Effects of γ-irradiation on PVC/mica Electrical Insulation

TRAIAN ZAHARESCU[1], SILVIU JIPA[1,2], EMIL D. POPESCU[3], WILHELM KAPPEL[1], GHEORGHE SAMOILESCU[4]
[1] INCDIE ICPE CA, 313 Splaiul Unirii, 030138, Bucharest, Romania
[2] "Valahia" University, Faculty of Sciences, 1 Carol Av., 130024, Targoviste, Romania
[3] Technical Military Academy, 81 - 83 G. Cosbuc Str., 050141, Bucharest, Romania
[4] "Mircea cel Batrân" Naval Academy, 1 Fulgerului Str, 900218, Constanta, Romania

This paper presents the effects of high energy irradiation on polyvinylchloride samples, some of them containing filler (1 and 5 % mica). The generation of dipoles as oxygenated radiolysis products modifies electrical behavior of polymer matrix. The presence of mica influences the rate of oxidation by decreasing the progress in the accumulation of oxygenated products. The values of volume resistivity, dielectric constant and loss factors are consequently changed as the mica content differs due to the adsorbent action of filler.

Keywords: PVC, mica, irradiation, volume resitivity, dielectric constant, loss factors

Polymer materials represent a large category of dielectrics, which cover a wide range of applications. The usage of polyvinylchloride in the electrical protection of wires and plates destined to electronic equipments and to several kinds of sealants in nuclear range requires a detailed investigation on the modifications induced by high energy radiation. These types of assays include also the characterization of durability for neat and modified PVC for the evaluation of the consequences caused by fast and intense energetic transfer onto electrical insulations.

Some papers dealing with the evaluation of functional properties of irradiated polymers used as electrical insulations were reported [1-10]. The necessity on the evaluation of quality control and durability of the electrical insulations imposes the enlarging area of research on various formulations of materials. The compounding process offers to manufacturers the alternatives for "classical" compositions. The addition of various fillers determines important modifications in the chemical and electrical behavior of dielectrics. Under these circumstances, the investigation on various levels of degradation emphasizes the involvement of filler in the degrading polymer matrix. Some papers on the radiation effects upon polyvinylchloride were published [11-15]. Although the technologies of addition of fillers to polymers to enhance a particular property have been reported for a long time [16, 17], the effects of filler composition on the dielectric properties have not been fully understood.

The most important conclusions concerning the influence of degrading conditions on the conductive and dielectric properties have to clarify the direct relations between the cause and the effects, which determine the service regime of insulations and the durability of polymeric covers on the metallic central wires. The purpose of this work is the correlation between chemical modifications induced during degradation and the level of electrical characteristics, the effect of mica on the evolution of degradation in polyvinylchloride bulk.

Experimental part

Sheets of polyvinylchloride with and without mica were obtained by pressing of neat material at 180^{0}C, 250 bars for 10 min. PVC was manufactured by OLTCHIM Rm. Vâlcea as the "impact sort". Three types of samples: neat polymer and 1 and 5% mica content materials were prepared. Sheets of 150 mm thickness were obtained.

They were subjected to the action of γ-rays provided by ^{137}Cs source incorporated in GAMMATOR M-38-2 installation (USA) at a dose rate of 0.4 KGy/h. Irradiation/measurement cycles were applied because of the accumulation of dose. Spectral measurements were carried out with JASCO 4200A (Japan) FTIR spectrophotometer. Conduction investigations were performed with Keithley 6517A (USA) electrometer and dielectric measurements were carried out with Hioki 3532-50 (Japan) RLC bridge.

Results and discussion

The degradation of polyvinylchloride is characterized by the elimination of hydrochloric acid from initial macromolecules and the formation of double bonds. The effect of energetic treatment with ionizing radiation consists of the reactions involving active sites placed on macromolecules and molecular oxygen that exists or it is diffused into irradiated material. The formation of oxygenated products, hydroperoxides and carbonyl compounds is correlated with the modification occurred in IR spectra. In figure 1 two FTIR spectra of initial and irradiated samples are presented comparatively; in figure 2 three FTIR spectra of the PVC samples containing mica are illustrated. The enlargement of 3350 cm^{-1} band that is ascribed to bond hydroxyls and the increasing of absorbance for 1720 cm^{-1} band is accompanied by the extension of 1650 cm^{-1} band, which is attributed to double bond accumulation. Because mica is an inert compound in relation with the radiolysis behavior of polyvinylchloride, the spectral contribution of this component can be disregarded. The progress in the oxidative degradation of polyvinylchloride containing mica takes place with unlike rate due to the involvement of inorganic filler in the scavenging of evolved hydrochloric acid. The differences that exist between the increasing of oxygenated compound contents are justified by the hindering of certain reactions, like the addition of hydrochloric acid or the decrease in the probability of the conversion reaction between oxygenated structures. The quantitative evolution of the oxygenated structures in irradiated PVC/mica samples is presented in figures 3a and 3b.

The difference in the rates of concentration increases for the both types of oxygenated products is justified by the mechanistic ways on which they are formed. According with the Bolland and Gee's scheme [18] reported for the formation of oxygen-containing products in the thermal

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* *email address: zaharescu@icpe-ca.ro*

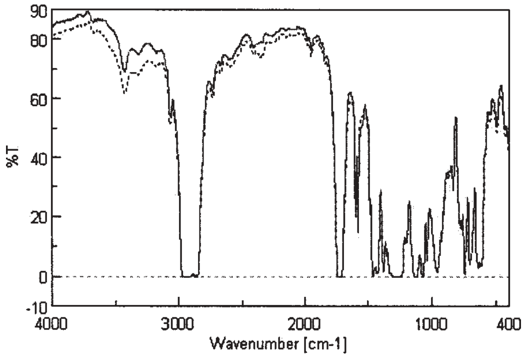

Fig. 1. FTIR spectra of PVC samples at different exposed doses (0 and 50 kGy)

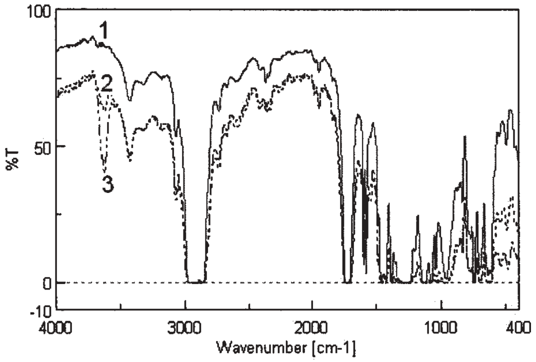

Fig. 2. FTIR spectra of PVC/mica samples exposed at the same dose

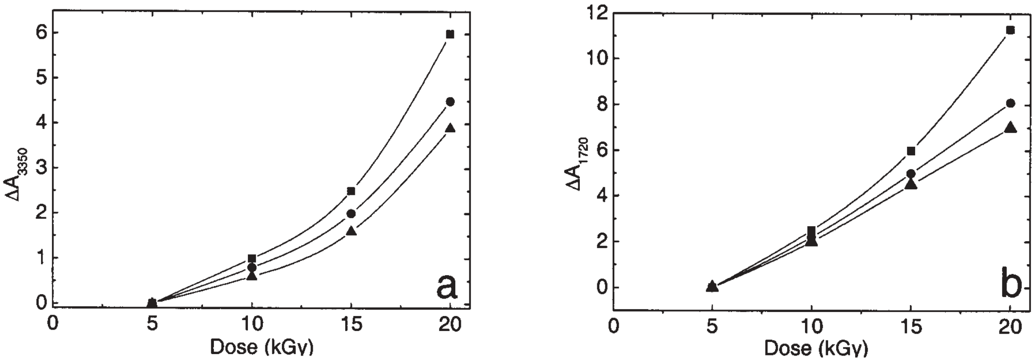

Fig. 3. The accumulation of oxygenated products (a: hydroperoxides; b: carbonyl compounds) in irradiated PVC samples. (■) neat material; (●) PVC/mica 1 %; (▲) PVC/mica 5%

degradation of polyolefins and related compounds, hydroperoxides are generated by the direct reaction of molecular oxygen, while carbonyl structures, especially ketones, are obtained either by the conversion of hydroperoxides, by the reaction between hydrocarbonate free radicals (R·) and alkoxy entity (RO·) or by the extraction of one proton during the reaction between two alkoxy radicals. The two simultaneous increases in the main oxygenated products occur with the accumulation/depletion of ROOH and the cumulation of $R_1R_2C=O$ structures.

The changes in 1650 cm^{-1} band would be quantitatively evaluated, but double bonds that are generated by dehydrochlorination react and on the low dose range selected in this study they did not attend a large extent.

The content of filler modifies the conductivity of polyvinylchloride. The comparison between the different levels of volume resistivity obtained from unirradiated and γ-exposed polyvinylchloride samples (figs. 4a and b) suggests not only the presence of inorganic component in the blends, but also the contribution of chemical modifications occurred in processed materials by the result of sharp energetic transfer. According to the energy band theory [19], the electrical conduction in polymeric insulators can be determined by the interaction between bonding electrons and applied electric field. In high energy irradiated polymers other source of charge carriers are δ-electrons that could be trapped either by the entangled macromolecules, or by the electronegative sites (double bonds and oxygen atoms). These electrons can be released from the attaching positions and their contribution to the conduction level is revealed by the significant diminution in the resistivity of samples.

The conduction of PVC/mica samples is modified in the close relation with applied tension (figs. 5a, b and c). It can be noticed that there is no any proportionality between electrical resistance (expressed by volume resistivity) and applied tension. The upper regions of these figures is occupied by the curves drown at low tensions. They are closer when the amount of filler increases. The smaller distances between the curves $\rho_v = f(t)$ due to the presence of mica, which plays the role of springboard. At higher tension the consequence of the difference in the conduction band energies of the two components (polymer insulator and inorganic filler) can be taken into consideration. However, the mechanisms of conduction in inorganic crystalline compounds and polymers are similar, but the widths of conduction bands explain the

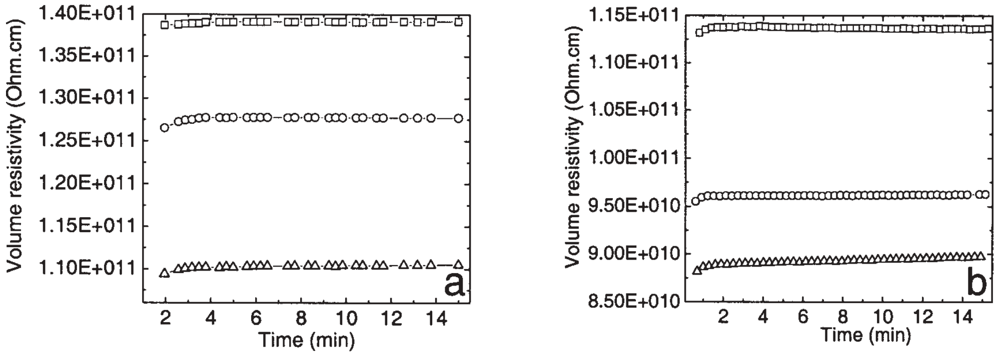

Fig. 4. Variation in the volume resistivity of PVC compounds (□ neat material, ○ PVC/mica 1 %, Δ PVC/mica 5 %). (a) nonirradiated samples; (b) specimens γ-irradiated at 10 kGy

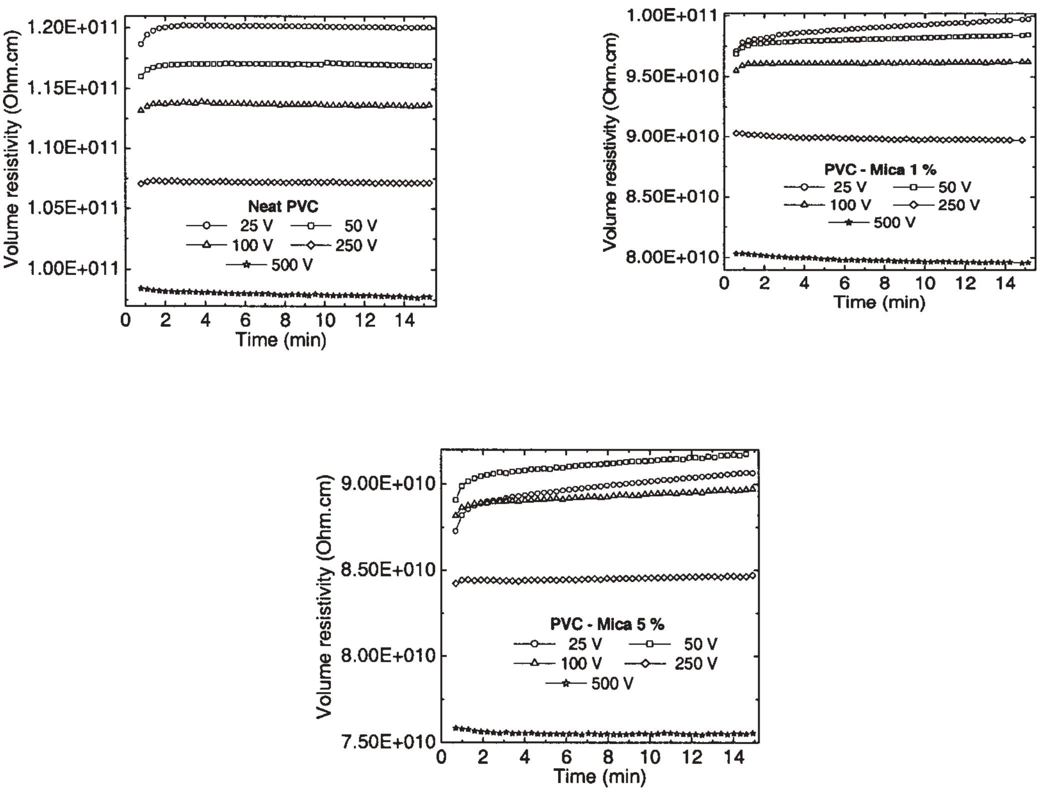

Fig. 5. Variation in the volume resistivity of PVC/mica systems exposed to the action of 15 kGy γ-dose in air

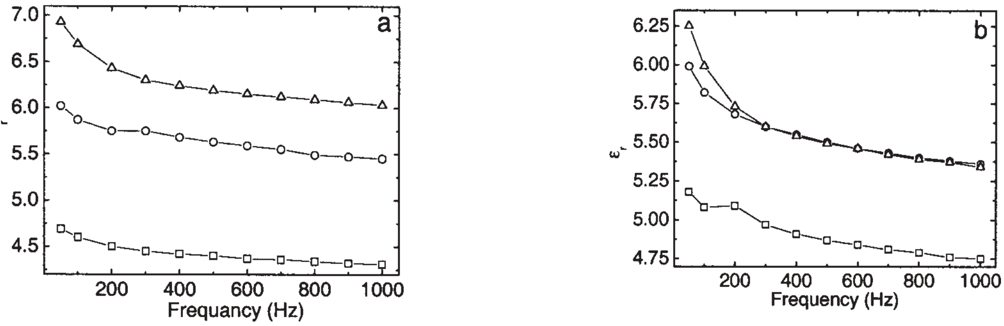

Fig. 6. Changes in the permittivity of two different PVC samples.
(a) neat PVC; (b) PVC + mica 5 % (□) nonirradiated sample; (o) dose: 5 kGy; (Δ) dose: 15 kGy

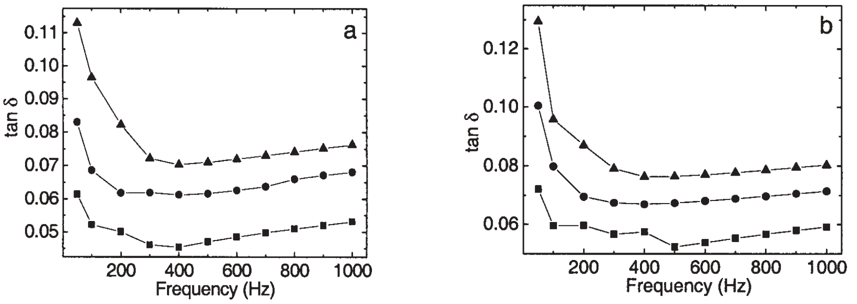

Fig. 7. Changes in dielectric loss of two different PVC samples.
(a) neat PVC; (b) PVC + mica 5 % (■) nonirradiated sample; (●) dose: 5 kGy; (▲) dose: 15 kGy

larger separation space between conduction curves at higher tensions.

The alteration in the distribution of oxygenated products causes the modifications in electrical behavior, either conduction or polarization. In spite of the presence of chloride atoms that brings about a certain level of polarizability, the new products formed during γ-irradiation promote large changes in the electrical replies of materials. In PVC/mica samples dielectric constant increases due to the exposure to γ-radiation because the quantity of oxygen appeared in irradiated samples is enhanced during radiolysis (fig. 6). The samples containing mica present a gathering of values for medium frequency range in contrast with neat probe, where the spread of values is somewhat similar to each other. The loss tangent dependencies on frequency look similar for neat and modified polyvinylchloride samples (fig. 7). The functions tan δ are slightly gathered in the case of irradiated samples. It may be explained the removing of expelled hydrochloric acid from polymer phase into the filler regions and, consequently, the diminution of the interaction between polymer macromolecules and removed chloride atoms from them.

Conclusion

The addition of mica as filler in polyvinylchloride does not substantially modify the electrical characteristics of host material in the undegraded state. However, the exposure to the action of γ-radiation brings about a slight alteration of resistivity values. The most important aspect that can be taken into account from irradiation information is the attestation of radiation processing in the cable manufacture.

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