The Assessment on Insulation Behaviour of Multilayer EPDM/Paper Composite

TRAIAN ZAHARESCU[A], FLORIN BUSE[B], SILVIU JIPA[A,C], ILONA PLESA[D], FLORIN CIUPRINA[D]

[a] INCDIE, ICPE CA, 313 Splaiul Unirii, 030138, Bucharest, Romania

[b] Technical Military Academy, 81 – 83 G. Coşbuc Bd., 050141, Bucharest, Romania

[c] "Valachia" University of Târgovişte, 18-22 Unirii Av., 130082, Târgovişte, Romania

[d] Politehnica University, Faculty of Electrical Engineering, 313 Splaiul Independenţei, 060032, Bucharest, Romania

The multilayer structure consisting of alternative sheets of paper and ethylene-propylene elastomers was investigated for electrical applications. The changes in the main electrical characteristics, namely volume resistivity, dielectric loss, permittivity were determined for the evaluation of material stability under accelerated degradation promoted by γ irradiation. The satisfactory response of this sandwich structure is illustrated by sample resistivity placed around 10^{15} Ω.m, permittivity less 2.025 and dielectric loss not higher than 0.04. The correlation between degradation effects and electrical properties is presented.

Keywords: electrical insulation, synthetic rubber, cellulose, multilayer structure

The electrical insulation used for the manufacture of capacitors must have certain features, which assure the charge accumulation on the plates without breakdown. These characteristics suppose a long term service that determine the lifetime of equipment. Several polymeric materials (polyethylene, polypropylene, polyvinyl chloride, synthetic rubbers, polyesters) are suitable dielectrics [1, 2].

The understanding of the functionality of long term service of electrical insulations requires endurance investigations to be performed. The most important aspects are related to the modifications induced by various damaging factors that act during the operation of electric assembly. The accelerated testing applied to studied material must emphasize the ability to degradation in the direct relation with the intensity and duration of action, the chemical structure, formulation and morphology of samples [3, 4].

The absorbed energy transferred onto materials causes scissions and, consequently, free radicals are decayed through crosslinking or degrading processes. For dielectric materials, the changes occurred in the electrical properties of irradiated material are the effects of structural modifications [5, 6]. Of a great importance for the alteration in the material properties is the oxidation through which dipoles are formed; the accumulation of oxygenated products defines the material behaviour under overcharge regime.

This paper presents the effects on the electrical performances of multilayer (EPDM/paper) structure subjected to a sustained energetic transfer by γ irradiation.

Experimental part

A 10 layers structure consisting of alternative sheets of ethylene-propylene-diene terpolymer (EPDM, Terpit C® delivered by ARPECHIM Piteşti, Romania) was prepared. Polymer films were obtained by the removal of chloroform from EPDM solution cast on capacitor paper (TUKO-W, Schöller & Hösch). Raw elastomers contained 3.5 % (w/w) of 2-ethylidene norbornene as added diene and the ratio of ethylene to propylene units was 3:2.

* *Tel.: 0726636222*

FTIR spectra were recorded on JASCO 4000 spectrometer immediately after the end of irradiation.

The irradiation of samples was carried out in an irradiator GAMMACELL provided with ^{137}Cs source. Dose rate was 0.4 kGy.h^{-1}. The exposures were done in air at room temperatures. For avoiding experimental errors, the irradiations were carried out by accumulation on the same specimens.

The electrical measurements were performed with Keithley 7600A multimeter for the determination of resistivity and with Novocontrol dielectric spectrometer for permittivity and loss tangent. All investigations were accomplished 24 h after the end of irradiations.

Three similar samples were prepared and subject to study for the comparison of recorded results.

Results and discussion

The radiolysis of each component of multilayer structure is the background that initiates the modifications inside layers. Ethylene-propylene diene belongs to the class of crosslinkable polymers [7]. The mechanism through which this polymer is transformed by the action of ionizing radiation was previously reported [8,9]. By contrary, paper that is a cellulose material belongs to the group of degradable materials [10]. The mechanism followed in the radiochemical degradation of cellulose has already been presented [11, 12]. The opposite behaviours of EPDM and cellulose compete for the evolution of degradation state of samples.

The conductivity of irradiated polymers would be based on the tree electrons formed by the ionization of excited molecules as the primary intermediates [14]. The multilayer probe is significantly modified since the amount of δ electrons expelled during irradiation increases as the dose enhances. The contribution of electrons to the conduction is demonstrated in figure 1, where a difference between the shape of the two functions $log\ \rho = f(t)$ recorded on the same sample at different times in relation to the end of irradiation look unlike.

In figure 2 the dependences of volume resistivity on measuring time for different exposure dose are illustrated. The increase in the sample resistivity for low dose (8 kGy)

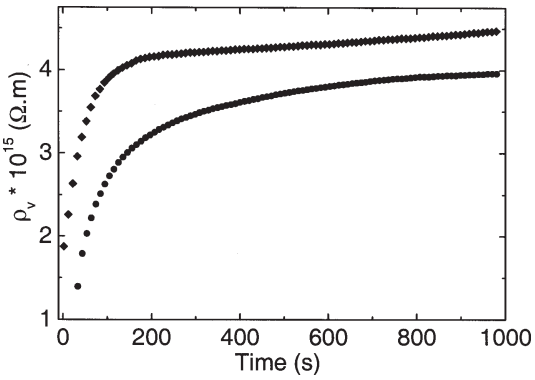


Fig. 1. The variation in volume resistivity of EPDM/paper multilayer sample irradiated in air at 15 kGy measured after two different times elapsed after irradiation (◇) after 20 h; (o) after 72 h

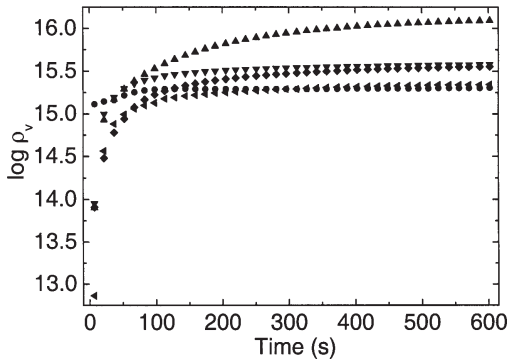


Fig. 2. Resistivity dependences on testing time at different exposure doses (•) 0 kGy; (▲) 8 kGy; (▼) 15 kGy; (♦) 26 kGy; (◄) 50 kGy.

can be explained by the radiation crosslinking of elastomers sheets. This process starts as about 5 kGy, the gel dose for ethylene-propylene diene terpolymer [13].

Due to the proportionality of resistivity on the number of collisions between charge carriers and macromolecules, the relevant decrease in the electrical conduction of low dose irradiated EPDM is displayed. The movement of charge carriers through the enriched hardened phase is prevented by the increased number of new intermolecular bridges and the steady state value of conduction current is attended much later than it is happened in the pristine samples.

The light increase of resistivity in the neat sample on the first 100 s would be caused by the residual trapped electrons that appear during the randomly applied mechanical stress. The irradiation of multilayer structure creates free electrons, which may be scavenged by molecule entanglement or may be trapped by any electronegative impurities. After the application of tension during measurement these electrons are selectively released function of the binding strength. For superior doses (for example 15 kGy), the initial value of resistivity is significantly lower than the similar figure for 8 kGy. The noticeable difference between the steady state values of resistivity consists of the upper conductivity in the 15 kGy irradiated specimen. The decrease in the resistivity of advanced exposed sample can be explained by the start of degradation either by higher rate of scission in comparison with the crosslinking rate, on one hand and the progress in the oxidative degradation of ethylene-propylene terpolymer (fig. 3) on the other hand.

The exposure of sample to increased doses grows the amount of charge carriers and the number of dipoles, which bring about significant diminishing in the resistivity of sample. The elastomers component which is more affected by the action of high energy radiation than cellulose

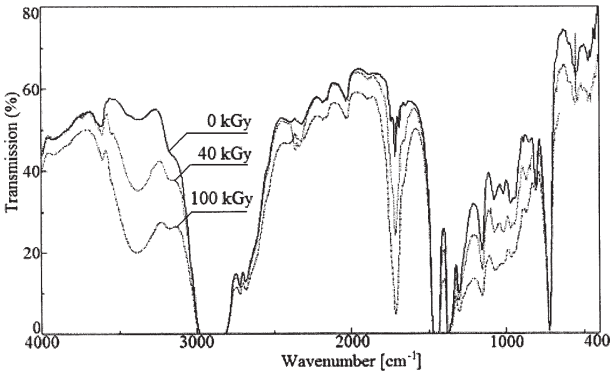


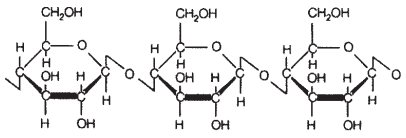
Fig. 3. FTIR spectra recorded for one sheet EPDM/paper for different irradiation levels

[15] contributes in a larger extent to the modifications occurred in electrical properties. For the absorbed dose of 50 kGy the resistivity is two orders of magnitude lower that the same property measured on the sample receiving low doses (8 and 15 kGy, fig. 2.).

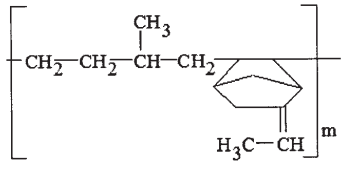
After the majority of charge carriers are neutralized after their recombination with the low movable anions (macromolecular entities), the resistivity of 50 kGy irradiated specimen attains the value corresponding to the pristine sample. The other resistivities are higher than they are for unirradiated specimen. The involvement of energy transfer onto polymer molecules affects only the initial conductivity. This behaviour can be improved by the application of short term heat treatment (about 30 min at 70-80^{0}C). The high values of resistivities (about 10^{15} Ω.m) allow large range of applications for this type of multilayer (EPDM/paper) structure. If in elastomers sheets would be added low quantity of proper stabilizer (0.25 or 0.50 % w/w of hindered phenol) the oxidation is diminished and the contribution of polarization and the association with the appearance of mobility band instead of forbidden band.

The evaluation of dielectric behavior of EPDM/paper insulation points out some features, which emphasize the peculiarities of the irradiation effects in hydrocarbon elastomers. The variation in the permittivity for all applied doses presents several maxima, which may be supposed that they are associated with the interaction between different units belonging to the two unlike macromolecules (ethylene propylene diene terpolymer and cellulose), whose structures are presented in figure 4.

The four peaks that appear in the records of permittivity on the high frequency range would be the result of the vicinity of D-glucose units with the unlike macromolecules



cellulose



ethylene-propylene diene terpolymer

Fig. 4. Molecular structures of the two materials consisting studied multilayer system

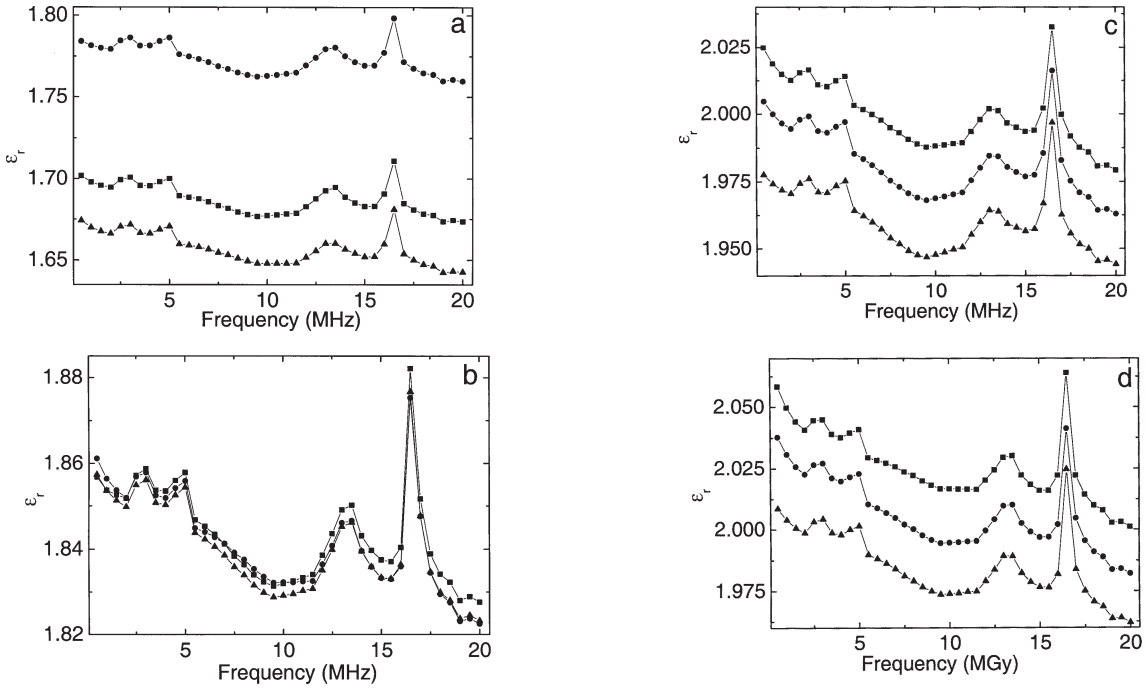


Fig. 5. Variation in the relative permittivity of EPDM/paper at different applied doses.
(a) 0 kGy; (b) 10 kGy; (c) 20 kGy; (d) 50 kGy testing temperatures:(■) 298 K; (●) 313 K; (▲) 328 K

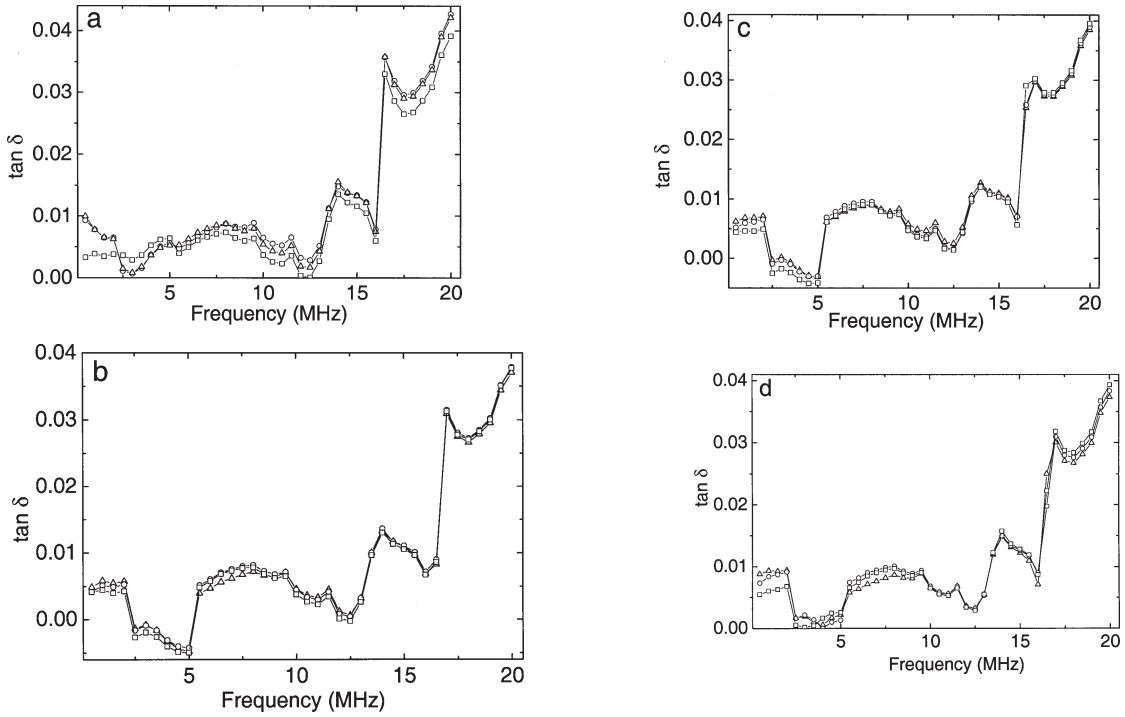


Fig. 6. Variation in the dielectric loss of EPDM/paper measured at different applied doses.
(a) 0 kGy; (b) 10 kGy; (c) 20 kGy; (d) 50 kGy testing temperatures:(□) 298 K; (o) 313 K; (Δ) 328 K

of EPDM. The comparative analysis of the curves from figures 5 (a-d) points out some particular aspects:

- γ irradiation induced an increased order in the elastomers sheets due to the crosslinking of this component of tested structure; this behavior would be explained by the augmentation of peak heights [16, 17];

- the oxidation started from the beginning of exposure had generated dipoles (oxygen- containing molecules), which interact with the oxygen atoms belonging to hydroxyl groups and ether bridges of cellulose;

- the degradation of cellulose brings about new structures in cellulose layers as citric acid and dicarboxylic acids [18];

- as the consequence of γ irradiation, some small fragments which would be trapped in the solid texture exhibit individual dielectric transitions [19];

- the noticeable differences between the permittivity of EPDM/paper multilayer structure can be remarked, because the accumulation of oxygenated products during radiation ageing increases in the polarizability of material. For dielectric loss, the differences between the curves shown for various temperatures (298, 313 and 328 K) are very small (almost insignificant) due to the high frequency of applied tension. The movement of dipoles does not follow the fast modification in the electric field direction;

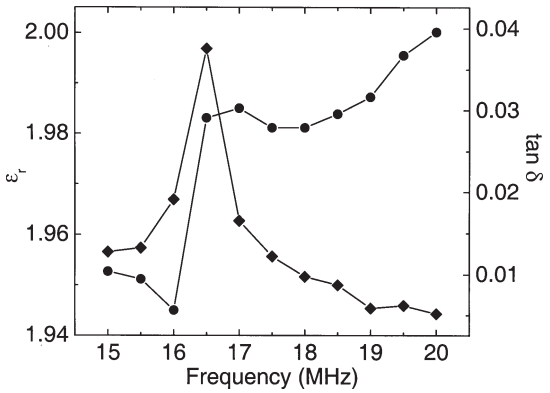


Fig. 7. Dielectric properties measured at 328 K on EPDM/paper multilayer structure subjected to γ-irradiation at 20 kGy (-♦-) permittivity; (•) dielectric loss

- the same value of frequency, 16.5 MHz, sharp modifications in the values of permittivity and dielectric loss happen (fig. 7). This jump frequency can be noticed for all absorbed doses and applied temperatures. It seems that this threshold is characteristic for the accumulation of carbonyl groups (dipole moment, μ = 2.8 Debye [20]) in the amorphous phase of both component materials.

· the reverse order in the relative positions of curves drawn for the three temperatures for unirradiated sample, on one hand and radiation exposed specimens, on the other hand describes the modifications occurred in the components of sandwich structure. It means that the crosslinking imposes certain rigidity in the relative movement of molecular units and the increase of temperature induces more fast vibrations of polarizable atoms diminishing the level of polarization.

The modifications appeared in dielectric loss values are essentially unlike on the frequency range from 1 MHz to 2.5 MHz. It means that these frequencies are characteristic features for material degradation. The influence of radiation action is less emphasized that the effect induced in the permittivity values of tested material. However, the most affected component of our multilayer system is the sheets of elastomers, which expose an advanced accumulation of dipoles.

The electrical behaviour under irradiation offers suitable information on the reliability of dielectrics that operate in hard conditions [21 – 24], i. e. in equipment placed in nuclear power plants.

Conclusion

The multilayer structure consisting of alternative sheets of ethylene-propylene terpolymer and paper preserves on satisfactory limits the values of electrical properties, permittivity and dielectric loss after the exposure to γ-radiation up to 50 kGy. However, the insulation behaviour is improved for low dose (8 kGy). Despite of the low resistivity measures on the first 100 s of current measurement, when available charge carriers retained into shallow traps are released, the steady state conduction shows similar values of resistivity for pristine sample and 50 kGy exposed specimen.

The present results underline that the γ-exposure of this insulation structure possible happened during accidental over-irradiation does not affect the good performances of this type of dielectric structure.

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