ELECTRICAL CONDUCTION IN PLASTICIZED POLYVINYLCHLORIDE EXPOSED TO HIGH ENERGY RADIATIONS AND ITS POST-IRRADIATION EFFECT

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Abstract: The volume resistivity of plasticized polyvinylchloride exposed to three kinds of radiation field, (atomic pile, gamma ray and electron) have been investigated over the range of temperature, 20°C to 70°C and of specimen thickness, 0.1 mm to 2 mm. On the volume resistivity measured for about a year after irradiation, there exists a remarkable post-irradiation effect which depends markedly upon both the specimen thickness and the plasticizer concentration mixed in P.V.C. The experimental results also show that the creation of charge carries, such as H^+ and Cl^- coming from the degradation of P.V.C. caused by radiation makes the decreasing volume resistivity with increasing radiation dose through the ionic conduction. And the post-irradiation phenomena showing a recovery on the reduced volume resistivity are related to the disappearance of the created charge carriers both due to their diffusion out of the specimen and the capturing of them into the trapping centers in the specimen, but not due to the change of ion mobility.

1. Introduction

High molecular materials having important applications as a electric insulator undergo semi-parmanent change of their physical properties resulting from alteration in the chemical structure by the exposure to high energy ionization radiations. In this experiment succeeding a previous one[1], the electric conduction after irradiation in plasticized P.V.C. have been investigated and especially the post-irradiation effect on the volume resistivity have been measured for about a year. Also, the effects of the specimen thickness and the plasticizer concentration in specimens on the post-irradiation phenomena and the apparent activation energy for the electric conduction have been studied in order to clarify a conduction mechanism in irradiated specimens.

2. Experimental

Formulations of the specimens used are given in Table 1. Each specimen was moulded into a sheet form with five different thickness in the range of 0.1 ~2 mm. Irradions were performed, in the presence of air, in the radiation field enumerated in Table 2. The maximum dosage of irradiation was 4 W (corresponding to the exposure time of 56 hrs at 40 KW output), 40 Mr, and 40 Mrad for atomic pile, γ ray and electron respectively. Thin alluminum foil was attached with a little amount of vaselinum on the specimens to form the parallel plane circular electrodes, which was surrounded by the guard electrode to take

TABLE 1. Formulation of Specimens

No. of specimen	1	2	3	4	5	6
P.V.C.	100*	100	100	100	100	100
Plasticizer DOP	20	35	50			
DOA				20	35	50
Stabilizer**	2	2	2	2	2	2
Lublicant***	0.5	0.5	0.5	0.5	0.5	0.5

* Parts by weight ** Dibutyltindilaulate *** Stearic acid

TABLE 2. Radiation Sources

Atomic pile (JRR-1)	$(3\sim4)\times10^{11}$ slow neutrons/cm^2•sec. plus the associated fast neutrons and gammas
γ ray	C_0^{60}, 3000 C, 0.33×10^6 r/hr.
Electron	Electron accelarator (N-S type) 1.5 MV, 200 μA

out the surface current. The conduction current passing through the specimen when applied D.C. 100 volts was estimated from the value at a minute after voltage application, in which the part of absorption current was to be negligible, and was observed over the temperature range, 20°~70°C to define the apparent activation energy for the electric conduction. The absorption spectrum in visible ray region, 300~900 mμ of wave length, was measured, which had a close relation to amounts of polyen structure existing in the specimen, in order to consider the mechanism of the electric couduction.

3. Experimental Results and Discussion

1) Radiation dose and volume resistivity (ρ)

ρ of plasticized P.V.C. is generally decreased with radiation dosage and this behavior is observed in the specimens irradiated here without depending on the radiation sources used. A typical example of the observed ρ versus radiation dose (proportional to the exposure time to the radiation field) is shown in Fig. 1 for the specimens with different concentrations of the plasticizer, Di-2 ethylhexylphthalate (D.O.P.) which are illustrated in the figure with $\overline{PL}$ (parts by weight). Generally, ρ measured 10 days after the irradiation indicates a saturation of decrease at some dose [1 W (15.4 hrs) for atomic pile, 10 Mrad for electron, and 10 Mr for γ ray] within the experimental dosage. (See, solid line in Fig. 1) On the other hand, although ρ measured about one year after

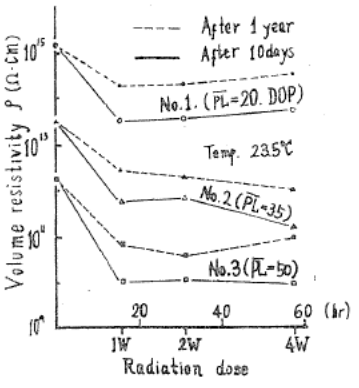

FIG. 1. Variations of volume resistivity of the pile irradiated specimens, measured 10 days and 1 year after irradiation as a function of the radiation dose.

the irradiation has the similar tendency to mentioned above, as shown by broken lines in Fig. 1, the absolute value of ρ increases compared with ρ given by the solid line. This results mean that ρ decreased by the radiation changes with the time passed and has a so-called "post-irraidation effect." The time effect of ρ over a year after irradiation is illustrated in Fig. 2 for the specimens with 4 W pile irradiation. The recovery of ρ decreased by the radiation appears more remarkably and at earlier times after irradiation for specimens with large amounts of plasticizer than those with small one. These behaviors are also observed in the specimens irradiated by other fields.

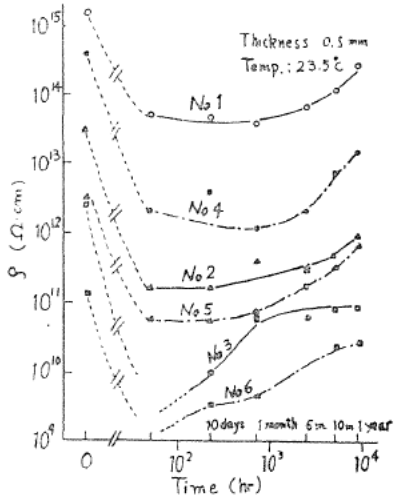

FIG. 2. Time effect on volume resistivity of various specimens with 56 hours (4 W) pile irradiation.

2) Apparent activation energy for electric conduction

In the irradiadted specimens, the temperature dependence of the volume resistivity is given by the following formula as in the unirradiated one.

$$\rho = \rho_0 \exp(E_c/kT), \tag{1}$$

where E_c is apparent activation energy, T absolute temperature, k Boltsman constant and ρ_0 a constant. As an example, E_c of electron irradiated specimens is given in Table 3 and these variations for the radiation doses are similar to those of γ ray or pile irradited specimens.[1] Generally, E_c is gradually increased with radiation dose for specimens with small amount of plasticizer, while it is decreased for specimens with large amount of plasticizer. However, the variation of E_c due to irradiation is not so large compared with that of the irradiated polyethylene in which it becomes two or three times E_c for the unirradiated in spite of comparatively small radiation dose.[2)3)]

TABLE 3. Apparent Activation Energy E_c (Kcal/mol) for Electric Conduction of Specimens Irradiated by Electron

No. of specimen	Unirradiated	10 Mrad	20 Mrad	40 Mrad
1	39.5	47.4	46.0	51.0
2	28.6	32.8	31.9	31.6
3	23.4	25.6	27.0	27.0
4	27.9	33.5	31.7	38.1
5	21.7	21.2	20.8	21.0
6	15.0	11.1	12.4	11.3

3) Thickness effect of specimens

Fig. 3 shows a thickness effect of specimens irradiated by 40 Mr γ ray. ρ measured 2 days after irradiation slightly depends on thickness of the specimens

both with the plasticizer concentrations, $\overline{PL}=20$ parts by weight and $\overline{PL}=50$ parts. However, the thickness effect on ρ a year after irradiation is different between the specimens with $\overline{PL}=50$ parts and with 20 parts and in the former case ρ is markedly decreased with the specimen thickness. If a radiation effect on the volume resistivity of plasticized P.V.C. is subjected to a surface effect as in the change of a dielectric loss factor of the polyethylene irradiated in air which is caused by the oxidation at the surface of the specimen,[1] the ρ increasing with thickness must be observed. Then, it may be suggested that the variation of the volume resistivity is based on the volume effect, but not on the surface, resulting from the change of the inner part of specimen caused by the radiation.

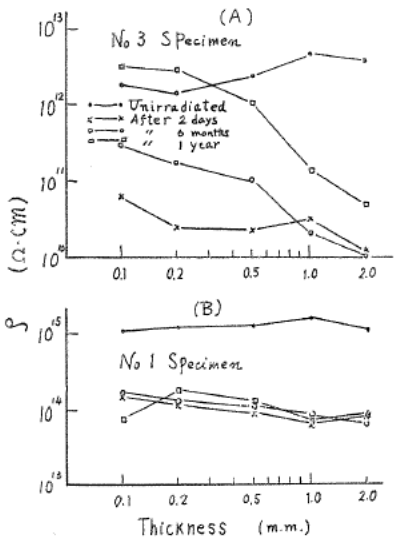

FIG. 3. Thickness effect on volume resistivity of 40 Mr γ ray irradiated specimens.

4) Discussion

Generally, plasticized P.V.C. is colored into from yellow brown to dark brown with increasing radiation dose. The specimen with small concentration of plasticizer has a large amount of absorption over the region from visible ray to ultraviolet ray, which is related to the creation of the polyen structure associated with de-hydrogenchloride in P.V.C. On the other hand, as pointed out by the authors,[4] the electric conduction in plasticized P.V.C. at low electric field is ionic and then, the conductivity (σ) is given by the following equation,

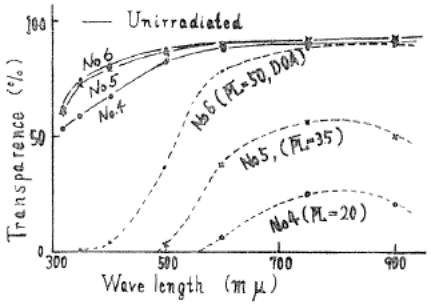

FIG. 4. Variations of transparence in the region of visible ray for 56 hours pile irradiated specimens.

$$\sigma=1/\rho=qN\mu, \tag{2}$$

where μ is ion mobility, N ion density and q charge of ion. Eq. (1) on ρ in irradiated specimens qualitatively agrees with the temperature dependence for the ionic conduction. Moreover, since the variation of E_c is comparatively small within the experimental dosage it may be suggested that the variation of the mobiltiy induced by irradiation is not enough to explain the change of ρ appearing after irradiation. Then, the change of ρ may roughly corresponds to a change of ionic density (N), which comes from the dissociation of hydrogen chloride that is the decomposition product of polymer.

According to the consideration mentioned above and to the results on the thickness effect and on the recovering tendency of ρ given in the previous section

it may be suggested that, the post-irradiation effect of ρ in the irradiated specimens is resulted from the disappearance of hydrogen chloride as a source of the charge carriers, due to the extinction out of the specimen and capture into some trapping centers in the specimen, which is closely related to the diffusion process of hydrogen chloride.

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