Studies of Polymer Electrets. III. Charge Decay Behavior in Polar Polymer Homoelectrets

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Synopsis

Charge stabilities of various polar polymer homoelectrets were determined. Although these electrets are reasonably stable in dry environments, they rapidly discharge when exposed to humidity. The rate of charge decay was found to depend directly on the ability of these polymers to absorb water under equilibrium conditions. Protection from humidity is obtained if these polar polymers are coated on both sides with nonpolar polymers. If, however, two different polymer films are laminated, the electret behavior follows a pattern that can be explained on the basis of charging at the interface. Difference in stabilities of the electrets of polar and nonpolar polymers is attributed to the differing natures of the charge traps present in these two classes of polymers.

INTRODUCTION

Investigations of homoelectrets derived from polyolefins[1] and polystyrenes[2] have shown that the charged particles are stabilized through interaction with chemical functional groups. Discharge of the electrets of the nonpolar polymers have been found to depend mostly on thermally activated processes. However, if the charge sites themselves are modified, then nonthermal discharge can take place. For example, in the cases of γ-ray-irradiated polyethylene[1] and polystyrene containing electron-acceptor impurities,[2] the charge sites are modified, so that they do not stabilize the charged particles to the same extent. Rather, the most dramatic result is that they rapidly discharge under humid conditions.

This behavior is also exhibited by the electrets obtained from polar polymers. We therefore became interested in finding out why humidity is so deleterious in these systems and if its harmful effects could be minimized.
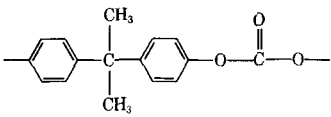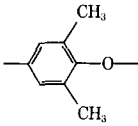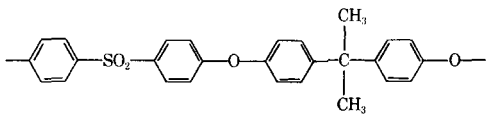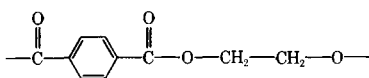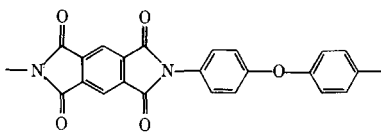
EXPERIMENTAL
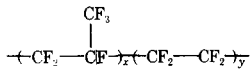
Table I lists the materials studied in this work.

The following laminates were prepared by mold pressing of the materials at a temperature where the lower melting material could be made to flow under pressure: polyethylene/polyimide laminate: 4 mils PE/1 mil PI; polyethylene/polyimide/polyethylene laminate: 4 mils PE/1 mil PI/4 mils PE; polyimide/polycarbonate laminate: 1 mil PI/5 mils PC.

Polymer films were coated with commercial polystyrene material from a 5% solution of polystyrene (general purpose) in a 1:1 mixture of chloroform and toluene by dipping, followed by slow withdrawal. The coated films were hung to dry, and the residual solvents were removed at 60°C/vacuum for 24 h.

Preparation and charge stability determination of the electrets were performed by following the methods described earlier.[1]

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TABLE I
Materials Used in This Work

Common name	Chemical structure	Supplier/other characteristics
Polycarbonate (PC)	structure: bisphenol A carbonate unit with CH₃ groups on central C and O—C(=O)—O	General Electric, 15-mil-thick sheet
Poly(phenylene oxide)	2,6-dimethylphenylene oxide unit (CH₃ groups, —O—)	General Electric, mold pressed, 15-mil-thick sheet
Polysulfone	—C₆H₄—SO₂—C₆H₄—O—C₆H₄—C(CH₃)₂—C₆H₄—O—	1C1, mold pressed, 15-mil-thick sheet
Mylar	—C(=O)—C₆H₄—C(=O)—O—CH₂—CH₂—O—	du Pont, 1-mil-thick film
Polyimide (P1)	pyromellitic diimide unit —N(CO)₂C₆H₂(CO)₂N—C₆H₄—O—C₆H₄—	du Pont, 1-mil-thick film
Kapton HF	polyimide (P1)/fluorinated ethylene–propylene copolymer (FEP) laminate	du Pont, 1.5-mil-thick film; 1 mil Pl/0.5 mil FEP
Polyethylene (PE)	—CH₂—CH₂—	Johnston Plastics, Toronto, 10-mil extruded sheet
Teflon FEP	$+CF_2-CF(CF_3)+_x+CF_2-CF_2+_y$	du Pont, type A, 1-mil-thick film

Aluminum was deposited on the polymer films by the standard vacuum deposition technique.

Temperatures are in degrees Celsius.

RESULTS AND DISCUSSION

If the chemical functional groups are important in the formation and stability of polymer electrets, the most obvious sites for charge trapping in polar polymers should be the dipolar groups present in these molecules. It stands to reason that dipolar water molecules should also interact with these dipolar groups, and this should be reflected by the amount of water that these polymers can absorb under equilibrium conditions.

Table II lists the polymers in order of their water adsorption abilities. Tables III to VII list the charge decay characteristics of the electrets of these polymers.

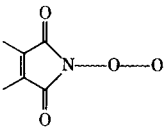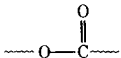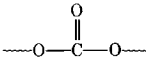TABLE II
Water Absorption by Polar Polymers
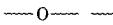
Polymer	Dipolar group	% Water absorption[3] in 24 h
Polyimide		2.90 (film)
Mylar		0.80 (film)
Polysulfone	—SO$_2$—O—	0.43
Polycarbonate		0.15
Poly(phenylene oxide)	—O— —	0.07

TABLE III
Charge Decay Characteristics of Polycarbonate Electrets (Thickness 15 mils)

Time, Days	Room temperature, dry		Room temperature, 98% relative humidity	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	1200	1.00	1150	1.00
1	1170	0.98	950	0.83
5	1150	0.96	700	0.61
10	1150	0.96	650	0.57
15	1140	0.95	460	0.40
25	1140	0.95	400	0.35
100	1140	0.95	180	0.16
125	1120	0.93	140	0.12
160	1080	0.90	—	——

TABLE IV
Charge Decay Characteristics of Poly(phenylene Oxide) Electrets (Thickness 15 mils)

Time, days	Room temperature, dry		Room temperature, 98% relative humidity	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	1500	1.00	1200	1.00
1	1420	0.95	1070	0.89
4	1350	0.90	940	0.78
10	1200	0.80	750	0.63
40	1100	0.73	650	0.54
60	1020	0.68	600	0.50
100	1020	0.68	540	0.45
130	1000	0.67	—	—
200	1000	0.67	—	—

TABLE V
Charge Decay Characteristics of Polysulfone Electrets (Thickness 15 mils)

Time, days	Room temperature, dry		Room temperature, 98% relative humidity	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	1800	1.00	1400	1.00
1	1700	0.94	1000	0.71
5	1350	0.75	400	0.29
60	710	0.39	180	0.13
80	650	0.36	90	0.06

The charge decay rates of these polymer electrets under 98% relative humidity are plotted against time in Figure 1. It shows that the rate follows the order poly(phenylene oxide) < polycarbonate < polysulfone < Mylar $\cong$ polyimide, indicating that charge decay and water absorption are directly related.

It is reasonable to assume that the discharge of polar polymer electrets caused by moisture is through dipole–dipole interaction of water and the polar functional groups, which in turn are the sites where the charged particles are trapped.

Obviously, similar mechanism should operate in the case of charge-transfer complexes produced in the styrene polymers[2] and γ-ray irradiation of polyethylene.[1] It seems, therefore, that groups that have charged characteristics, such as dipoles, charge-transfer complexes, etc., do not give rise to stable electrets, especially in presence of water. In contrast, stable interaction seems to arise between charged particles and molecular orbitals derived from n- and π-electrons, as in the case of polyolefins, polyfluoroolefins, and polystyrenes.

At this stage, we became interested in improving the charge stabilities of polar polymer electrets by protecting one or both sides of the polymer film by means of lamination or coating with another polymer. We selected polyimide as the

TABLE VI
Charge Decay Characteristics of Polyimide Electrets (Thickness 1 mil)

Time, days	Room temperature, dry		Room temperature, 98% relative humidity	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	500	1.00	500	1.00
1	350	0.70	10	0.02
2	270	0.54	—	—
30	230	0.46	—	—
60	190	0.38	—	—

TABLE VII
Charge Decay Characteristics of Mylar Electrets (Thickness 1 mil)

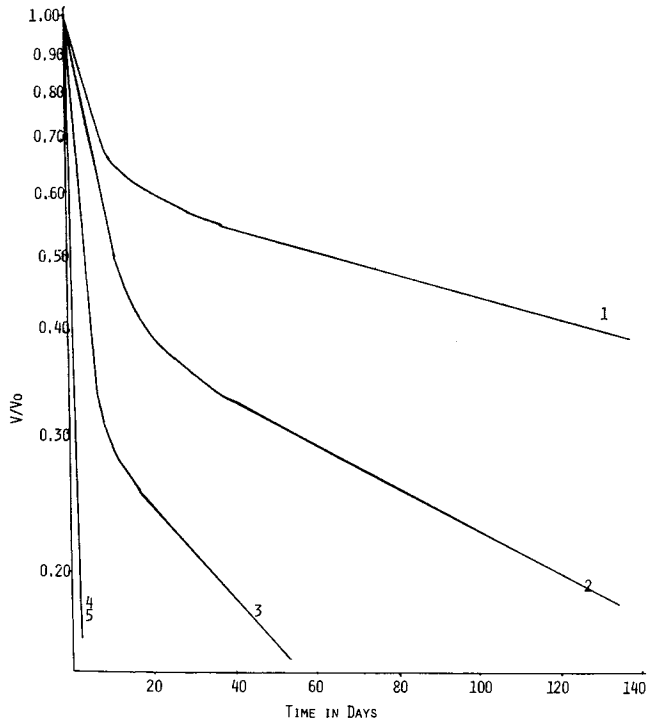| Time, days	Room temperature, dry		Room temperature, 98% relative humidity	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	600	1.00	600	1.00
1	450	0.75	100	0.17
5	270	0.45	20	0.03
60	110	0.18	—	—

Fig. 1. Charge decay characteristics of polar polymer electrets under 98% relative humidity and room temperature: 1, poly(phenylene oxide); 2, polycarbonate; 3, polysulfone; 4, Mylar; 5, polyimide.

target polymer, because it produces the least stable electret.   Under humid conditions, polyimide electrets discharge overnight.   Table VIII shows that a slight improvement in the stabilities of the electrets is achieved when polyimide is laminated with polycarbonate; but a comparison between Tables VIII and III indicates that the charge decay characteristics of the composite electret is similar to that of polycarbonate electrets, and therefore very little charge is left in the polyimide portion of the laminate.

From the above result, one would think that lamination with polyimide-like material might improve physical properties such as flexural strength, creep, etc., of stable electret-producing nonpolar polymers such as polyethylene, Teflon FEP,

TABLE VIII
Charge Decay Characteristics of Polyimide/Polycarbonate (1 mil/4 mils) Electrets[a]

Time, days	Polyimide side negatively charged		Polyimide side positively charged	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	1600	1.00	1100	1.00
1	1300	0.81	1050	0.95
2	1100	0.69	850	0.77
7	900	0.56	750	0.68
21	650	0.41	560	0.51
35	550	0.34	520	0.47
75	400	0.25	360	0.33
135	250	0.16	200	0.18

[a] Environment: room temperature, 98% relative humidity.

etc., without adversely affecting their electret charge decays. Unfortunately, however, this was found not to be the case, as shown in Tables IX and X. Polyimide is adversely affecting the behavior of the composite electrets.

On the other hand, if polyimide is protected on both sides by nonpolar materials such as polyethylene and polystyrene, the charge decay is controlled by the materials on the outside surface as shown in Tables XI and XII. This is not surprising, because in this situation, polyimide is not directly exposed to the atmosphere.

The most interesting laminate for our present study has been presented by du Pont's Kapton HF, a laminate of Teflon FEP, and polyimide. Teflon FEP is one of the best electret material, and we wanted to see why lamination with polyimide affects it electret behavior.

TABLE IX

Charge Decay Characteristics of Polyimide/Polyethylene (1 mil/4 mils) Electrets[a]

Time, days	Polyimide side negatively charged		Polyimide side positively charged	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	700	1.00	800	1.00
1	430	0.61	530	0.66
2	350	0.50	410	0.51
7	310	0.44	280	0.35
21	240	0.34	190	0.24
35	210	0.30	120	0.15

[a] Environment: room temperature, 98% relative humidity.

TABLE X

Charge Decay Characteristics of Polyimide/FEP (1 mil/0.5 mil) Electrets[a]

Time, days	Polyimide side negatively charged		Polyimide side positively charged	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	600	1.00	700	1.00
1	650	1.08	1100	1.57
9	400	0.67	750	1.07
26	370	0.62	570	0.81
54	300	0.50	450	0.64
87	250	0.42	400	0.57
147	250	0.42	350	0.50

[a] Environment: ambient conditions.

TABLE XI

Charge Decay Characteristics of Polyethylene (10 mils) and Polyethylene/Polyimide/
Polyethylene (4 mils/1 mil/4 mils) Electrets[a]

Time, days	Polyethylene (10 mils)		Laminate (9 mils)	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	1300	1.00	1300	1.00
3	1250	0.96	1250	0.96
10	1200	0.92	1200	0.94
24	1200	0.92	1200	0.92
38	1200	0.92	1200	0.92
70	1150	0.88	1190	0.92

[a] Environment: room temperature, 98% relative humidity.

TABLE XII
Charge Decay Characteristics of Polystyrene and Polystyrene-Coated Polyimide Electrets[a]

Time, days	Commercial polystyrene (5 mils)		Polyimide coated with polystyrene (1 mil)	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	1400	1.00	900	1.00
1	630	0.45	350	0.39
3	330	0.24	240	0.27
13	180	0.13	145	0.16
30	140	0.10	85	0.09

[a] Environment: room temperature, 98% relative humidity.

Table XIII shows that in FEP electrets, negative charge carriers are preferred. In experiments with FEP and FEP/PI laminates, we have allowed the higher initial charge to dissipate without wrapping the laminates with an aluminum foil, because we considered the higher initial driving voltage would allow us to notice any real difference much more clearly. We also used films metalized with aluminum on one side to see whether unipolar homoelectrets differ from bipolar homoelectrets with respect to charge decay processes.

TABLE XIII
Charge Decay Characteristics of FEP/Aluminum (1 mil) under Ambient Conditions

Time, days	FEP side negatively charged		FEP side positively charged	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	2000	1.00	1600	1.00
4	1900	0.95	1280	0.80
11	1720	0.86	650	0.41
25	1540	0.77	—	—
60	1260	0.63	—	—

TABLE XIV
Charge Decay Characteristics of FEP/PI Laminate (1.5 mils) under Ambient Conditions

	FEP/PI Laminate							
	FEP side positively charged				FEP side negatively charged			
Time, days	PI(−)		FEP(+)		FEP(−)		PI(+)	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	3700	1.00	3700	1.00	3700	1.00	3600	1.00
6	3000	0.81	3000	0.81	2700	0.73	2700	0.75
14	2700	0.73	2700	0.73	2600	0.70	2570	0.71
34	2550	0.69	2510	0.68	2500	0.68	2400	0.67
62	2200	0.60	2200	0.60	2100	0.57	2000	0.56

	FEP/PI/Aluminum				PI/FEP/Aluminum			
Time, days	FEP(+)		FEP (−)		PI(+)		PI(−)	
	Voltage (V)	V/V_0	Voltage (V)	V/V_0	Voltage (V)	V/V_0	Voltage (V)	V/V_0
0	3200	1.00	3200	1.00	3000	1.00	2500	1.00
6	2500	0.78	2400	0.75	2500	0.83	1900	0.76
14	2300	0.72	2100	0.66	2350	0.78	1700	0.68
34	2100	0.66	2000	0.63	2250	0.75	1600	0.64
62	1900	0.59	1700	0.53	2050	0.68	1100	0.44

(a)

−1380 | FEP / P1 | +1300 → peeling → +1100 FEP −850 ; −300 P1 +270

+1200 FEP / P1 −1150 → peeling → −300 FEP +1100 ; +310 P1 −210

(b)

−620 FEP / P1 +820 → peeling → +1400 FEP +1150 ; 0 P1 +240

+580 FEP / P1 −530 → peeling → +750 FEP +1380 ; +270 P1 +100

(c)

−300 FEP / P1 +700 → peeling → +500 FEP −300 ; −220 P1 −140

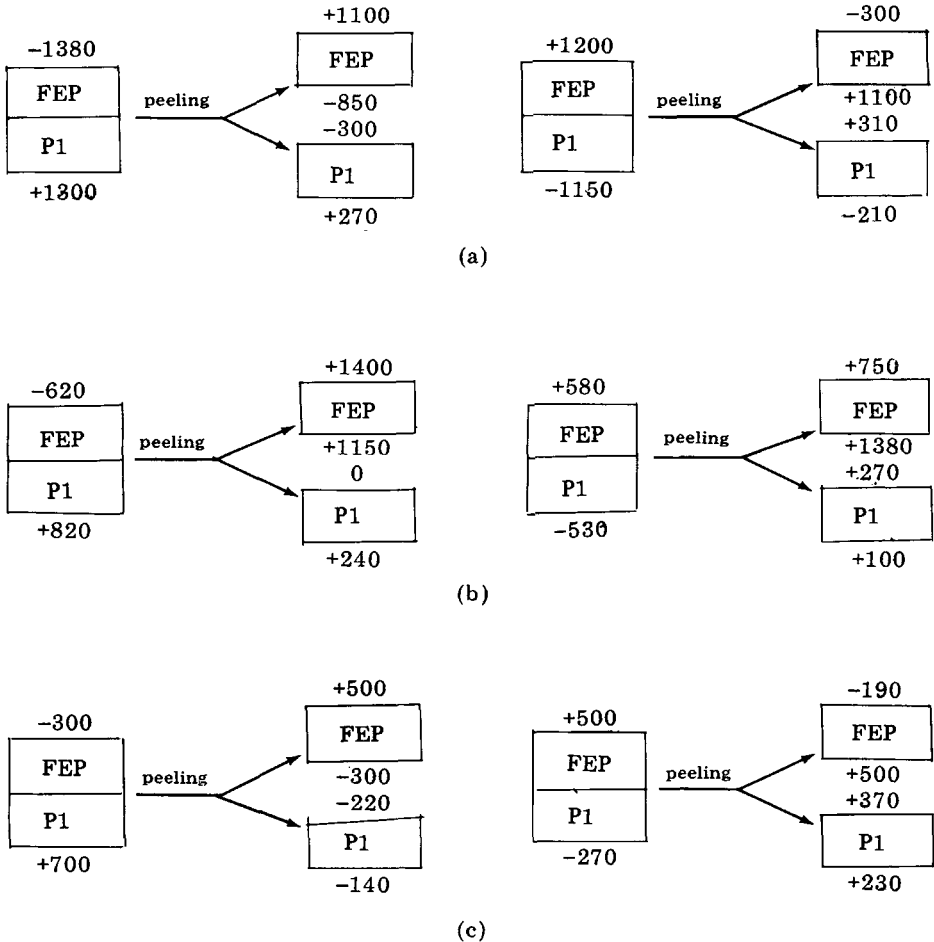+500 FEP / P1 −270 → peeling → −190 FEP +500 ; +370 P1 +230

Fig. 2. Distribution of charges on PI and FEP films after they are peeled off at ambient conditions from FEP/PI electrets (average of three samples). (a) Immediately after charging followed by wrapping with an aluminum foil. (b) After samples in (a) have been aged for three days/dry box. (c) After samples in (a) have been aged for three days/98% relative humidity. Values are in volts as measured by the chopper method.[1]

In Table XIV, it can be seen that FEP/PI laminate behaves like a single entity, and it does not have any directional sense with regard to positive and negative charge carriers.

Results from Tables X and XIV, when compared to those in Table XIII, indicate that polyimide plays an important part of the FEP/PI laminate electret, and probably charge development and decay in FEP and FEP/PI electret systems are different. We therefore decided to physically peel off the FEP and PI parts from FEP/PI laminate electrets and see how the charges are distributed in each component. Figure 2 shows the results.

Sectioning of polymer electrets has been done before[4] to determine the spatial distribution of space charges and dipole orientation inside these materials. In these experiments, sectioning was done with a thin circular saw, care being taken not to heat up the samples. It was noticed that the amount of frictional charging found was negligible, and a good estimate of charge distribution inside these

materials could be made by studying the thermally stimulated discharge (TSD) spectrum of the various sections of the original electret.

Peeling of two polymer films from their laminate electrets can be considered as a process similar to sectioning, except that in the peeling, sectioning of two dissimilar polymers is performed at the interface. Still, there is a real possibility that the two films when pulled apart can be recharged if the field strength near the interface just being destroyed exceeds the breakdown voltages. The speed of the peeling, thickness of the films, as well as the charge density of the laminate electret would likely determine this behavior.

Our peeling experiments can at best be described in qualitative terms, since we measured only the surface voltages, not the total charge contents of these materials by TSD techniques. However, the following observations tend to show that charging of polymer laminates presents an interesting situation that involves the interface.

In Figure 2, although the nature of surface charges on the two sides of the laminate electret remains the same with respect to time and environmental conditions, those of the component films when separated are not. They are highly susceptible to time and environment, indicating that internal interfacial charge reorganization occurs that does not affect the outside surface charges of the laminate electret.

In Figure 2, the behavior is the same, irrespective of whether one or the other surface is positively or negatively charged. This again shows the importance of interface because, as we have seen earlier (Table XIII), there is a preference for negative charge in FEP polymer.

When pulled apart, the surfaces involved in the interface have the same type of surface charge. This shows that the charged species are in thermodynamic equilibrium across the interface.

References

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