VARIATION OF ELECTRICAL PROPERTIES ON POLYMERS BY HIGH ENERGY RADIATION

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1. Introduction

Accompanied by the rapid development in the use of atomic energy, a number of investigations on the interaction between high energy radiations and materials have been made during recent years.[1] Generally speaking, the electrical insulation in the electrical machinery and apparatus located near nuclear reactors requires a highly stabilized level for the deterioration induced by radiation. The purpose of this study is to determine the effects of high energy radiation on the electrical properties of polymers, which have made remarkable progress as electrical insulating materials in recent years. In this paper, the variation of the electrical properties, namely dielectric constant, dielectric loss factor, conductivity and dielectric strength induced by gamma-ray and neutron radiation on polyethylene (non-polar) and polyvinyl chloride compound (polar) will be considered.

2. Specimen and Irradiation Procedure

Irradiated polymers used in this experiment were moulded into a sheet form with the thickness range 0.1–0.6 mm in order to make the measurements of various electrical properties and irradiation convenient to take. As a radiation source, the gamma-ray from 3,000 Curie Cobalt-60 and the thermal neutron flux with the associated fast neutron and gammas produced in the atomic pile JRR-1 (Japan Research Reactor) at Tokai-mura, Japan, were used. The irradiation intensity is 5×10^5 r (roentgen)/hr. for the gamma-ray and $\approx 5 \times 10^{11}$ n (neutron)/cm²-sec. at 50 KW out-put for the thermal neutron, respectively. All of the measurements were made after taking out the specimens with some radiation dose from the radiation field and, therefore, were of the static means.

3. Experimental Results and Discussion

3.1. Polyethylene

The relation between the dielectric characteristics and the radiation dosage, the influence of the radiation atmosphere and the effect of various additioners which are mixed into pure polyethylene were studied. The polyethylene used was of the high pressure method (trade name, DFD-2,005, made of Union Carbide Co.) with the sheet form of 0.6 mm thickness. Both dielectric constant (ε) and dielectric dissipation factor (tan δ) increase with gamma-ray and neutron radiation dosage, but the increasing of tan δ is more remarkable than that of ε. Fig. 1 shows the variation of tan δ measured with the frequency of 1 Mega-cycle per sec.

(M.C.) induced by the gamma radiation on several kinds of specimens with the different additioners. The value of $\tan \delta$ increases markedly with the radiation dosage for all specimens tested in this experiment. However, from the comparison with the four specimens cited in Fig. 1, it is to be noted that the antioxidant manufactured under the trade name "Akroflex-C" suppresses the increasing of $\tan \delta$ considerably, while carbon black has very little effect on it.
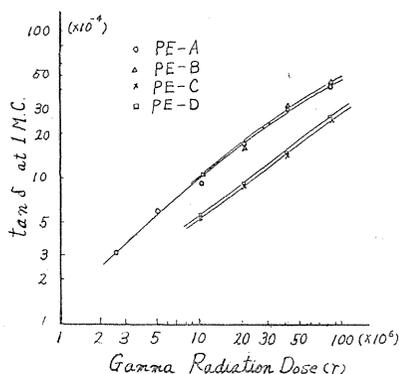
FIG. 1. Variation of $\tan \delta$ at 1 M.C. with gamma-radiation dose for polyethylenes with different formulation as follows:

Component	Parts by weight			
	PE-A	PE-B	PE-C	PE-D
Polyethylene (DFD 2005)	100	100	100	100
Antioxidant (Akroflex-C)			2	2
Carbon Black		2		2

The variation of dielectric characteristics on the irradiated polyethylene in the atomic pile, JRR-1, is nearly the same as in the case of the gamma irradiation as shown in Table 1. From these results, the radiation dosage showing the same effect on $\tan \delta$ is 7.8×10^{16} n/cm² for the pile radiation and 23×10^6 r for the gamma radiation, respectively; this relation agrees in the same order with the result obtained in the atomic pile, BEPO, at Harwell by Charlesby,[2] (10^{17} n/cm² $\rightarrow 46 \times 10^6$ r).

TABLE 1. Effect of Pile Radiation on Dielectric Characteristics of Polyethylene Specimens*

Irradiation time, hours	Specimen-A**		Specimen-B**		Specimen-C**	
	ε	$\tan \delta$	ε	$\tan \delta$	ε	$\tan \delta$
		$(\times 10^{-4})$		$(\times 10^{-4})$		$(\times 10^{-4})$
0	2.33	1.3	2.42	1.1	2.36	1.4
16	2.34	2.8	2.43	2.2	2.36	1.7
57	2.37	19.5	2.45	19.7	2.39	15.4

* Irradiations were carried out in the atomic pile, JRR-1: radiation intensity approximately 4×10^{11} n/cm²-sec. Measurements were made at the frequency, 1 M.C.
** Specimen-A: Polyethylene (DFD-2005).
  // -B: Polyethylene (DFD-2005) with White Pigment (TiO₂).
  // -C: Polyethylene (DFD-2401) with Antioxidant (Akroflex-C) and Carbon Black.

To find the mechanism of increasing $\tan \delta$ on the irradiated polyethylene, the effect of the atmospheric conditions under the irradiation was also investigated. Four specimens were enclosed in 30 mm diameter, 200 mm length glass tubes, the inside of each kept in a vacuum, air (1 atm.), nitrogen (1 atm.) and oxygen

(1 atm.), respectively, which had been irradiated with the same radiation dose 20×10^6 r of the gamma-ray. The value of $\tan \delta$ was changed markedly by the atmospheric conditions as shown in Table 2, the effect of oxygen being the most extensive compared with the others.

TABLE 2. Effect of Atmospheric Condition on Dielectric Dissipation Factor for Irradiated Polyethylene*

Atmospheric condition under irradiation	Nitrogen	Vacuum	Air	Oxygen
$\tan \delta$ at 1 M.C. (unit in 10^{-4})	2.2	2.6	22	26

* Each specimen was irradiated with the same radiation dose of gamma-ray, 20×10^6 r.

Also the infrared absorption spectrums in the region of wave number 75–4,500 cm^{-1} on the specimens irradiated in nitrogen, oxygen and also on the non-irradiated materials are shown in Fig. 2. The specimen kept in nitrogen and the non-irradiated specimen both show nearly the same absorption spectrums, while only a weak absorption, induced by double bond formation within the chain molecule "–RCH $=$ CHR–" (960 cm^{-1}), appears on the spectrum of the specimen kept in nitrogen. On the specimen kept in oxygen, however, a sharp and strong absorption induced by the CO bond (1,701 cm^{-1}) and a rather wide absorption of the OH group (3,290 cm^{-1}) are detectable. From these experimental results, it is concluded that the above-mentioned phenomena is explained by the creation of a number of dipolar groups due to the oxidation of polyethylene which is substantially non-polar material before irradiation. Fig. 3 shows the frequency characteristics of ε and $\tan \delta$ on the irradiated polyethylene, and, within the frequency region 100 K.C.–10 M.C., both ε and $\tan \delta$ are a constant concerning the frequency.

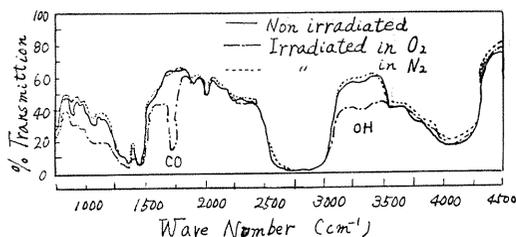
FIG. 2   FIG. 3

FIG. 2. Infrared absorption spectrum for polyethylenes irradiated in various atmospheres.
(Each specimen is irradiated with the same dosage of gamma-ray, 20×10^6 r.)
FIG. 3. Frequency characteristics of dielectric constant (ε) and dielectric dissipation factor ($\tan \delta$) for the polyethylene irradiated with 20×10^6 r, gamma-ray.
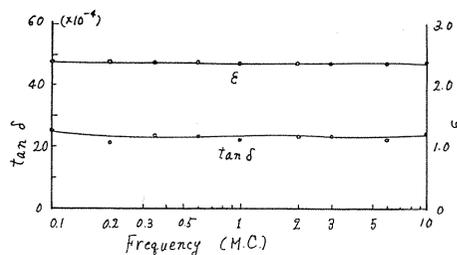
On the other hand, $\tan \delta$ induced by irradiation largely depends upon the specimen thickness, whereas ε doesn't. To explain the thickness effect, a comparison between the analysis by the equivalent electric circuit, which is based on the results of the infrared absorption spectrum mentioned above and the weight

change caused by irradiation, on an irradiated specimen as shown in Fig. 4 and the experimental results on the thickness effect was made. If the thickness of the surface oxidation part ① of the equivalent circuit in Fig. 4 is considerably thinner than that of the inside non-oxidation part ②, $C_2' \ll C_1'$, therefore, the series circuit (B) is transformed into the circuit (C) in Fig. 4. As a result, the equivalent capacity and dielectric dissipation factor as a whole (see, (D) in Fig. 4) are shown as follows:

$$C = \frac{C_2'}{1 + \tan^2 \delta} = C_2 \frac{1 + \tan^2 \delta_2}{1 + \tan^2 \delta} \doteqdot C_2,$$

$$\tan \delta = \omega C_2'(R_1' + R_2') \doteqdot \omega C_2 R_1' + \tan \delta_2 \doteqdot \omega C R_1' + \tan \delta_2,$$

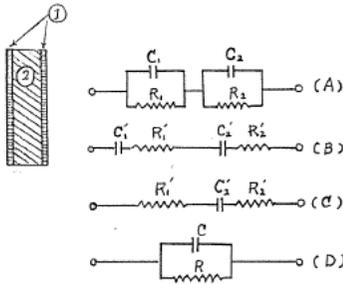where $\tan^2 \delta \ll 1$, $\tan^2 \delta_2 \ll 1$.

FIG. 4. Equivalent electric circuit for irradiated polyethylene. (Suffix 1 or 2 have a concern in the surface part ① or the volume part ②, respectively.)

From the above formulas, it is easy to reach the conclusion that total capacity is almost equal to the capacity of the non-oxidation part and for that reason ε doesn't depend on the specimen thickness. Also, $\Delta \tan \delta$ ($= \tan \delta - \tan \delta_2$) is proportional to $\omega C R_1'$, where R_1' is $\tan \delta_1 / \omega C_1'$ and necessarily

$$\Delta \tan \delta = (C/C_1') \cdot \tan \delta_1.$$

That is to say, $\Delta \tan \delta \propto 1/d$, because of the relation $C \propto 1/d$ (d: specimen thickness) which can be approximately used for the sheet form specimen.

Fig. 5 shows the thickness effect, and the results coincide with the formula obtained from the above analysis. On the other hand, it is expected from the analysis that with the very thin film polyethylene, the thickness effect is negligible, because of the inconsistency of the relation $C_1' \gg C_2'$.

As a fruit of these discussions and experimental results we have come to the final definition that the variation of $\tan \delta$ induced by irradi-
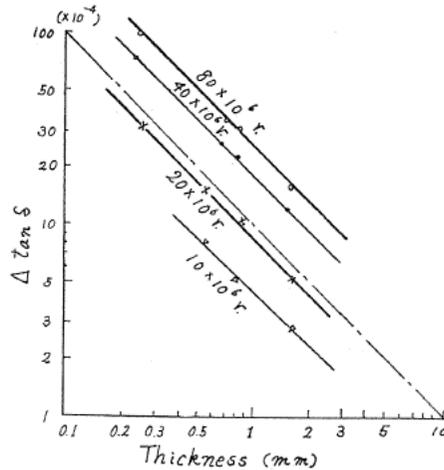

FIG. 5. Thickness effect of $\Delta \tan \delta$ for irradiated polyethylene.

ation is based on the surface effect, not a volume one.

3.2. Polyvinyl chloride

Generally, when polyvinyl chloride resin are moulded into a practical form, various additioners, such as stabilizer, plasticizer, filler, pigment etc. should be mixed during the heat moulding process. Among them, stabilizers are used for the purpose of preventing the thermal decomposition of the polymer, and also plasticizers, which give plasticity to the polymer at a rather lower temperature, are employed. Experiments were carried out on dielectric characteristics of the compound with two series, that is, "P.V.C. (polyvinyl chloride)-Stabilizer" and "P.V.C.-Plasticizer-Stabilizer".

In the former series, there is a critical radiation dose, at which $\tan \delta$ runs up rapidly with the said dose and its critical value increases with the stabilizer concen-
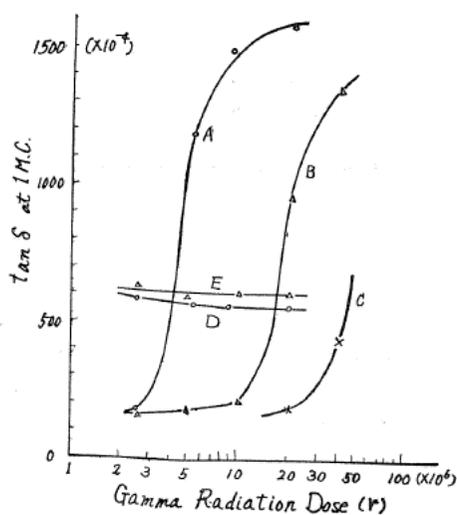

FIG. 6. Variation of $\tan \delta$ at 1 M.C. with gamma radiation dose for P.V.C. compounds with different formulation as follows:

Component	Parts by weight				
	A	B	C	D	E
P.V.C.	100	100	100	100	100
Stabilizer (Tribase)	2	4	6	2	4
Pasticizer (D.O.P.)				50	50

TABLE 3.   Effect of Pile Radiation of Dielectric Characteristics
of Polyvinyl Chloride*

Irradiation Time, hours	Un-plasticized Specimen				Plasticized Specimen			
	A**		B**		C**		D**	
	ε	$\tan \delta$	ε	$\tan \delta$	ε	$\tan \delta$	ε	$\tan \delta$
		$(\times 10^{-4})$		$(\times 10^{-4})$		$(\times 10^{-4})$		$(\times 10^{-4})$
0	2.94	142	2.94	142	3.20	635	3.20	638
14	3.66	230	3.07	146	—	—	—	—
63	8.07	2,015	8.02	2,000	3.20	633	3.20	615

* Irradiations were carried out in the atomic pile, JRR-1: radiation intensity approximately 4×10^{11} n/cm²·sec. Measurements were made at the frequency, 1 M.C.
** Specimen-A: P.V.C. (100 parts) with Stabilizer "Tribase" (2 parts).
  // -B: P.V.C. (100 parts) with "Tribase" (4 parts).
  // -C: P.V.C. (100 parts) with Plasticizer "D.O.P." (50 parts) and "Tribase" (2 parts).
  // -D: P.V.C. (100 parts) with "D.O.P." (50 parts) and "Tribase" (4 parts).

tration as shown in Fig. 6. Also, data irradiated in the atomic pile JRR-1 is shown in Table 3. For both the gamma-ray and the neutron radiation, the change of ε and $\tan\delta$ on the largely plasticized P.V.C. compound is very small within the region of our experimental radiation dosage.

The exsistence of the dispersion frequency at the mega cycle region of the frequency characteristics of the dielectric loss factor ($\varepsilon \times \tan\delta$), as shown in Fig. 7, on the irradiated specimens suggest that the hydro-chloride (HCl) molecule, induced from the decomposition of the polymer, plays an important rôle.
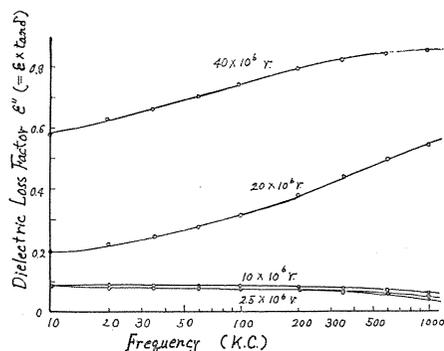

FIG. 7. Frequency characteristics of dielectric loss factor for gamma irradiated P.V.C.
(P.V.C., 100 parts-Tribase, 4 parts.)

To find out the effect of this in electrical conduction and dielectric breakdown, the specimen is formed with 0.1 mm thickness by using the heat moulding device, while di-butyl tin di-laulate, in the liquid state, is used as a stabilizer for the convenience of the measurements of the electrical properties mentioned above and of the infrared absorption spectrum. The specimens made by the above procedure are transparent. Fig. 8 shows the relation between the electrical volume resistivity and the irradiation time in the pile on the plasticized P.V.C. with di-2-ethylhexyl phthalate (D.O.P.) as a plasticizer. In general, the volume resistivity decreases with the irradiation time, but this inclination slows down with the increasing of the plasticizer concentration. Furthermore, it is to be noted that on the specimen with 60 parts of plasticizer for 100 parts of polymer, the volume resistivity induced by irradiation shows a minimum value at some irradiation time. Fig. 9 also shows the result on the specimens with the different molecular structure of plasticizer, that is, tricresyl phosphate (T.C.P.) and di-2-ethylhexyl adipate (D.O.A.), from which the former includes the benzen ring in its molecular structure similar to D.O.P., while the latter does not. For these specimens, volume resistivity only decreases with irradiation time notwithstanding the larger concentration of the plasticizer, and never increases.

Given the facts that, one, the relation between volume resistivity and plasticizer concentration for a non-irradiated specimen agrees with that induced from the analysis based on Flory's viscosity formula as reported by Boyer,[3] and, two, the temperature dependence of volume resistivity is considerably larger as mentioned later, the moving particle making the electric conduction in the specimens tested has the tendency to be the ion. Suppose this is true. then volume resistivity follows to the next relation:
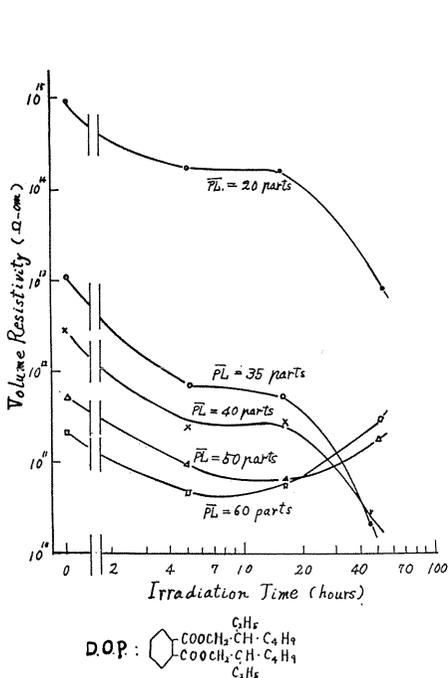
DOP : (structure) COOCH₂·CH·C₄H₉
                   COOCH₂·CH·C₄H₉

FIG. 8

T.C.P. : (CH₃—〈 〉)₃·PO
                  CH₃

D.O.A. : C₄H₉(C₂H₅)CHCH₂ OOC·
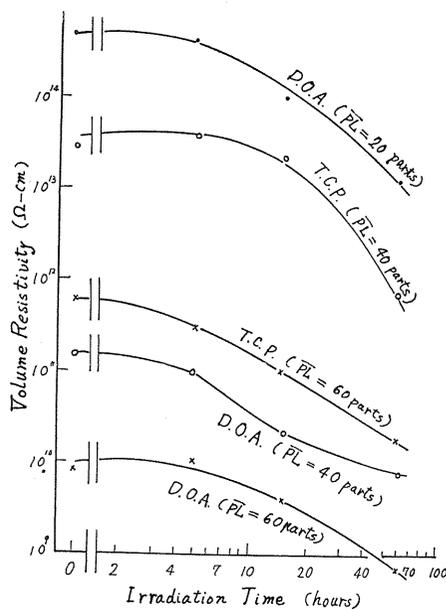   (CH₂)₄COOCH₂CH(C₂H₅)C₄H₉

FIG. 9

FIG. 8. Variation of volume resistivity as a function of pile irradiation time for P.V.C. compounds with plasticizer D.O.P., whose chemical formula is given in the figure. Radiation intensity is approximately 4×10^{11} n/cm²-sec. $\overline{PL}$ in the figure represents the plasticizer concentration in parts by weight for 100 parts of polymer.

FIG. 9. Variation of volume resistivity as a function of pile irradiation time for P.V.C. compounds with plasticizer T.C.P. and D.O.A., respectively. Radiation intensity is approximately 4×10^{11} n/cm²-sec. $\overline{PL}$ in the figure represents the plasticizer concentration in parts by weight for 100 parts of polymer.

$$\rho \propto 1/I \propto 1/N\mu,$$

where ρ is volume resistivity, I electric current, N ion density and μ ion mobility.

Usually, decomposition and crosslinking of the polymer are expected by the irradiation where the former, mainly, has an influence upon ion density and the latter upon ion mobility. On the plasticized compound, also, one may expect the degradation of the plasticizer itself. However, the facts that, one, the effect of irradiation on the volume resistivity goes down with the increasing plasticizer concentration, and, two, a qualitative change of the coloring of the specimens to light brown due to the irradiation (which means the creation of the double bond in the P.V.C. molecule by the decomposition of the polymer accompanied with hydro-chloride) has a co-relation with the variation of volume resistivity, show that the increasing of the ion density induced by the irradiation is caused mainly by the decomposition of the polymer, not by that of the plasticizer. On the other

hand, in this experiment, the evaporation of the plasticizer, which is one of the important factors in causing the decreasing ion mobility under the test of thermal degradation at higher temperatures, was neglected, because the temperature in the atomic pile, JRR-1, which operated at a constant out-put was approximately below 60-70° C, and the weight change of the irradiated specimen was below about 1% of the original weight.　Accordingly, in the specimen with D.O.P. (60 parts), the increasing volume resistivity at the region of rather long irradiation time, as shown in Fig. 8 may be accompanied by the increasing of the trapping centres of moving ions created by the chemical change of D.O.P.[4]　The activation energy for volume resistivity on the irradiated specimens, which is calculated from the equation, $\rho = K \exp. (E/RT)$, where ρ is volume resistivity, K constant, E activation energy, R gas constant and T absolute temperature, is shown in Fig. 10 with the plasticizer concentration as a parameter.　The variation of activation energy by irradiation on the specimen with a small quantity of plasticizer in it is more than those with a large quantity of plasticizer in them.

　　The variation of the dielectric breakdown strength induced by the irradiation is similar to that of the volume resistivity, as shown in Fig. 11.
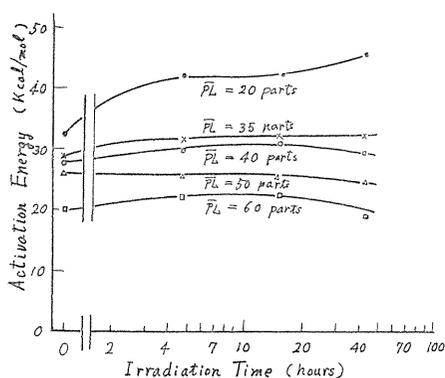

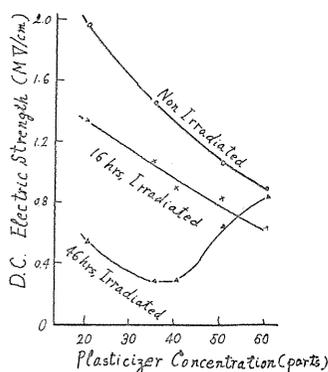FIG. 10   FIG. 11

　　FIG. 10.　Activation energy of volume resistivity given in Fig. 8.

　　FIG. 11.　Variation of direct current electric strength as a function of plasticizer concentration for P.V.C. compounds with plasticizer, D.O.P., irradiated in the atomic pile, JRR-1, operated by the same conditions with those given in Fig. 8.

4. Acknowledgments

References

1) For instance, Charlesby, A., Proc. Roy. Soc., *A 215*, 187 (1952); Bopp, C. D. *et al.*, Nucleonics, *13*, 28 (1955); Klein, P. H. *et al.*, A.I.E.E. Transactions (Comm. and Elect.), No. 22,

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2) Alexander, P. *et al.*, Proc. Roy. Soc., *A 223*, 392 (1954).

3) Boyer, R. F., J. Chem. Phys., *20*, 540 (1949).

4) Warner, A. J. *et al.*, J. Appl. Phys., *25*, 131 (1955).