ATEE - 2004

INFLUENCE OF WATER, ELECTRIC FIELD AND IONIZING RADIATION ON ELECTRICAL PROPERITIES OF PVC INSULATIONS

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Abstract

The effects of water, electric field and high energy radiation exposure (γ-irradiation) on electrical and mechanical properties of poly(vinyl chloride) blended with fillers (plasticizer, lead stabilizer and mica) are presented. The present investigations were carried out on plate samples (disks), a part of them receiving radiation doses of maximum 160 kGy. Because mica plays a role of absorbent for hydrochloric acid formed by PVC degradation, favorable properties are obtained for dose up to 120 kGy. The volume resistivity decreases constantly while tan δ remains unchanged for a large frequency range (10^2-10^5 Hz). The increase in mica content of 14 % induces a decrease of resistivity in unirradiated PVC of one order of magnitude. After irradiation at 160 kGy volume resistivity increases by about five times relative to 40 kGy irradiated samples. At 150 kGy tensile strength decreases only with 10 %, and elongation at break presents a light modification in the selected dose range. At 40 kGy, when the degradation becomes relevant, the dipoles are not efficiently trapped by mica and the current does not attend a steady state for a long period (more than half an hour). Some considerations concerning the consequences of high energy exposure of poly(vinyl chloride) on electrical behaviour are presented. Water treeing tests (sample exposure to water and electric field) reveal no consistent difference in abosrption currents determined by mica content in PVC blends.

1. INTRODUCTION

The radiation treatment of polymers started since 1950, when Charlesby discovered the crosslinking of polyethylene [1]. The continuous efforts directed to the modification induced by high energy radiation have provided the useful information on final characteristics of processed materials. Polymer dielectrics may exhibit an improvement in functional parameters like crosslinking or hardening [2-4]. Electrical insulations may be defined as good materials by accelerated testing using radiochemical investigations [5-7]. Special attention has been paid for polymer materials that are inserted in electrical equipments destined to the electrical power stations [8]. Nowadays, several companies have adopted applications of radiation processing of polymers used in cable manufacturing [9, 10]. Figure 1 shows a section area obtained from multilayer insulated cable.

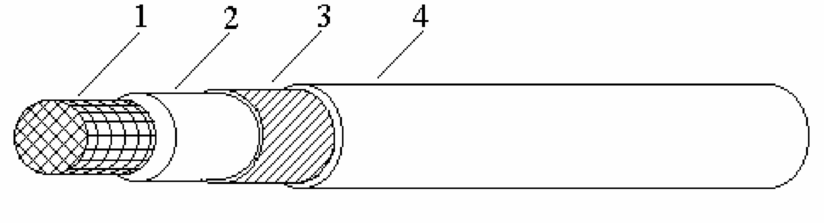

Fig. 1 Structural configuration of low and medium voltage range
(1) metallic wire; (2) irradiated PVC insulation; (3) metallic screen; (4) unmodified PVC insulation

Electrical applications of poly(vinyl chloride) demands accelerated tests for characterizing the alterations occurred during ageing. Several studies concerning thermal degradation [11-14], photostability [15-18] and electrical behaviour [17, 19, 20] of various sorts of PVC were performed. They have emphasized the susceptibility of this macromolecular compound to preserve the initial features as long as the double bond content does not exceed a critical concentration. Two of the practical solutions for ameliorating functional parameters are: blending with other polymers [21, 22] or high energy irradiation [23, 24].

This paper presents changes in mechanical (tensile strength and elongation at break) and electrical (volume resistivity, dielectric constant and dielectric loss) properties of the poly(vinyl chloride) in the presence of mica as hydrochloric acid absorbent.

2. EXPERIMENTAL

Four formulations consisting of poly(vinyl chloride) (OLTCHIM, Romania), mica ($K_2O.3Al_2O_3.6SiO_2.2H_2O$, Mining Ltd, Rm. Valcea, Romania) and plasticizer (lead octoate) were prepared (Table 1). PVC was mixed with the other blending components in a double screws extruder

Sample mark	PVC (parts))	Plasticizer (parts)	Mica (parts)
I	100	4	-
II	100	4	4
III	100	4	10
IV	100	4	14

Table **1**. Sample formulations

Irradiation was performed in the radiochemical equipment GAMMACELL (USA) provided with ^{137}Cs source. Dose rate was 0.4 kGy/h. All exposures were carried out in air at room temperature. Four total doses (40, 80, 120 and160 kGy) were applied to assess the changes in material properties. Unirradiated specimens were also analyzed as references. Each value represents an average of ten determinations.

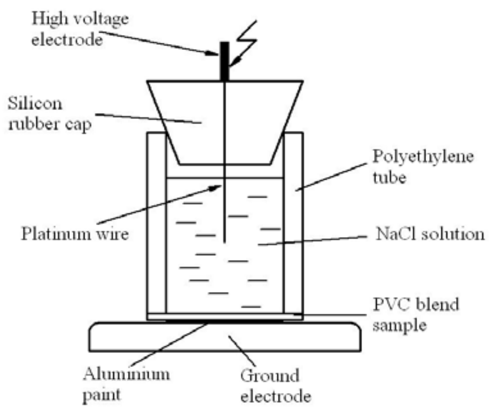

Fig. 2 Cell used to produce water trees [25]

Unirradiated samples were submitted to water treeing tests in cells (figure 2), having as electrolyte a NaCl solution (0,1 mol/l) and an electric field of intensity 3 kV/mm and frequency 5 kHz, for 24 h. Absorption currents through samples were measured both before and after water treeing ageing.

Mechanical properties were obtained by means of INSTRON mechanical tester under the specifications of ASTM 620E. Electrical investigation were done with Keithley electrometer (U. K.), type 6517 at 100 V working tension for volume resistivity, and with multifunctional bridge, Hewlett Packard (USA), model 4263B for dielectric properties, namely permittivity and loss factor.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

Exposure of PVC samples to the action of gamma radiation decreases tensile strength and elongation at break because the macromolecules are cut into several moieties and, in the same time, the entanglement of fragments trends to maintain certain elasticity of materials. In figure 3 the modification in tensile strength and elongation at break by irradiation of PVC samples are illustrated.

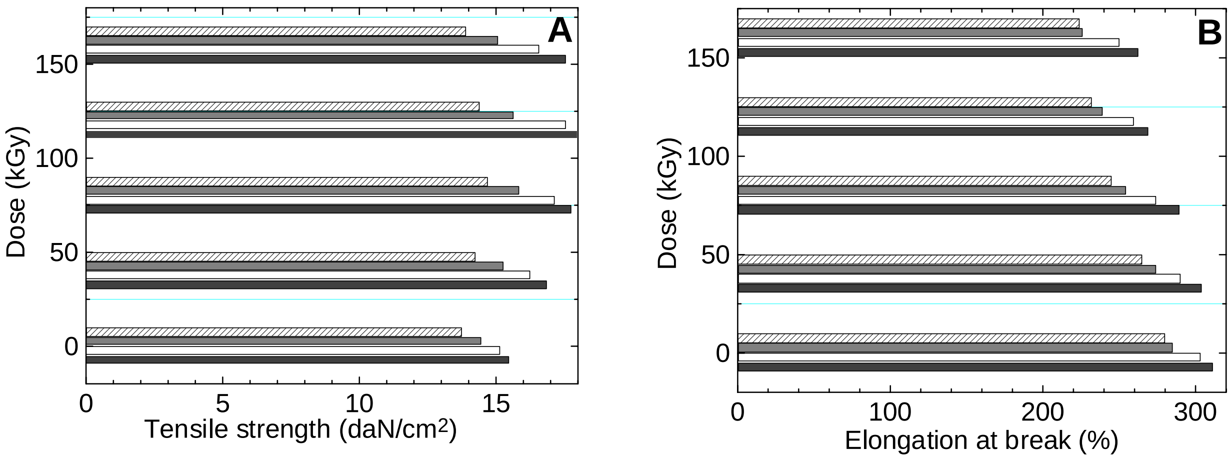

Fig. 3 Modification in tensile strength and elongation at break by irradiation of PVC samples. Samples: (I) black; (II) white; (III) light grey; (IV) hatched.

3.2. Electrical properties

The behaviour of PVC/mica specimens in electrical field is characterised by the changes in the values of relative permittivity. The dependencies of permittivity on irradiation dose and on the testing frequency are shown in figure 4. The increase in this property of irradiated PVC/mica compounds is probably due to the transfer of chlorine atoms from poly(vinyl)chloride into mica component. This displacement leads to the decrease in the values of ε_r for PVC, but it is not compensated by the accumulation of this polarisable atoms

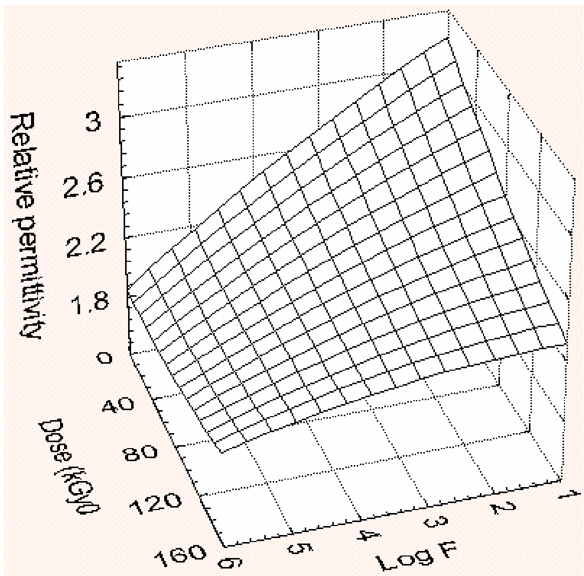

Fig. 4 Dependencies of relative permittivity on irradiation dose and measurement frequency

in mica fraction. The values of dielectric loss are slightly modified by irradiation. The explanation of this stability is based on the constant content of chlorine in the samples.

Electrical resistivity is influenced by radiation treatment because during exposure the oxidative degradation of polymers occurs. For low irradiation dose, when the amount of oxidation products does not reach a measurable value, poly(vinyl)chloride may be crosslinked. The formation of double bonds by dehydrochlorination brings about new reactive positions capable to be split and to generate radicals. In this stage of irradiation the resistivity of sample is increased (figures 5), while the dose of 40 kGy gets a real difference between the four types of PVC/mica samples (figure 5a).

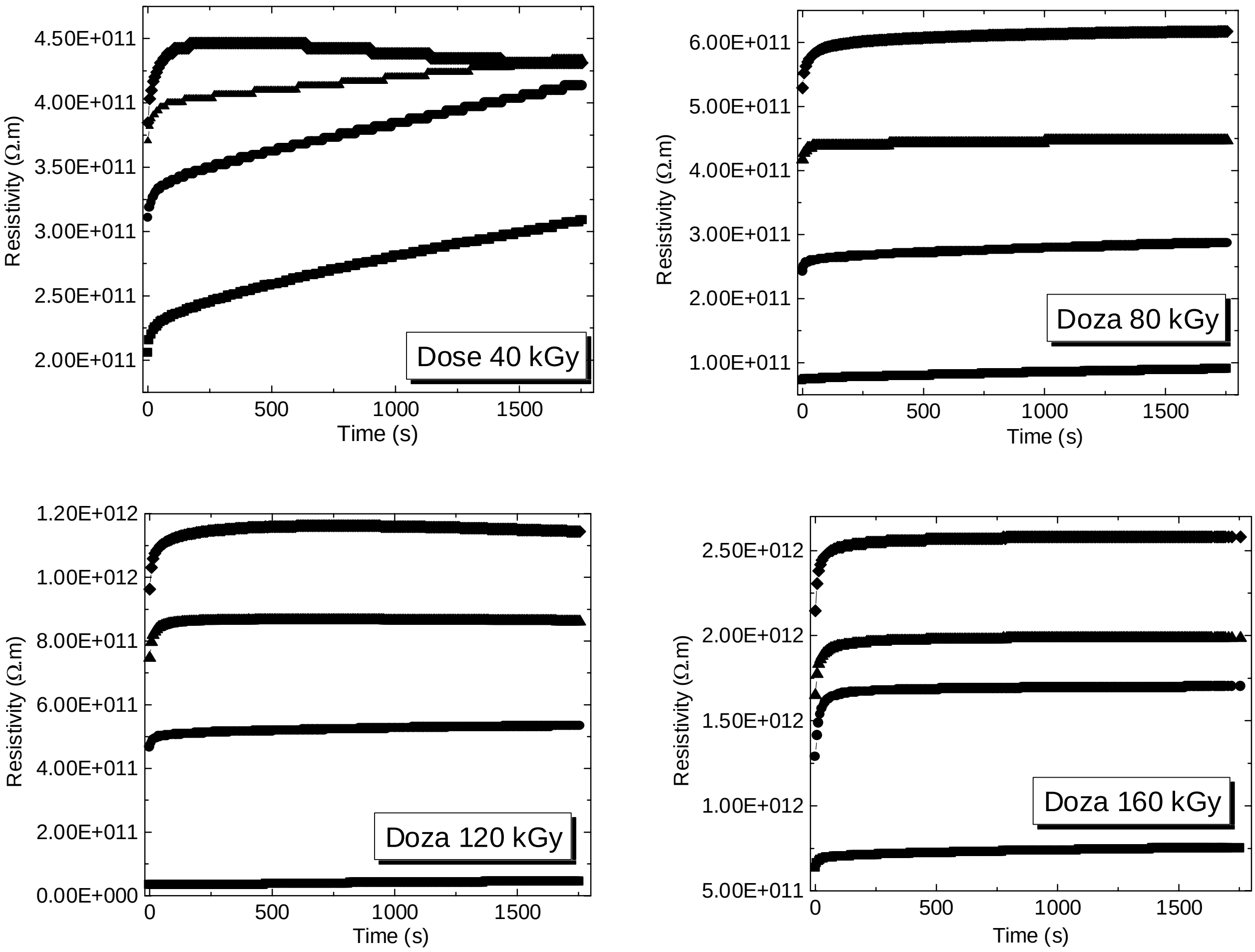

Fig. **5** Time dependencies of resistivity on sample composition and irradiation dose.
(■) sample IV; (●) sample III; (▲) sample II; (♦) sample I.

The differences that may be noted from figures 5 emphasise the ascendant tendency of current values as irradiation dose increases. This behaviour may be due to the accumulation of hydrochloric acid in the inorganic phase as the result of polymer dehydrochlorination. The most suggestive comportment for radiation-induced modification in PVC matrix is depicted by the 40 kGy irradiated sample. While the PVC sample containing 14 % mica exhibits an evident current diminish on the first stage of measurement (increased resitivity), followed by slight decrease in the current value, the sample free of mica displays a monotone augmentation in resistivity. Samples containing different amounts of mica reveal unlike behaviour in relation to resistivity variation. While chemically unmodified PVC (figure 6a) exhibits a large difference between unirradiated and exposed samples, the formulation consisting of PVC with 14 % mica presents more spread placement onto the $\rho(t)$ space.

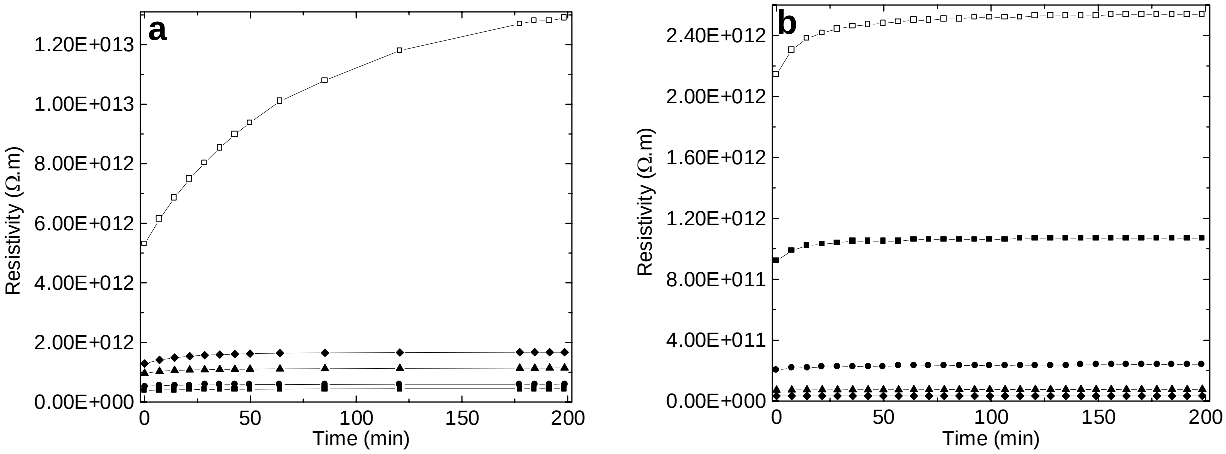

Fig. 6 Distribution of resistivity for various irradiation doses.
(□) unirradiated; (■) 40 kGy; (●) 80 kGy; (▲) 120 kGy; (♦) 260 kGy.

3.2. Water treeing

The water treeing resistance of PVC-mica samples was assessed by the changes of the absorption currents values. The absorption currents variations for 100 % PVC and for 86 % PVC + 14 % mica samples are shown in figure 7. One can remark that the salted water diffusion through the samples leads to absorption current values of 3 - 4 times higher than in reference samples, but the increase of current values in the treed samples is quite the same in both cases presented, with no consistent difference due to mica content. The accumulation of double bonds in the PVC phase develops a larger availability of polymer to damage. The simultaneous action of natrium chloride and electric field would accelerates the attach rate of ions on the weaker positions in polymer macromolecules (double bonds). But, these circumstances are favourable not only for the initiation of water treeing, but also to propagate it. The same was observed for all blending concentrations.

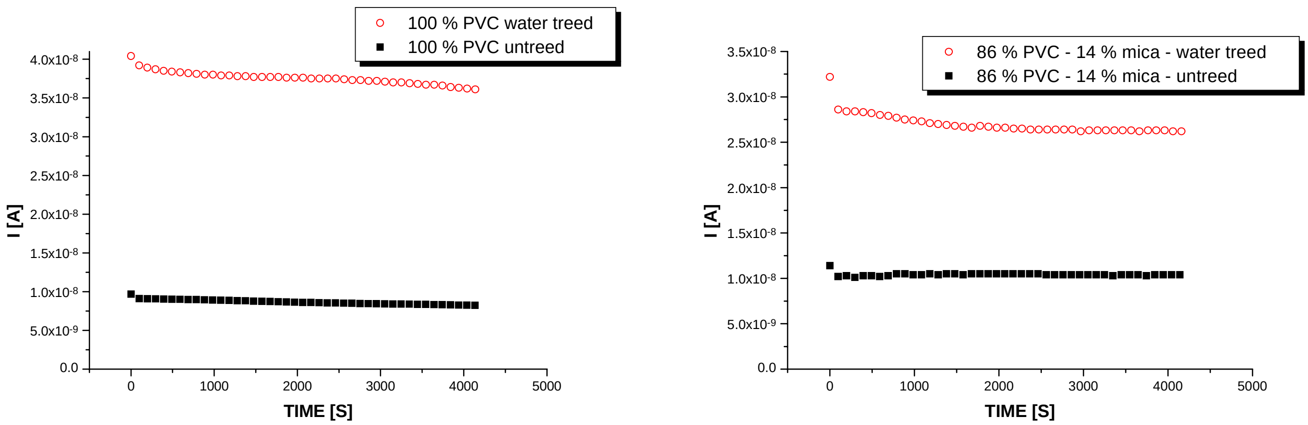

Fig. 7 Absorption current variations.

4. CONCLUSION

Water treeing tests reveal that mica content does not have an obvious influence on the increase of the absorption currents values in treed samples compared to untreed ones.

Radiation processing of PVC for electrical purposes produces modifications in the behaviour of material, but the changes in resistivity values do not influence the life time of this kind of insulations for long term service.

Accelerated testing of PVC dielectric material emphasises the proper behaviour in the damaging conditions. The addition of inorganic filler, mica, anticipates proper condition for the abstraction of hydrochloric acid from polymer phase decreasing the probability of its attack on the more reactive positions (double bonds) generated in PVC molecules by γ-irradiation.

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