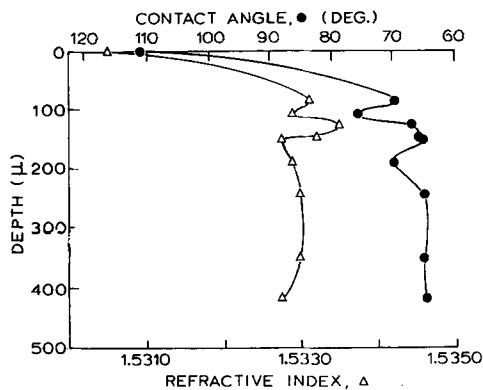

Fig. 12. Plots of (△) surface refractive index and (●) water contact angle on the polyol-modified epoxy as a function of the depth of the measurement plane from the polymer–polytetrafluoroethylene mold surface.
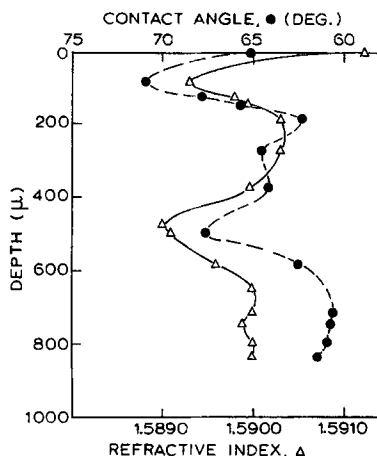
Fig. 13. Plots of (△) surface refractive index and (●) water contact angle on the TETA–828 epoxy as a function of the depth of the measurement plane from the polymer–air interface.

DISCUSSION

When a given polymer was cured in molds of different materials, the water drop contact angle on the mold surface was matched by that on the polymer surface (Table II). Upon aging the polymers after separation from the mold, the contact angle changed as a function of time (Figs. 5–8). The progression was in a direction toward the higher surface energy associated with the air interface (contact angle = 65°). For the polyol-modified epoxy cured against polytetrafluoroethylene (contact angle = 110°) the change was observed to occur over a period of about 30 days at 23°C. (Fig. 4, curve A), and was accelerated to a few hours at 71°C. (Fig. 5). The process could be reversed; for a stable polymer–air interface (exhibiting a 65° contact angle), when clamped against polytetrafluoroethylene, the contact angle increased as a function of time (Fig. 4, curve B). This phenomenon is ascribed to a mobile polymer phase. Varying rates of change of surface contact angle (associated with degree of mobility) were observed (Figs. 6 and 7) in the order: polyol-modified epoxy > DEA–828 > poly(methyl methacrylate) > polyethylene. The different surface contact angles are indicative of the presence of mixed constituents in the polymers containing both polar and nonpolar groups. The interface matching phenomena are interpreted as the orientation polarization of these mobile polymer constituents effected by the external environment. The result of this process is a minimum free energy discontinuity at the interface.

High-sensitivity infrared analysis of the sample surface layer failed to show a transfer of polytetrafluoroethylene from the mold to the epoxy polymers. A radically different trend in the contact angle measurements at the molded surfaces was observed in experiments where a transfer of

material would be expected.   Figure 8 shows the measurements for the polyol-modified epoxy cured in molds coated with a silicone fluid mold-release agent.   The upper curve indicates that the mold release agent diffused away from the polytetrafluoroethylene mold during cure (the characteristic water–polytetrafluoroethylene contact angle was obtained on the polymer surface).   The three curves show a deviation from the behavior observed in the absence of mold-release agents (Figs. 4 and 5), in that a much higher equilibrium contact angle was obtained (about 103°). This result is consistent with the assumption that the mold-release agent reappeared at the surface after about 7 days.   Zisman et al.[4] have shown that surface-active additives of this type diffuse to the surface and have a pronounced effect upon the friction characteristics of polymeric materials.

The contact angle gradient is interpreted as an orientation polarization and concentration gradient induced by the mold in the epoxy polymers and extends from the mold interface to several hundred microns below the surface.   Figure 9 shows this gradient from the polymer surface (where the mold contact angle value was matched by the polymer) to points in the polymer bulk (as successive polymer layers were removed), where a bulk contact angle value of about 83° was obtained for the polyol-modified epoxy.   The contact angle oscillations indicative of a layered structure are superimposed upon this surface-to-bulk gradient and will be treated in a subsequent paper.   A similar gradient indicated by both contact angle and surface refractive index measurements is shown in Figure 12 for the polyol-modified epoxy and in Figure 13 for the TETA–828 epoxy polymer. Machine-sanding was required in order to obtain surfaces sufficiently flat and smooth for the refractive index measurements.   This technique heated the sample surface to a greater extent than did the hand-sanding technique normally used in making the contact angle–depth measurements.   The effect of this additional heating on the polyol-modified epoxy (which is characterized by a phase transition near room temperature) is shown in Figure 12.   The bulk equilibrium contact angle obtained by machine sanding was about 65° (the same as that for the air interface), rather than 83°.   This difference indicates that the heating was sufficient to displace the whole curve toward higher energy values similar to the behavior noted at the polymer surface in Figures 4 and 5.   After taking the last measurement shown at the bottom of Figure 12, the sample surface was sanded by hand and the normal bulk contact angle value (83°) was obtained.   Figure 11 shows the results of contact angle–depth measurements made on a thin sheet of plasticized polyethylene after melting it on a steel surface.   Polar material appears to be concentrated near the high energy interfaces (steel and air).

The matching at the interface appears to be a function of the amounts and types of impurities or low molecular weight fractions present in the polymers.   The polymers characterized by a narrower molecular weight range or greater purity show a decreased matching capability (the 2500 molecular weight polyethylene, Figs. 6 and 7, and the polyethylene film,

Fig. 11). The contact angle changes that occur at the surface when the mold material is removed or replaced are rapid for samples polymerized from low-viscosity starting materials (the mobile polymer phase is thought to be a mixture of the starting materials, low molecular weight polymer, and impurities) and slow for harder or high-viscosity component systems (Figs. 6 and 7).

CONCLUSIONS

The mold in which polymers are cured or solidified produces a material gradient in the surface region of the polymer which is thought to be similar to the diffuse electric double layer found at phase boundaries in colloidal systems. The changes that occur in the surface region (as shown by contact angle and refractive index measurements) when the mold material is changed or removed are consistent with an assumed change in polarization of the diffuse double layer. Recent experiments, which will be described in a subsequent paper, show a correlation between the surface contact angle and the current generated by mechanical impact and may be interpreted in terms of this postulated orientation of dipoles induced by the external environment.

References

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4. R. C. Bowers, N. L. Jarvis, and W. A. Zisman, Naval Research Laboratory Report 6227, March 1965.

Résumé

De nombreux polymères époxy, le polyméthacrylate de méthyle, le polyéthylène fortement plastifié et le polyéthylène de poids moléculaire 2500, sont influencés jusqu'à une profondeur considérable de leur surface par le matériau moulu ou par l'environnement atmosphérique. Les résultats présentés sont interprétés sur la base d'une double couche diffuse induite par la fusion à la région superficielle du polymère. Ces effets d'environnement sont les plus forts pour les systèmes époxy et appraissent dans une mesure moindre, progressivement, lorsque le polymère fondu est modifié au départ de matériaux de pureté plus grande et de poids moléculaire plus étroit.

Zusammenfassung

Einige Epoxypolymere, Polymethylmethacrylat, ein stark weichgemachtes Polyäthylen und ein Polyäthylen vom Molekulargewicht 2500 zeigten bis zu einer beträchtlichen Tiefe von der Oberfläche eine Beeinflussung durch das Formmaterial oder die umgebende Atmosphäre. Die Ergebnisse werden im Sinne einer durch die Form in Ober-

flächenbereich des Polymeren induzierten diffusen Doppelschichte interpretiert. Diese Milieueffekte scheinen für das Epoxysystem am grössten zu sein und machen sich beim Übergang zu Polymeren höherer Reinheit oder mit engerem Molekulargewichtsbereich immer weniger bemerkbar.