

## Electromechanical Hysteresis Measurements: A New Tool for Investigation of the Properties of Plastics

EDWARD L. KERN\* and SELBY M. SKINNER†

*Case Institute of Technology, Cleveland, Ohio*

A net charge occurs on the surface of a plastic specimen when it is subjected to mechanical strain.<sup>7</sup> This charge has not been disclosed in any systematic way in the usual experimental techniques which are applied to study or testing of plastics, probably because of two factors: (a) the charge is usually distributed over a large surface and charge density is not large; (b) the charge gradually disappears. Its existence may be shown by the use of charged, luminescent powders,<sup>5,8,10</sup> these also reveal the charge topology. Instrumental observation may be made by special equipment and techniques, in which the charge is recorded as a function of time by its inductive effect upon an electrode at a small distance from the surface. This relation between distortion of the specimen and resultant charge distribution can be observed by simultaneous recording of both upon an X-Y recorder, an electrometer being used for the latter, and a linear variable differential transformer for the former. Tension and compression yield opposite signs of charge.

The charging has been observed in both the tensile mode and the flexural mode of strain. The latter has the advantage that opposite portions of contiguous material are stressed in tension and in compression, so that electrical source and sink are close to each other. The flexural strain-charge phenomenon has been studied in detail; as is described below, it is a simple experimental technique reproducible, but sensitive to chemical structure and composition, as well as to other parameters.

The charge observed at a given strain is different if the strain is increasing from that when it is decreasing. The phase lag responsible for this is apparently caused by the finite resistivity of the plastic material. A charge-strain plot exhibits hysteresis and in a reversing cycle shows a charac-

teristic hysteresis loop. The hysteresis effect has been observed and investigated for fifty-eight plastic and elastic compositions and exists in other than plastic materials, such as mica. The precise hysteresis curve is dependent upon the electrical and viscoelastic properties, the composition and heterogeneous nature of the material, and upon controllable experimental parameters. The composition dependence provides a practical method for comparing plastics and of screening individual batches of a single plastic in order to match the material to the processing characteristics desired. Dependence of the hysteresis curve upon phase heterogeneities and recycling promises to be an indicator and technique for study of fatigue.

Reciprocal interactions between electrical and mechanical effects present a challenging field of research in plastics and solid state theory. Displacement of charge by mechanical strain resembles the piezoelectric effect in crystals; the differences are due to the dissimilar electrical characteristics of crystals and insulating plastics. Related effects have recently been reported by the authors: the effect of the electrical field in modifying tensile properties<sup>8</sup> and a correlation of the experimentally measured mechanical forces in adhesion and in friction to charge transfer between surfaces.<sup>2,4,6</sup>

### EXPERIMENTAL

#### Sample Preparation

Fifty-eight different materials were tested with at least five samples for each material. These included: three series each made up of a common basic composition with minor variations, silicone rubbers, mica sheets, fiber-reinforced phenolics and polyesters, filler-reinforced polymers, homopolymers, and copolymers.

Most of the samples were either injection-molded or milled from molded sheet  $\frac{1}{8}$  in. thick, in accordance with A.S.T.M. D-638-52T (dumbbell ten-

\* Present address: Aeronautical Research Laboratories, Wright-Patterson AFB, Ohio.

† Present address: Air Arm Division, Westinghouse Electric Corp., Baltimore, Md.

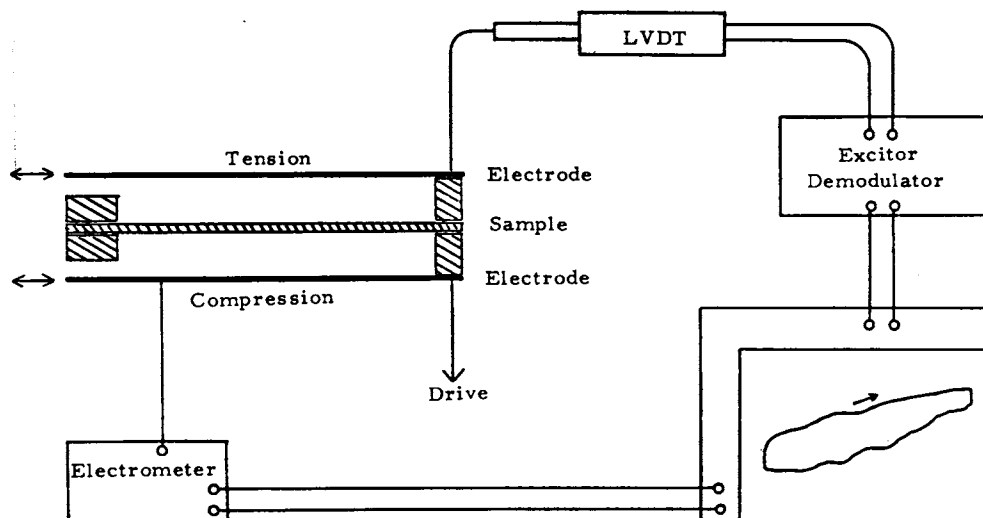


Fig. 1. Charge-strain hysteresis apparatus.

sile samples). To reduce the effects of machine release agents, grease due to handling, water and laboratory vapors, and dirt, the samples were washed for 5 min. each in (1) absolute diethyl ether, (2) *n*-heptane, C.P., and (2) absolute ethyl alcohol. If the polymer composition would have been solvated by any step, that step was omitted. The samples were vacuum dried and kept in a desiccator until used.

### Apparatus

The charge on the plastic surface was observed by placing a metal electrode surface parallel to and slightly distant from the plastic. An equal and opposite sign charge was induced on the metal surface. A high input resistance electrometer (Keithley model 210) was connected to the metal electrode, producing an output voltage of the same sign as the charge on the plastic surface.<sup>2</sup> One electrode was on the tension side and one on the compression side of the flexing sample (Fig. 1).

The distance between electrode and sample was 1 in., and both were constrained to move in a parallel manner. The sample was placed with its length vertical in order to facilitate the testing of elastomeric materials. The lower end of the sample and electrode were moved perpendicularly to their length by a slow, constant strain rate at displacement of 1 in. in 7 sec. A linear variable differential transformer (LVDT) (connected to the displacing sample) with its excitor-demodulator, indicated the displacement of the sample end. Its output feeds the *X*-axis of an *X*-*Y* plotter; the output of the electrometer, the *Y* axis (Fig. 1).

### Testing Technique

The samples were mounted between the plastic plates, top and bottom, which form the holder, with 5 in. between to be strained. Five minutes were allowed for the electrometer to rezero and the sample to come into equilibrium with the atmosphere and electrical equilibrium with the sample holder.<sup>9</sup> The experiment consisted of displacing one end of the sample in flexure, thus creating a compression on one side and tension on the other.

Data were taken from the electrode on the sample's compressing side, thus eliminating the effects of slight differences in electrodes. A maximum end displacement of 1 in. (0.40 strain units) was used, with cycling period of 15 sec. Between each cycle, a 1-min. rest period was allowed for re-establishment of original conditions. After several cycles had been completed, the sample was reversed in the holder, and the charge and hysteresis curve resulting from compression of the other side was recorded for an equal number of cycles. The effect of many repeated cycles was observed by continuously cycling the sample and periodically recording the hysteresis curves.

### DISCUSSION

#### The Charge-Strain Hysteresis Curve

A typical charge-flexural strain hysteresis curve is shown in Figure 2. (A) shows the appearance of a large charge produced by a very small strain (0.01 strain units). The charge increases with strain (B), usually approaching an asymptotic

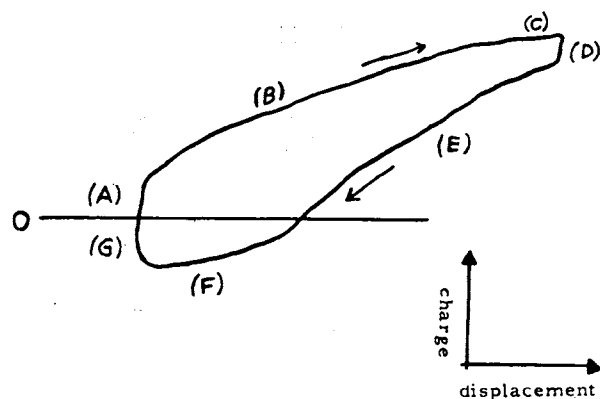


Fig. 2. A general charge-strain hysteresis curve. Initial zero charge is indicated. During decreasing strain, the charge goes from positive to negative values. The charge shown is for the compression side of a sample being strained in flexure.

limit (C). This increase may be smooth, as the diagram indicates, or discontinuous, depending upon the material being tested. The constant rate of flexing is reversed at (D), often with a sudden decrease in charge (with a strain change of about 0.01 units). The charge decreases with decreasing strain (E), usually with the same characteristic curve shape as when the charge increased. The charge usually approaches an asymptotic value (F) which is usually below the charge value at the start of the cycle. The charge gradually returns to its original value while at zero strain (G).

The charge increase exhibited on compression may be positive or negative, depending upon the material and its history and surface condition. The charge on the compression side is opposite to that on the tension side, and curve shapes are apparently identical if the materials are identical on the two sides, but differ if they are different. Thus, injection-molded samples show nearly identical hysteresis curves for both sides, while samples cut from commercial sheetmolded materials or milled samples show a considerable difference. In the latter case, there may be differences in the contacting materials at the two surfaces and one side stays in the mold longer than does the other.

#### Experimental Factors Affecting the Hysteresis Curve

The effect of a number of controllable experimental factors upon the hysteresis curves was studied. On variation of the amplitude of the hysteresis curve by doubling the maximum flexural strain from 0.40 to 0.80, the maximum change did

TABLE I  
Effect of Maximum Strain on Hysteresis Curve Characteristics

Material	Ratio of maximum charge at 0.80 strain/0.40 strain	Rank <sup>a</sup>	Ratio of hysteresis areas at 0.80 strain/0.40 strain	Rank <sup>a</sup>
Styrene-acrylonitrile-nitrile-rubber-2	1.6 ± 0.1	1	2.5 ± 0.5	7
Poly-styrene-GRS-2	—	—	2.9 ± 0.1	6
Acrylonitrile-butadiene-styrene	1.4 ± 0.1	2	3.1 ± 0.4	2
Poly-ethylene	1.3 ± 0.1	3	2.4 ± 0.2	5
Styrene-acrylonitrile-nitrile-rubber-1	1.3 ± 0.1	4	2.65 ± 0.05	4
Poly-styrene-GRS-1	1.32 ± 0.02	5	3.0 ± 0.1	3
Rigid PVC	1.25 ± 0.02	6	3.9 ± 0.2	1

<sup>a</sup> Ranked according to descending values.

not double, while the area more than doubled (Table I). The materials with the high maximum charge ratios have the low hysteresis area ratios, the order being reversed with but one exception. The materials which tend to keep charging significantly at higher strains, i.e., do not approach an asymptotic charge value as soon, also have higher charge relaxation (by resistive flow) times, so that the charge cannot diminish from the surface as fast with time.

Variation with rate of straining was observed for polyethylene and acrylonitrile-butadiene-styrene, for which a slower rate of straining decreased the charge attained at maximum strain. Although the charge increased with the magnitude of strain, a longer cycling period gave the charge being displaced more time to drain from the surface, and the hysteresis area was correspondingly decreased.

Continuous recycling for the same cycle period and strain values, without intervening rest periods between cycles, resulted in several effects. If a positive charge was produced on the compression side, and, if at the end of each cycle the charge had

not returned to the original value, each succeeding cycle started at a lower initial charge value than the preceding; if there was negative charging, then there was a more positive initial charge. This shift with the number of cycles was rapid at first, falling off asymptotically, so that after many cycles the charge values of succeeding cycles were superimposable. The shift depended on the straining rate, since the charge difference between the onset and end of a strain cycle was speed-dependent.

The hysteresis area decreased with the number of cycles: the charge difference between minimum and maximum strain (hysteresis curve height) and, therefore, the average slope of the curve, decrease with continuous cycling. (See Appendix.) After many cycles (30–50 and more), allowing the sample to rest for a considerable period (24 hr.) does not restore the ability to give the type of hysteresis curve it initially demonstrated.

When a sample is held at constant strain, the charge on the surface diminishes. If the sample showed a positive charging with increasing strain (on one side), the charge became less positive at constant strain and often became more negative than the initial charge before straining. Polystyrene-GRS, held for 3 min. at a strain of 0.40, the strain then being reduced to zero, had a charge decrease (at 0.40 strain) to a value lower than the original charge, and, in three out of four cases, well below the normal decrease observed at strain reversal. Polyethylene (medium density), held 5 min. at maximum strain, showed a charge drop to below the value before the start of the cycle and considerably more drop than at strain reversal in normal cycling. Polytetrafluoroethylene held 5 min. at maximum strain decreased considerably more than at normal strain reversal but not below the charge value at the beginning of cycling. The subsequent hysteresis curves with normal cycling were altered only slightly.

During the time span at constant strain, phenomena of charge flow and material flow occurred simultaneously, charge flow paralleling the initial stages of plastic flow.

### Effect of Reinforcing Materials

The amount and type of filler in polymer produced definite effects. One filler for silicone rubber produced a different hysteresis curve than another of the same volume concentration, as observed in both magnitude and changes of characteristic features (Fig. 7). The effect of epoxide and silicone binders in mica is observed in Figure 4, for both

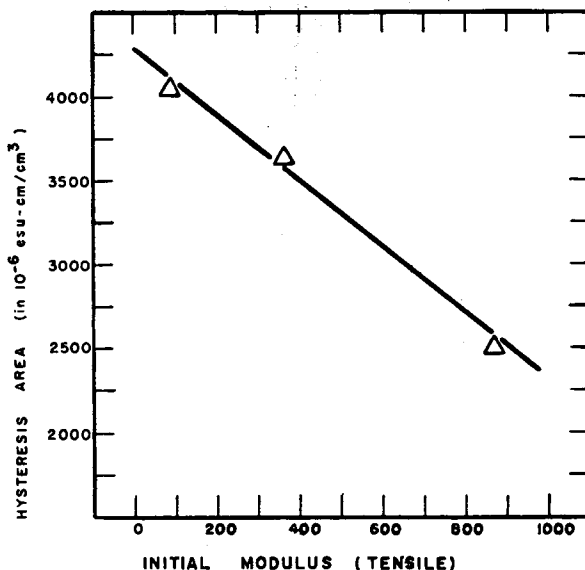


Fig. 3. Hysteresis area vs. initial modulus for silicone rubber.

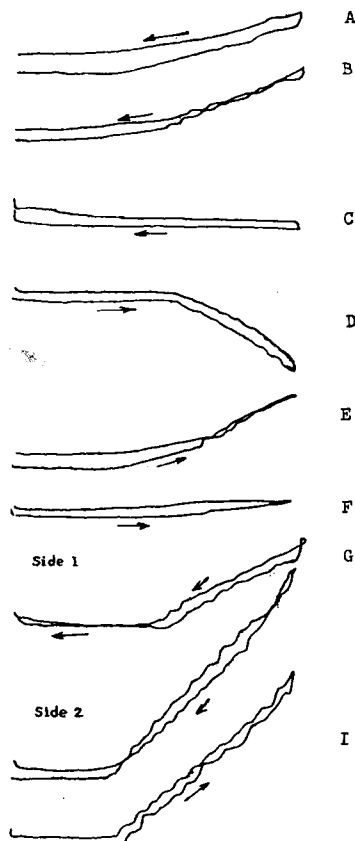


Fig. 4. Comparison of hysteresis areas for materials of slightly different composition: (A) bonded mica, 15% silicone bonded; (B) bonded mica, 25% silicone bonded; (C) bonded mica, 35% epoxy bonded; (D), (E), (F) glass-filled polyesters; (G), (H), (I) Buna S-coated phenolics, See Table II for hysteresis area values.

TABLE II  
Comparison of Hysteresis Areas for Materials of Slightly  
Different Composition

Curve in Fig. 4	Material	Hysteresis area, $10^{-6}$ esu-cm./cm. <sup>3</sup>
A	Bonded mica 5% Silicone bonded	-646
		-946
		-1462
B	25% Silicone bonded	-2070
		-670
		-532
		-706
C	35% Epoxy bonded (semi-cured) (one side only)	-666
		+240
		+274
		+288
D	Glass-filled polyesters 1.	+462
		-241
		-236
E	2.	-283
		-240
		-317
F	3.	-349
		-362
		-247
G	Buna S-coated phenolics One side coated	-183
		-578
		-256
		+126
		+80
		+46
I	Two sides coated <sup>a</sup> Both sides	-352
		-369
		-570

<sup>a</sup> Note direction of charge flow in Figure 4.

different concentrations of filler and different fillers. In large enough concentrations, the filler can be expected to change the ease of charge flow. In formerly homogeneous polymers, filler introduces a heterogeneous phase which, as experimentally observed, produces a curve with discontinuous charge buildups and decreases.

The effect of mechanical properties of the material upon the charge-strain hysteresis was studied by means of a series of silicone rubbers with different amounts and types of fillers. Hysteresis area decreased with increasing filler content and corresponding higher modulus, the type of filler determining the rate of area change with concentration change. Figure 3 illustrates this effect for one

unfilled sample and two samples with different concentration of the same filler. Changing the filler content also changes the ultimate strength and ultimate elongation; the hysteresis area decreased as the ultimate elongation and the ultimate strength increased.

The resin-reinforcing fiber combination directly influences the hysteresis characteristics. The effect of using the same fiber (glass) and changing the resin (different polyester compositions) is illustrated in Figure 4 and Table II. In phenolic samples, the fiber was changed (nylon to linen), changing the shape of the hysteresis curve, but not the area. The fibers introduce a heterogeneous phase, different in both electrical and mechanical properties, and this is reflected in differences of the electromechanical effect.

### Effect of Composition

The most powerful influence on the hysteresis curve was the composition of the plastic material. Changing the composition can change the hysteresis area from a very small quantity to a large one and can change the charge at a specific strain from negative to positive; the hysteresis curve from a smooth curve to one with steplike charge changes. Table

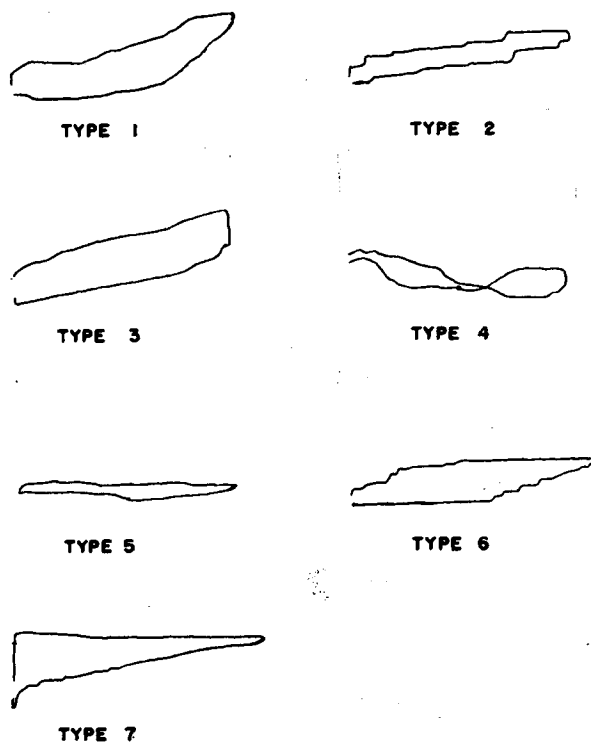


Fig. 5. General types of charge-strain hysteresis curves.

III shows the variation of hysteresis area for different materials and its reproducibility for replicate samples (see Figs. 6, 7, and 8).

TABLE III

Hysteresis Areas of Commercial Plastics. Reproducibility of Measurements for Replicate Samples

Plastic	Area of hysteresis curve, $10^{-6}$ esu-cm./cm. <sup>2a</sup>
Polytetrafluoroethylene	310
	323
Polyethylene	803
	740
	558
	540
Polystyrene-GRS-1 <sup>b</sup>	224
	229
	243
	232
Polystyrene-GRS-2 <sup>b</sup>	925
	903
	924
	910
Polystyrene-GRS-3 <sup>b</sup>	592
	570
	556
	559
	421
Phenolic-nylon base	321
	266
	375
	781
Nylon 6	748
	100
Nylon 66	119
	119
Nylon 610	132
	190
	144
	112
Acrylonitrile-styrene-nitrile rubber-1 <sup>b</sup>	-133
	-127
	204
Acrylonitrile-styrene-nitrile rubber-2 <sup>b</sup>	227
	259
	168
Polystyrene-polymethyl methacrylate	172
	203
	165
Polymethyl methacrylate	166
	196
	165
	165

<sup>a</sup> Each value is the average area for two sides of the sample and different values are for different specimens of the same composition.

<sup>b</sup> Commercial samples from different producers with slight composition differences.

### Classes of Hysteresis Curves

The shape of a hysteresis curve can also be used to classify the charge-strain properties of a sample. Seven types of curves adequately classify the variations caused by both changes in polymer composition and in reinforcing materials. Curves sometimes have characteristics of more than one type. When sample preparation conditions are different for the two sides of a sample, they can have one type of behavior for one side, another type for the other side.

TABLE IV

Classification of Hysteresis Curves for Plastics According to General Types

Type	Polymer
Type 1	Acrylonitrile-styrene-nitrile rubber (2 types)
	Polypropylene (1 type)
	Polyethylene (3 types)
	Polytrifluorochloroethylene
	Epoxide resins (2 types)
	Epoxide-bonded mica
	Black-stained india mica (1 side) <sup>a</sup>
	Nylon reinforced phenolic
	Nylon 6
	Nylon 66
	Nylon 610
	Polymethyl methacrylate (1 side)
	Polystyrene
	Glass-filled polyester (1 type)
Type 2	Polytetrafluoroethylene
	Polyethylene (2 types)
	Polystyrene-polymethyl methacrylate
	Polystyrene-GRS (1 type)
	Polymethyl methacrylate latex
	Silicone rubber (unfilled)
	Epoxide resins (4 types)
Type 3	Linen-reinforced phenolic
	Black-stained india mica (1 side)
	Cellulose acetate
	Polystyrene-GRS (2 types)
	Polyethylene (1 type)
	Epoxide resins (3 types)
	Nylon 610
Type 4	Polymethyl methacrylate (1 side)
	Epoxide resins (3 types)
	Silicone rubber, (filled, 4 types)
	Glass-filled polyester (2 types)
Type 5	Buna S-coated phenolics
	Silicone rubber (filled, 1 type)
	Polypropylene (2 types)
Type 6	Silicone rubber (filled, 1 type)
	Polypropylene (1 type, 1 side)
	Polyethylene (1 type, 1 side)
Type 7	Silicone rubber (filled, 1 type)
	Polypropylene (1 type, 1 side)
	Polyethylene (1 type, 1 side)

<sup>a</sup> A material may have more than one general type of curve depending on the side of the sample tested and variations between samples.

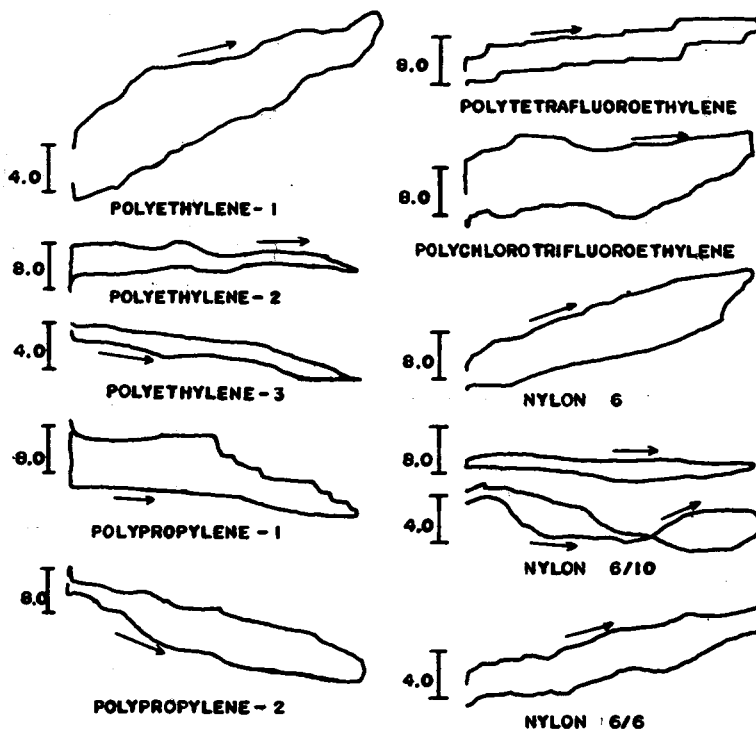


Fig. 6. Charge-strain hysteresis curves for flexible polymers. The nylon samples had one type of behavior on one side, a different type on the other. Scale on left is in charge units of  $10^{-6}$  esu/cm.<sup>2</sup>. Arrows indicate the increasing strain part of curve.

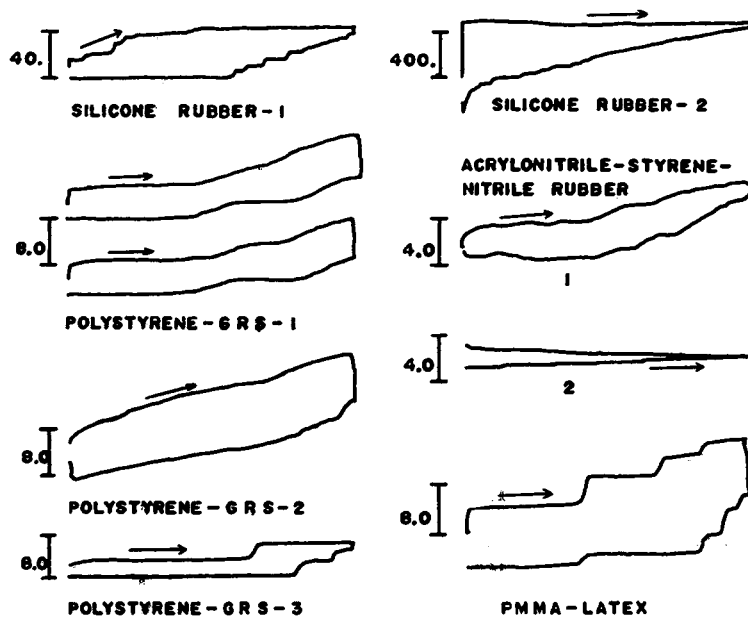


Fig. 7. Charge-strain hysteresis curves for rubber compounds. Low modulus silicone rubbers have much larger hysteresis curves than more rigid plastics. The type of curve also changes going from the flexible to the rigid materials. The two curves for polystyrene-GRS-1 are successive cycles on the same sample. Scale on the left is in charge units of  $10^{-6}$  esu/cm.<sup>2</sup>.

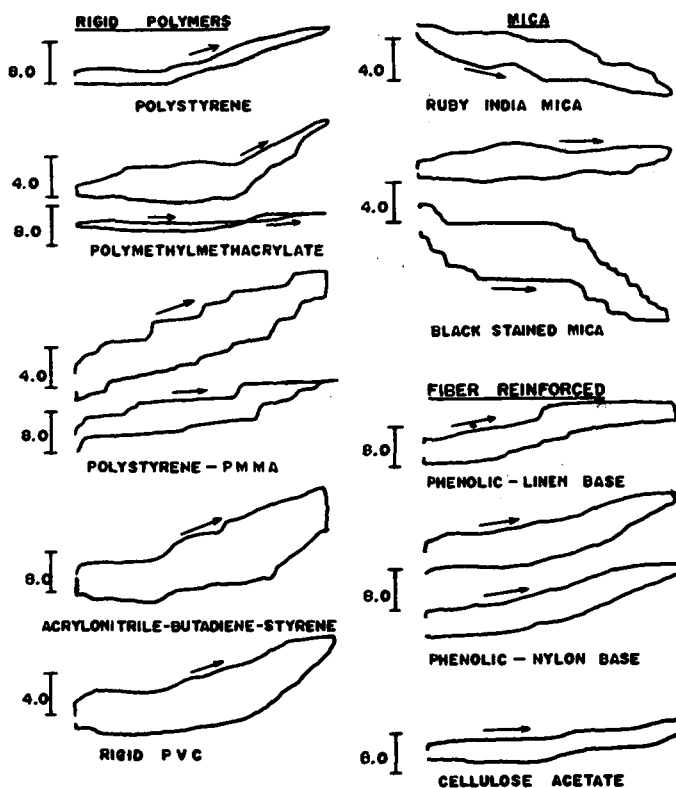


Fig. 8. Charge-strain hysteresis curves for rigid plastics and mica. The two curves for nylon-reinforced phenolic are for two different samples cut from a uniform sheet. Scale on the left is in charge units of  $10^{-6}$  esu/cm.<sup>2</sup>.

**Type 1.** An appreciable charge appears at a very small strain, followed by a continuous increase toward an almost asymptotic value at maximum strain (Fig. 5). Upon reversal of strain, the charge decays in a continuous manner and approaches asymptotically a value below the original charge value. The charge returns to the initial value in several minutes while at zero strain. Half of the materials showing Type 1 characteristics are amorphous homopolymers without phase heterogeneity (Table IV). The other half contain phase heterogeneity, but differences in phase properties are much lower than for Types 2, 3, 5, 6, and 7 to be described. The more homogeneous and rigid materials, such as polystyrene, polyethylene, and nylon 610 have a charge effect small in magnitude compared to that of the other types.

**Type 2.** An appreciable charge builds up at very small strains, after which the charge increases in well defined steps, instead of monotonically. There is an appreciable decrease of charge immediately following reversal of strain, proportional to the magnitude of increase at the beginning of the

cycle. The decrease of charge, during decrease of strain, is in steps which occur at the same strain values as the increasing charge steps. The nature, and probably cause, of these step increases is related to the composition and history of the samples. The charge, after return to zero strain, is below the initial value, returning to it in the same manner as for Type 1.

**Type 3.** The same type of charge buildup occurs as for Types 1 and 2, but the decrease at strain reversal is much larger than for these types, and occurs in a very short period of time corresponding to a strain change of less than 0.01. The charge often drops well below the original value.

**Type 4.** A smooth charge increase and decay usually occurs, even at strain reversal, but a cross-over of the curve appears, i.e., from a positive curve (positive charge increase with increasing strain) to a negative curve (negative charge increase with increasing strain), or vice-versa.

**Type 5.** A step increase in charge occurs, similar to Type 2; the change between the increasing strain and decreasing strain curves, how-



TABLE V

Comparison of Hysteresis Areas for Slightly Different Compositions of Epoxide Resin Coatings

Series	Hysteresis area, $10^{-4}$ esu-cm./cm. <sup>2</sup>
1	-326
	-312
	-322
	-444
2	-630
	-470
	-510
	-551
3	-660
	-652
	-873
	-882
4	-702
	-848
	-748
	-742
5	-1233
	-1208
	-1230
6	-1305
	-1395
	-1495
7 (2 sides)	-698
	-918
	-951
	-712
	-664
7 (Side 1)	-1290
	-1366
	-1260
	-936
7 (Side 2)	-940
	-536
	-576
	-484
	-392
	-106

TABLE VI

Comparison of Polyolefins by the Hysteresis Area. Effect of Minor Variations in Catalyst Residue

Polymer	Hysteresis area, $10^{-4}$ esu-cm./cm. <sup>2</sup>	
Polypropylene 1.	-74	
	-34	
	-276	
	-130	
	2.	+246
		+232
		+121
	3.	+159
		-253
		-202
Polyethylene 1.	-283	
	+507	
	+631	
	+455	
	+354	
	+414	
	2.	+485
		+579
	3.	+533
		+291
+115		
4.	+255	
	-248	
	-258	
	-278	
	-244	
5.	-267	
	-227	
	+127	
	+122	
	+95	
	+83	

ever, is much smaller than for Type 2. These materials are usually fiber- or filler-reinforced, with phases of distinctly different properties.

**Type 6.** An initial surge of charge appears at a small strain, followed by step increase of Type 2 and reaching a constant value at strains less than half the maximum. The charge decrease at straining reversal is like Type 2, a constant charge value being reached considerably before the strain returns to zero. The materials exhibiting this behavior are moderately to highly heterogeneous.

**Type 7.** This type of behavior, observed thus far for only one type of silicone rubber and a few samples of polyethylene, is characterized by the maximum charge being produced at small initial

strains; thereafter the charge remains constant or decreases slightly until reversal of straining. It then decreases gradually as the strain decreases. The magnitude of charge for this type is considerably higher than for the other types.

Table IV classifies some of the materials tested according to the seven general types of curves. Several significant factors should be noted. Samples of a highly heterogeneous type, such as the fiber-reinforced plastics, or samples in which glassy polymer is blended with an elastomeric material, and certain heterogeneous foam structures (polytetrafluoroethylene, polyethylene) have curves in which the charge increases by steps (Types 2, 5, 6, and 7). These are samples in which two distinct phases or two large agglomerates slip when the sample is strained. The smoothly varying curves usually are for materials which are more homogeneous (Types 1, 3, and 4). Very large hysteresis area

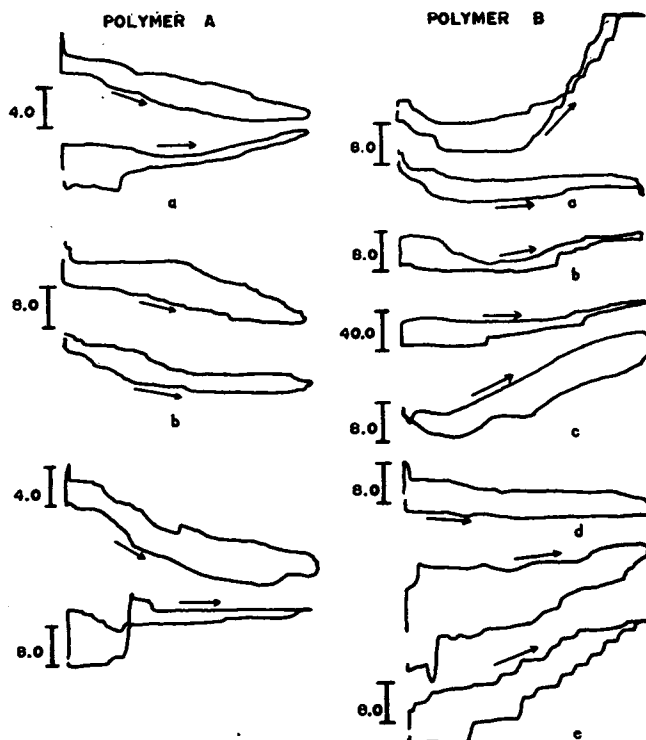


Fig. 9. Hysteresis curves for crystalline polyolefins. The distinctly different behavior between samples with minor variations and the reproducibility for specimens prepared from a uniform sample can be utilized as a comparison method. Scale on the left is in charge units of  $10^{-6}$  esu/cm.<sup>2</sup>. Where the two sample sides differ in hysteresis behavior, a curve is shown for each side. Arrows indicate the increasing strain part of curve.

and the large changes which occur in a limited range of initial strains are produced by the more flexible materials (including some of the elastomers) which are heterophase.

The electromechanical effects observed seem to be strongest where the rheological structure involves interactions between polyphase domains. Such interactions affect observed flow and creep properties and the response of polymers to impact.<sup>3</sup> The most evident case of polyphase domains exists in material containing fillers or reinforcing fibers; less evident phase or quasi-phase structure may be the result of poor compatibility between monomers and of certain polymerization schedules and techniques.

#### Differentiating Plastics

**Single Cycling.** Samples of some series of polymers where a constituent is changed slightly (so that physical properties and appearance remain the same), show distinctly different hysteresis areas and curve shapes. Tables III, V, VI show

the sensitivity to chemical composition, illustrating the sensitivity of this type of comparison method. Figure 9 shows the effect that slightly different processes have on curve shape for two polyolefins.

Comparison of hysteresis areas provides a method for differentiating between materials of very slightly different composition and structure. Use in quality control is possible. A series of laboratory standards for the material in question (which are usually available) may be used to determine a reference set of curves, and the test sample curves are compared against them. This method is relatively easy to carry out and requires far less time than other tests which are routine in many laboratories. The quantity of sample needed, being quite small, is another distinct advantage, and often the sample is undamaged and so may be used in other, e.g., destructive, tests.

**Continuous Cycling.** The manner in which the hysteresis area decreased with number of cycles can be used as a differentiation method for materials with slight composition differences. This method

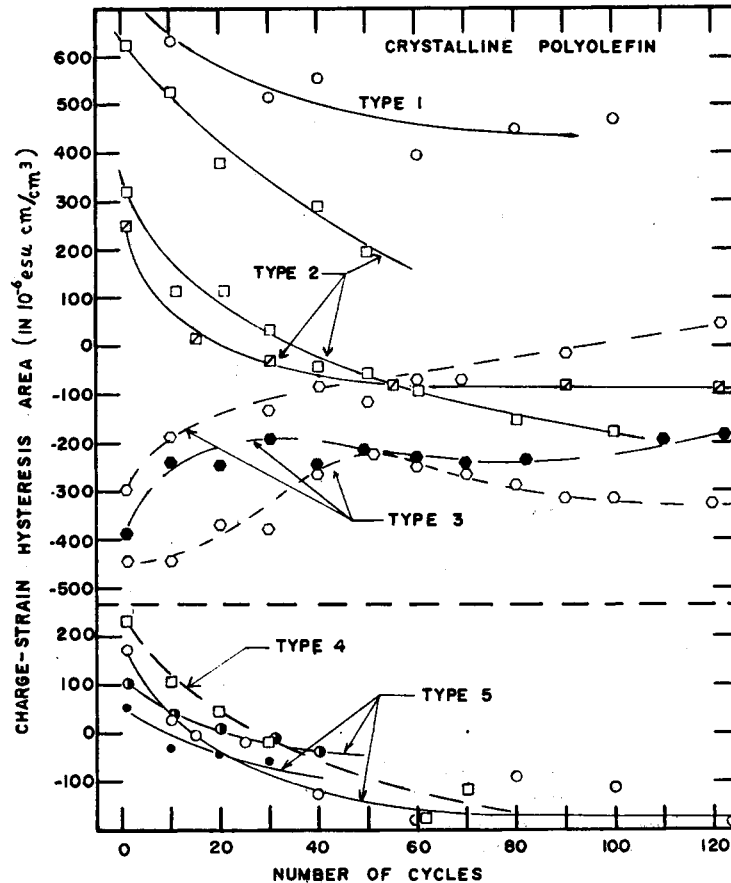


Fig. 10. Decrease of hysteresis area with cycling: crystalline polyolefin.

is usually more definitive for commercial plastic samples than is the method utilizing single hysteresis curves and areas. Figure 10 shows the hysteresis decline for a series of slightly different polyolefins. Figure 11 shows the decline for types of epoxide resin coatings (flexible) which were compounded slightly differently. Figure 12 shows curves of the way in which hysteresis area variation differs for different types of organic binder in bonded mica sheet.

### Flexural Fatigue

A permanent change in the charge-strain hysteresis curves was introduced by cycling the sample without intervening relaxation periods. It is reasonable to suppose that a permanent effect is taking place in the structure and mechanical properties, which is part of the phenomenon of mechanical fatigue. If it can be proved that these two effects are related, then changes in the hysteresis area should provide a means for observing some aspects of the mechanism of very early stages of flexural fatigue. The hysteresis area usually decreased

rapidly toward a steady state value with lower surface charge or even to a reversal of charge sign (after going through zero). Sometimes there was an increase in the hysteresis area (Fig. 12). The usual gradual decline of hysteresis area (Fig. 13) indicates that the fatigue phenomenon in plastics is a very gradual effect that arises because the cyclic variation slowly changes the mechanical (and also electrical) properties. The general features of the hysteresis curves usually did not change except for magnitude. (See Figs. 14 and 15.)

### CONCLUSION

The electromechanical properties observed in amorphous solids are a research tool in associating charge flow characteristics with material flow characteristics. Experimental tools are needed which consider amorphous solids on a microscopic scale, as is theory which relates practical behavior to fundamental properties; the complexity introduced by the statistically arranged structure of plastic materials has limited the number of available investigative techniques. One insight into elec-

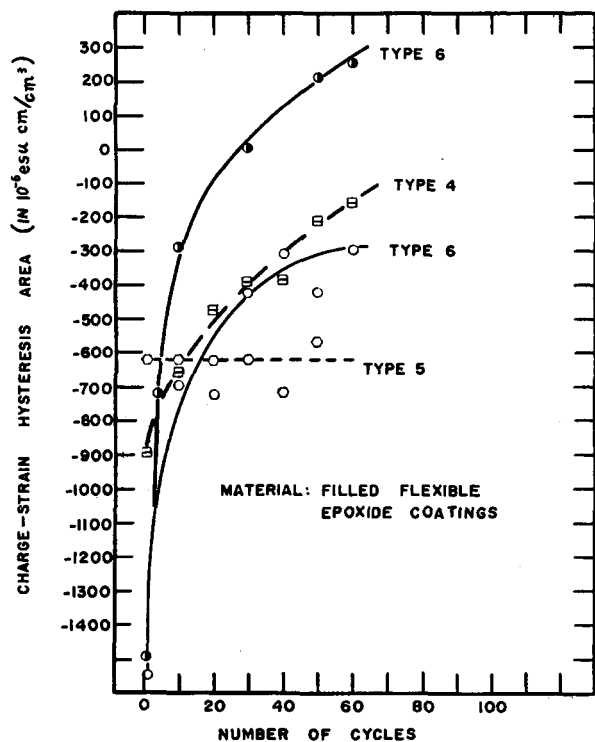


Fig. 11. Hysteresis area decrease with cycling: filled flexible epoxide coatings.

tromechanical relationship is the work of Fitzgerald and Ferry,<sup>1</sup> in which equivalent activation energies have been found for mechanical and electrical flow at higher frequencies. The present hysteresis and electromechanical curve-shape method is a new and distinct approach which offers both fundamental insight into behavior of materials and a number of very practical direct uses in commercial materials processing.

#### SUMMARY

The charge-strain hysteresis curve can be measured by simple apparatus. While fundamental interpretation of the effect may be complex, the use of the curves for practical purposes such as investigation of fatigue, quality control, differentiation between materials or methods of preparation or surface characteristics is simple. The effect shows indication of being related to the chemical nature of the material, its composition and structure, and particularly the phase or quasi-phase structure.

Charge-strain hysteresis curves have been measured. These are quite reproducible if the samples from which specimens are prepared are uniform. The shape of the hysteresis curve is affected by:

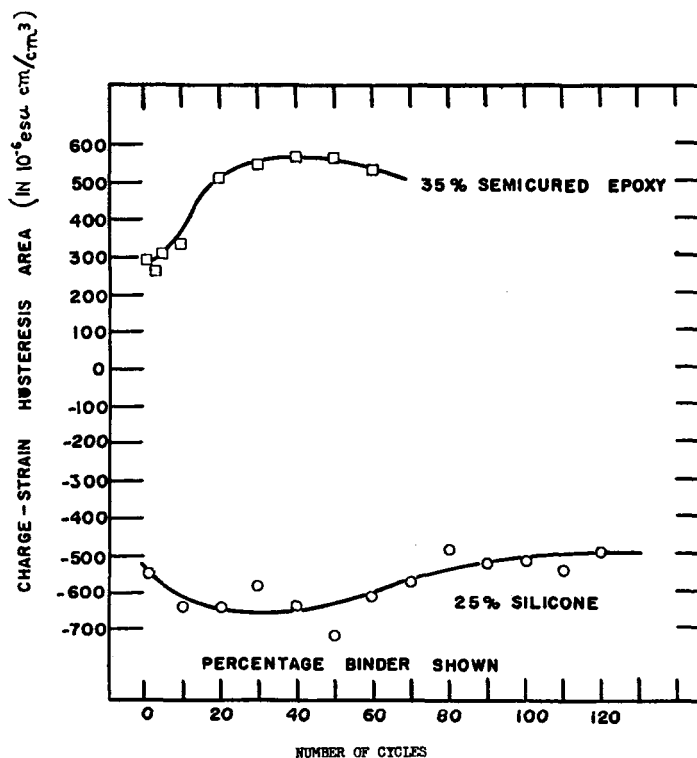


Fig. 12. Hysteresis area decrease with cycling: bonded micas.

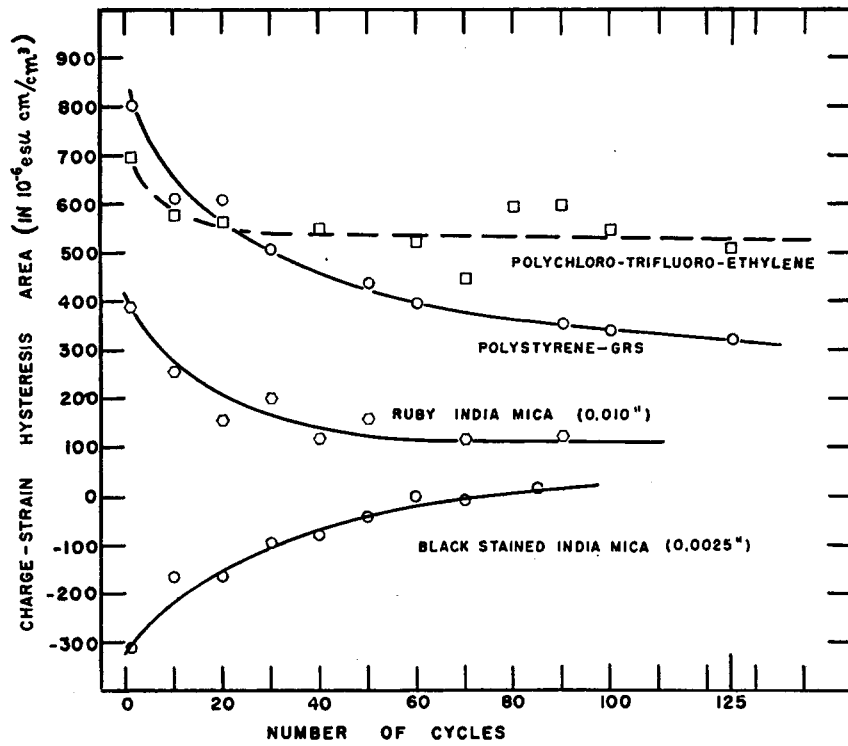


Fig. 13. Hysteresis area decrease with flexural fatigue.

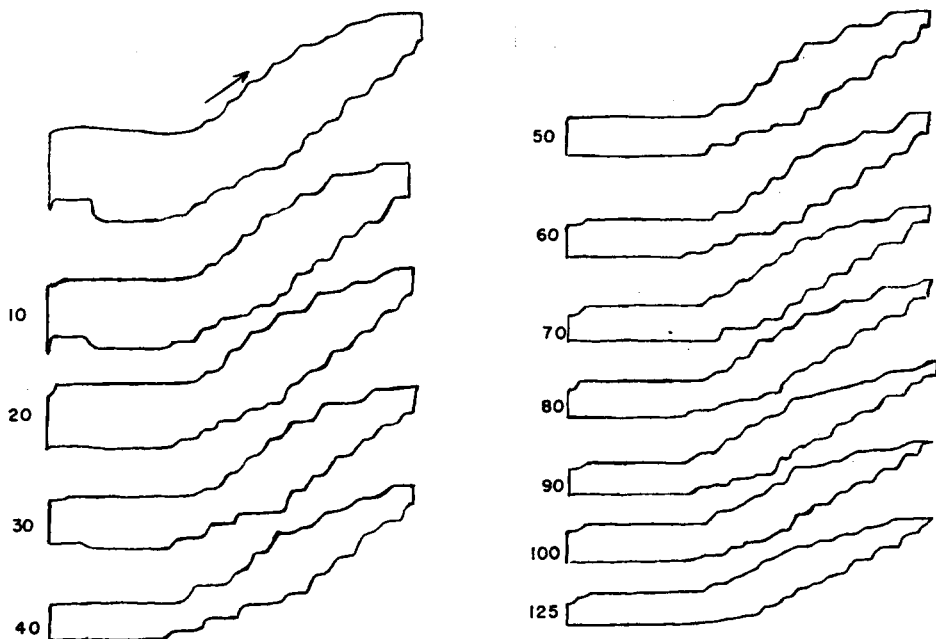


Fig. 14. Flexural fatigue and decrease of the charge-strain hysteresis area. Number of cycles given; note decrease in height with cycling. Numerical decrease in area given in Fig. 13. Material: polystyrene-GRS.

(1) amplitude of strain; (2) rate of straining, including constant strains; (3) the functional dependence of strain upon time; (4) repeated cycling; (5) incorporation of fillers; (6) incorporation of reinforcing fibers; (7) the mechanical properties of the plastic; (8) detailed composition of the polymers; (9) temperature (see appendix).

Seven general types of hysteresis curve are observed. The general features of the curve and the hysteresis area are sensitive to slight changes in composition. This method of sample differentiation is illustrated with examples showing the magnitude and sensitivity of the effect.

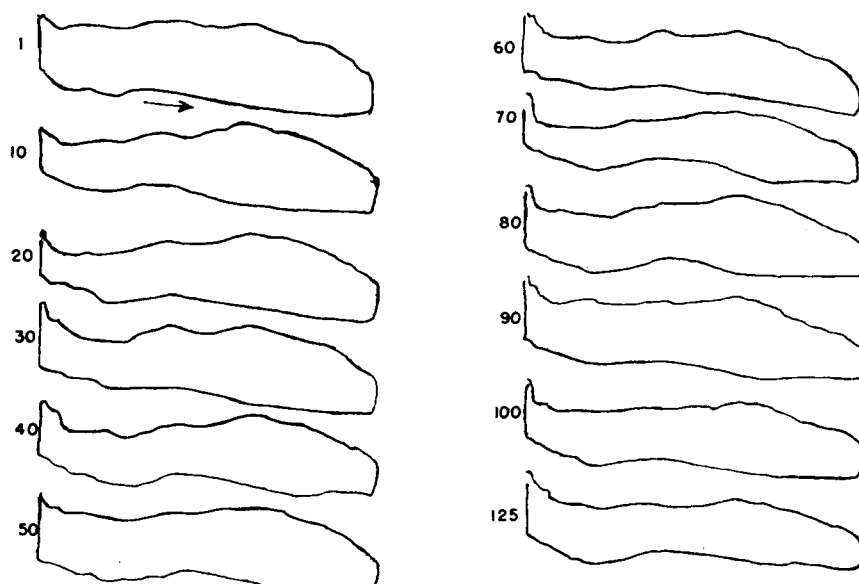


Fig. 15. Flexural fatigue and decrease of the charge-strain hysteresis area. Number of cycles shown; numerical decrease in area given in Fig. 13. Material: polychlorotrifluoroethylene.

When a sample was held at a given strain, the charge decreased; this suggests that both resistivity and the initial stages of mechanical plastic flow may be observed indirectly through this phenomenon. Continuously repeated cycling shows a change in charging-strain response, related apparently to the initial stages of flexural fatigue. A regular decrease of hysteresis area is observed with repeated cycling, with the area decrease depending upon the plastic composition. The rate of decline of the area with repeated cycling is a second method for differentiating between materials, particularly when differences are obscured in other methods of testing.

## APPENDIX. THEORY

The equations characterizing the basic hysteresis curve features will be described. Since no consideration is taken of heterogeneities within the material, smooth curves of Type 1 will be expected. Abrupt changes during increasing or decreasing strain or at strain commencement or reversal will not be explained, since these are due to material heterogeneity. The dependence of hysteresis behavior upon material flexibility is not included since this depends upon the specific nature of charge production by straining, whereas a general

relationship is used herein. Therefore, the general features of an ideal hysteresis curve are described.

Two cases of straining which are most frequently encountered are discussed. The first is a constant strain rate which is periodically reversed. The second is a sinusoidal straining.

### Constant Rate of Strain

#### The Increasing Strain Portion of the Cycle.

Let  $\gamma$  be the strain. Depending upon the type of strain,  $\gamma$  will take different functional forms. The strain results in a charge distribution which is observed at the surface. This charge distribution tends to decrease because of flow through the re-

sistance represented by the strained material. The equivalent resistance of the material is designated by  $R$  and the equivalent capacitance (actual capacitance or depleted layer capacitance) by  $C$ . The charge production is determined by the rate of strain and is set equal to  $\alpha\dot{\gamma}$ .

$$C(dq/dt) = -(q/R) + C\alpha\dot{\gamma} \quad (1)$$

If the plastic is initially uncharged,

$$\gamma = \beta t$$

$$q = \alpha\dot{\gamma}RC(1 - \exp\{-t/RC\}) \quad 0 \leq t \leq t_0 \quad (2)$$

where  $t_0$  is the time of strain stopping or reversal. The amplitude of the strain is  $\dot{\gamma}t$ , and therefore the charge for a given amplitude increases as the rate of distortion increases, as is experimentally observed. Physically this occurs because the distortion produces the charge in a smaller time and therefore less time is available for neutralizing flow.

**The Decreasing Strain Portion of the Cycle.** If the direction of strain is reversed at time  $t_0$ , the charge observed at that instant is that given by eq. (2), and both  $q$  and  $t$  are given the subscript zero. From this moment on, eq. (1) must be replaced by

$$C(dq/dt) = (-q/R) - \alpha C\dot{\gamma} \quad (3)$$

since the strain is now in the opposite direction and tends to cancel the charges previously produced. Therefore,

$$\gamma = \beta(2t_0 - t) \quad t_0 \leq t \leq 2t_0 \quad (4)$$

$$q = \alpha\dot{\gamma}RC[-1 - \exp\{-t/RC\} - 2 \exp\{-(t - t_0)/RC\}]$$

When the strain has again become zero there is a residual charge value and, hence, the value does not return to its original value.

$$q = -\alpha\dot{\gamma}RC(1 - \exp\{-t_0/RC\})^2 \quad (5)$$

The negative value is indicative of a hysteresis curve. The moment at which zero charge was present, before the return of strain to zero, was

$$t = RC \ln [2 \exp\{t_0/RC\} - 1] \quad (6)$$

which for slow distortion ( $t_0/RC \gg 1$ ) this is ( $t_0 + RC \ln 2$ ), and for rapid distortion ( $t_0/RC \ll 1$ ) it is nearly  $2t_0$ . Rapid distortion and recovery permit little charge to flow in charge relaxation.

**Constant Strain.** If the strain is kept constant, no charge production is observed, but rather, there is a decay in the total amount of charge (see ex-

perimental discussion). When time is  $t_1$  and  $\dot{\gamma}$  is zero,

$$C(dq/dt) = -q/R$$

$$\text{and} \quad q = q_1 \exp\{-(t - t_1)/RC\} \quad (7)$$

### Sinusoidal Strain

**The Area of the Hysteresis Curve.** A sinusoidal straining is of practical interest and results in less complicated expressions for the area of the curve:

$$\gamma = \sin bt$$

$$\dot{\gamma} = b \cos bt \quad (8)$$

Equation (1) is now valid throughout the successive cycles, except for the charge present at the beginning of each cycle, and

$$q = \alpha b \frac{RC \sin(bt + \theta)}{(1 + b^2R^2C^2)^{1/2}} + \exp\{-t/RC\} \phi(\alpha, b, R, C) \quad (9)$$

where

$$\cot \theta = bRC$$

in which the last term rapidly becomes negligible during continuous cycling. The area of the hysteresis loop is

$$A = \pi b^2 \alpha R^2 C^2 / (1 + b^2 R^2 C^2) \quad (10)$$

There is also present the usual phase lag which accompanies hysteresis.

**Change in Hysteresis Curve Area with Number of Deformations.** The type of change in area of hysteresis curve with repeated flexing should be roughly equivalent in sinusoidal and in constant rate periodic flexing. Repeated flexing causes two general types of effects. The first is increase of temperature, and the second is mechanical flow or creation of defects. It may be assumed that, in eq. (10), the defects affect the factor  $\alpha$ , and therefore the rate of production of charge. Since the generation of charge is most likely a result of the deformation of material, i.e., of the temporary or permanent flow of material over or against material with which it was formerly not in contact, it is functionally related to the viscosity of the material, e.g.,

$$\alpha = p\eta$$

where  $p$  is a constant. Additional considerations must be included if the overall sample is heterogeneous, for example, through the inclusion of reinforcing material.

The resistivity of the material, in general, is an exponential function of temperature, and the viscosity is a similar function of temperature. "In plastic solids the rate at which cohesive flow of chain segments past one another takes place is . . . given by an exponential function,  $\lambda = B \exp \{V/kT\}$ ."<sup>3</sup> Accordingly,

$$R = R_0 \exp \{B/kT\} \quad (11)$$

and

$$\eta = \eta_0 \exp \{D/kT\} \quad (11)$$

so that

$$\Delta R = -(RB/kT^2)\Delta T \quad (12)$$

and

$$\Delta \alpha = -(\alpha D/kT^2)\Delta T \quad (12)$$

It is possible, therefore, to consider the change in the area of the hysteresis curve as being directly or indirectly caused by the change in temperature resulting from the flexing. The component which causes change in electrical resistance is probably reversible, whereas that which causes change in viscosity is probably irreversible, in that the material flow is not retrieved when the ambient temperature is again attained, and a period of rest at ambient temperature is given the sample.

By eq. (10), the change in area of the hysteresis curve is:

$$\begin{aligned} A &= \frac{2\pi\alpha RC^2b^2}{(1+b^2R^2C^2)^2} \Delta R + \frac{\pi R^2C^2b^2}{1+b^2R^2C^2} \Delta \alpha \quad (13) \\ &= \frac{-\pi\alpha R^2C^2b^2[2B+D(1+b^2R^2C^2)]}{(1+b^2R^2C^2)^2kT^2} \Delta T \end{aligned} \quad (13')$$

At any moment, the increase in temperature is given by

$$\rho\tilde{C}\Delta T = nQ - n(2\pi/b)K\Delta T \quad (14)$$

in which the term on the left represents the total heat received and retained by the plastic,  $Q$  is the heat dissipated in the plastic per cycle, and  $n$  is the number of deformation cycles which have taken place.  $K$  is the constant in Newton's law of cooling. Thus,

$$\Delta T = nQ/[\tilde{C}\rho + (2\pi nK/b)] \quad (15)$$

If it is assumed that the heat dissipation in the

material is primarily resistive dissipation from the current flow,

$$Q = \oint i^2 R dt = \frac{\pi\alpha^2 R^3 C^2 b^2}{b(1+b^2R^2C^2)} \quad (16)$$

Substituting eq. (16) into eq. (15) and the latter into eq. (13), we obtain

$$\Delta A = -fn/(g+hn) \quad (17)$$

where

$$f = [2B + D(1 - b^2R^2C^2)]A^3$$

$$g = \pi bRC kT^2 \rho\tilde{C}$$

$$h = 2\pi^2RCkT^2K$$

The experimental curves show a dependence of area upon the number of flexures similar to that of eq. (17), and in many cases the agreement is precise. If the two independent constants are calculated from two points, the best curve passing through the experimental points may be obtained from eq. (17). For complete generality, other factors may need to be included; however, their inclusion should alter the general functional form of the relation (17) only slightly if agreement with experiment is to be retained.

**Slope Decrease with Cycling.** The effect of successive cycles heating the material is seen by differentiating eq. (9), neglecting the last term.

$$dq/d\gamma = \left[ \frac{\alpha R^2 C^2 b^2}{(1+b^2R^2C^2)} \right] \left[ \frac{\cos(bt+\theta)}{\cos bt} \right] \quad (18)$$

In the case of  $R^2C^2b^2 \gg 1$ ,

$$\frac{dq}{d\gamma} = \alpha \frac{b \cos(bt+\theta)}{\cos bt}$$

For small quantities of heat produced (small number of cycles),  $\alpha$  decreases.  $\alpha$  for the cycle in question is  $\alpha_0 + \Delta\alpha$ . From eq. (12)  $\Delta\alpha$  is negative and increases in magnitude with temperature rise. Experimental data show that  $\alpha$  decreases with continuous cycling.

## Discussion

This theoretical treatment has described the general features of the charge-flexural strain hysteresis curves and has not taken material structural features into account. It shows correspondence with the following experimentally observed behavior.

(a) If a sample is flexed, a charge density is observed which increases with increased amplitude of flexing.



(b) If the amplitude of flexing is doubled, the charge increases but is not doubled.

(c) If a sample is maintained at constant strain, the charge on the surface diminishes.

(d) Slower rate of straining decreases the charge attained at maximum strain, and more rapid straining increases this charge.

(e) The phase lag which is usual in the hysteresis type of experiment is predicted.

(f) It is predicted that the charge does not return to zero at the same time as the strain. Each succeeding cycle will start at a lower initial charge value than the preceding one.

(g) The hysteresis area decreases with an increase in the number of cycles. Functional form and values of the decrease are represented by the relationships derived.

(h) It is shown that the average slope of the hysteresis curve decreases with continuous cycling.

The plausible direct relationship between hysteresis area decrease and the initial stages of fatigue indicates that the tendency for a material to fatigue can be coupled to a set of fundamental properties of the material. These include the equivalent resistance and capacitance, heat capacity and cooling constant for the material, and the activation energies for charge and material flow, in addition to the ambient temperature and frequency of cycling. Effect of phase boundaries will add terms dependent upon differences in the properties of the respective phases.

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## Synopsis

The charge-strain hysteresis curve can be measured by simple apparatus. While fundamental interpretation of the effect may be complex, the use of the curves for practical purposes such as investigation of fatigue, quality control, differentiation between materials or methods of preparation or surface characteristics, is simple. The effect shows indication of being related to the chemical nature of the material, its composition and structure, and particularly the phase or quasi-phase structure. Charge-strain hysteresis curves have been measured. These are quite reproducible if the samples from which specimens are prepared are uniform. The shape of the hysteresis curve is affected by (1) amplitude of strain, (2) rate of straining, including constant strains, (3) the functional dependence of strain upon time, (4) repeated cycling, (5) incorporation of fillers, (6) incorporation of reinforcing fibers, (7) the mechanical properties of the plastic, (8) detailed composition of the polymers, and (9) temperature. Seven general types of hysteresis curve are observed. The general features of the curve, and the hysteresis area are sensitive methods for detecting slight changes for composition. This method of sample differentiation was illustrated with examples showing the magnitude and sensitivity of the effect. When a sample was held at a given strain, the charge decreased; this suggests that both resistivity, and the initial stages of mechanical plastic flow may be observed indirectly through this phenomenon. Continuously repeated cycling shows a change in charging-strain response related apparently to the initial stages of flexural fatigue. A regular decrease of hysteresis area is observed with repeated cycling, with the area decrease depending upon the plastic composition. The rate of decline of the area with repeated cycling is a second method for differentiating between materials, particularly when differences are obscured in other methods of testing.

## Résumé

La courbe d'hystérésis charge-élongation peut être mesurée au moyen d'un appareillage simple. Alors que l'interprétation fondamentale de l'effet peut être complexe, l'emploi des courbes dans un but pratique tel que l'étude de la fatigue, le contrôle de la qualité, l'étude de la différence existante entre différents matériaux, les méthodes de préparation ou la nature de la surface, est simple. L'effet donne une indication qui est reliée à la nature chimique du matériau, à sa composition et à sa structure et particulièrement à la structure de la phase ou de la quasi-phase. On a

mesuré les courbes d'hystérésis charge-élongation. Elles sont tout à fait reproductibles si les échantillons, à partir desquels on prépare les spécimens, sont uniformes. La forme de la courbe d'hystérésis est modifiée par l'amplitude de la tension, la vitesse de la tension, y compris les tensions constantes, la dépendance fonctionnelle de la tension sur le temps, le recyclage, l'incorporation de substance de charge, l'incorporation de fibres de renforcement, les propriétés mécaniques du plastique, la composition détaillée des polymères et la température. On a observé six types généraux de courbe d'hystérésis. Les caractéristiques de la courbe et de la surface de l'hystérésis sont des méthodes sensibles pour détecter de faibles changements de composition. Cette méthode de différenciation a été illustrée par des exemples montrant l'importance et la sensibilité de l'effet. Lorsqu'un échantillon a été maintenu à une tension donnée, la charge diminue; cela montre que la résistance et la mise en oeuvre initiale de l'écoulement mécanique du plastique peuvent être indirectement observés au moyen de ce phénomène. Un recyclage répété montre un changement dans le réponse de la tension de charge apparemment reliée à la mise en oeuvre initiale de la fatigue due aux flexions. On observe une diminution régulière de la surface d'hystérésis avec le recyclage répété, ainsi qu'une diminution de la surface dépendant de la composition du plastique. La vitesse de diminution de la surface avec le recyclage répété est une seconde méthode pour différencier les matériaux, spécialement lorsque ces différences sont masquées dans le cas des autres méthodes d'investigation.

### Zusammenfassung

Die Verformungs-Hysteresiskurve bei Belastung kann mit einem einfachen Apparat aufgenommen werden. Während eine grundlegende Behandlung des Effektes schwierig ist, ist die Verwendung der Kurven für praktische Zwecke wie Untersuchung der Ermüdung, Qualitätskon-

trolle, Unterscheidung zwischen Materialien oder Darstellungsmethoden oder Oberflächencharakterisierung einfach. Der Effekt scheint mit der chemischen Natur des Materials, seiner Zusammensetzung und Struktur und besonders mit dem Phasen- oder Quasiphasenaufbau in Beziehung zu stehen. Verformungs-Hysteresiskurven bei Belastung wurden gemessen. Sie sind reproduzierbar, wenn die für die Proben verwendeten Materialien einheitlich sind. Die Form der Hysteresiskurve wird beeinflusst durch: (1) Verformungsamplitude, (2) Verformungsgeschwindigkeit, (3) funktionelle Abhängigkeit der Verformung von der Zeit, (4) Wiederholung der Cyclen, (5) Einbau von Füllstoffen, (6) Einbau von Verstärkerfasern, (7) mechanische Eigenschaften, (8) genaue Zusammensetzung der Polymeren und (9) Temperatur. Es wurden sieben allgemeine Typen von Hysteresiskurven beobachtet. Das allgemeine Aussehen der Kurve sowie die Hysteresisfläche stellen ein empfindliches Mittel zur Auffindung geringer Zusammensetzungsänderungen dar. Diese Methode zur Unterscheidung von Proben wurde mit Beispielen für die Grösse und Empfindlichkeit des Effektes belegt. Wurde die Probe bei einer bestimmten Verformung gehalten, so nahm die Spannung ab; dies deutet darauf hin, dass sowohl der Widerstand als auch die Anfangsstadien des mechanischen, plastischen Fließens durch diese Erscheinung indirekt beobachtet werden können. Bei fortlaufend wiederholten Cyclen ändern sich die Spannungs-Verformungs-Verhältnisse, was offenbar in Beziehung zu den Anfangsstadien der Biegsamkeitsermüdung steht. Es wird eine regelmässige Abnahme der Hysteresisfläche bei wiederholten Cyclen beobachtet; die Flächenabnahme ist von der Zusammensetzung des plastischen Stoffes abhängig. Die Geschwindigkeit der Flächenabnahme bei wiederholten Cyclen ist ein weiteres Mittel zur Unterscheidung von Materialien, wenn die nach anderen Testmethoden ermittelten Unterscheidungsmerkmale unklar sind.

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