

Epoxy Polymers. IV. Impact-Induced Voltage Generation

R. E. CUTHRELL, *Surface Chemistry and Electrical Properties Division, Sandia Corporation, Albuquerque, New Mexico 87115*

Synopsis

Mechanical-stress-induced voltage or current in epoxy polymers appears to be a function of the state of order of dipoles in the surface layer. The sign and magnitude of the voltage is correlated with the surface layer characteristics. The time required for the impact voltage to decay to its original value appears to correlate with dipole orientation relaxation times obtained by dielectric constant and loss measurements.

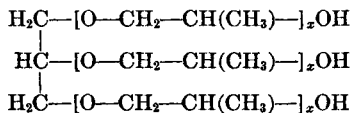
INTRODUCTION

Many investigators have reported recently on the stress-induced voltage generation or current output of dielectric materials¹⁻²⁰ and, earlier, on the behavior of electrets.¹¹⁻²⁰ There are many similarities between electrets, as classically defined, and the "piezoelectric" plastic materials. The common basis may be the ordering of dipoles which result in bound charges at the surfaces of capacitors containing dielectric solids or liquids. Recent results indicate that the stress-induced voltage phenomenon is related to the characteristics of the surface layer rather than the bulk in epoxy polymers.

EXPERIMENTAL

Chemicals

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



The average value of x is 3.6. The curing agents were benzyldimethylamine and hexahydrophthalic anhydride. After parts A and B were heated 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 give different properties. Table I lists sources of other materials

TABLE I
Materials and Sources

Materials	Source
Epichlorhydrin-bisphenol A (828)	Shell Chemical Company
Curing agent, diethanolamine (DEA)	Fisher Scientific Company
Glycerol (analytical reagent grade)	Mallinckrodt Chemical Works
Ice	Twice-distilled water

tested. These materials were used as obtained, without further purification.

Equipment

A bar pendulum was constructed for impacting the samples by suspending an 800 g. steel rod, 1 in. in diameter and 9 in. long, by four woven copper wires, 12 in. in length, two at each end of the rod. Each pair of suspension wires formed a V (with the rod at the apex), such that pendulum yaw was

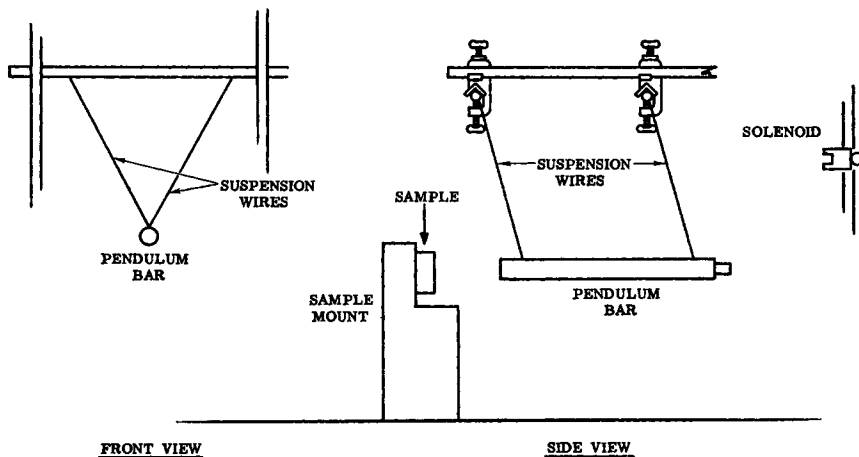


Fig. 1. Bar pendulum and sample holder.

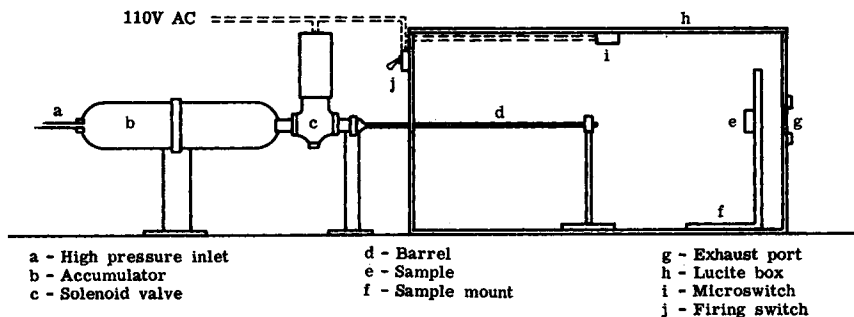


Fig. 2. Air gun for high-velocity impact.

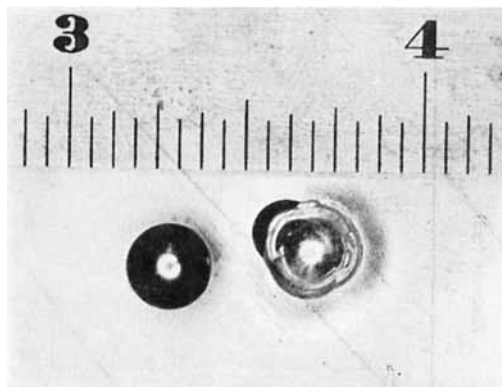


Fig. 3. Effect of (right) twenty impacts on a brass plate with (left) a $\frac{1}{4}$ -in. steel ball projectile.

minimized, and the point and angle of impact were maintained constant. The front of the rod was machined flat and aligned parallel to the sample surface by adjusting the upper wire suspension points. A near plane wave was obtained upon sample impact; deviations from planarity were dependent primarily upon the sample-to-rod alignment. The rod was held in the high pendulum position by a solenoid, so that the start of the swing was reproducible with respect to height and lateral position. The impact momentum was varied by changing the height at the start of the pendulum swing or by adding mass to the bar (in the form of U-shaped lead weights). The sample mount, positioned at the low point of the pendulum swing, was machined from a brass rod 3 in. in diameter and 8 in. in length. Figure 1 shows a diagram of the pendulum and sample holder arrangement.

For higher impact velocities an air gun was constructed as shown in Figure 2. An argon lecture bottle (used as a gas accumulator) was fitted at one end, so that air could be admitted at 75 psig through $\frac{1}{4}$ in. copper tubing, and at the other end with a short brass coupling to a solenoid-operated water valve ($\frac{1}{2}$ in. bore, rated at 150 psi). The valve led to a steel tube 22 in. in length $\frac{5}{16}$ in. i.d., and of 0.012 in. wall thickness, which was attached to the solenoid valve with flare fittings. A copper wire was soldered across the bore in the brass fittings at the breech, to prevent a muzzle-loaded ball from entering the solenoid valve. The sample was attached to the brass sample mount at the target point 28 in. from the muzzle of the gun barrel. A lucite box constructed, as shown in Figure 2, served as a safety shield and prevented loss of the steel ball projectile ($\frac{1}{4}$ in. diameter) after impact. The lucite box was vented by a screen-covered aperture 3 in. in diameter, located in the protected area behind the brass sample mount. A hinged lucite lid allowed access to the box for loading the projectile and for sample positioning. The gun was fired by actuating the solenoid valve with a two-position switch, spring-loaded to the "off" position. The hinged lid actuated a microswitch, in series with the firing switch, so that the gun could not be fired when the lid was in the "open" position.

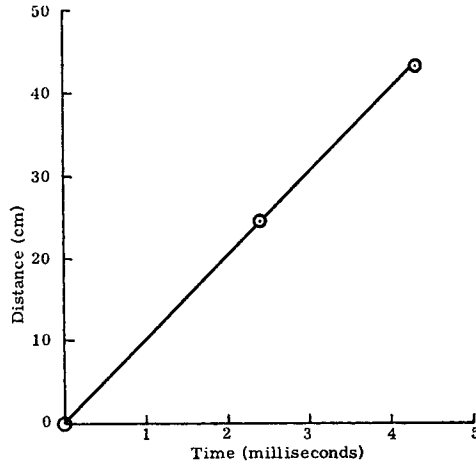


Fig. 4. Time required for projectile to travel a measured distance from the air-gun muzzle.

Figure 3 shows the effect of twenty impacts (on the right) on a brass plate with the steel ball projectile (on the left). The accuracy in striking the target can be estimated from the photograph; all twenty impacts fell within a circle 0.309 in. in diameter (1.24 times the diameter of the ball).

The average velocity over the 44 cm. path between the gun muzzle and the sample was determined experimentally to be 100.8 ± 0.2 m./sec. The

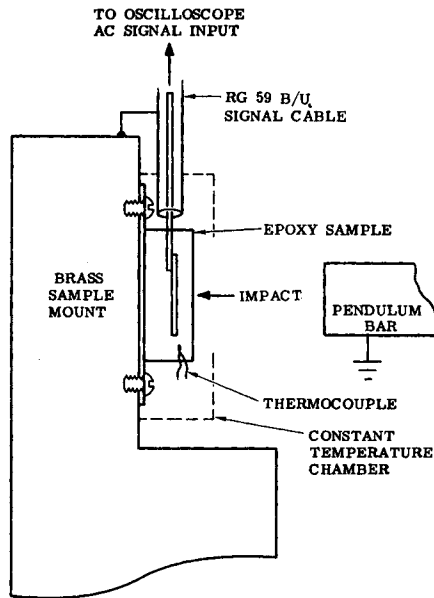


Fig. 5. Sample configuration and sample mount.

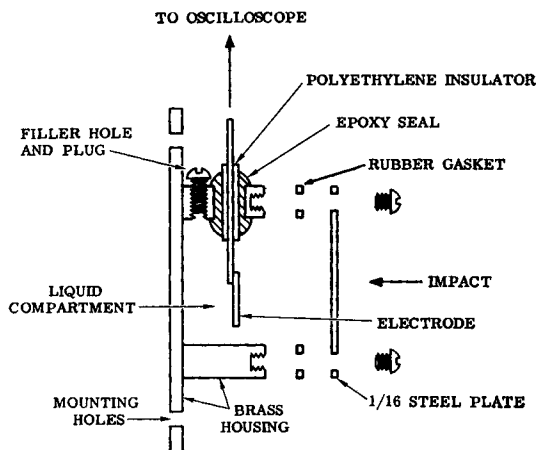


Fig. 6. Sample cell for liquids (expanded view).

time of travel over the measured distance from the gun muzzle to the sample was obtained by using the projectile to trigger an oscilloscope trace as it left the muzzle and to produce a change in voltage upon impacting the sample. The sample was moved closer to the muzzle, and this procedure was repeated. The average velocity was calculated from the distance-time measurements (four measurements at each muzzle-to-sample distance). The linearity of the curve shown in Figure 4 indicates that the projectile velocity is very nearly constant over these short distances. The average velocity over the shot path may then be assumed to be equivalent to the projectile velocity at the time of impact.

The sample and holder configuration is shown in Figure 5. A copper electrode, 1 in.² in area, was located in the interior of the epoxy samples $\frac{1}{4}$ in. from the impacted surface.

Figure 6 shows the cell used for testing samples, which were liquid at room temperature (ice and glycerol).

The sample temperature was varied by passing nitrogen gas through copper coils and then into the constant-temperature chamber. The coils were either cooled by immersion in a liquid nitrogen bath or heated by an oil bath. The sample temperature was recorded during the test using an iron-constantan thermocouple embedded in the sample material, a Minneapolis-Honeywell Reg. Co. potentiometer, and a potentiometric T-Y recorder.

RESULTS

The current produced on impact loading the dielectric samples resulted in a change in potential across the 1 Mohm oscilloscope resistor. The voltage-time curve obtained with the pendulum for a DEA-828 epoxy sample is shown in Figure 7. Similar curves were obtained with all the samples tested by both the pendulum bar impact and the air-gun projectile

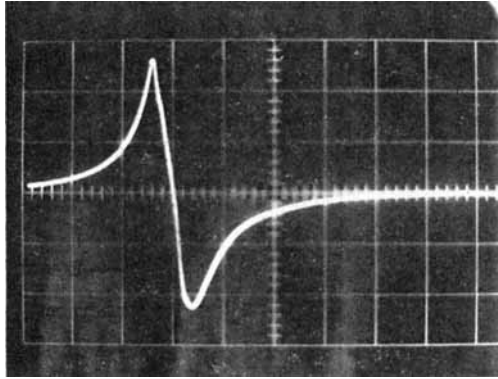


Fig. 7. Oscilloscope trace showing voltage-time curve obtained by pendulum bar impact on DEA-828 epoxy sample.

impact. Figure 8 shows the potential maximum of the first peak as a function of the number of consecutive impacts on the polyol-modified epoxy. The first 150-200 impact voltages were averaged, and these average values are shown plotted in Figure 9 as a function of the impact force and the cure schedule for the DEA-828 and the polyol-modified epoxy samples. The polyol-modified epoxy was impact tested at various sample tempera-

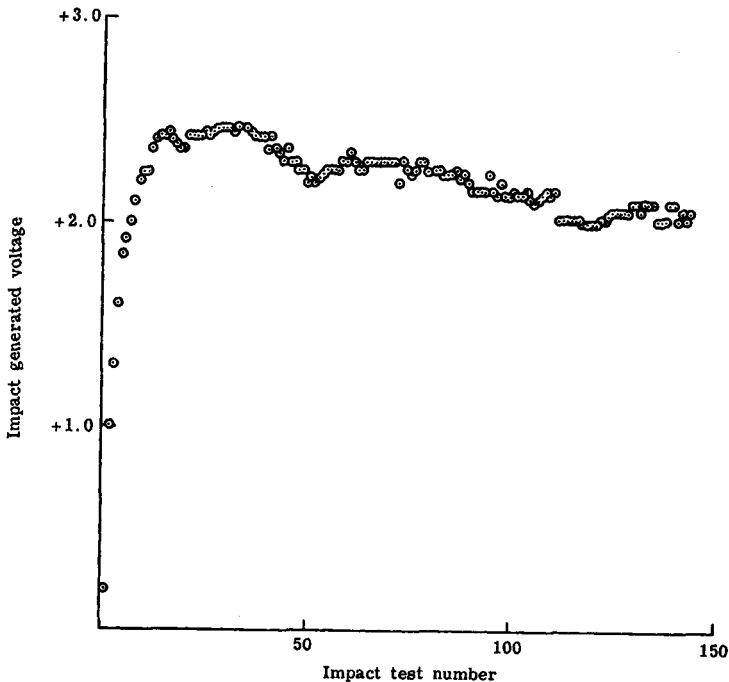


Fig. 8. Impact voltage as a function of number of consecutive impacts on polyol-modified sample.

tures; these results are shown in Figures 10-13. In a prior report²¹ it was shown that the water drop contact angle on polymer surfaces varies with the mold material. A series of samples of the DEA-828 and the polyol-modified epoxy were prepared in different molds, and the molded surface

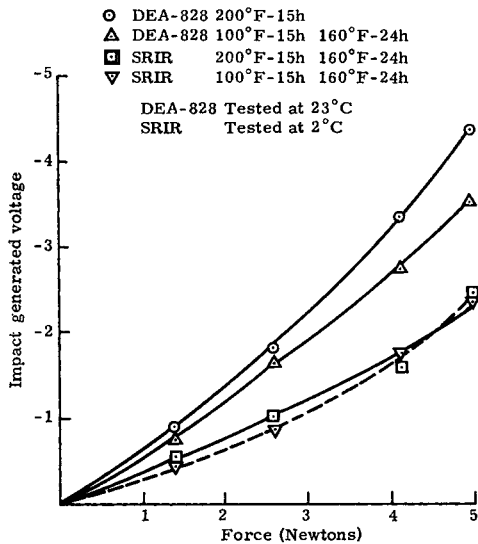


Fig. 9. Impact voltage as a function of impact force and cure schedule for polyol-modified epoxy (SRIR) and for DEA-828 epoxy polymerized in silicone-coated steel molds.

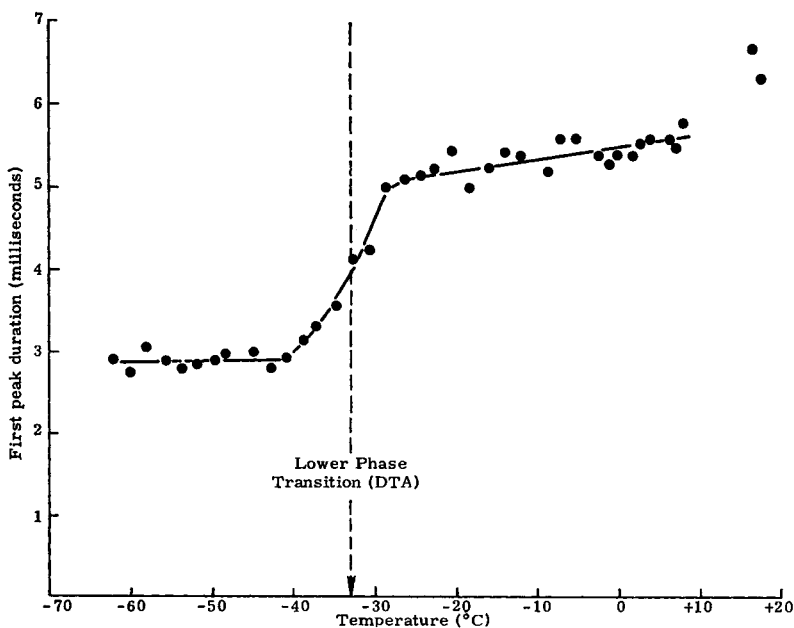


Fig. 10. Duration of first impact voltage peak as a function of sample temperature.

was impact-tested. Figure 14 shows the correlation between the impact-generated voltage magnitude and sign with the contact angle on the surface tested. The data points represent first impact voltage only.

Auty and Cole²² obtained the dipole relaxation times for ice at various temperatures by dielectric constant and loss measurements as a function of

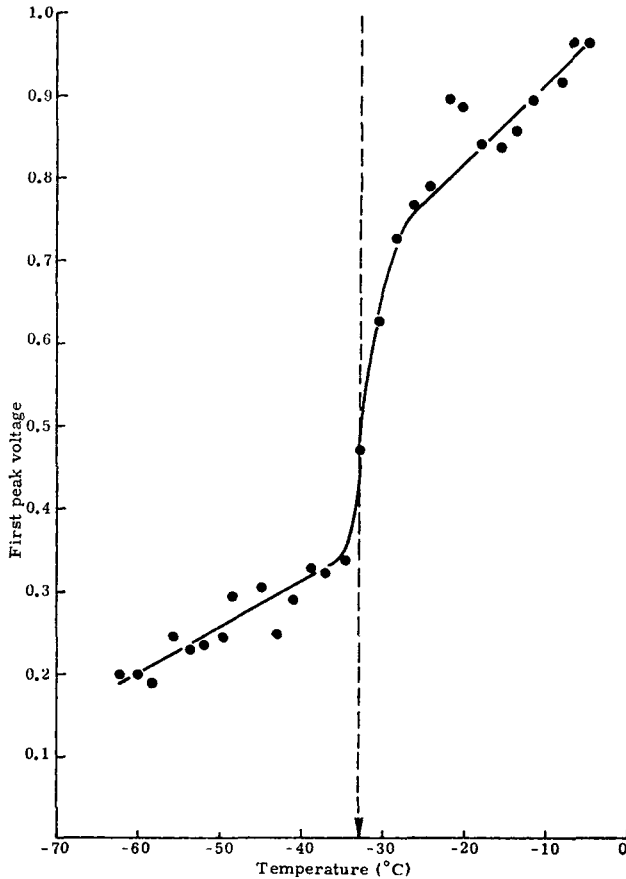


Fig. 11. First peak impact voltage as a function of sample temperature for polyol-modified epoxy.

frequency and temperature. Figure 15 shows their data and the voltage decay time (second voltage peak on the oscilloscope trace) obtained by mechanical impact on the surface of ice at various temperatures.

The time required for the second voltage peak to decay is assumed to be that required for the surface charge to return to its original value prior to impact. Relaxation times as a function of temperature for glycerol were calculated from the data published by Morgan and Yager²³ by eq. (1).²⁴

$$\tau = 1/(2\pi f_m) \quad (1)$$

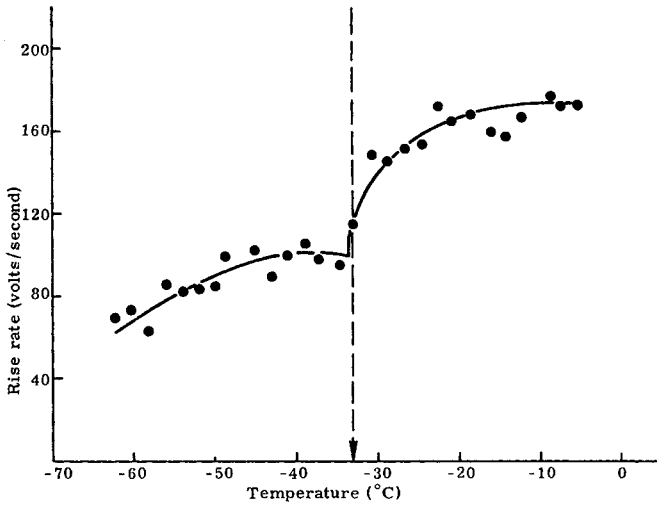


Fig. 12. Rise rate of first impact voltage peak as a function of sample temperature for polyol-modified epoxy.

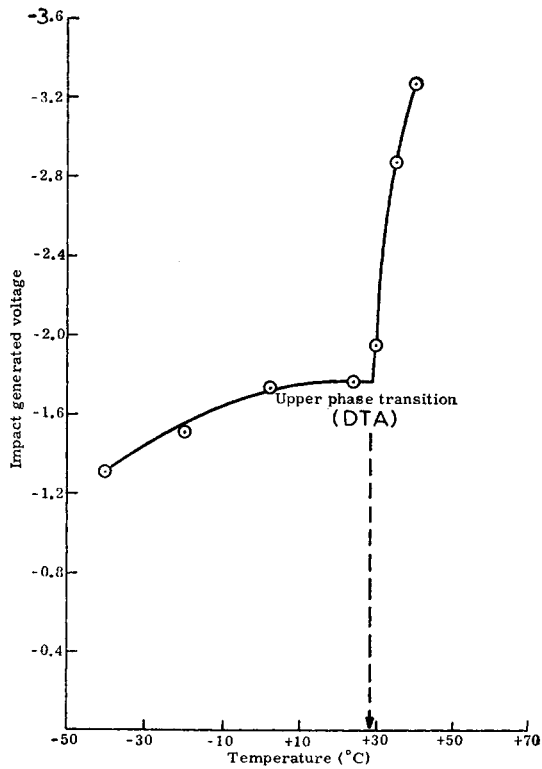


Fig. 13. Impact voltage as a function of sample temperature for polyol-modified epoxy.

where τ is the dipole orientation relaxation time, and f_m is the frequency for which a maximum occurs at a given temperature in the loss factor-temperature curve. These values are shown in Figure 16 with the voltage decay times obtained by mechanical impact on the surface of glycerol at various temperatures.

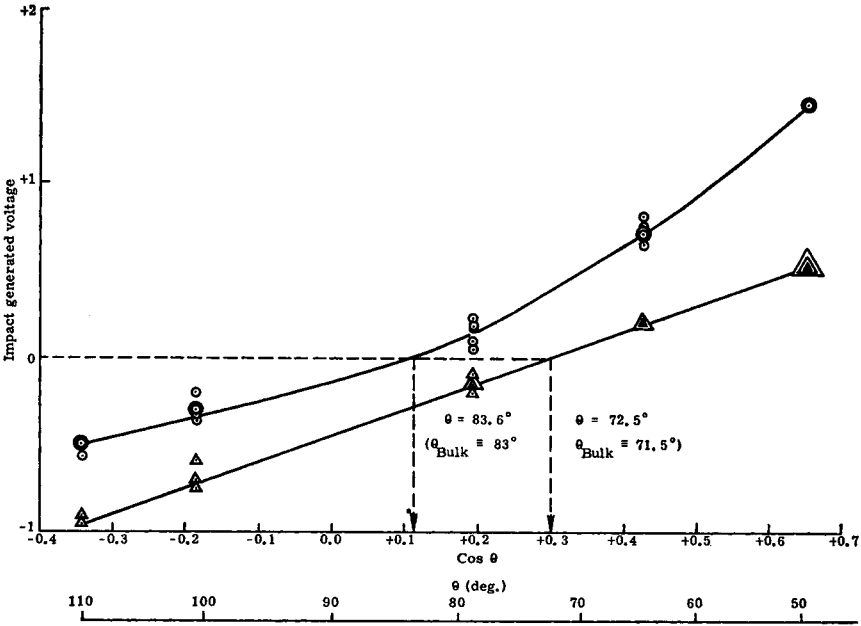


Fig. 14. Impact voltage as a function of surface contact angle for (Δ) DEA-828 and (O) polyol-modified epoxy.

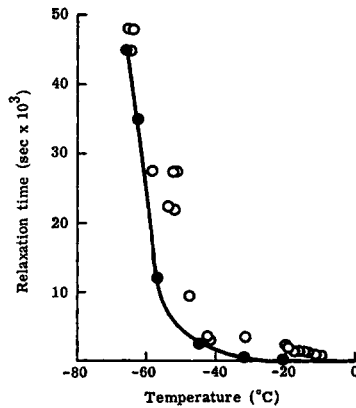


Fig. 15. Dipole relaxation times for ice at various temperatures: (●) Auty and Cole²²; (○) impact voltage output, second peak duration.

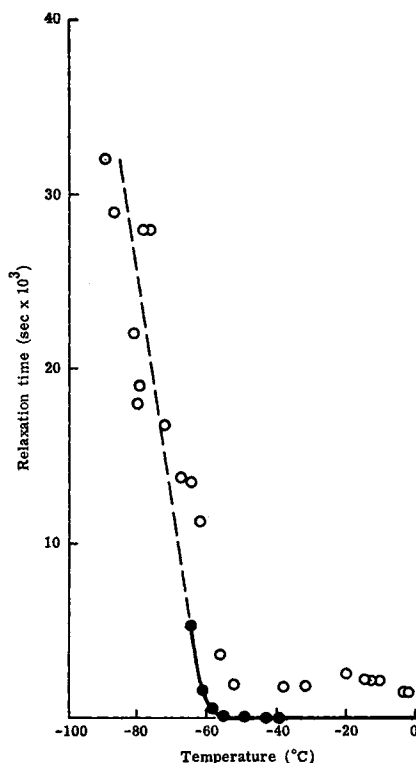


Fig. 16. Dipole relaxation times for glycerol at various temperatures: (●) Morgan and Yager²³; (○) impact voltage output, second peak duration.

DISCUSSION

Figure 17 shows a circuit schematic, in which the face of the pendulum bar and the electrode embedded in the sample form a capacitor with an epoxy medium between the plates.

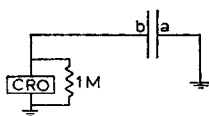


Fig. 17. Circuit schematic.

A typical oscilloscope (CRO) trace of the change in potential that occurs at plate *b* when the pendulum strikes the epoxy sample is shown in Figure 7. Plate *b* is connected to ground through a 1 Mohm resistor in the CRO. If the voltage values on the *y* axis in Figure 7 are divided by this resistance, the data are then represented by a current-time curve which, upon integration, indicates a change in charge on impact from some static value to a positive

value and then back to the original value. This can be accounted for qualitatively by the following simple equations:

$$Q = CV \quad (2)$$

$$C = \epsilon A/D \quad (3)$$

$$Q = V\epsilon A/D \quad (4)$$

were Q and V are the charge and potential, respectively, on the capacitor plates of area A and separation distance D . The constant ϵ is the permittivity, a function of the dielectric constant of the epoxy medium. Assuming the potential and the area are constant, a decrease in the distance between the plates as a result of sample compression on impact would cause an increase in Q . A decrease in Q to the original value would be expected after pendulum rebound, if the epoxy material exhibited completely elastic behavior.

The symmetry of the voltage-time curve (Fig. 7) and the barely detectable sample deformation after several thousand impacts indicate that the epoxy systems studied are subject to only very small plastic deformation under the reported testing conditions. The sign of ΔQ , or the sign of the first potential peak (Fig. 7), is dependent upon the sign of the initial charge on the capacitor plate a of Figure 17. This surface was charged negatively with respect to ground with a battery, the battery disconnected, and the surface struck with the pendulum. A curve showing a positive first peak was obtained (the charge on plate b is of equal magnitude and opposite in sign to that on plate a). A negative first peak was obtained when surface a was positively charged.

Equation (5) can be obtained by differentiating eq. (4):

$$dV = (D/A\epsilon)dQ + (Q/A\epsilon)dD - (QD/A^2\epsilon)dA - (QD/A\epsilon^2)d\epsilon \quad (5)$$

The constants in eq. (5) represent the initial values and can be expressed as shown in eq. (6) by combining eqs. (4) and (5):

$$dV = (V/Q)dQ + (V/D)dD - (V/A)dA - (V/\epsilon)d\epsilon \quad (6)$$

It is interesting to note that the initial potential appears in each term. A surface charge may give rise to this potential. The second term contains dD/D , which can be related to the impact pressure by Hooke's law,

$$F/A = K(dD/D) \quad (7)$$

where K is Young's modulus for compression. An increase in the impact force caused a corresponding increase in the measured voltage (Fig. 9). This result is consistent with a greater sample deformation (decrease in capacitor plate spacing) at higher forces. According to eq. (6), the magnitude of the impact-voltage increment due to sample compression would be dependent upon the initial potential or surface charge in addition to the amount of compression. The velocity of impact was changed from 2.25 m./sec for the pendulum to 100.8 m./sec for the air gun, and the mass was

changed from 535 g. (pendulum) to 1.0433 g. (air-gun projectile). The ratio of impact voltage to momentum remained constant (about 3.0v./kg. m. sec.⁻¹, indicating an approximately linear relationship between the impact voltage and the momentum of the impacting mass.

Previous measurements indicate that the hardness and density of the polymers can be changed by varying the curing temperature.²⁵ Figure 9 shows a relatively small but predictable dependence of impact voltage upon the hardness of the polymers. For each polymer a greater hardness was obtained in curing at a lower temperature. The pendulum impact would result in less sample deformation for the harder samples and, according to eqs. (6) and (7), a lower impact voltage.

The degree of sample deformation accompanying an impact should be directly proportional to the sample temperature and should reflect the polymer phase transitions. Two phase transitions were found independently in each epoxy system by differential thermal analysis and by linear thermal expansion measurements.²⁵ Figures 10, 11, and 12 show a discontinuity for the first peak duration (the time measured on the oscilloscope trace for the first half-cycle, Fig. 7), voltage, and rise time, respectively, in the region where the low-temperature phase transition occurs in the polyol-modified epoxy. Similar data are shown in Figure 13 for the high-temperature phase transition. The overall positive slopes of these curves are consistent with the assumption that an impact can deform the sample to a greater extent at higher temperatures.

The results showing the contact angle matching that occurs at interfaces in molded epoxy systems are reported elsewhere.²¹ This matching phenomenon was interpreted as indicative of the orientation polarization of dipoles in the surface layers induced by the mold materials. A surface-to-bulk gradient in properties such as contact angle, refractive index, hardness,²¹ and dielectric constant²⁶ was found to extend over several hundred microns into the polymers. These measurements may be interpreted as showing a gradient in chemical constitution as well as a gradient in dipole ordering. Samples of the polyol-modified epoxy and of DEA-828 exhibiting various surface contact angles with water (cured against molds of different materials and surface energy) were tested by pendulum impact. The correlation of both the sign and magnitude of the impact voltage and the contact angle at epoxy surface *a* (Fig. 17) are shown in Figure 14. The reference electrode (capacitor plate *b* of Fig. 17) is maintained at ground potential through the CRO and is cast in the polymer bulk. It is interesting to note that the curves shown in Figure 14 pass through the zero voltage level at contact angle values typical of those found in the bulk polymers (83° for the polyol-modified epoxy and 71.5° for the DEA-828 epoxy). These results are interpreted as follows.

(1) Impact-voltage sign and magnitude are dependent upon the characteristics of the impacted surface (the surface at *a* of Fig. 17) rather than the characteristics of the bulk polymer. This conclusion stems from the impact-voltage correlation with the surface contact angle rather than the

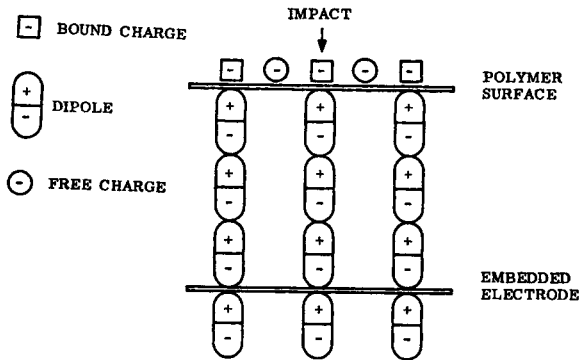


Fig. 18. Schematic representation of dipole polarization: minus sign in square, bound charge; minus sign in circle, free charge; plus and minus signs in oval, dipole.

bulk contact angle or any intermediate contact angle in the surface-to-bulk gradient.

(2) The electric charge on the sample surface is partially dependent upon the state of order of the dipoles in the dielectric sample. This concept is treated more fully by Condon and Odishaw.²⁷ The text is illustrated by a figure similar to Figure 18. The results shown in Figure 14 are interpreted, therefore, as indicative of the dependence of the impact voltage upon the degree of ordering of dipoles in the surface layer of the epoxy samples. The three regions in the epoxy samples (the surface layer, the bulk, and the layer adjacent to the inner electrode) may be analogous to a three-layer capacitor. The equivalent circuit diagram might then be three capacitors connected in series. Both the bound surface charge and the contact angle are assumed to be dependent upon dipole orientation in the surface layer.

The possibility of reordering the dipoles by repetitive impact was investigated. Figure 8 shows a typical impact-voltage trend as the sample is struck repetitively at a rate of about 60 impacts per minute. By this procedure the impact voltage could be changed from negative values, such as those shown at the lower left in Figure 14 (for samples cured against polytetrafluoroethylene, exhibiting a 110° water contact angle), to values shown on the curve at the upper right of Figure 14. The pendulum bar was machined from a steel rod. A contact angle of about $46\text{--}49^\circ$ was found on steel surfaces. A change in the contact angle at the impacted sample surface was noted to accompany the change in impact voltage and a stable contact angle value of about 49° was obtained after several hundred impacts. This change is interpreted as indicative of a change in dipole ordering, from that obtained by the influence of the mold during cure to that characteristic of the new sample environment (the steel interface on impact). When the samples were aged in air after being taken from the mold and were not subjected to repetitive impacts, the change in contact angle and in impact voltage approached that characteristic of the air interface (65° contact angle). The impact voltage obtained with the polyol-modified epoxy can be mini-

mized by curing the polymer in steel molds coated with a chlorophenyl silicon mold release agent (this composite surface most nearly approaches the polymer bulk in water contact angle).

The polymer samples are compressed on impact. The motion of the surface may result in a slight change in the orientation of the dipoles in the surface layer and a return to approximately the original orientation after impact. If this occurs, the time required for the impact voltage to decay to $1/e$ of its maximum value (approximately the time on the horizontal axis under the second peak in Fig. 7) should show some correlation with relaxation times for dipole orientation. An approximate correlation is shown for ice and for glycerol in Figures 15 and 16, respectively, over the temperature range of -100 to 0°C .

CONCLUSIONS

The voltage or currents generated on impact loading two epoxy polymeric systems were determined and were found to reflect the mechanical and molecular properties of the materials, such as hardness, phase-transition temperatures, and postulated surface dipole ordering. A correlation was obtained between the magnitude of the impact voltage and the momentum of the impact over a wide range of impact velocity and projectile mass. The results indicate that the impact-voltage sign and magnitude are strongly influenced by the characteristics of the polymer surface layer rather than those of the polymer bulk. Interpretations in terms of the degree of ordering of dipoles are presented. A correlation between the impact-voltage decay time and relaxation times for dipole orientation was obtained for ice and glycerol (materials for which dielectric constant and loss measurements as a function of frequency and temperature are reported in the literature). The impact-voltage phenomena are thought to be closely related to the phenomena observed in electrets (both could be considered a function of dipole ordering).

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