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The Effect of High Energy Radiation on the Electrical Characteristics of Pyrrone Polymers

P. J. REUCROFT,* H. SCOTT, P. L. KRONICK, and F. L. SERAFIN
The Franklin Institute Research Laboratories, Philadelphia, Pennsylvania, 19103

Synopsis

Gamma radiation-induced conductivity and permanent conductivity effects produced by high doses of 2 MeV electrons have been measured in two polyimidazopyrrolone polymers. Radiation-induced conductivity levels are small compared to those found in many common insulating polymers. Permanent increases in dark conductivity produced by accumulated doses of 5×10^9 rad at temperatures up to 300°C are not sufficient to inhibit ultraviolet-visible photoconductivity. High doses of 2 MeV electrons (5×10^9 rad) under the same temperature conditions produce no discernible effect on dielectric properties. Both radiation-induced conductivity and permanent dark conductivity increases were much smaller in one polymer (BTDA–DAB), suggesting the possibility of optimizing radiation resistance in this class of polymers by means of chemical structure variation. The radiolytic and thermal stability reported previously for this class of polymers has been generally confirmed, with particular reference to electrical properties.

INTRODUCTION

Two general effects are usually found when common commercial polymeric insulating materials are exposed to high energy radiation.[1,8] An induced conductivity, δ', is observed when the sample is placed in the radiant beam. It is related to the radiation dose rate R according to the following equation:

$$\delta' \propto R^n \tag{1}$$

where n is less than 1 and is usually in the range 0.57 to 0.82.

For total accumulated doses in excess of 10^8 rad, permanent changes in conductivity are found in addition, usually reflecting permanent chemical changes in the solid produced by radiation damage. In these materials, a deterioration of the electrical properties is generally preceded by mechanical failure.

The polyimidazopyrrolone or "pyrrone" polymers, a new class of aromatic heterocyclic polymers, have been found to display excellent thermal and radiolytic stability in a preliminary evaluation of their mechanical and

* Present address: Department of Materials Science and Metallurgical Engineering, University of Kentucky, Lexington, Kentucky 40506.

electrical characteristics.[2–5] In these polymers, mechanical properties were found to be substantially unchanged by accumulated radiation doses up to 10^{10} rad. More detailed studies of gamma radiation-induced conductivity and permanent effects produced by 2 MeV electrons on the dc conductivity and dielectric properties have been carried out in order to characterize the effects of high energy radiation on two pyrrone polymer films, PMDA–DAB and BTDA–DAB. Some preliminary indication of chemical structure features necessary for optimization of radiation resistance, with particular reference to electrical properties, has been obtained.

EXPERIMENTAL

Materials

The pyrrone polymers were prepared by procedures similar to those described previously.[2–4] BTDA–DAB was prepared by adding 95 ml of a solution of 12.89 g (0.04*M*) of sublimed 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA) in 100 ml of dimethylacetamide (DMAC) to a stirred, hot (~60°C) solution of 8.56 g (0.04*M*) of recrystallized 3,3′-diaminobenzidine (DAB) in 100 ml DMAC in a preheated high-speed blender under nitrogen. After 30 min of stirring, the remainder of the BTDA solution was added dropwise. Stirring and heating were continued for 7 hr. The polymer was then centrifuged and the supernatant was decanted off and stored under nitrogen in a Dry Ice chest. PMDA–DAB was prepared in a similar way using pyromellitic dianhydride (PMDA) and DAB. In this case the reaction vessel was not heated and upon completion of addition of the PMDA solution, stirring at room temperature was continued for about $^1/_2$ hr.

Films were cast from these solutions with an adjustable clearance film applicator set at 6.0 mils clearance, on a Pyrex glass plate polished on one side to 10 bands. After the films were cast, gentle heat was applied beneath the plates from two infrared heating elements. After $1^1/_2$ hr, the plate was placed in a forced-air oven set at 100°C. The films were cured at

TABLE I
Prepolymer Viscosity[a] and Elemental Analysis[b] of PMDA–DAB and BTDA–DAB Films

	[η]	C	H	N
PMDA–DAB	1.02			
Calc. for $C_{22}H_8N_4O_2$		73.33	2.22	15.56
Found		69.28	3.44	15.58
BTDA–DAB	1.70			
Calc. for $C_{29}H_{12}N_4O_3$		75.00	2.59	12.07
Found		71.29	2.79	11.77

[a] Final intrinsic viscosity in dl/g of a blend of smaller prepolymer dopes prepared from equimolar amounts of the amine and anhydride.

[b] Percentages; average of duplicate determinations by Galbraith Laboratories.

100°C for 3 hr, at 200°C for 2 hr, and at 300°C for 1 hr. After the curing cycle, the films were stripped from the glass plate while it was submerged in a water bath to facilitate removal. The films were then cured for another 24 hr at 300°C. Film thickness ranged from 10 μ to 50 μ. The intrinsic viscosity of the polymer dopes and elemental analyses of cast films are shown in Table I. Thermogravimetric analysis showed negligible weight loss up to 500°C for both polymer films. At 800°C, BTDA–DAB films showed a 20% weight loss and PMDA–DAB films, a 40% weight loss.

Electrical Measurements

Samples for electrical measurements were obtained by vacuum evaporating gold electrodes, 1 cm^2 in area, on both sides of polymer film samples. A grounded guard ring electrode was deposited around the perimeter of the electrode on one side to eliminate surface conductivity.

Direct currents through the sample were measured at applied field strengths in the range 10^2–10^6 V/cm with a Cary model 31/31v Vibrating Reed Electrometer. A Keithley Model 240 dc power supply was used to supply voltage to the sample.

The dielectric constant and dissipation factor of polymer film samples were measured at frequencies ranging from 10^2 to 10^5 Hz by means of a General Radio type 1615A capacitance bridge used with a General Radio type 1232-A tuned amplifier and null detector. The dielectric constant was calculated directly from the capacitance by means of the following relationship:

$$C = 8.84\times10^{-8}\frac{KA}{d}$$

where C = capacitance in microfarads (μF), K = dielectric constant, A = area in cm^2, and D = dielectric thickness in cm.

The dissipation factor was read directly from the bridge. Radiation-induced conductivity was determined using a 4000-Ci gamma beam 150 C irradiation facility supplied by Atomic Energy of Canada, Ltd. Radiation dose rates in the range 10 to 1000 rad/min were employed.

Radiation was allowed to fall normal to one electrode. The radiation dose rate was measured inside the conductivity cell at the sample location by means of thermoluminescent dosimetry. TLD-100 LF thermoluminescent powder, supplied by Harshaw Chemical Company, was used in the calibration.

Samples with high accumulated doses of high energy radiation were obtained by irradiating at temperatures ranging from 20°C to 300°C with 2 MeV electrons at the radiation facilities at Electronized Chemicals, Burlington, Massachusetts. Doses ranging from 10^7 rad to 5×10^9 rad were accumulated. The samples were maintained in vacuo at 10^{-3} torr or less and at the specified temperature throughout the dose accumulation. After accumulating the radiation dose, samples were transferred from the

irradiation chamber to glass containers under an ultrapure-grade argon atmosphere. The samples were maintained under an argon atmosphere until they were removed for conductivity evaluation. Electrical characteristic evaluation consisted of measuring the dc dark and photocurrent at applied fields in the range 10^2–10^6 V/cm at room temperature as described previously,[6] the dielectric constant, and the dissipation factor and comparing the data with similar data obtained for unirradiated samples.

In all conductivity measurements, samples were evacuated overnight at 10^{-3} torr before electrical measurements were carried out.

RESULTS AND DISCUSSION

Radiation-Induced Conductivity

Typical current voltage characteristics illustrating the radiation-induced conductivity effect are shown for PMDA–DAB in Figure 1. Steady state radiation-induced currents were established 20–30 sec after applying radia-

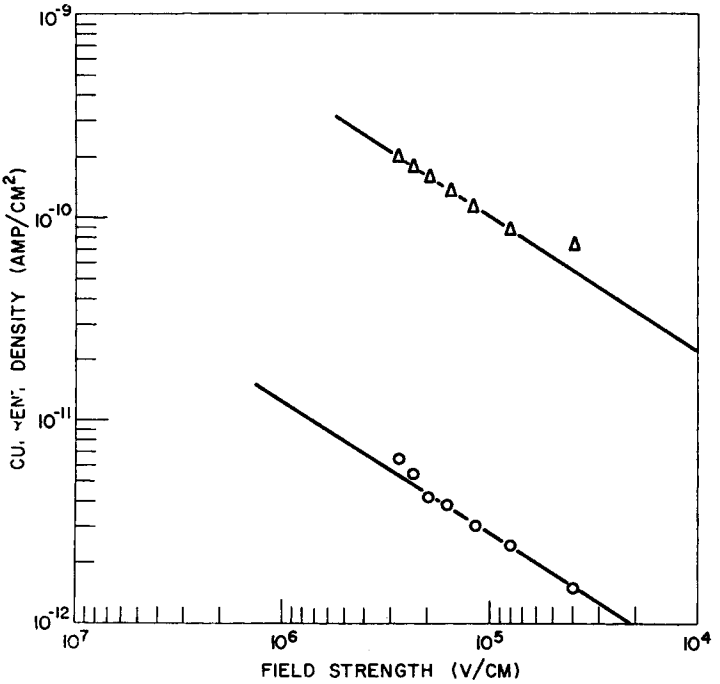

Fig. 1. Radiation-induced current characteristics (PMDA–DAB): (O) dark current; (Δ) radiation-induced current. Dose rate 900 rad/min. Negative voltage applied.

tion. After removing radiation, the current decayed about 90% of its value within 20–30 sec. Similar results were obtained for BTDA–DAB.*

* More detailed information in graphical form can be obtained from *NASA Contractor Report, NASA CR-1367*, "Electrical Characteristics of Pyrrone Polymers," by P. J. Reucroft, H. Scott, P. L. Kronick, and F. L. Serafin.

TABLE II
Radiation-Induced Current Data for PMDA–DAB[a]

Distance from source, cm	Dose rate, rad/min	Positive Voltage Applied				Negative Voltage Applied				Zero Voltage Applied
		I_R	I_D	I_+	$(I_+ - I_0)$	I_R	I_D	I_-	$(I_- - I_0)$	I_0
150	33	+0.88	+0.20	+0.68	+1.28	−2.0	−0.24	−1.76	−1.16	−0.60
150	33	+3.40	+2.80	+0.60	+1.44	−4.75	−2.60	−2.15	−1.31	−0.84
100	80	+1.56	+0.28	+1.28	+1.88	−2.45	−0.38	−2.07	−1.47	−0.60
75	120	+1.80	+0.22	+1.58	+2.25	−2.90	−0.26	−2.64	−1.97	−0.67
50	350	+1.60	+0.21	+1.39	+2.34	−5.40	−0.27	−5.13	−4.18	−0.95
29	900	+1.65	+0.15	+1.50	+3.95	−10.00	−0.27	−9.73	−6.28	−2.45

Field strength = 10^5 V/cm; currents in amp/cm^2 $\times 10^{11}$.

[a] I_R = measured current in radiant field with voltage applied; I_D = dark current before and after irradiation with voltage applied; $I_+, I_- = I_R - I_D$; I_0 = current measured in radiant field with no voltage applied. Radiation was incident upon the electrode to which the voltage was applied; a sandwich arrangement was used for all measurements.

TABLE III
Radiation-Induced Current Data for BTDA–DAB[a]

Distance from source, cm	Dose rate, rad/min	Positive Voltage Applied			Negative Voltage Applied			Zero Voltage Applied
		$I_R - I_0$	I_D	$I_+ - I_0$	$I_R - I_0$	I_D	$I_- - I_0$	I_0
150	33	+4.3	+0.97	+3.33	−3.1	−1.13	−1.97	−7.4
100	80	+5.2	+0.73	+4.47	−6.1	−1.18	−4.92	−6.0
75	120	+7.7	+0.87	+6.83	−6.9	−1.0	−5.9	−8.3
75	120	+6.8	+0.7	+6.1	−8.0	−0.78	−7.22	−8.3
50	350	+8.0	+0.58	+7.42	−13.0	−1.0	−12.0	−15
29	900	+15.7	+0.35	+15.35	−21.9	−1.44	−20.46	−42

Field strength = 10^5 V/cm; currents in amp/cm$^2 \times 10^{12}$.

[a] I_R = measured current in radiant field with voltage applied; I_D = dark current before and after irradiation with voltage applied; $I_+, I_- = I_R - I_D$; I_0 = current measured in radiant field with no voltage applied. Radiation was incident upon the electrode to which the voltage was applied; a sandwich arrangement was used for all measurements.

The dark current level in the samples before irradiation was greater than radiation-induced currents produced in the lead cables to the conductivity cell. Radiation-induced currents produced with the samples present were thus interpreted as arising from the interaction of radiation with the pyrrone polymer sample.

A greater radiation current level was produced when a negative voltage was applied to the incident electrode. This was interpreted as being due to the motion of Compton electrons reinforcing the current owing to the motion of free electrons in one direction (negative voltage) and subtracting from it in the other direction (positive voltage). The free electrons are produced by interaction of the radiation with the material. Support for this interpretation was obtained from the observation that a net negative current was obtained in the sample with no applied field. This current arises from the motion of Compton electrons and is an effect associated with the momentum of impinging photons. Correcting the measured radiation-induced current (I_R) for this zero voltage current (I_0) and the background dark current (I_D) gave radiation-induced currents ($I_+ - I_0$) and ($I_- - I_0$) that were approximately symmetrical with respect to sign of applied voltage and depended upon R^n, where $n < 1$. Tables II and III summarize radiation-induced conductivity data for PMDA–DAB and BTDA–DAB, respectively, for an applied field strength of 10^5 V/cm. The data were taken

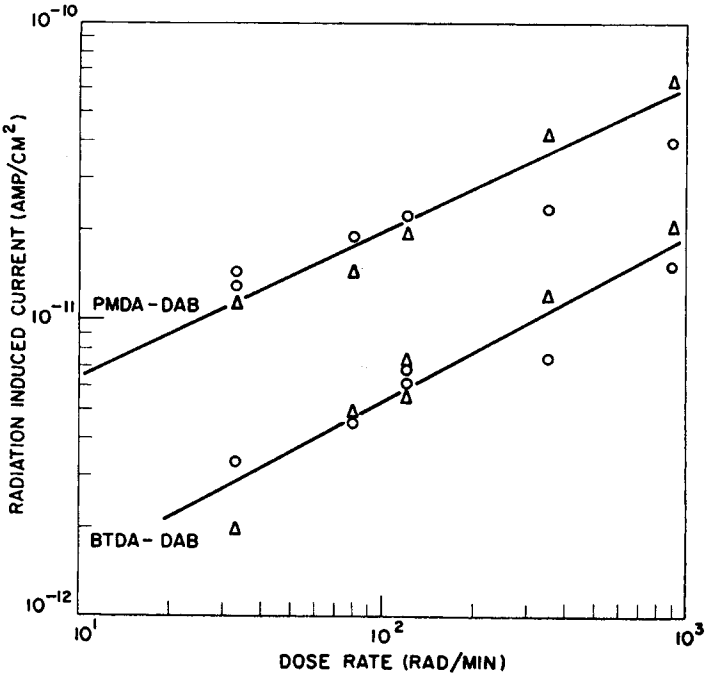

Fig. 2. Radiation-induced current as function of radiation dose rate for PMDA–DAB and BTDA–DAB: (○) ($I_+ - I_0$); (△) ($I_- - I_0$).

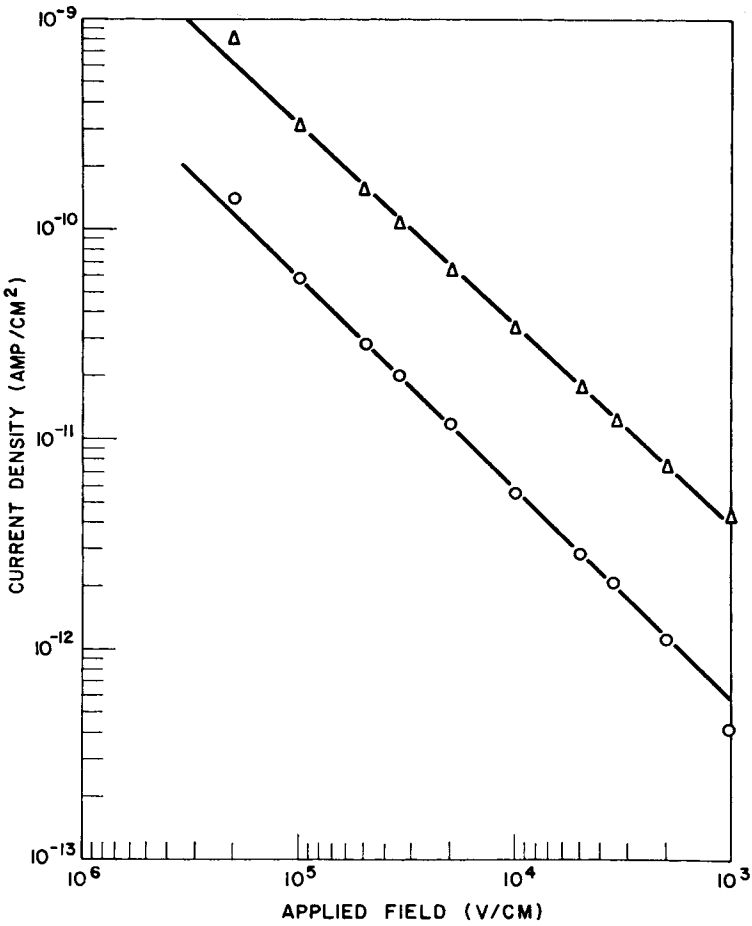

Fig. 3. Current–voltage characteristics for irradiated PMDA–DAB: (O) dark current; (Δ) photo current; radiation dose = 5×10^9 rad at 300°C; incident intensity of polychromatic light = 31–36 m W/cm²; sample thickness = 0.0020 cm; sample electrode area = 1.0 cm².

from plots similar to those shown in Figure 1. The radiation-induced current for BTDA–DAB, i.e., $(I+ - I_0)$, $(I- - I_0)$, was approximately three to four times smaller than that induced in PMDA–DAB. The current due to the Compton effect was similar for both polymers, however. This resulted in net negative radiation-induced currents being measured when BTDA–DAB samples were irradiated with a positive voltage applied to the electrode receiving radiation. On correcting for I_0, it was found that the radiation-induced current was again symmetrical with respect to sign of applied voltage as shown in Table III. Figure 2 shows the corrected radiation-induced current plotted against radiation dose rate. Fitting the data to eq. (1) gives $n = 0.5$.

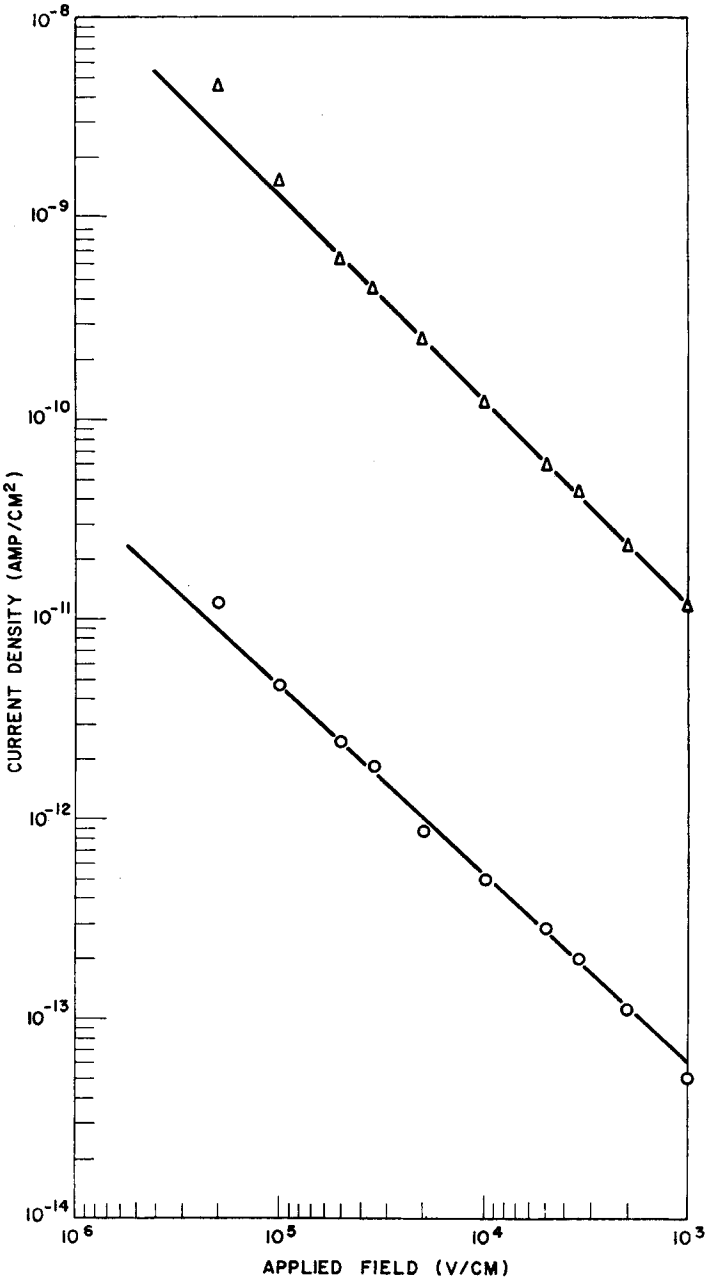

Fig. 4. Current–voltage characteristics for irradiated BTDA–DAB: (O) dark current; (Δ) photo current; radiation dose = 5×10^9 rad at 300°C; incident intensity of polychromatic light = 23–31 mW/cm²; sample thickness = 0.0020 cm; sample electrode area = 1.0 cm².

TABLE IV
Dark and Photocurrent Level at 10^3 V/cm for Irradiated Pyrrone Samples

		PMDA–DAB			BTDA–DAB		
		Photocurrent (I_p), amp/cm²	Dark current (I_D), amp/cm²	$I_p - I_D$, amp/cm²	Photocurrent (I_p), amp/cm²	Dark current (I_D), amp/cm²	$I_p - I_D$, amp/cm²
Unirradiated		2.5×10^{-12}	8×10^{-14}	2.42×10^{-12}	2×10^{-12}	9×10^{-15}	2×10^{-12}
1×10^7 rad	20°C	1×10^{-9}	6×10^{-10}	4×10^{-10}	1×10^{-12}	2.5×10^{-14}	1×10^{-12}
	100°C	4×10^{-12}	1.4×10^{-12}	2.6×10^{-12}	1.1×10^{-12}	1.7×10^{-14}	1.1×10^{-12}
	200°C	9.8×10^{-12}	4×10^{-12}	5.8×10^{-12}	1.7×10^{-12}	3.2×10^{-14}	1.7×10^{-12}
	300°C	4.2×10^{-12}	3×10^{-12}	1.2×10^{-12}	1.5×10^{-12}	2×10^{-14}	1.5×10^{-12}
1×10^9 rad	20°C	8×10^{-11}	7×10^{-11}	1×10^{-11}	3.5×10^{-12}	4×10^{-14}	3.5×10^{-12}
5×10^9 rad	20°C	1.4×10^{-11}	7×10^{-12}	7×10^{-12}	3.5×10^{-12}	3×10^{-14}	3.5×10^{-12}
	100°C	1.6×10^{-11}	1×10^{-11}	6×10^{-12}	6×10^{-12}	3×10^{-14}	6×10^{-12}
	200°C	1.5×10^{-11}	3×10^{-12}	1.2×10^{-11}	—	—	—
	300°C	3.5×10^{-12}	6×10^{-13}	2.9×10^{-12}	1.2×10^{-11}	5×10^{-14}	1.2×10^{-11}

TABLE V
Dielectric Properties of Irradiated Pyrrones

PMDA–DAB				BTDA–DAB			
Frequency, Hz	Dissipation factor	Capacitance, pf	K	Frequency (Hz)	Dissipation factor	Capacitance (pf)	K
No Irradiation				No Irradiation			
10^2	5×10^{-2}	105	4.5	10^2	1×10^{-2}	148	3.1
10^3	4×10^{-2}	99	4.2	10^3	1×10^{-2}	176	3.0
10^4	4×10^{-2}	93	4.0	10^4	1×10^{-2}	173	3.0
10^5	3×10^{-2}	90	3.9	10^5	1×10^{-2}	168	2.9
5×10^9 rad at 20°C				5×10^9 rad at 20°C			
10^2	5×10^{-2}	144	5.0	10^2	7×10^{-3}	205	3.5
10^3	4×10^{-2}	133	4.6	10^3	7×10^{-3}	203	3.5
10^4	3×10^{-2}	127	4.4	10^4	7×10^{-3}	201	3.4
10^5	2.5×10^{-2}	122	4.2	10^5	7×10^{-3}	199	3.4
5×10^9 rad at 300°C				5×10^9 rad at 300°C			
10^2	2×10^{-2}	230	3.6	10^2	1×10^{-2}	192	3.3
10^3	2×10^{-2}	233	3.5	10^3	1×10^{-2}	189	3.3
10^4	1.7×10^{-2}	217	3.4	10^4	1×10^{-2}	186	3.2
10^5	1.6×10^{-2}	210	3.3	10^5	8×10^{-3}	184	3.2

Permanent Electrical Changes

The conditions of measurement for the irradiated samples were chosen to approximate as closely as possible those used in measuring unirradiated samples. The same light source was used for all measurements and was placed at the same distance from the sample in all cases.

Current–voltage characteristics for PMDA–DAB and BTDA–DAB samples that were irradiated with 5×10^9 rad at 300°C are shown in Figures 3 and 4, respectively. Similar data were obtained for samples irradiated with 5×10^9 rad at 20°, 100°, and 200°C, with 1×10^9 rad at 20°C and with 1×10^7 rad at 20°, 100°, 200°, and 300°C. (See footnote on p. 1364.)

On comparing the results with data on unirradiated samples,[6] it was found, in general, that the irradiated samples showed a higher dark current level. Table IV lists current levels obtained for irradiated samples at 10^3 V/cm compared to unirradiated samples. The observed increase in the case of BTDA–DAB was much less than that in PMDA–DAB, the dark current for irradiated samples in no case being more than a factor of 5 above that of the unirradiated samples. The dark current level was much greater in the case of irradiated PMDA–DAB, being a factor of 10 to 1000 above that of the unirradiated samples. The effect of temperature at which the radiation was accumulated was such that the dark current increase was highest at the lowest temperature for PMDA–DAB with a constant radiation dose. In the case of BTDA–DAB, no significant influence of temperature was found on the dark current increase produced.

All samples showed photoconductivity on illumination, the net increase in current produced, i.e., I_p-I_D, falling in the range 10^{-12}–10^{-11} amp/cm^2 for all samples but one PMDA–DAB sample. This sample had accumulated 10^7 rad at 20°C and had abnormally high photocurrent and dark current. In the case of BTDA–DAB, the photocurrent–dark current ratio was little changed from that observed for unirradiated samples. The photocurrent–dark current ratio for PMDA–DAB was generally much reduced compared to unirradiated samples in view of the increased dark current level.

Dielectric constant (K) and dissipation factor data for irradiated samples of PMDA–DAB and BTDA–DAB are given in Table V. The measurements were carried out at room temperature in air. In general, no marked effect of radiation could be seen on comparing the results with similar data obtained on unirradiated samples (also shown in Table V). The unirradiated polymer samples used as controls had dissipation factors similar to those found in irradiated samples. The dielectric constant variations fell within the range of values obtained for several samples of these polymer films, the variations being due to errors in measuring sample thickness.

SUMMARY AND CONCLUSIONS

Radiation-induced conductivity produced in pyrrone polymer samples by gamma radiation at dose rates up to 900 rad/min is on the lower range of

values reported for many engineering plastics.[1] Permanent increases in dark conductivity are produced in the polymers by accumulated doses of 2 MeV electrons ranging from 1×10^7 rad to 5×10^9 rad at temperatures up to 300°C. The dark conductivity increases produced are not sufficient to inhibit ultraviolet-visible photoconductivity exhibited by these polymers. No significant effect on the dielectric constant and dissipation factor can be detected by such accumulated doses.

Both radiation-induced conductivity effects and permanent effects produced by high accumulated doses are much less marked in BTDA–DAB than in PMDA–DAB. This suggests that it may be possible to optimize radiation resistance in this class of polymers by variation of chemical structure.

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