

Epoxy Polymers. V. Dielectric Strength

R. E. CUTHRELL, *Sandia Laboratories, Albuquerque, New Mexico 87115*

Synopsis

This report deals with material properties which determine dielectric strength rather than phenomena that occur during breakdown. We propose that the determining factors are the same for liquids and polymers. We report dielectric strengths calculated from measured breakdown potentials and sample thicknesses for liquids, ionic solutions, and epoxy polymers doped with ionizable materials. The breakdown field (in liquids and polymers) is hypothesized to be that which generates some critical current density value in the dielectric. The reasons for this value being critical and characteristic of the material are unknown; however, the ionic current density that the measured breakdown field produces can be calculated from the Onsager theory of high-field electrolytic conduction, and this ionic current density is assumed to be the critical threshold quantity involved. Because of field effects on the dissociative ionization and conductivity of electrolytes in organic systems, the *breakdown field* varies with concentration and solute species, but the *ionic current density* associated with the breakdown field is essentially constant for a wide range of species and molar concentrations in a given solvent.

INTRODUCTION

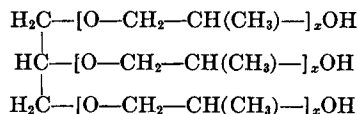
Milton observed that the pulse dielectric strength of epoxy polymers varies from about 2 kV/mil to near 8 kV/mil, depending on the curing temperature and the casting mold material.¹ We found that epoxy polymers do not cure completely and contain residual liquid constituents that are similar to the starting materials.² Since liquids exhibit lower dielectric strengths than this polymeric solid, we sought to determine those properties of organic solvent systems which influence the dielectric strength. These results are reported here for simple systems as well as for polymers doped with ionizable materials.

Previous investigations have indicated that the polymer contains a grain-like solid structure and a liquid confined in intergranular capillaries. The grain-to-liquid material ratio depends on grain size, which is a function of the curing rate prior to and during gelation. The thermal conductivity of the mold material is a factor affecting the cure rate.² Uncured epoxy materials dissolve significant quantities of acids, bases, and salts. Recrystallizations, acid-base reactions, oxidation-reduction reactions, and ion transport phenomena occur in the cured polymer.³ We believe these properties can be attributed to the polymer liquid phase, and we will show that dielectric strength is strongly dependent upon ionic concentration and conductivity.

EXPERIMENTAL

Chemicals

The casting compound C 13-009 in parts A and B, a polyol-modified epichlorhydrin-bisphenol A epoxy resin, was cured with hexahydrophthalic anhydride and benzyldimethylamine. The polyol structure is



where the average value of x is 3.6. After preheating, parts A and B were mixed in equal quantities by weight. Air bubbles were removed at reduced pressures, and the curing conditions were varied to obtain different properties. Table I shows the composition of parts A and B.⁴

Anhydrous acetic acid was prepared by the reduced-pressure fractional distillation of glacial acetic acid solutions of acetic anhydride. Other chemicals were obtained commercially in reagent grade or spectrograde and were used without further purification.

TABLE I
Epoxy Composition

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

Equipment and Procedure

Dielectric breakdown may be described as an event which gives rise to a catastrophic decrease in the potential across the sample and is accompanied by a flash of light, gas formation, and a loud explosion. We define the pulse dielectric strength as V_B/l , where V_B is the maximum voltage on the ascending portion of the pulse which can be developed in 1 to 3 μsec and is immediately followed by the breakdown event, and l is the sample thickness.

Electronic equipment designed by Kelly⁵ and a Rogowski sample geometry described by Milton⁶ were used to measure voltage as a function of time. A dc pulse was applied to the sample. The pulse voltage amplitude was controlled to cause dielectric breakdown on the ascending portion of the pulse at about 2 μsec after inception. The Rogowski sample geometry effectively eliminates dielectric breakdown at the electrode edges where the field is nonuniform. A glass cell was constructed to contain the liquids between gold-plated steel electrodes and is shown in Figure 1. The electrode spacing, typically 0.025 in., was measured microscopically



Fig. 1. Cell for measuring the dielectric strength of liquids.

with a precision of ± 0.0001 in., and dielectric strengths were calculated from breakdown voltages for various sample thicknesses. The sample cross-sectional area A , 11.33 cm^2 , was calculated using resistance measurements for anhydrous acetic acid in the relation $R = \rho l/A$, where R is the resistance, ρ is the specific resistance, and l is the electrode spacing. The specific resistance for acetic acid was obtained using standard cells calibrated by the National Bureau of Standards and an ac bridge operated at 1 kHz. Cured epoxy samples, cast in the Rogowski configuration, were doped with ionic impurities of known type and concentration using an electroosmosis cell similar to that described by Adamson.⁷ After dielectric strength measurements were completed, the epoxy samples were sectioned in the breakdown region to determine the dopant penetration depth using reflected light microscopy. The diffusion front in the epoxy was readily apparent because of differences in refractive index and was parallel to the sample surface.

RESULTS

Liquids and Solutions

Figure 2 shows the measured dielectric strengths of several liquids as a function of dielectric constant. The dielectric constants were obtained

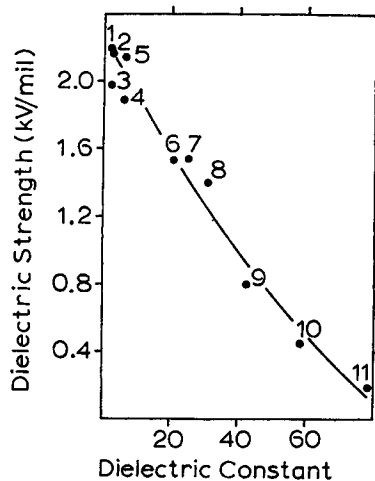


Fig. 2. Dielectric strength as a function of dielectric constant for *n*-hexane (1), carbon tetrachloride (2), benzene (3), ethyl acetate (4), acetic acid (5), acetone (6), ethanol (7), methanol (8), glycerol (9), formic acid (10), and water (11) at room temperature.

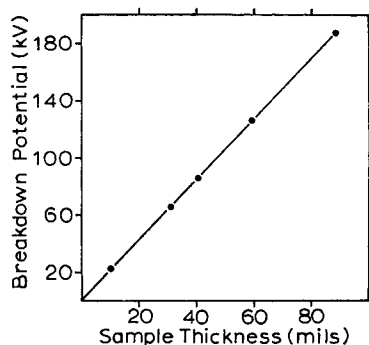


Fig. 3. Breakdown potential for acetic acid as a function of sample thickness.

from the *Handbook of Chemistry and Physics* and are intended to be the limiting values at low frequencies, the so-called static values. The average deviation was less than ± 0.04 kV/mil for 10 or more measurements with each liquid. Breakdown potentials for anhydrous acetic acid are shown in Figure 3 as a function of sample thickness. The dielectric strength is the slope of this curve. Figure 4 shows dielectric strengths for 0.02 molal solutions of electrolytes in anhydrous acetic acid as a function of the low-field specific resistances reported by Kolthoff and William.⁸ These electrolytes are all bases in the acetic acid solvent system. The effect of water, a weak electrolyte in acetic acid, on the dielectric strength is shown in Figure 5 as a function of the molal water concentration. We obtained similar results for acetic acid solutions of strong electrolytes, and these are shown in Figure 6. When the solutes could not be obtained in anhydrous

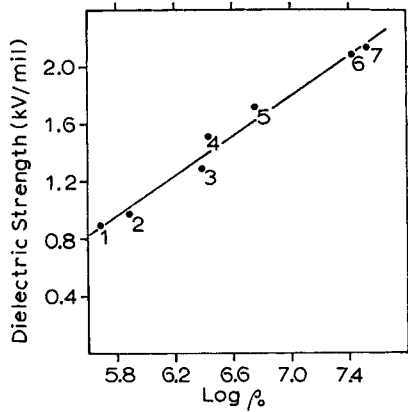


Fig. 4. Dielectric strength as a function of specific resistance for 0.02 molal anhydrous acetic acid solutions of ammonium acetate (1), sodium acetate (2), magnesium acetate (3), nickel acetate (4), lead acetate (5), and urea (6), and for acetic acid (7).

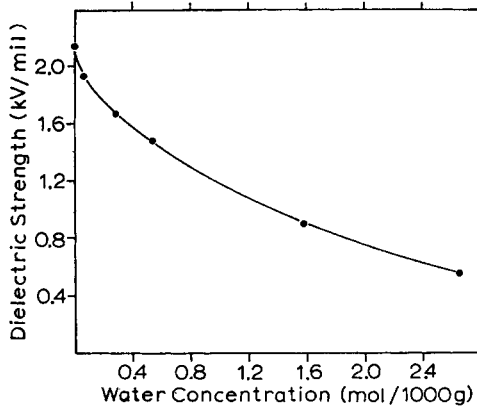


Fig. 5. Dielectric strength of acetic acid solutions as a function of water concentration.

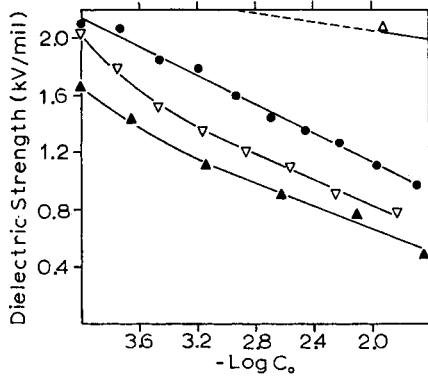


Fig. 6. Dielectric strength of acetic acid solutions as a function of concentration for water (Δ), sodium acetate (\bullet), ammonium acetate (∇), and perchloric acid (\blacktriangle).

form, we added a stoichiometric amount of acetic anhydride to react with the water. The solutions were carefully handled and tested immediately after mixing in order to avoid atmospheric contamination.

Epoxy Polymers

The dielectric strengths of a polyol-modified epoxy polymer were obtained by Milton and related to the cure temperatures.¹ We found the solid-phase polymer constituent to be distributed as small spherical floccules throughout the sample.² The floccule dimensions depend upon the rate of cure which in turn depends upon the cure temperature.² Milton's data are shown in Figure 7 as a function of the average floccule diameter and in Figure 8 as a function of the nominal interfloccular capillary dimensions. The floccules were assumed to be closely packed spheres.²

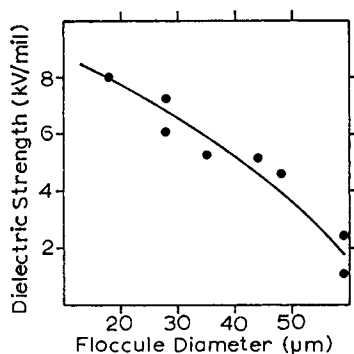


Fig. 7. Dielectric strength as a function of floccule diameter for the polyol-modified epoxy polymer.

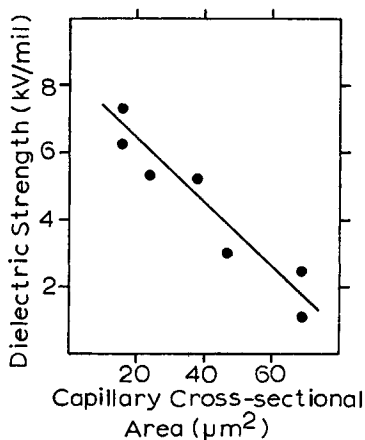


Fig. 8. Dielectric strength as a function of interfloccular capillary cross-sectional area for polyol-modified epoxy polymer.

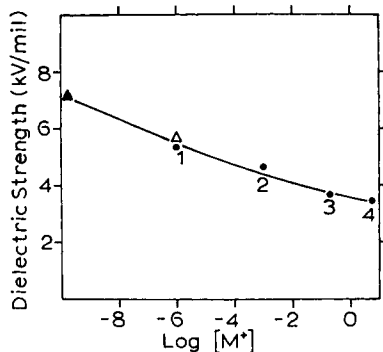


Fig. 9. Dielectric strength of the doped epoxy polymer as a function of ionic concentration in the dopants ethanol (\blacktriangle), distilled water (1), aqueous sodium hydroxide (2), and aqueous sodium chloride (3 and 4), compared with the nondoped epoxy (Δ).

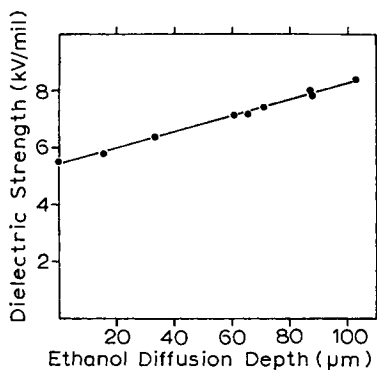


Fig. 10. Dielectric strength as a function of ethanol dopant diffusion depth in the epoxy polymer.

Epoxy samples, cured in the Rogowski geometry, were doped by electro-osmosis with water and aqueous electrolyte solutions. Doping was complete after about 19 days, as indicated by the liquid level in standpipes attached to the electro-osmosis cells. The dielectric strength for these doped samples decreased with increasing dopant ionic concentration. The electrolytic concentration due to self-ionization and ionic impurities in doubly distilled water was assumed to be about 10^{-6} mol/l.⁹ The dielectric strengths of undoped samples and those doped with distilled water were approximately equivalent. In order to deliberately produce a very low ionic concentration, the epoxy samples were doped with ethanol. Epoxy dielectric strengths are shown in Figure 9 for samples of equivalent dopant diffusion depth (about $70 \mu\text{m}$) and in Figure 10 as a function of ethanol diffusion depth. Self-ionization of ethanol ($K_i = 10^{-19.5}$) produces an ionic concentration of about $10^{-9.75}$ mole/l.¹⁰

DISCUSSION

Figure 3 is interpreted below, according to Ohm's law, to indicate that dielectric breakdown occurs in acetic acid when a critical current density is exceeded. Milton and Wentz obtained similar results for the polyol-modified polymer.¹¹ According to the Onsager theory for weak electrolytes, the specific resistance is a function of field strength, dielectric constant, absolute temperature, and electrolyte type.¹² Since these were constant in this experiment,

$$X_B = \frac{V_B}{l} = \rho \frac{i_B}{A} \quad (1)$$

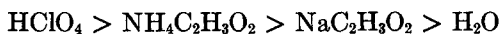
and

$$i_B/A = \text{constant.} \quad (2)$$

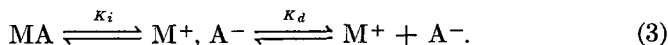
X_B is the breakdown field strength, V_B and i_B are the breakdown potential and current, respectively, ρ is the specific resistance, and A is the sample cross-sectional area.

We postulate that dielectric strength of a liquid depends upon those properties which determine the conductivity: the solvation of ions, the ionization and dissociation of neutral molecules, and the ionic mobilities. The dissociation of ion aggregates to form solvated ions proceeds to a limited extent in low-dielectric-constant media, and electrolytic conductivity is directly related to dielectric constant.¹³ Figure 2 shows that dielectric strength is inversely related to dielectric constant for a substantial number of liquids. The dielectric strength is directly related to the specific resistance of the solution (Fig. 4) and inversely related to the concentration of dissolved electrolytes (Figs. 5 and 6). These data indicate that the critical current density may be reached at lower field strengths for the more conductive solutions. In the following sections, we will relate the measured breakdown fields to the free ion concentrations and calculate the theoretical saturation current densities using the Onsager theory.

There is a logarithmic relation between the variables in Figure 4. This nonohmic behavior will be examined in detail. Figure 5 shows the effect of water on the dielectric strength of acetic acid. An extrapolation of this curve is indicated in Figure 6 for comparison with data for stronger electrolytes. The order of electrolyte strengths,^{8,14}



is the reverse of the order of dielectric strengths. The un-ionized form of a solute (MA) and the ion pair (M^+ , A^-) are nonconductive species in equilibrium with the solvated ions (M^+ and A^-),



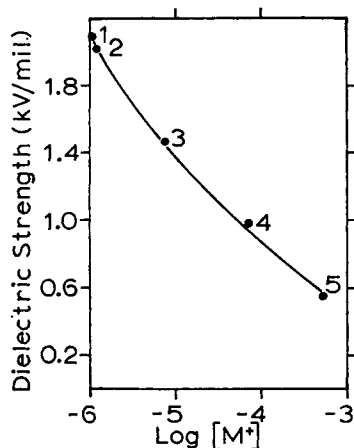


Fig. 11. Dielectric strength of 0.02 molal acetic acid solutions as a function of solvated ion concentration for urea (1), water (2), hydrochloric acid (3), sodium acetate (4), and perchloric acid (5).

The ionization constant K_i and dissociation constant K_a are given by

$$K_i = \frac{[M^+, A^-]}{[MA]} \quad (4)$$

and

$$K_a = \frac{[M^+][A^-]}{[M^+, A^-]} \quad (5)$$

where the brackets represent concentrations and the activity coefficients are omitted. The overall ionization-dissociation constant K_0 is usually expressed¹⁵ as follows:

$$K_0 = \frac{[M^+][A^-]}{[MA] + [M^+, A^-]} = \frac{K_i K_a}{1 + K_i} \quad (6)$$

Since $[MA] + [M^+, A^-] \gg [M^+]$, and $[M^+] = [A^-]$,

$$[M^+] \approx (C_0 K_0)^{1/2}, \quad (7)$$

where the total or formal solute concentration is given by $C_0 = [MA] + [M^+, A^-] + [M^+]$. Equation (7), expressed in logarithmic form, is

$$\log [M^+] = 1/2 \log K_0 + 1/2 \log C_0. \quad (8)$$

This treatment has led us to a linear relation between $\log [M^+]$ and $\log K_0$ at fixed total solute concentration. The overall ionization-dissociation constants reported by Bruckenstein and Kolthoff¹⁴ and the dielectric strengths for 0.02 molal acetic acid solutions are listed in Table II. Figure 11 shows the relation between dielectric strength and $\log [M^+]$ where we calculate the latter using eq. (8) and K_0 values from Table II.

TABLE II
Solute equilibrium Constants and Dielectric Strengths for 0.02 molal
Acetic Acid Solutions

Solute	K_0	Dielectric strength, kV/mil
Perchloric acid	$10^{-4.87}$	0.55
Sodium acetate	$10^{-6.68}$	0.98
Hydrochloric acid	$10^{-8.55}$	1.46
Water	$10^{-10.1}$	2.01
Urea	$10^{-10.24}$	2.09

The Debye-Hückel-Onsager theory of conductance for electrolytes stated in its simplest form is^{16,17}

$$\Lambda = \Lambda_0 - [A\Lambda_0 + B]\sqrt{C} \quad (9)$$

where Λ is the equivalent conductance for ionic concentration C ; Λ_0 is the equivalent conductance at infinite dilution; and A and B are factors which depend upon the field strength, viscosity, dielectric constant, absolute temperature, and the ion valence type. Since A and B decrease as the field strength increases, the equivalent conductance increases and, for very high field strengths, approaches Λ_0 .¹⁸ The limiting value is less than Λ_0 since the destruction of the ionic atmosphere by the high field is not accompanied by complete elimination of the electrophoretic effect.¹⁹ This phenomenon is known as the Wien effect and results in an exponentially decreasing specific resistance with increasing field strength. Ohm's law, then, has only limited range of validity for ionic solutions. High external electric fields increase both the velocities of ions and the dissociation of weak electrolytes. "The effect of an external electric field on the electrolytic dissociation [was] computed kinetically [by Onsager] from the equations for Brownian motion in the combined coulomb and external fields...; the theory [was] quantitatively confirmed by the deviations from Ohm's law which [were] observed for solutions of weak electrolytes in water ($D = 78.54$) [dielectric constant] and in benzene ($D = 2.28$). For solutions of salts in acetone ($D = 20.7$), and for solid electrolytes such as glass, mica, celluloid, etc., the observed increments of conductance [were] smaller than those expected from the theory, but still of the predicted type and order of magnitude."¹² The validity of the theory was confirmed for solutions of tetrabutylammonium picrate in diphenyl ether ($D = 3.53$) by Mead and Fuoss,²⁰ and for a variety of electrolytes in water by Bailey and Patterson.²¹ The ratio of the dissociation constants at high field strengths $K(X)$ to low field strengths $K(0)$ was expressed by Onsager,¹²

$$\frac{K(X)}{K(0)} = 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \frac{b^5}{2700} + \frac{b^6}{56700} + \dots \quad (10)$$

or, for large values of b ,

$$\frac{K(X)}{K(0)} = (2/\Pi)^{1/2} (8b)^{-3/4} e^{(8b)^{1/2}} \times \left\{ 1 - \frac{3}{8(8b)^{1/2}} - \frac{15}{128(8b)} - \frac{105}{1024(8b)^{3/2}} - \dots \right\} \quad (11)$$

where b is defined in eq. (12),

$$b = \frac{Z_1^2 Z_2^2 (\lambda_1 + \lambda_2)}{|Z_2| \lambda_1 + |Z_1| \lambda_2} 9.695 \frac{X}{DT^2} \quad (12)$$

where Z_i and λ_i are the valence and equivalent conductance, respectively for ion i ; X is the field strength in volts/cm; D is the dielectric constant for the solution; and T is the absolute temperature. For 1-1 electrolytes, $Z_1 = Z_2 = 1$, and eq. (12) reduces to

$$b = 9.695 \frac{X}{DT^2}. \quad (13)$$

Onsager predicted that if the saturation current is measured before any great fraction of the ion pairs have been electrolyzed, then we shall expect the saturation current to increase with field intensity X in the ratio¹²

$$\frac{i(X)}{i(0)} = \frac{K(X)}{K(0)} \quad (14)$$

or

$$i(X) = i(0) \frac{K(X)}{K(0)}. \quad (15)$$

Then, from Ohm's law,

$$\frac{i(0)}{A} = \frac{X}{\rho_0} \quad (16)$$

and

$$\frac{i(X)}{A} = \frac{X}{\rho_0} \frac{K(X)}{K(0)} \quad (17)$$

where ρ_0 is the specific resistance at low field strengths. The factor $K(X)/K(0)$ is the high-field Wein-Onsager correction to Ohm's law. The relative importance of this factor is shown in Figure 12 for 1-1 electrolytes in solutions of different dielectric constant. The values for $K(X)/K(0)$ were calculated using eqs. (11) and (13) for $T = 298.2^\circ\text{K}$.

Table III lists the results obtained using Onsager's theory and the data from Figure 4. The critical current densities were the same within $\pm 3.8\%$ for the acetic acid solutions. It is of interest to note that the correction factor $K(X)/K(0)$ ranged from about 47 to 1272.

TABLE III
Calculated Current Density and Dissociation Constant Ratio for Acetic Acid Solutions

Solute	X , kV/mil	ρ_0 , ^a Ω -cm	$K(X)/K(0)$ ^b	i/A , ^c amp/cm ²
Ammonium acetate	0.896	4.926×10^5	47.26	33.84
Sodium acetate	1.025	7.752×10^5	70.16	36.52
Magnesium acetate	1.37	2.451×10^6	185.3	40.77
Nickel acetate	1.405	2.755×10^6	203.3	40.81
Lead acetate	1.63	5.848×10^6	361.2	39.64
Urea	2.095	2.703×10^7	1077.	32.86
Acetic acid	2.17	3.376×10^7	1272.	32.18
Average $i/A_{(1-1)} = 33.8 \pm 1.3$				

^a Kolthoff and William.⁸

^b Calculated using eqs. (11) and (13).

^c Calculated using eq. (17).

Note: Equation (13) is not valid for 2-1 electrolytes; the values enclosed in the boxes are therefore in error.

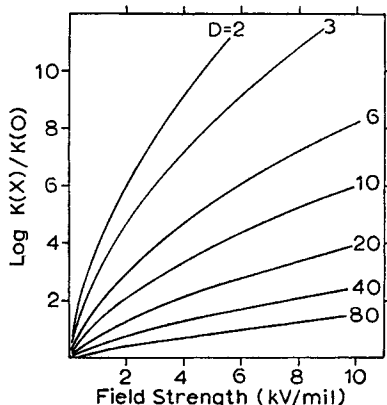


Fig. 12. The ratio of dissociation constants at high field strength $K(X)$ to low field strength $K(0)$ as a function of field strength and dielectric constant D .

We believe that dielectric strengths of epoxy polymers and liquids are determined by the same factors. Milton's data for the polyol-modified epoxy are very similar to those shown in Figure 3 which we interpret as dielectric breakdown upon exceeding a critical or saturation current. This polymer consists of roughly spherical floccules closely packed to form an interfloccular capillary network in which a liquid is confined.² The effect of small capillaries to reduce the rate of liquid diffusion^{2,22} is postulated also to reduce the conductivity of the liquid through wall adsorption and flow drag. The higher dielectric strengths found for polymers (Fig. 7) as compared to those for free liquids and the dependence upon capillary size (Fig. 8) are consistent with this point of view.

When ionic materials are diffused into the epoxy polymer, the effect on the dielectric strength (Fig. 9) is very similar to that for acetic acid

(Figs. 5 and 6). The small effect of water may be due to polymer pre-saturation as indicated by the presence of many small hexahydrophthalic acid crystals. Hexahydrophthalic anhydride is a curing agent in the polymer mix and reacts with water to form the acid.

The discussion presented thus far has been concerned with dielectric breakdown phenomena occasioned by single short (10^{-6} sec) pulses. In the case where the sample is subjected to a slowly increasing dc potential, a somewhat different condition develops. According to Onsager,¹²

“the kinetic constants of dissociation [of ion aggregates] and recombination can be computed separately on the assumption that the recombination proceeds as rapidly as the mutual approach of two ions due to the coulomb attraction. The derivation is equivalent to that of Langevin and leads to the same result. In the Langevin case, the coefficient of recombination is independent of the field; that of dissociation is increased by a factor $F(b)$, [$=K(X)/K(0)$]. Slower reactions may occur when a [chemical] rearrangement of ion pairs is involved. In the most general case, it is necessary to consider the successive reversible reactions ions \rightleftharpoons pairs \rightleftharpoons molecules, where the former takes place with the Langevin velocity; only the reaction rate pairs \rightarrow ions depends on the field. . . . We now recognize that when a considerable chemical time lag exists (molecules \rightarrow pairs), the saturation phenomena will develop through two essentially different stages. At first, the ions removed by electrolysis will be replaced by dissociation of ion pairs at the Langevin rate. The modifications of the field by space charges will be moderate (a factor of the order 2), as long as the concentration of the ion pairs is nowhere greatly reduced. However, after the electrode regions have been depleted of ion pairs, the subsequent production of ions in these regions will be determined by the slower transformation of molecules, and the electrode layers will expand accordingly. *The conditions in this second stage permit the development of much greater fields, so that even the concentration of cations near the cathode and that of anions near the anode will be greatly lowered due to their high velocities.*”

These considerations may explain the much higher dielectric strengths found for the same polymer (the polyol-modified epoxy) when subjected to slowly rising (20 min) dc potentials.²³

According to the theory of Debye and Falkenhagen, both the dielectric constant and the conductance are increased by alternating potentials.²⁴⁻²⁶ These changes would result in a lower dielectric strength, and this has been observed by Milton for the epoxy polymer when tested using alternating potentials.²³

CONCLUSIONS

The dielectric strengths of liquids, electrolyte solutions, and epoxy polymers are inversely related to the concentration and conductance of dissolved ionic species. Breakdown is hypothesized to occur when a critical current density is exceeded. The reasons for this value being critical are unknown. According to Onsager's theory for high field electrolytic conduction, the field strength required to produce the saturation current density depends upon the rate of ion removal by electrolysis and the kinetics of ion production by ionization and field-dependent dissociation of ion pairs. Dielectric strengths are dependent upon the kinetics

of these processes, and predictable effects have been observed for dielectric breakdown by pulses, slowly rising potentials, and alternating potentials. We believe the critical current density for dielectric breakdown and the saturation current density computed according to Onsager's theory are the same for the pulse breakdown case.

This work was supported by the U.S. Atomic Energy Commission.

References

1. O. Milton, *Insulation*, 59 (November 1967).
2. R. E. Cuthrell, *J. Appl. Polym. Sci.*, **12**, 955 (1968); *ibid.*, **12**, 1263 (1968).
3. *Idem*, Sandia Corporation, Albuquerque, New Mexico, in press.
4. B. Carroll and J. Smatana, *Transparent Cold-Shock-Resistant Epoxy Casting Resin*, Sandia Corporation Report SC-R-60-173, Albuquerque, New Mexico, 1960.
5. R. D. Kelly, *A High-Voltage Pulse Generator for Testing Dielectric Samples*, Sandia Corporation Report SC-TM-203-60, Albuquerque, New Mexico, 1960.
6. O. Milton, *ASTM Proceedings*, **65**, 831 (1965).
7. A. W. Adamson, *Physical Chemistry of Surfaces*, Interscience, New York, 1960, p. 193.
8. I. M. Kolthoff and A. William, *J. Amer. Chem. Soc.*, **56**, 1014 (1934).
9. H. R. Kruyt, *Colloid Science*, Vol. 1, Elsevier, New York, 1952, p. 70.
10. S. Kilpi and H. Warsila, *Z. Phys. Chem. (Leipzig)*, **A177**, 427 (1936).
11. O. Milton and J. L. Wentz, *Insulation*, 71 (May 1966).
12. L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).
13. R. E. Barker, Jr., and A. H. Sharbaugh, *J. Polym. Sci. C*, **No. 10**, 134 (1965).
14. S. Bruckenstein and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **78**, 10 (1956); *idem*, p. 2974.
15. H. A. Laitinen, *Chemical Analysis*, McGraw-Hill, New York, 1960, p. 73.
16. P. Debye and E. Hückel, *Z. Phys.*, **24**, 185, 305 (1923).
17. L. Onsager, *Z. Phys.*, **27**, 388 (1926); *ibid.*, **28**, 277 (1927).
18. H. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1963, pp. 184-185.
19. H. Harned and B. B. Owen, *ibid.*, p. 320.
20. D. J. Mead and R. M. Fuoss, *J. Amer. Chem. Soc.*, **61**, 2047 (1939); *ibid.*, **61**, 3589 (1939).
21. F. E. Bailey, Jr., and A. Patterson, Jr., *J. Amer. Chem. Soc.*, **74**, 4428 (1952).
22. S. B. Tuwiner, *Diffusion and Membrane Technology*, Reinhold, New York, 1962, pp. 40-74.
23. O. Milton, personal communication, Sandia Corporation, Albuquerque, New Mexico.
24. P. Debye and H. Falkenhagen, *Z. Phys.*, **29**, 121, 401 (1928); *idem*, *Z. Elektrochem.*, **34**, 562 (1928).
25. H. Falkenhagen, *Electrolytes*, Clarendon, Oxford, 1934, pp. 181-192.
26. H. S. Harned and B. B. Owen, *op. cit.*, pp. 126-127.

Received February 14, 1972