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Contributed Paper

X-RAY-INDUCED PHOTOCONDUCTIVITY IN DIELECTRIC MATERIALS*

R. S. Lee,[†]G. A. Fulk,^{**}, R. H. Barlett, D. J. Meeker, and R. C. Weingart

Lawrence Livermore Laboratory, University of California Livermore, California 94550

ABSTRACT

X-ray-induced photoconductivity has been meas-

ured in low-density polyethylene, Tefzel[‡] (Dupont fluorocarbon), Durasan (Dupont fluorocarbon), polychlorotrifluoroethylene (Kel-F), polystyrene, polypropylene, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl chloride and mica. Dose rates varied in the range $10^9 - 5 \times 10^{10}$ rad/s. The observed photoconductivity showed no apparent dependence on the molecular structure of the materials. The photoconductivity of polyethylene and Kel-F was observed to depend on the degree of crystallinity in these materials.

INTRODUCTION

In an earlier paper¹ we reported measurements of x-ray-induced photoconductivity in six common dielectric materials. We have completed measurements on a number of additional dielectrics, and we wish to add these data to our earlier published data. The experimental procedure we used is described in detail in the earlier paper and will not be repeated here. Dose rates varied in the range $10^9 - 5 \times 10^{10}$ rad/s and were produced by a pulsed x-ray-generator from a design by Blumlein.²

The purpose of the investigation was twofold. First, we wished to study as many common dielectric materials as was conveniently possible in order to provide information useful for designing systems which must operate in a radiation environment. Whenever possible we used commercially available dielectric films. In some cases commercially produced films were not available and samples were made at Bendix Corporation, Kansas City, Mo., using commercially available resins. It is expected that the samples prepared at Bendix would correspond closely to commercial films from the same resins. Any variations should be limited to impurities either introduced by handling or carried over by solvents. rather than fundamental differences in polymerization reactions. We have listed the composition, source, and method of preparation of the films in Table I.

Our second objective was to investigate the effect of the chemical composition, molecular structure, and degree of crystallinity on the photoconductivity. We were particularly interested in investigating polymers with the same molecular structure, but

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^TPresent address: Kansas State University, Department of Physics, Manhattan, Kansas.

[°]Cmdr., U. S. Navy.

¹Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable. differing chemical composition, e.g., polyethylene $(C_2H_4)_n$, Teflon $(C_2F_4)_n$, polyvinyl chloride $(C_2H_3Cl)_n$, Kel-F $(C_2F_3Cl)_n$, polyvinylidene fluoride $(C_2H_2F_2)_n$, and polyvinylidene chloride $(C_2H_2Cl_2)_n$. It is also possible, for some polymers, to vary the degree of crystallinity. This was done for Kel-F, where amorphous and partially crystalline samples were prepared from the same starting resin by controlling the rate of cooling after the material had been heated above the glassy transition temperature. Amorphous (low-density) and crystalline (high-density) polyethylene were also studied, but the low-density and high-density samples were commercial films obtained from different sources.

RESULTS AND DISCUSSION

The photoconductivity data are summarized in Table II. All of the samples exhibited a linear variation of peak photocurrent with electric field. Delayed conductivity was negligible in all but four of the materials studied. Since the dose rates in the various materials varied by over an order of magnitude, a comparison of the materials is best made by normalizing the peak conductivities to the same dose rate. Figure 1 shows the peak conductivities of all of the materials we have studied, normalized to a dose rate of 5×10^9 rads. The data for Teflon, polyethylene, Mylar, Kapton, epoxy and

borosilicate glass are from an earlier study.¹

The photoconductivity appears to depend on the degree of crystallinity of the material. The high density polyethylene (Marlex) is more crystalline than the low density polyethylene and exhibited a higher photoconductivity. The crystalline Kel-F samples showed a larger photoconductivity than the amorphous Kel-F samples. The materials which showed the highest photoconductivities were Teflon and high-density polyethylene, and these are both highly ordered materials.

We can discern no apparent dependence of photoconductivity on the molecular structure of the materials we studied. One might expect, for example, that polyvinylidene fluoride $(C_2 H_2 F_2)_n$ would have electrical properties intermediate between Teflon $(C_2 F_4)_n$ and polyethylene $(C_2 H_4)_n$. Polyvinylidene fluoride has a photoconductivity nearly two orders of magnitude less than either polyethylene or Teflon.

The lack of correlation between photoconductivity and molecular structure may be due to electrically active impurities in the materials studied. The presence of trapping centers in photoconductors can change the mobility of charge carrier by many orders of magnitude. If impurity centers are present in sufficient number, the material properties can be completely masked by the impurities. A high impurity level is to be expected in the materials studied because of side reactions during polymerization, end groups in the polymer chains, and as a result of impurities deliberately added to control the properties of the polymer.

Material	Thiekness	Composition	Source	Method of preparation	
Low-density polyethylene (Visqueen)	0.050 mm	$(C_2H_4)_n$	Phillips Petroleum	Commercial film	
Tefzel	0.050	$(C_4H_4F_4)_n$	Dupont Corporation	Commercial film	
Durasan	0.050	$(C_4H_4F_3C1)_n$	Dupont Corporation	Commercial film	
Kel-F (Amorphous)	0.125	$(C_2F_3Cl)_n$	Shamban, Inc. (sheet made from Allied Chemical Type 22 granules)	A 0.127 mm thick strip was placed in a heated platen press for 2 min $(250^{\circ}\text{C} \text{ and } 1.4 \times 10^4)$	
				N/cm^2 pressure. It was then removed from the press and cooled by immersion in water.	
Kel-F (Crystalline)	0.125	$(C_2F_3Cl)_n$	Shamban, Inc. (sheet made from Allied Chemical Type 22 granules)	The procedure was the same as for amorphous Kel-F, except that the samples were cooled slowly in air after removal from the press.	
Polystyrene (Type IV, Class II)	0.070-0.080	(C ₈ H ₈) _n	Monsanto Corp- oration	Material was dissolved in toluene, then solvent cast in a polyethylene container.	
Polypropylene (Profax 6523)	0,050	(C ₃ H ₆) _n	Hercules Inc. (pellets)	Bars were molded from the pellets. The bars were then backed with Al foil and pressed between ferrotype plates for 10 min @200°C, 0.7×10^4 N/cm ² pressure.	
Polyvinylidene chloride (Saran)	0.050	$(C_2H_2C)_2)_n$	Dow Chemical Corp- oration	Sheet Saran was dissolved in a solution of 25% cyclohexane, 75% tetrahydrofuran. Films were solvent cast from the decanted top of the solution.	
Polyvinyl chloride (Type 7042)	0.125	$(C_2H_3CI)_n$	Ethyl Corporation, Polymer Division	Pellets were dissolved in tetrahydrofuran and allowed to stand. Films were solvent cast from the decanted top of the solution.	
Polyvinylidene fluoride (Kynar,	0.080	$(\mathbf{C}_{2}\mathbf{H}_{2}\mathbf{F}_{2})_{n}$	Penwalt Inc.	A layer of pellets was backed with Al foil on sides and pressed between ferrotype plates for 2 min @ 250°C, 3.5×10^4 N/cm ² pressure.	
grade 300)				101 2 min @ 250°C, 3.5 × 10 N/ cm pressure.	
Mica (Muscovite)	0.037-0.063	${ m K_2Al_6Al_2Si_6} - { m O_{20}(OH)_4} + { m impurities}$	Spruce Pine Mica	Commercial sheet, Victor Type I (ASTM Standard).	

Table I. Composition, source, and method of preparation of the dielectric samples. The dielectric samples were fabricated at Bendix Corporation, Kansas City, Missouri.

Material	Peak ^a dose rate (rad/s)	Peak conductivity (Ohm-cm) ⁻¹	Delayed conductivity ^b (Ohm-cm) ⁻¹	Decay time ^c (ns)
Low-density polyethylene	3.9 × 10 ⁹	1.25×10^{-9}	2.1×10^{-10} @4 × 10 ⁵ V/cm	~50
Tefzel	1.0×10^{10}	2.98×10^{-10}	negligible	
Durasan	2.9×10^{10}	6.37×10^{-10}	negligible	
Kel-F (amorphous)	3.5×10^{10}	8.82×10^{-10}	1.48×10^{-10} @ 1.8×10^5 V/cm	~50
Kel-F (crystalline)	3.5×10^{10}	1.46×10^{-9}	1.65×10^{-10} @ 2.2×10^5 V/cm	~50
Polystyrene	3.6×10^9	2.37×10^{-10}	3.45×10^{-11} @ 2.6 × 10 ⁵ V/cm	~50
Polypropylene	3.3×10^{9}	1.02×10^{-9}	negligible	
Polyvinylidene chloride (Saran)	6.14×10^{10}	1.29×10^{-9}	negligible	
Polyvinyl chloride	5.1×10^{10}	6.4×10^{-10}	negligible	
Polyvinylidene fluoride (Kynar)	9.80×10^{9}	1.78×10^{-10}	negligible	
Mica	4.1 × 10 ¹⁰	6.39×10^{-9}	negligible	

Table II. A summary of the photoconductivity data.

^aThe dose rate normalization was from a monitor pulse that was recorded at the same time as the sample signal. The monitor pulse was calibrated to dose rate in a separate experiment, as detailed in Ref. 1.

^bDelayed conductivity was measured at the end of the radiation pulse. The electric field at which it was measured is also given, since delayed conductivity is often field-dependent.

^CDecay time is defined to be the time for the conductivity persisting at the end of the radiation pulse to decay to half its value.

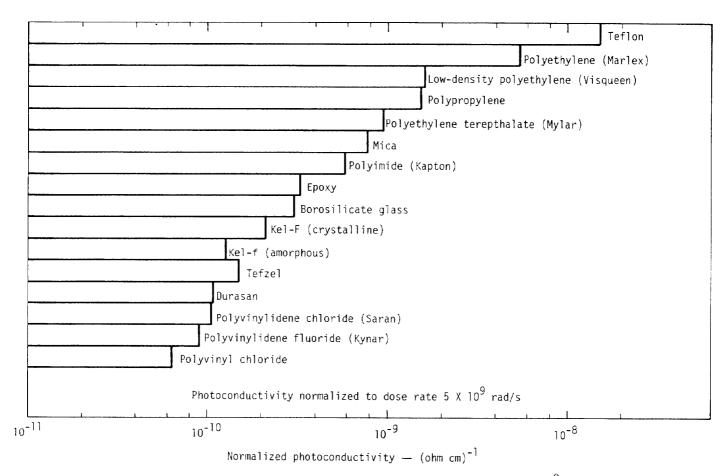


Fig. 1. Summary of peak photoconductivity data normalized to a dose rate of 5×10^9 rad/s. Data for Teflon, polyethylene, Mylar, Kapton, epoxy and borosilicate glass are from an earlier study.

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Ronald S. Lee received the Ph. D. degree in physics from Iowa State University, Ames, in 1967.

He joined the Department of Physics, Kansas State University, Manhattan, in 1967, and is currently an Associate Professor of Physics. Since 1970, he has been associated with the Lawrence Livermore Laboratory, University of California, Livermore, as a Consultant and Summer Employee. There, he has been concerned with problems involving the interaction of ionizing radiation with solids. His publications are mainly in the area of ionization effects in insulating materials.

Dr. Lee is a member of the American Association of University Professors and the American Physical Society.



Gerald A. Fulk received the B.S. degree from the United States Naval Academy, Annapolis, Md., in 1956, the M.S.E.E. and Professional Electrical Engineer degrees from the Naval Postgraduate School, Monterey, Calif., in 1969.

For the next ten years following his graduation from the United States Naval Academy, he served in various billets at sea, including a tour, first, as an Engineer Officer, then, as an Executive Officer aboard the nuclear powered frigate USS Bainbridge DLGN/25. He spent two years as a Military Research Associate at the Lawrence Livermore Laboratory, University of California, Livermore. Cmdr. Fulk is presently serving as commanding officer of USS Pabsons (DDG-33).



Robert H. Barlett received the Ph. D. degree from The Pennsylvania State University, University Park, in 1963.

Since 1963, he has been with the Lawrence Livermore Laboratory, University of California, Livermore. His primary research interests have been concerned with the physical phenomena arising from intense X-ray pulses and shock waves in condensed media.



Donald J. Meeker (S'68-M'72) received the Ph. D. degree in the area of plasma diagnostics in 1972 from the University of Illinois, Urbana.

In 1972 he joined the Lawrence Livermore Laboratory, University of California, Livermore, where he has worked in the area of relativistic electron beam machines, plasma diagnostics, and radiation transport.

Dr. Meeker is a member of the American Physical Society.



<u>Richard C. Weingart</u> received the Ph.D. degree in physics from the University of California, Berkeley, in 1958.

He joined the Lawrence Livermore Laboratory, University of California, Livermore, in 1958. Presently, he is a Staff Physicist and Leader of physics group. In addition to cadiation-induced phenomena, his specific areas of interest include shock hydronamics, pulsed energy systems, and radiation diagnostic techniques.