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Degradation effects in EPDM/cellulose sandwich structures

F. BUŞE, T. ZAHARESCU[a*], S. JIPA[a,b]
Technical Military Academy, 81 – 83 G. Cosbuc Bd., Bucharest 050141
[a]INCDIE ICPE C A, 313 Splaiul Unirii, Bucharest 030138
[b]Valahia University, Faculty of Sciences, 18 – 22 Unirii Av., Targoviste 130082

The ethylene-propylene terpolymer (EPDM) has been used for the preparation of cellulose sandwich structure. It is shown that the electrical insulation of the energy sandwich is characterized by slow aging during high energy particle irradiation.

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1. Introduction

The dielectric materials inserted into condensers allow the increase in the accumulated charge on the plates due to its proportionality with permittivity. The variation in the electrical behavior of electrical insulators limits the application ranges and the durability of items where they are the components that determine the extension of usage.

The most materials that play the role of electrical insulation are oxidized under the action of various stressors such as oxygen, heat, humidity, electrical field, mechanical charge. The duration and the intensity of damaging agent are the main factors that influence the progress in the degradation processes [1]. The important aspect which contributes to the worsening in the material quality is the molecular scissions. The multilayer compounds preserve their stabilization, if the components are simultaneously sufficient stable; otherwise this kind of systems is subjected to the propagation of oxidation from one component to the other. The weakest compound will provide oxidation initiators, which are spread into the own material and onto the interlayer boundary.

The paper with good electrical properties is generally used for the manufacture of condensers. The characterization of electrical properties for paper may be found elsewhere [2, 3]. The relative easy damage of paper was presented in an earlier report [4].

Due to the necessity of the decrease in the oxidation rate, the impregnation of paper is applied. Usually, the polyester resins are inserted in the electrical systems [5], but other solution would be selected.

Polyolefins like polyethylenes or ethylene – propylene elastomers are the best organic polymers that provide satisfactory electrical properties. The values of electrical strength, permittivity, volume and surface resistivities are good features for electrical insulations. Additional proper characteristics are their stabilities under oxidation [6, 7]. The prevention of advanced degradation is the main condition that the impregnation material must satisfy for a long term applications. The processes that define the structural modifications occurred in polyolefins degraded under the more or less accelerated conditions may be depicted by the correlation between the information provided by several procedures.

The choice of ethylene – propylene terpolymer (EPDM) for the impregnation and the preparation of sandwich structure was the purpose of this paper. The behavior of the alternation of organic polymer and cellulose layers is a suitable check for the employment in the electrical insulating. Two degradation regimes under thermal conditions and ionizing radiation exposure were applied for particularization of the answers of compounds to different rate transfer of energy.

2. Experimental

The sandwich structures were prepared by the alternation of ten paper sheets and nine layers of synthetic elastomers (EPDM). The condenser paper provided by EXPORTLES (Russia) destined for winding, shielding and copper insulation was used. Ethylene-propylene terpolymer was the sort Terpit C, whose ratio between ethylene and propylene units was initially 3:2.

For the preparation of sandwich structures, the polymer was brought in chloroform solution for easy removal of solvent by evaporation. Square leaves (70x70 mm/mm) of paper were cut and a proper amount of polymer solution, which corresponded to a thickness of 0.1 mm in dry state, was spread on the paper pieces. After the evaporation of chloroform, but when the polymer deposit was still with high consistency, the next paper sheet covered polymer stratum. The following paper was strongly pressed by the translation of ruler for the elimination of any air bubble that would disturb the conduction results.

Heat treatment was applied in an air-circulation oven maintained at 80^0C for all periods of heating. High energy exposure was performed in an irradiator GAMMATOR M-38-2 (USA) provided with a ^{137}Cs source. The dose rate was 0.4 kGy/h, which represents a low dose rate and it is peculiar for accidental event simulation.

FTIR spectra were recorded with JASCO 4200A spectrometer with 20 scans and 4 cm^{-1} resolution. The UV spectra were recorded with JASCO 570spectrophotometer. The spectral investigations were managed by transmission through individual sheets: paper (100μm thickness), ethylene-propylene elastomers film (150μm thickness) and polymer-impregnated paper (110μm thickness).

Electrical measurements were done with Keithley electrometer 6517A (USA) provided with resistivity test chamber 8009 and impedance analyzer 4294A produced by Agilent Technologies (USA).

All the electrical and spectral investigations were carried out immediately after the end of each kind of energetic treatment in order to avoid the modification of sample state by storage and the recombination of radicals of medium lifetime.

3. Results and discussion

The thermal and radiochemical degradation occurs either for ethylene-propylene terpolymer (EPDM) or cellulose by radical mechanisms. The detailed approach on the sequence of reactions that occur during the radiolysis of EPDM was previously reported [8]. For the correct understanding on the evolution of oxidation during the exposure of polymer, paper and their sandwich structure to the accelerated oxidative degradation, in Fig. 1 the FTIR spectra recorded on the EPDM film and in Fig. 2 the evolution of 1720 cm^{-1} band ascribed to carbonyl stretching are respectively presented.

Fig. 1 depicts the fast evolution in the 1720 and 3360 cm^{-1} bands, which illustrates the accumulation of large amounts of ketonic compounds and hydroperoxides. Additional to the oxidation reactions, there were occurred some other reaction involving free radicals, namely the disproportionation. This process revealed by the variation in the absorbances at 968 cm^{-1} represents the other start point for oxidation. The simultaneous generation and decay of unsaturation explain the small increase in the absorbance at 968 cm^{-1} band and a significant enhance in the carbonyl stretching. These intermediates have a major contribution to the decay of free radical because of their reaction with forming double bonds during irradiation.

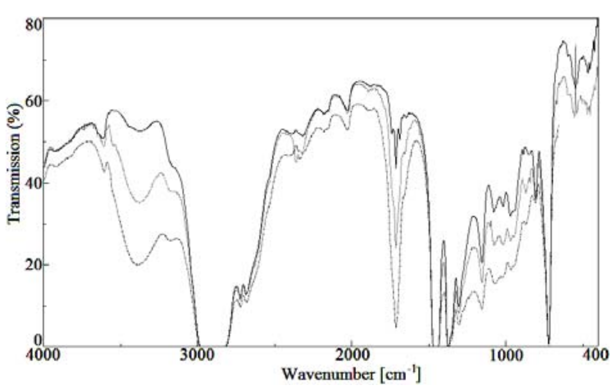

Fig. 1. FTIR spectra recorded on EPDM film (full line: unirradiated polymer; dot line: polymer exposed to 40 kGy; dash line: polymer exposed to 100 kGy).

The variation in the absorbance at 1720 cm^{-1} for the neat and impregnated papers (Fig. 2) emphasizes the role of cellulose layer as the absorbent of free radicals. On the dot line from Fig. 2 (b), a prominent maximum can be noticed, which demonstrated the formation of esters as the result of the reactions between the radiolysis oxygenated products (acids and alcohols).

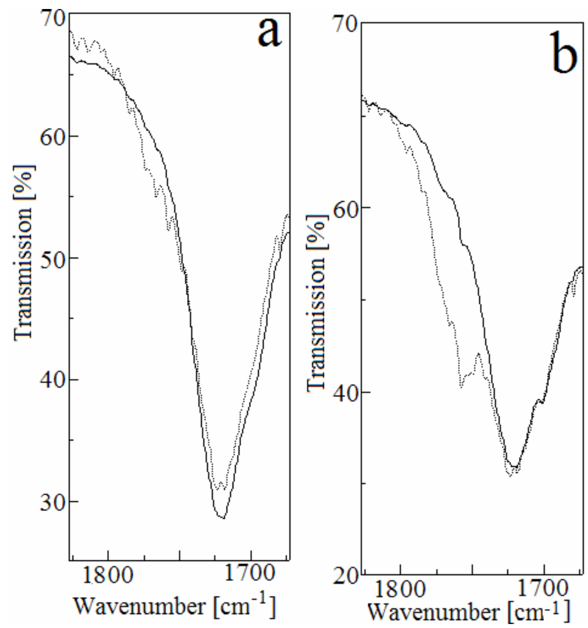

Fig. 2. Carbonyl peak in the FTIR spectra recorded on paper sheet: (a) and EPDM-impregnated foil; (b) Solid line: unirradiated samples and dot line: exposure dose 100 kGy.

This behavior is quite important for the electrical applications of EPDM-impregnated paper sheets. The slower development in the oxidation state recommends these structures as proper electrical insulators for various kinds of condensers.

The UV-Viz spectra recorded on EPDM film, neat paper and EPDM-impregnated paper (Fig. 3 (a), (b) and (c), respectively) sustains the statement of high stability of EPDM/paper sandwich structures on which the paper layers have limited the progress in the oxidation process of polymer component. The thin layer sequence of EPDM component and impregnated paper with good electrical features presents the remarkable stability to oxidation even during their exposure to the action of high energy radiation. The accumulation of nonconjugated ketones [9] in elastomers film (Fig. 3 (a)) is severely diminished by the presence of cellulose form neat sheets, which confer a noticeable effect on the preservation of initial characteristics of electrical insulation structure. In fact, the diminution observed in the rate of oxidation involves the slowing down accumulation of dipoles (the oxygenated products that are formed by oxidative degradation). The consequences in the electrical properties of studied structures can be reported in the changes occurred.

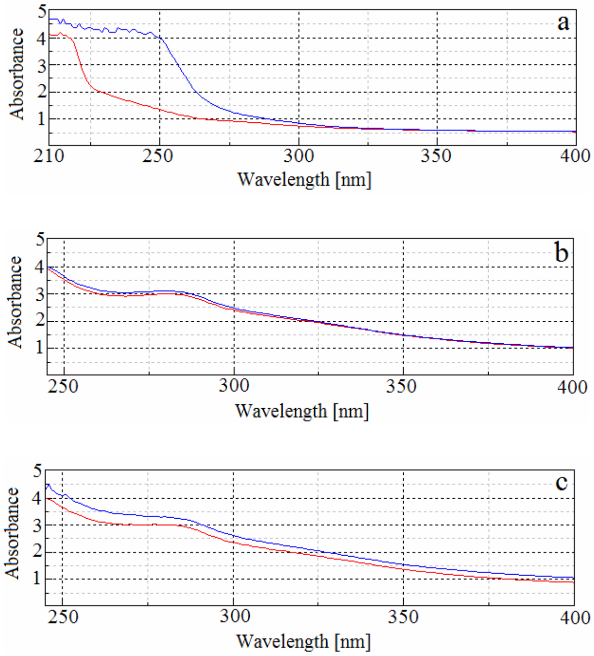

Fig. 3. UV-Viz spectra recorded on EPDM film (a), neat paper (b) and EPDM-impregnated paper (c) for unirradiated samples (lower curves) and 100 kGy exposed specimens (upper curves).

The electric properties of EPDM/paper sandwich depict this kind of insulation as a proper structure for the covering and/or spatial separation of electrical conductors. Fig. 4 presents the variation of impedance, permittivity and dielectric loss for 10 paper sheets place between 9 layers of polymeric material (EPDM). The decrease noticed for all these three parameters as the measurement frequency enhances denotes that over the value of about 0.1 MHz the impedance becomes to be reduced after a large range of its constancy. The explanation of this behavior involves the diffusion of dipoles formed in polymer matrix into paper foils. The alternative component of established current would follow the profile revealed by tan δ. This characteristic does not monotonically decrease like permittivity does. The higher frequency would induce a certain orientation, because the movement (rotation) of dipoles that initially exist in polymer materials and, of course, in cellulose beds does not perform similar alternations as the applied electrical field. The smooth alteration occurred in the values of permittivity recommends the sandwich polymeric structures as good insulation for medium voltage range, which is frequently selected for electronic circuits. The low values obtained over the high frequency domain represent a great advantage for the application of these structures in the manufacture of radars.

The oxygenated products appeared during the high energy exposure of sandwich structures as the result of the oxidation reactions between free radicals and diffused molecular oxygen bring about similar features in the electrical field. Fig. 5 presents the changes recorded in the permittivity and tan δ of sandwich structure subjected to a γ-dose of 100 kGy. The received energy is significant high, which correspond to an accelerated degradation of polymer (Fig. 1). The energy of 23.8 kcal that is received by 1 kg of polymer induces the accumulation of oxidation products that are the polarizable moieties. They establish higher values of permittivity and tanδ, but their increase relative to initial values doe not determine a sharp diminishing in the quality of insulation.

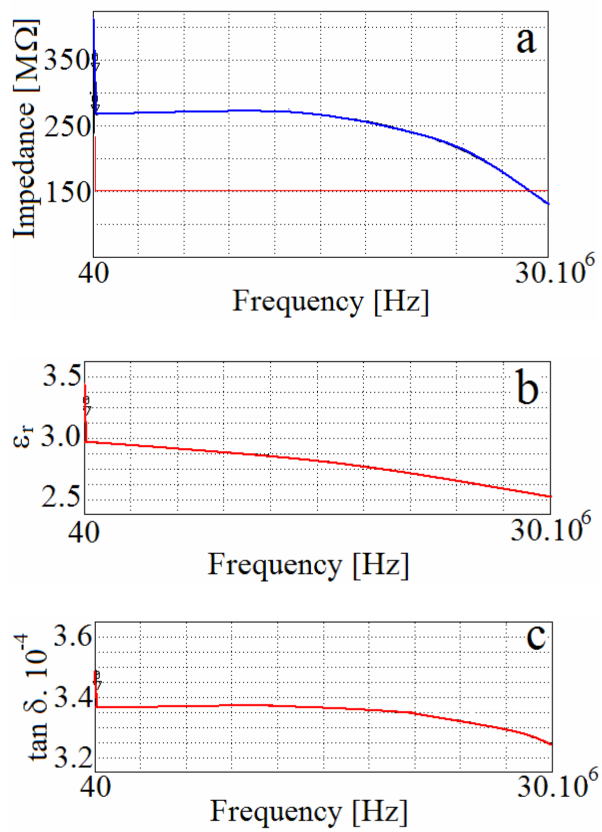

Fig. 4. The modification in the values of impedance (a), permittivity (b) and dielectric loss (c) obtained for EPDM/paper sandwich structure.

The changes in electrical properties are correlated with the chemical modifications revealed by the FTIR investigations. In spite if the high susceptibility of ethylene-propylene elastomers (EPDM) for the radiochemical oxidation (Fig. 1), the adsorption of oxygenated products on paper sheets at the interface regions promotes a relative preservation of initial properties of materials.

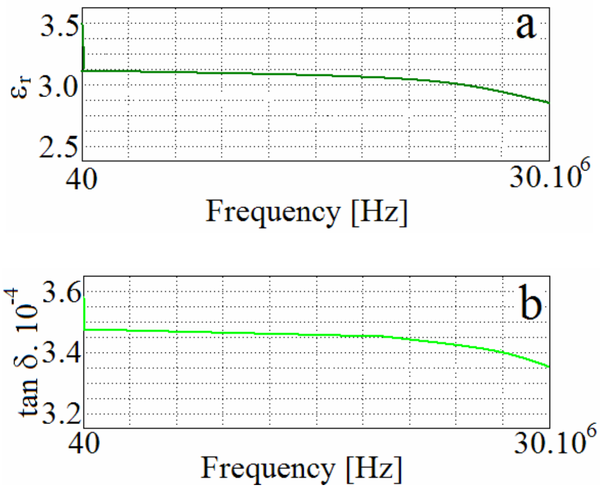

Fig. 5. Modifications in the permittivity and dielectric loss of EPDM/paper sandwich structures irradiated at 100 kGy.

The retention at an acceptable constant values level of dielectric properties during the high energy irradiation illustrates the possibility of these structures for applications in hard operation conditions.

The conduction of sandwich samples is changed during external treatment because the high energy radiation promotes the formation of δ-electrons. After thermalization, these electrons are attached to trapping centers, where they remain till a sufficient energy is transferred. The application of electrical field may remove these electrons. Because they received sufficient energy for withdrawing and the excess is available for their movement inside the polymer matrix. On the other side, the measured current may be established as the result of polarization. In time, either amount of free electrons or the increasing number of oriented dipoles is diminished and the resistivity is increased (Fig. 6). For the unirradiated sample, the increase in the resistivity value is much smaller for nondegraded ethylene-propylene elastomers than the variation range for the pure material. This difference represents the contribution of expelled electrons from the polymer molecules.

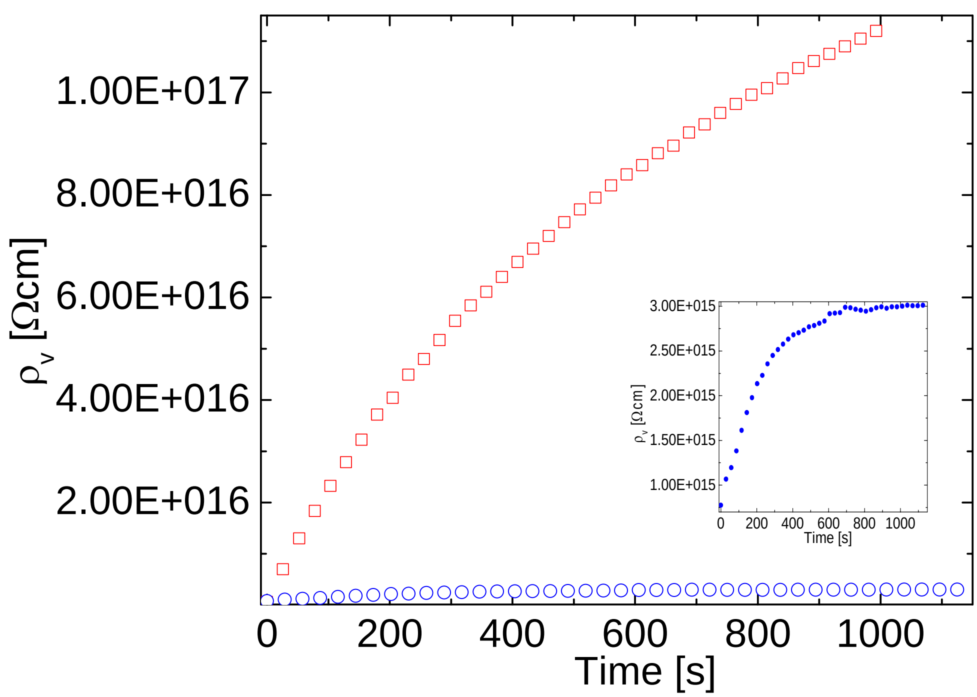

Fig. 6. The dependency of volume resistivity on measuring time for two levels of irradiation (circle: unirradiated state; square: 100 kGy exposure).

The intensity of energetic transfer is illustrated in Fig. 7, where similar EPDM/paper sandwich structures were degraded by different treatments (thermal ageing and radiation exposure). The increase in the resistivity values for γ-irradiated sample is much larger than that of the heated sample.

Consequently, the measured current becomes more intense in the case of radiochemically processed structure and the ageing in the radiation field is more pronounced than in the case of heat treatement.

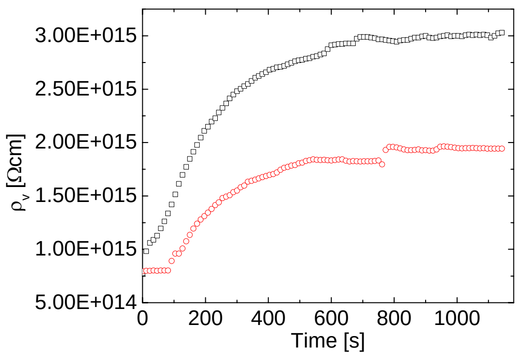

Fig. 7. The modification in the resistivity of aged EPDM/paper sandwich probes (square: sample irradiated at 25 kGy; circle: sample heated 100 h at 80^0C in air).

The most important aspect in the ageing of EPDM/paper sandwich is the smaller variation in the resistivity during thermal treatment, which is accompanied by light modification in the dielectric characteristics.

4. Conclusions

The EPDM/paper sandwich structure is a proper insulation system which may be applied in electric and electronic devices subjected to low and medium voltages. The interfaces between polymer layers and paper sheets represent suitable vicinity, where the dipoles formed in polymer can interact with cellulose molecules in the benefit of electrical properties.

This kind of electrical insulation reveals slower ageing during high energy irradiation in comparison with individual components. The correlation between the information obtained by electrical measurements and by spectroscopic investigation points out the satisfactory features of sandwich structures.

References

[1] R. L. Clough, N. C. Billingham, K. T. Gillen, Polymer Durability. Degradation, Stabilization, and Lifetime Prediction, ACS, Washington DC, 1996.
[2] P. V. Noţingher, Materials for Electrical Engineering. Technical Properties and Applications. Politehnica Press, Bucharest, 145, 2005.
[3] L. Matisová-Rychla, L., V., Bukovsky, J. Rychly, Pletenikova, M., Macromol. Symp. **247**, 340 (2007).
[4] V. Bondareva, V. Komarov, A. Selivester, R. Ershov, M. L'vov, S. Trifonova, High Energy Chem. **39**, 196 (2005).
[5] P. Zagoreki, P. Flodin, Polym. Composites **7**, 170 (1986).
[6] S. Jipa, L. M. Gorghiu, C. Dumitrescu, R. Olteanu, T. Zaharescu, R. Setnescu, Rev. Chim. (Bucharest) **56**, 254, (2005).
[7] T. Zaharescu, F. Ciuprina, Mat. Plast. (Bucharest) **43**, 59 (2006).
[8] T. Zaharescu, M. Giurginca, S. Jipa, Polym. Degrad. Stabil. **63**, 245 (1999).
[9] A. T. Balaban, M. Banciu, I. I. Pogany (eds), Applications of physical methods in organic chemistry, Scientific and Encyclopedic House Printing, Bucharest, 1983.

*Corresponding author: traian_zaharescu@yahoo.com