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Radiation modification of functional properties in PVC/mica electrical insulations

Traian Zaharescu[a] (✉), E. Nemeş[b], M. Râpa[b], E. Grosu[b]

[a]Advance Research Institute for Electrical Engineering, 313 Splaiul Unirii, Bucharest 030138, Romania
[b]INCERPLAST, 23 Ziduri Moşi, Bucharest, Romania
e-mail: traian@gw-chimie.math.unibuc.ro, fax: 0040-1-346-8299

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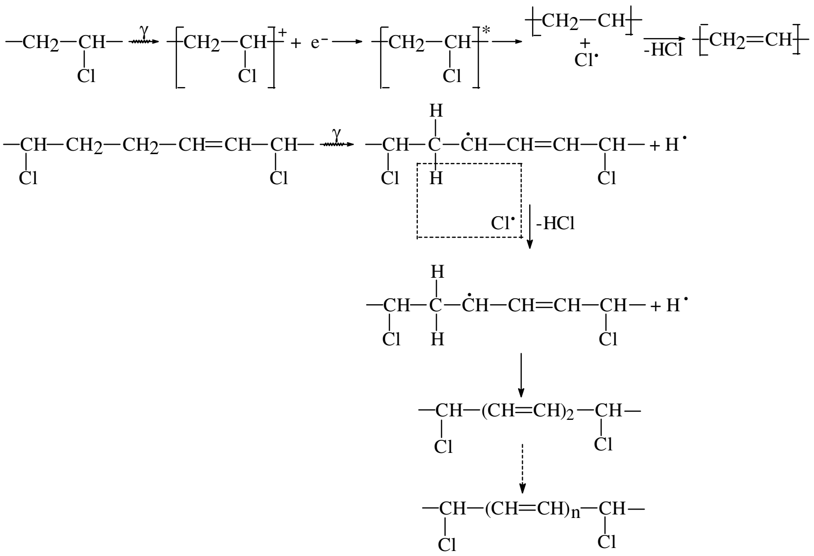
Summary

The effects of γ-irradiation on poly(vinyl chloride) blended with fillers (plasticizer, lead stabilizer and mica) are presented. Mechanical and electrical investigations were carried out on samples that received doses of maximum 160 kGy. The results on tensile strength, volume resistivity and loss factor prove that poly(vinyl chloride) may be used as electrical insulator after short γ-exposure. 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 cps). Mica content of 14 % induces a decrease in unirradiated PVC of one order of magnitude. After irradiation at 160 kGy volume resistivity increases of 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. The largest differences between the maximum current values obtained for applied doses are presented by PVC with the highest concentration of mica (14 %). 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). For higher doses the steady-state current is reached after only 1-3 minutes, due to crosslinking. Some considerations concerning the consequences of high energy exposure of poly(vinyl chloride) on electrical behaviour are presented.

Introduction

Endurance investigations on polymers represent a permanent task for material characterization. Several ways of degradation lead to the damage of products. Of a great importance is the long-term stability of electrical wire and cable insulators. The action of permanent mechanical stress, humidity, oxygen, and other environmental factors shorten the life time of goods. The intensity and the duration of ageing induce significant changes in material properties.

Poly(vinyl chloride) has a high demand on the polymer market, even if it is processed as monocomponent or as blend raw materials. The understanding the property-structure correlation helps either the manufacturers to produce high quality polymer, or customers to use proper material required for any particular application. For PVC the simplest and the most general description on radiation degradation is dehydrochlorination. This process occurs via allyl radicals as precursors of conjugated polyene macroradicals [1, 2]:



The large scale manufacture of PVC-based electrical insulators technologically starts from the laboratory investigations. Natural weathering applied to poly(vinyl chloride) induces not only yellowing and oxidation, but also material rigidizing and increase in T_g values [3, 4]. On the other hand, high energy irradiation of PVC induces an increase in gel content, and, consequently, an enhanced hardness and tan δ_{max}. [5-7]. The improvement in the durability of PVC products is obtained by including additives like antioxidants [8] or inorganic compounds: oxides [9] or carbonates [10].

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 [21-24] or high energy irradiation [6, 25-29]. The last procedure has been adopted by several industrial companies for the fabrication of different classes of electrical cables.

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.

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 foreseen with four temperature zones to ensure the homogeneity of samples [22, 23]. After extrusion the composites were kept in plaque form by pressing at 150 atm for 10 min, from which dumbs and round pieces were obtained for mechanical tests and electrical studies, respectively.

Table 1. Sample formulations

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

The exposure to high energy radiation was performed in the radiochemical equipment GAMMACELL (USA) irradiator 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 and 160 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. For electrical study a cumulative experiments were carried out, each sample being replaced in the irradiation zone for additional exposure after electrical measurements. On the interval when samples are neither irradiated, nor under determination, they are placed in a dissector to avoid the humidity adherence on surface. 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 [24].

Results and discussion

It is generally admitted that the use of polymers is limited by technological conditions under which they are manufactured. The radiochemical processing of polymers must be managed under strict irradiation parameters, because any deviation from optimal exposure circumstances may cause irreversible and unacceptable changes in the functional features. For electrical applications, any difference in the order of magnitude for operational properties leads to the modification of insulation class in which studied material may be included. The behaviour of processed poly(vinyl chloride) as electrical insulation is peculiarly influenced by structural modifications at various irradiation doses, because the elimination of hydrochloric acid and the generation of double bonds will alter the polarizability of material.

3.1. Mechanical properties

Poly(vinyl chloride) belongs to the class of radiation crosslinkable polymers [25]. The mechanical properties: tensile strength and elongation at break will depend not only on the sample formulation, but also on the irradiation dose. Figure 1 presents these properties for all tested compositions. The decrease in the both mechanical peculiarities is due to the lack of chemical interaction between mica and polymer matrix. The analysis of these data reveals linear dependency of tensile strength and elongation at break on the concentration of mica. This aspect proves not only the homogenous distribution of mica particles in PVC, but also the efficient packaging of additive by the entangled macromolecules. The increase in mica content contributes to the enlargement of intermolecular distance worsening the mechanical resistance of PVC dumbs.

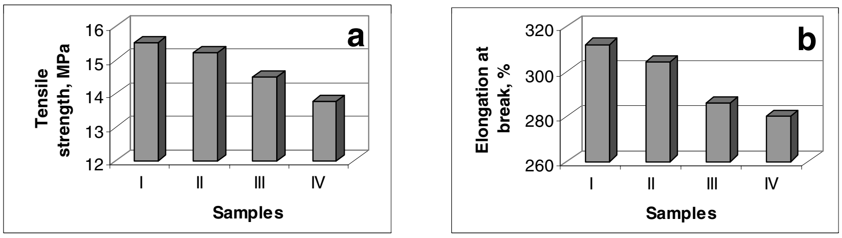


Figure 1. Changes in tensile strength (a) and elongation at break (b) for various PVC/mica formulations subjected to γ-irradiation at 120 kGy.

The γ-exposure of PVC/mica specimens brings about an increase in tensile strength and a simultaneous decrease in elongation at break. The low irradiation doses up to 100 kGy are proper for developing crosslinking. The intermolecular bridges formed during irradiation enhance the stress value, while the strain of radiation modified poly(vinyl chloride) composites falls down progressively. Samples irradiated at 160 kGy show a lower contribution to the tensile strength values because the rate of degradation would exceed the rate of crosslinking. However, the samples irradiated at this dose present higher mechanical resistance in comparison with unirradiated samples. The exposure to a total dose of 100 kGy confers satisfactory mechanical parameters to the electrical insulations consisting of PVC and mica. It means that 1 m of PVC cable insulation with an outer diameter of 3 mm and a material thickness of 1 mm may support a longitudinal mechanical charge 3.10^4 times greater than it weight.

3.2. Electrical properties

The presence of chlorine atoms in the poly(vinyl chloride) molecules determines an increased polarizability in comparison with polyolefins. The amount of mica included in polymer substrate will decrease the permittivity. In figure 2 the dependencies of dielectric constant on measuring frequency are presented. It can be remarked that the formulations with less than 10 % mica exhibit significant differences in ε_r. The advanced dilution of chlorine concentration does not influence other increase in the permittivity values. It can be considered that 10 % represents a threshold in the modification of this parameter relative to the additive concentration.

The unlike behaviour has been noticed by the determination of loss factor at various frequencies. Because of the independence of tan δ on additive concentration (figure 3), it may be supposed that the electrical field is not deformed in the inner part of samples by the mica particles. At different measuring frequencies, the loss factor increases due to the higher effort spent for the periodical deformation of electron cloud.

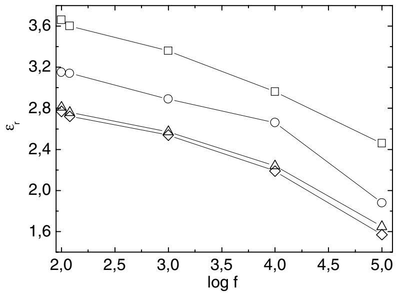


Figure 2. Modification in dielectric constant for γ-irradiated various PVC/mica blends. (□) free of mica; (○) 4 % mica; (Δ) 10 % mica; (◊) 14 % mica.

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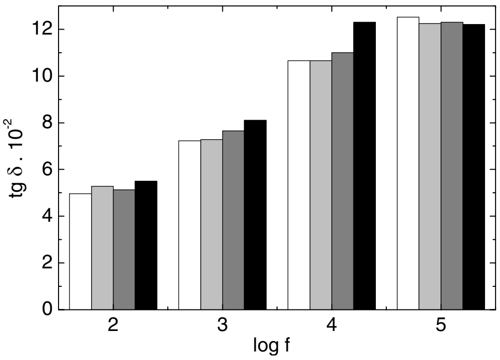

Figure 3. Modification in dielectric loss for γ-irradiated various PVC/mica blends. (white) free of mica; (light grey) 4 % mica; (dark grey) 10 % mica; (black) 14 % mica.

Electrical resistivity is the most representative characteristic for cable insulations. It depicts the structural integrity under the action of electrical field, and the electron availability as charge carrier. For poly(vinyl chloride) the energy transfer from γ-radiation is consumed for bond scission, which is followed by the remote of hydrochloric acid, and the increase in unsaturation level, or by crosslinking. Consequently, the electrical resistance will take certain values according to the modification degree induced during irradiation.

Figure 4 presents the time dependences of electrical resistance for irradiated PVC samples containing various amounts of mica.

The highest mica concentration of 14 % promotes a decrease of one order of magnitude in the values of this parameter. This effect may be due mainly to the presence of inorganic ions (potassium), but aluminum atoms that are constitutive components of additive would also cause it. The steady state conductivity is reached easier in the samples with high mica content in comparison with unmodified poly(vinyl chloride) specimens, because the electrons that participate at the conduction process would be scavenged by the crystalline silicate network after several collisions. The process is assisted by the loss of kinetic energy by the interaction with electronegative atoms (oxygen atoms) existing in silicate structure.

The consequence of γ-irradiation on the modification occurred in electrical resistance of modified-PVC samples may be remarked in figure 5. The low rate removal of chlorine (Fig.5a) is followed by mitigation in the resistivity of mica-free sample. By contrary, the PVC probes containing mica present a continuous increase in electrical resistance, because the inorganic filler act as scavenging phase withdrawing hydrochloric acid from polymer substrate. However, a slight rise of resistivity (Figs 5b – 5c) may be noticed in the resistivity obtained for irradiated and modified PVC samples. This behaviour of studied systems would be due to the limited motion of chloride ions in mica phase and the hindering contribution of three dimensions network (crosslinked phase) grown during irradiation.

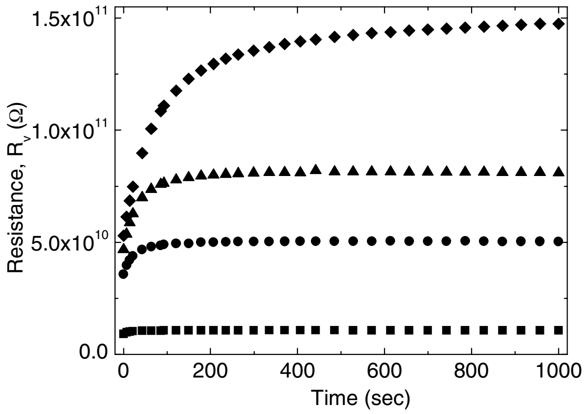

Figure 4. Time dependencies of electrical resistance for the unirradiated PVC/mica specimens with similar thicknesses.

(♦) free of mica; (▲) 4 % mica; (●) 10 % mica; (■) 14 % mica.

The higher content of filler emphasizes the tendency of the improvement in the resistivity values obtained for the polymer samples irradiated at 80 and 120 kGy. At 160 kGy, the resistivity range covers low values, probably due to an advanced stage of degradation. This electrical measurements indicate the role of light crosslinking in the radiation treatment of poly(vinyl chloride). The higher dose rate would induce a higher crosslinking level, which will contributes to a proper adjustment of resistivity. The quality of electrical insulators will be upgraded allowing to be used for higher voltage range.

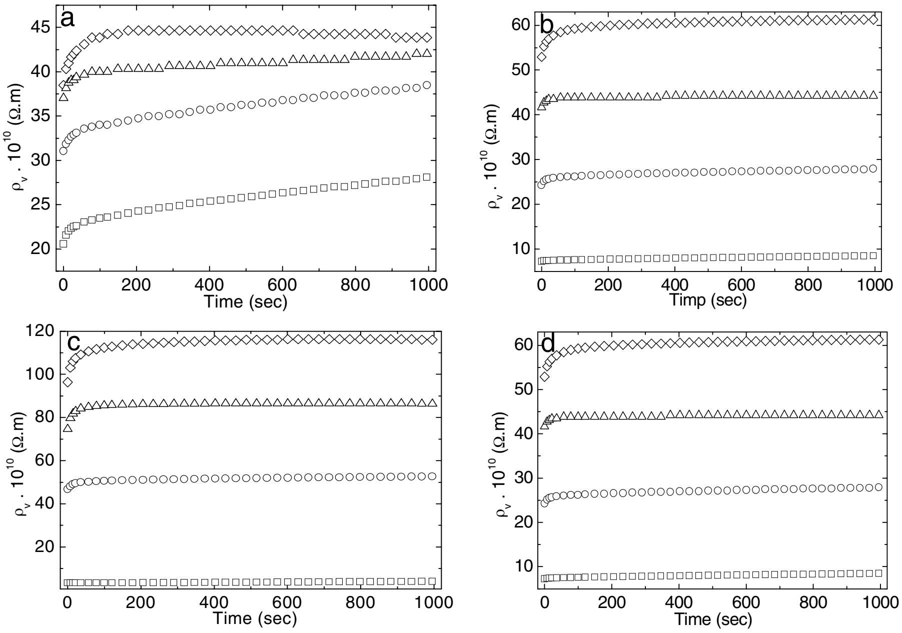

Figure 5. Dependencies of the resistivity on measuring time for PVC/mica formulations at various irradiation doses.
(◊) free of mica; (Δ) 4 % mica; (○) 10 % mica; (□) 14 % mica.
(a) dose: 40 kGy; (b) dose: 80 kGy; (c) dose: 120 kGy; (d) dose: 160 kGy.

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Conclusion

High energy irradiation of poly(vinyl) chloride brings about an improvement in electrical resistance, when exposed probes contain an inorganic filler that plays the role of absorbent of removed hydrochloric acid. Even though the dielectric loss of γ-irradiated PVC/mica formulations keeps constant values for the same blending composition, the dielectric permittivity decreases when the concentration of filler rises with some percents, or the measurement frequency is higher.

The electrical insulations manufactured by PVC/mica blends present improved mechanical strength in the dose range of 100 kGy due to a partial crosslinking of polymer phase, while the elongation at break decrease as the value of absorbed dose increases.

The high energy irradiation offers a good alternative for manufacture of electrical insulators made from poly(vinyl) chloride and the quality of radiation modified material displays favorable characteristics for several applications in the range of low tensions.

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