Irradiation of Poly(vinyl Chloride) with H_2 Plasma. II

A. H. ZAHRAN and E. NOFAL, *Atomic Energy Authority, National Centre For Radiation Technology, Cairo, Egypt,* M. A. EL-AZMIRLY, *National Research Centre, Laboratory of Polymers, Dokki, Cairo, Egypt,* and M. Z. ELSABEE, *Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt*

Synopsis

Poly(vinyl chloride) films blended with plasticizers, stabilizers, and fillers are irradiated with a beam of H_2 plasma. The polymer partially loses its solubility in cyclohexanone. The viscosity of the soluble part decreases in the initial stages and then increases on further irradiation. Crosslinking was followed by dehydrochlorination and discoloration of the polymer. The electrical conductivity was measured as a function of the irradiation dose and time. The plasticizers enhanced the action of plasma while the stabilizers and fillers reduced it.

INTRODUCTION

Bombardment of polymers with plasma particles was found to induce crosslinking[1–5] as well as degradation[6–11] depending on the nature of the polymer and on the plasma used. Poly(vinyl chloride) (PVC) is one of the most frequently used thermoplastic polymers. Its big advantage is the high variability of properties which allows its application in rigid or soft products. PVC is used also as an electric insulator for wires and cables.

One of the main causes of premature insulation breakdown in strong electric fields is the effect of electric discharges originating in air inclusions in insulating pores, which is analogous to plasma irradiation. Nevertheless, very little attention has been given to the interaction of PVC with plasma particles. The present communication describes our observations on this interaction.

EXPERIMENTAL

The plasma source, its characteristics and irradiation procedure have been described in a previous communication.[12]

Materials

Pure-grade poly(vinyl chloride) supplied by the National Plastic Company, Egypt, was further purified by reprecipitation from cyclohexanone–methanol. The purified polymer was dried in vacuo at room temperature. Dibutyl phthalate (DBPhth), tricresyl phosphate (TCPhos), and dibasic lead phosphate (DBLPh) were obtained from Hopkin and Williams, Ltd. Laboratory Reagents, England, and were used without any further treatment. Calcium carbonate was supplied by the General Pharmaceutical Company, Sudbury, England. All the solvents were purified by known procedures.

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Poly(vinyl chloride) was compounded with the different plasticizers, stabilizer, and filler. PVC films 1 mm thick were prepared by casting the compounded PVC in cyclohexanone over a glass plate. These films were then cut into strips of approximately 2 × 1 cm, carefully dried in vacuo, and kept in a brown bottle in a desiccator.

Electrical Conductivity Measurements

After irradiation of the PVC of different compositions, the soluble part was isolated and prepared in the form of a disc 1 cm in diameter and 0.05 cm thick. Copper metal was coated on both sides of these samples to improve the electrical contact. The sample was placed between brass rods 1 cm in diameter. The rods are provided with a spring to press the sample between them and serve as a condenser. The test condenser was kept in a metallic box and connected to the measuring instrument through a short, low-capacitance coaxial cable to minimize the external noise. A vibrating reed electrometer Type V.A.J.5 made by Veb Vakutronik, Dresden, Germany, with a range of 10^8 to 10^{16} Ω was used for resistivity measurements. The resistance was calculated from the voltage drop using the formula

$$R_X = R_M\ (V_H/V_M - 1)$$

where R_X is the unknown resistance, R_M is the input resistance, V_H is the auxiliary voltage, and V_M is the voltage drop across the unknown resistance. All the other experimental details are described elsewhere.[12]

RESULTS

Plasma irradiation of PVC induces partial loss in its solubility in cyclohexanone due to the formation of crosslinks. The extent of crosslinking was followed after 8 min of irradiation with hydrogen plasma (plasma energy 7.5 eV). The effect of plasticizers, stabilizer, and filler on the extent of crosslinking was investigated.

When the irradiated samples were kept in dark bottles, the percent of the soluble part increased with time. The effect of storage time on the percent of the insoluble part of the polymer is shown in Figure 1. When the PVC was blended with dibutyl phthalate and irradiated, the insoluble part increased with the concentration of the plasticizer in the blend. The effect of the stabilizer on the extent of crosslinking is shown also in Figure 1. Obviously the stabilizer reduces the effect of plasma. Further, plasma irradiation was found to induce crosslinking to a greater extent in PVC blended with dibutyl phthalate than with tricresyl phosphate.

The extent of crosslinking was also followed by measuring the swelling ratio of the PVC gels formed after irradiation. Figure 2 shows the results of the swelling measurements for pure PVC and PVC blended with plasticizers, stabilizer, and filler. From this figure it is clear that the PVC samples blended with 20% plasticizer show the highest degree of crosslinking, while the PVC samples compounded with 10% stabilizer show the lowest degree of crosslinking.

The soluble part of the polymer was isolated and its intrinsic viscosity $[\eta]$ was measured. Figure 3 shows the $[\eta]$ as a function of the irradiation time for PVC

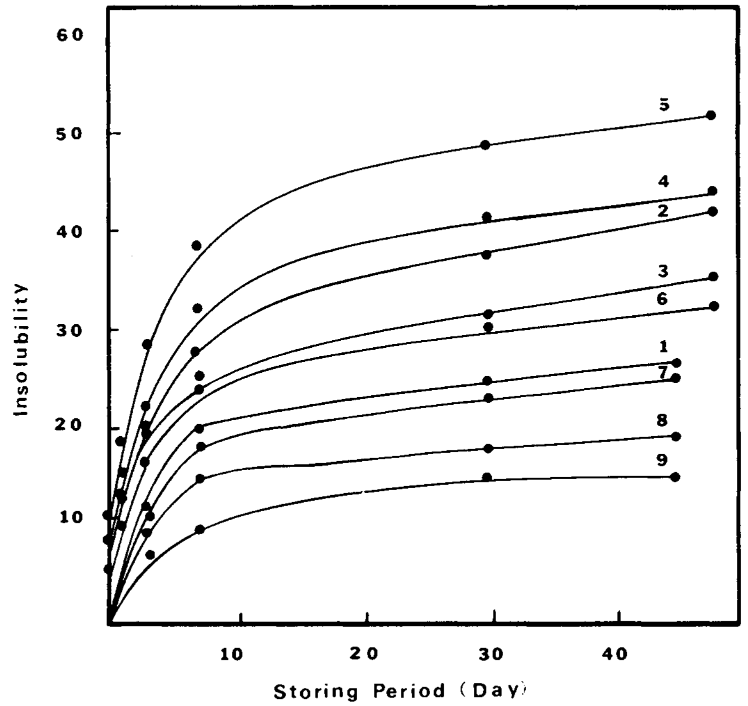


Fig. 1. Effect of storing period on solubility of irradiated PVC (irradiation time 8 min, plasma energy 7.5 eV): (1) pure PVC; (2) PVC + 10% DBPhth; (3) PVC + 20% DBPhth; (4) PVC + 30% DBPhth; (5) PVC + 40% DBPhth; (6) PVC + 20% TCPhos; (7) PVC + 20% TCPhos + 10% $CaCO_3$; (8) PVC + 20% TCPhos + 10% $CaCO_3$ + 5% DBLPh; (9) PVC + 20% TCPhos + 10% $CaCO_3$ + 10% DBLPh.

samples blended with plasticizers and stored for 10 min and seven days after irradiation. With the samples stored for 10 min after irradiation, the $[\eta]$ decreases at the initial stages of exposure to the plasma beam and then starts to increase with further irradiation. However, when the samples were stored for seven days, the viscosity increases pronouncedly, even at low irradiation doses, and reaches an ultimate value after an irradiation time of 8 min. Further, $[\eta]$ increases with increasing concentration of plasticizer in the irradiated sample; however, it decreases when the stabilizer is added to the PVC during irradiation.

The electrical conductance was measured at 25°C for samples of PVC irradiated with different doses of plasma (Fig. 4). The conductivity was found to increase enormously with the irradiation dose, particularly for samples irradiated for more than 8 min. The effect of storage time on conduction was also investigated. On standing, the conductivity increases directly with time. The same trend was also observed for the PVC samples blended with different ingredients. The effect of storage time on the electrical conductivity of PVC samples compounded with different additives and irradiated for 8 min is shown in Figure 5; the conductance reaches a maximum value after 20 days. The dose rate was also found to affect the conductivity (Fig. 6). Again, on standing, the conductivity of the samples increases steadily.

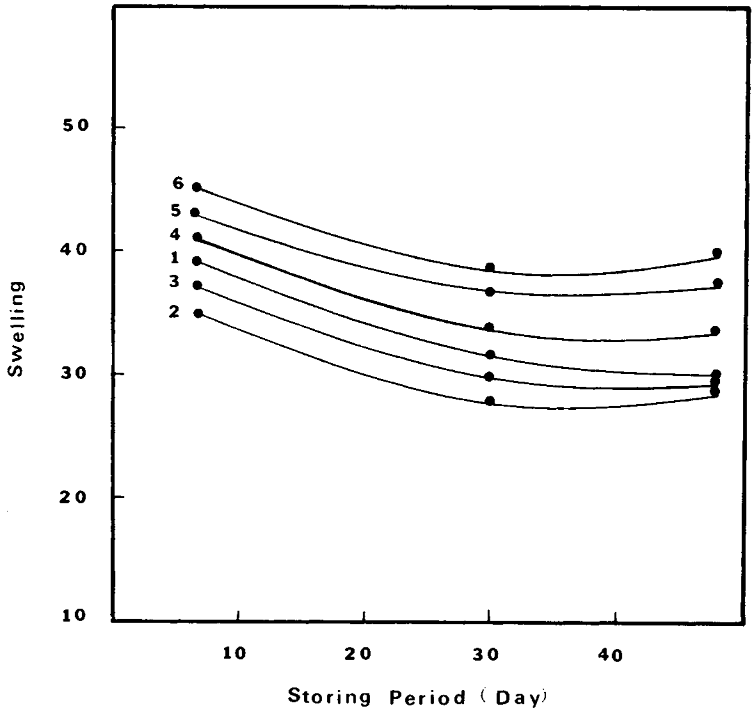


Fig. 2. Effect of storing period on swelling percent of irradiated PVC (irradiation time 8 min, plasma energy 7.5 eV): (1) pure PVC; (2) PVC + 20% DBPhth; (3) PVC + 20% TCPhos; (4) PVC + 20% TCPhos + 10% $CaCO_3$; (5) PVC + 20% TCPhos + 10% $CaCO_3$ + 5% DBLPh; (6) PVC + 20% TCPhos + 10% $CaCO_3$ + 10% DBLPh.

DISCUSSION

We have previously reported that irradiation of pure PVC films with hydrogen plasma results in the formation of crosslinked structures.[12] In the present work, we have examined the effect of some additives such as plasticizers, stabilizers, and fillers on the extent of the modification brought about in PVC by plasma irradiation. The plasma irradiation of solid solutions of PVC blended with these materials was found to result in partial loss in solubility of the polymer in cyclohexanone. Also the color of the material changed gradually to reddish brown and finally to black. Analysis of the solubility measurements (Fig. 1) indicates that the amount of the insoluble part increases as the amount of the plasticizer compounded with PVC increases. It is known that the unplasticized PVC is a hard, rigid material due to the strong forces holding the molecular chains together. The added plasticizers act as lubricants allowing the molecules to slip easily past each other. This increased mobility of the chains leads to a higher rate of migration of the free and trapped radicals and ions, which in turn increase the probability of radical collision. This explains the increase in the extent of crosslinking with the increased percentage of plasticizer added.

The viscosity measurements of the soluble part of PVC are in agreement with the solubility results. When the samples were stored for seven days after irradiation, the $[\eta]$ increases as the plasticizer percent increases, which indicates increased branching and finally crosslinking of the polymer chains. Both dibutyl phthalate and tricresyl phosphate are effective, but the intrinsic viscosity and

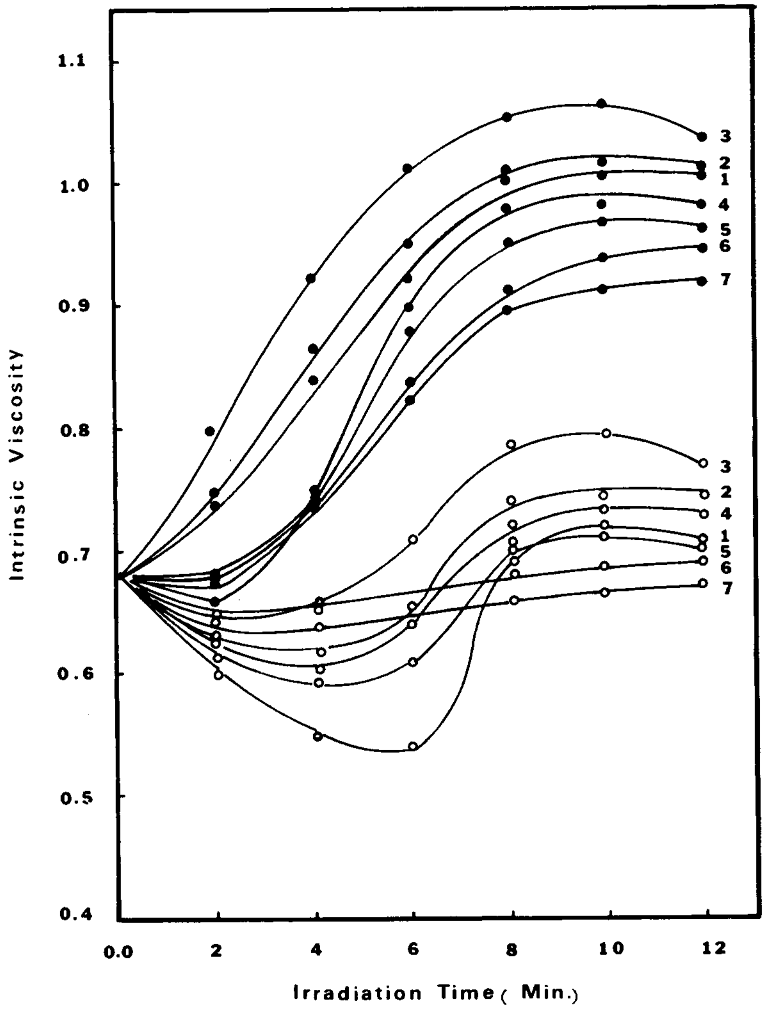
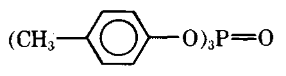
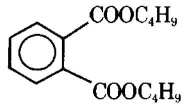


Fig. 3. Effect of irradiation time on intrinsic viscosity of PVC (plasma energy 7.5 eV): (●) storing period 7 days; (○) storing period 10 min; (1) pure PVC; (2) PVC + 20% DBPhth; (3) PVC + 40% DBPhth; (4) PVC + 20% TCPhos; (5) PVC + 20% TCPhos + 10% $CaCO_3$; (6) PVC + 20% TCPhos + 10% $CaCO_3$ + 5% DBLPh; (7) PVC + 20% TCPhos + 10% $CaCO_3$ + 10% DBLPh.

hence the extent of crosslinking is higher in the case of dibutyl phthalate. This may be easily explained as follows: The aromatic compounds which have a resisting nature to radiation are characterized by resonance-stabilized structures which apparently can absorb and dissipate energy through a vibration process.[13] More recent studies consider this problem from the point of view of C–H bond energy which is nearly equal to that of the lowest and most stable level.[14] Hence, on a weight basis, tricresyl phosphate (a) which contains more aromatic units than dibutyl phthalate (b) is less effective than the latter in bringing about the observed transformations:



a



b

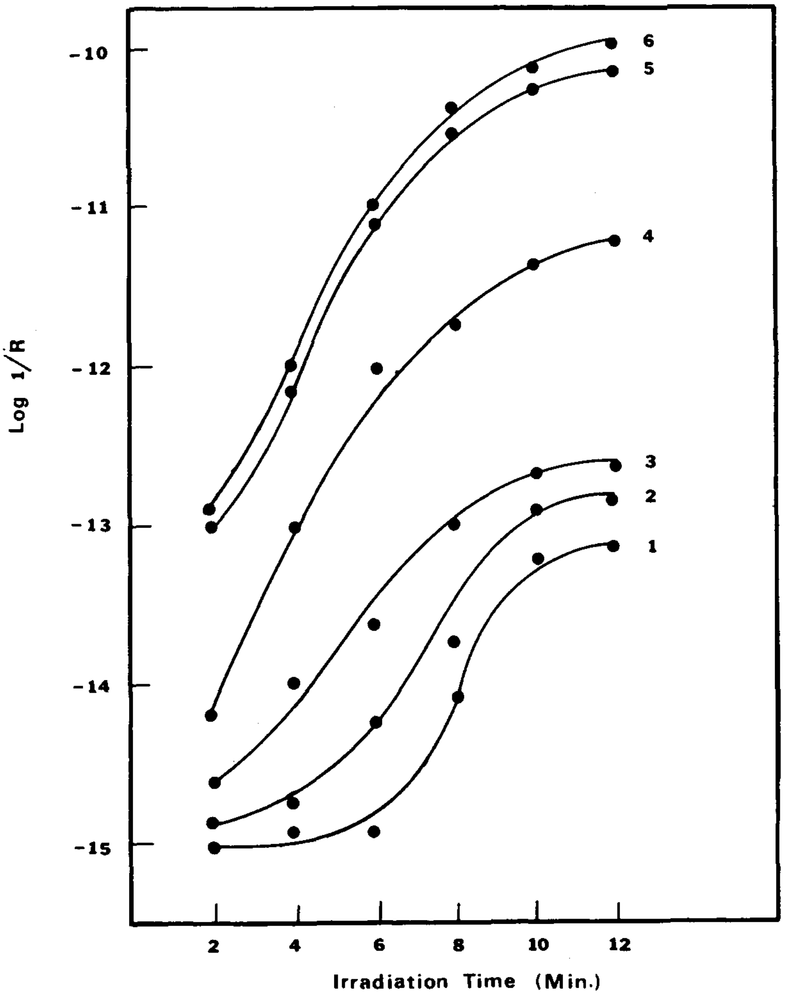


Fig. 4. Effect of irradiation time on conductivity of irradiated pure PVC (plasma energy 7.5 eV). Storing period: (1) 10 min; (2) 1 day; (3) 3 days; (4) 7 days; (5) 30 days; (6) 45 days.

Crosslinking was also followed by measuring the swelling ratio of the PVC gels formed after irradiation. The swelling properties of crosslinked polymers depend on the density of crosslinking or the average molecular weight between chains. It is clear from Figure 2 that the extent of swelling of PVC blended with plasticizers is less than that of pure PVC, suggesting that the presence of a plasticizer during irradiation promotes crosslinking to a greater extent.

Analysis of the solubility, intrinsic viscosity, and the swelling data shows that the postirradiation effect is an important factor. It affects the rate of crosslinking more than the irradiation dose itself. The high-energy plasma particles fall on the polymer surface, generating free and trapped radicals and ions, the concentration of which will be determined by the energy of the particles and the area of the polymer sample. On standing, these free radicals and ions migrate deeper into the sample.[15] The rate of propagation is proportional to the storing temperature and to the initial concentration of radicals and ions. The presence of plasticizers facilitates the migration process, thus giving a maximum response

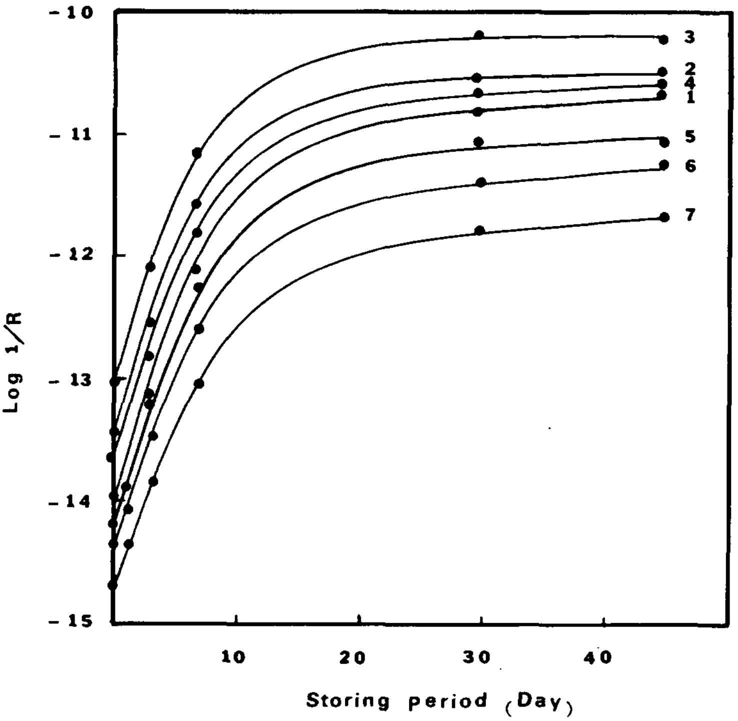


Fig. 5. Effect of storing period on conductivity of irradiated PVC (irradiation time 8 min, plasma energy 7.5 eV): (1) pure PVC; (2) PVC + 20% DBPhth; (3) PVC + 40% DBPhth; (4) PVC + 20% TCPhos; (5) PVC + 20% TCPhos + 10% $CaCO_3$; (6) PVC + 20% TCPhos + 10% $CaCO_3$ + 5% DBLPh; (7) PVC + 20% TCPhos + 10% $CaCO_3$ + 10% DBLPh.

to plasma. On the other hand, the presence of stabilizers and fillers reduces the effect of plasma. The filler increases the steric hindrance inside the polymer which decreases its response to radiation. Furthermore, the filler increases the internal viscosity of the polymer, which prevents free-radical migration. Moreover, the presence of stabilizers may disrupt the free-radical process.[16] This may suggest a free-radical mechanism for the crosslinking process.

From the kinetic investigations of the PVC dehydrochlorination reported in the literature[16-19] and from the results discussed above, a radical mechanism may generally be accepted. Many authors consider the chlorine atom from a direct homolytic cleavage of the C–Cl bond to be an active part of the chain reaction.[17] This assumption is reasonable as the C–Cl bond dissociation energy is about 20 kcal/mole less than the energy of either C–H bonds. The homolysis of the C–Cl bond is followed by reactions of the chlorine atom as suggested by Winkler[16]:

$$\text{—CH}_2\text{—CHCl—CH}_2\text{—CHCl— + Cl}^\cdot \rightarrow \text{—CH}_2\text{—CHCl—CH}^\cdot\text{—CHCl— + HCl}$$

The resulting radical is quite unstable and sustains the propagation of the chain reaction leading to the formation of HCl and conjugated unsaturation:

$$\text{—CHCl—CH}^\cdot\text{—CHCl—CH}_2\text{—} \rightarrow \text{—CHCl—CH=CH—CH}_2\text{— + Cl}^\cdot$$

$$\text{Cl}^\cdot + \text{—CHCl—CH=CH—CH}_2\text{—} \rightarrow \underset{\text{(allyl radical)}}{\text{—CHCl—CH=CH—CH}^\cdot\text{—}} + \text{HCl}$$

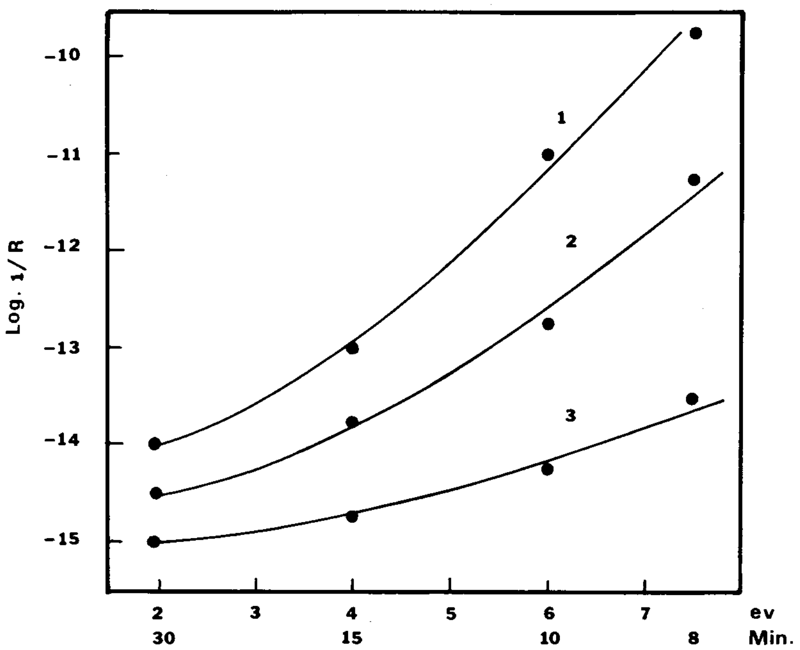


Fig. 6. Effect of dose rate on conductivity of irradiated PVC. Storing period: (1) 10 min; (2) 7 days; (3) 45 days.

$$\text{—CHCl}\!\left(\text{CH=CH}\right)_n\text{CH}^{\cdot}\text{—CHCl—CH}_2\text{—} \rightarrow \left(\text{CH=CH}\right)_{n+1}\text{CH}_2\text{—} + \text{Cl}^{\cdot}$$

(polyenyl radical)

$$\text{Cl}^{\cdot} + \text{—CHCl}\!\left(\text{CH=CH}\right)_{n+1}\text{CH}_2\text{—} \rightarrow \text{—CHCl}\!\left(\text{CH=CH}\right)_{n+1}\text{CH}^{\cdot}\text{—} + \text{HCl}$$

The resulting allyl and polyenyl radicals contain thermally labile allylic chlorine atoms which remain even after radical termination.[18] Under the action of energetic plasma particles, similar mechanisms may exist.

In the presence of oxygen, the formation of peroxides and hydroperoxides is possible. On subsequent dissolution the hydroperoxides may decompose to form an aldehyde and alcohol and produce main chain scission, which may also occur by rearrangement of the peroxy radicals.[19] This may explain the low intrinsic viscosity observed at the low irradiation doses. Moreover, as the polymer crosslinks, some molecular weight separation occurs as the higher molecular weight molecules have a higher probability of becoming insoluble than the lower ones. Accordingly, one would expect the soluble part to contain shorter molecules on the average. However, a systematic study of the ESR spectra of the PVC irradiated with energetic plasma particles remains to be undertaken.

The physical and chemical structures of the polymer were evidently changed after plasma irradiation. These structural changes are reflected in their electrical conductance. The persistence of conductivity after plasma irradiation is contradictory to the effect of gamma irradiation, in which the conductivity falls exponentially with time. Early attempts to ascribe conduction in PVC to ionic impurities can be refuted for the following reasons: Measurements carried out on purified polymer and plasticizer did not lead to an increase in resistivity in comparison with that of commercial samples. The values of conductivity in unplasticized PVC, at the same temperature, obtained by many authors are practically the same, which is hard to understand if the current is carried by an uncontrolled amount of ionic impurities. Further, equal activation energies for the dc conductance and dielectric loss are difficult to interpret if the steady current is carried by impurity ions. It is believed, therefore, that the steady conduction in PVC must be due to intrinsic carriers.

Recent reports propose different mechanisms for dc conductivity in PVC. For instance, Kosaki et al.[20] are in favor of hopping ionic conduction; and Fleming and Ranicare[21,22] favor electronic conduction, interpreting their results in terms of energy-band theory. Oster[23,24] accepts successive ionic and electronic conduction, while Parrini[25] contests the existence of a steady current at temperatures below the glass transition temperature and assumes an ionic conduction above this temperature.

The so-called hopping conduction mechanism, proposed by Lupu et al.,[26] seems to be a plausible one. They proposed the following explanation for the dc conduction in PVC: For every thermally activated segmental motion of the polymer chain which produces the dielectric α or β absorption (the high- and low-temperature regions, respectively), there exists some probability that a favorable configuration will be realized for the carrier to hop in the direction of the electric field. One may imagine that in such a hopping the carrier passes from a site corresponding to a potential minimum to another similar site possibly situated on another molecule. Thus, the molecular motion responsible for the dielectric absorption also allows dc conduction. After the application of an electric field, the steady state attained when the polarization current has dropped to zero must be imagined as a state of dynamic equilibrium with respect to micro-Brownian motion, thus creating the condition necessary for dc conduction. In the case of plasma irradiation, an additional factor contributing to conductance will be the trapped ions. The polyene structures formed will serve as a kind of a potential well in which these carriers move more easily.

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