Characterization of Ethylene-Propylene-Diene Terpolymer Based Electrical Insulation

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***Abstract*- The accelerated ageing by γ-irradiation was accomplished for the evaluation of ethylene-propylene-diene terpolymer (EPDM) as electrical insulation in the cable manufacture. Three complementary procedures: FT-IR spectroscopy, isothermal and nonisothermal chemiluminescence and absorption/resorption current measurements were applied on a certain formulation for depicting the main material characteristics foreseen in the applications as cable electrical insulations. The explanation of structural modifications in relation with the magnitude of received energy is presented.**

***Keywords*: EPDM, accelerated degradation, FT-IR, chemiluminescence, DC conductivity**

I. INTRODUCTION

The applications of polymer materials for the manufacture of electrical insulation are based on their favorable properties, which are related to their high stability [1]. The durability of cables is mainly defined by the integrity of insulation that protects central wire. During the ageing process happened in natural or accelerated conditions, the oxidation as the main degradation process generates polar entities, which change the functional properties of electrical insulations [2]. The fundamental problem of ageing polymer materials is the correlation between the structural modifications and the intensity of stressors: heat [3, 4], radiation exposure [5, 6], electrical field [7, 8].

The influence of electrical field on the polymeric insulators is an essential aspect of the endurance testing of polymer materials. In the most of cases the chemical degradation is associated to the formation of channels and water trees [9, 10] starting from chemical defects. The accumulation of polar entities, various oxygenated structures, as the result of reactions between free radicals and molecular oxygen, can be emphasized by, for example, TSDC investigations [11], which provide additional information on the presence and relaxation of various molecular structures and chains.

The electrical properties of polymer materials are determined by the bond strength. The ethylene-propylene elastomers manufactured by copolymerization of ethylene and propylene in various proportions are stable materials [12]. Their degradation rates depend on the ethylene/propylene ratio being known that tertiary and quaternary carbon atoms form the less stable bonds [13]. The ethylene-propylene-diene rubber (EPDM) consisting of three structures: ethylene, propylene and 5-ethylidene-2-norbornene as diene component, is a proper material for the applications in hard working conditions [14-16]. The degradation profiles were previously reported [17-20] by which the material durability can be assessed.

The chemical strength of EPDM depends strongly on the diffusion of oxygen penetrating material simultaneously with energetic transfer [21, 22]. This diffusion feeds the oxidation process and the ageing level is determined by the oxygen amount existing in degrading material. The electrical characteristics (low resistivity, low relative permittivity) were studied on different kinds of commercially available EPDMs [23-28], confirming the availability of EPDM for the manufacture of electrical insulations. The achievement of satisfactory behavior in electrical field may be attained by the well selected formulation, which consists of high performance materials [1, 29].

The present study is focused on the evaluation of functional features of EPDM formulation destined to the manufacture of low voltage cables in nuclear power plants.

II. EXPERIMENTAL

Ethylene-propylene-diene terpolymer (EPDM) was provided from Lanxess (USA) as KELTAN 5470. It can be characterized by ethylene content weight: 60 %, diene (5-ethylidene-2-norbornene, ENB) content: 4.5 %, Mooney viscosity ML(1+4) 125 ^{o}C: 55. The formulation of samples is presented in Table 1.

TABLE I
FORMULATION OF SAMPLES

Component	Percentage (phr)
EPDM 5470	100
Zinc oxide	3
Stearic acid	10
Irganox 1010	0.5
Retilink T-40	3
Dicup 40	2.3

Film samples were obtained by the evaporation of solvent, $CHCl_3$, at room temperature. Plaque samples were vulcanized for 15 minutes at 180 ^{o}C in an electrically heated press.

The exposure was accomplished in air at room temperature in irradiation machinery M-38 GAMMATOR (USA)

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provided with ^{137}Cs source. Dose rate was 0.4 kGy h^{-1}, which is proper for the investigations on accelerated degradation.

FT-IR spectra were recorded with JASCO 4000 spectrophotometer at 48 scans. The carbonyl and hydroxyl indexes were calculated accordingly with procedure earlier reported [30]. Isothermal and nonisothermal chemiluminescence (CL) determinations were accomplished using LUMIPOL 3 (Slovakia) equipment. The errors of temperature readings are in the limit of ± 0.5 ^{o}C. Isothermal CL measurements were carried out at 160 ^{o}C. The temperature range for nonisothermal measurements was 25-250 ^{o}C at a heating rate of 5 ^{o}C min^{-1}. The CL results were expressed in Hz g^{-1} for the normalization of emission intensities. Electrical measurements of currents were done on Keithley 6517 A electrometer. The applied voltage for all samples was 500 V. Dimensions of samples: 60x60x0.5 mm.

III. Results and Discussion

Ethylene-propylene-diene terpolymer (EPDM) has been widely used as efficient electrical insulator, because it shows high chemical stability and proper dielectric characteristics under high voltage direct current devices [31]. The dielectric features of studied polymer are determined by many factors, e.g., chemical composition, morphological configuration, the concentration and distribution of dipoles along the field direction [32]. The polymeric insulators are the proper materials with specific electrical characteristics, which must preserve the integrity of cable due to their mechanical and electrical strengths. By ageing process the diminution of item life time is noticed according with the level of degradation reached by the jacket. The commission of ethylene-propylene-diene terpolymer in the nuclear areas is controlled by the ability of material to maintain the low degradation state over a real exposure dose range [33]. The pivotal effect of electrical dipoles containing oxygen atoms is the electron driving by jumping [34].

A. FT-IR Spectroscopy Investigation

The oxidation stability of EPDM films can be evaluated by FT-IR records depicting the modifications in characteristic vibration bands [35]. The carbonyl (1718 cm^{-1}), bond hydroxyl (3350 cm^{-1}) or double bond from norbornene (880 cm^{-1}) bands are the main spectral regions, where the transmission values are significantly changed (Fig. 1). The accumulation of carbonyl- and hydroxyl-containing products is a measure of oxidation state defining the stability strength during normal or accelerated ageing. The degradation mechanism was earlier reported [35, 36], but the specificity of EPDM is identified by the accumulation rates of degradation products (Fig. 2).

The increase in the concentration of dipoles is practically mirrored in the changes of material stability. The formation of free radicals as the precursors of oxygenated products would determine a change in the thermal behavior of material, because the presence of peroxyl radicals as oxidation initiators makes possible the feeding of degradation chain.

The higher irradiation dose that means a greater amount of energy mitigates the oxidation induction time.

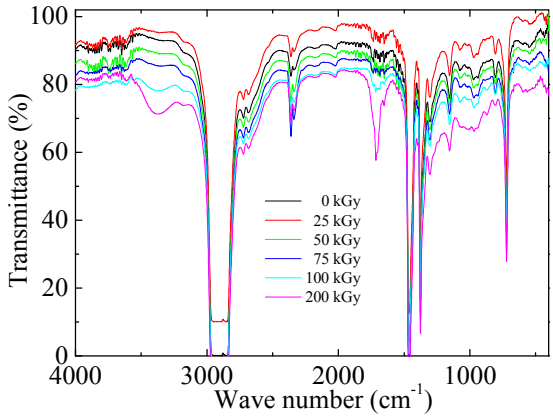

Fig. 1. FTIR spectra recorded on EPDM sample γ-irradiated at different doses.

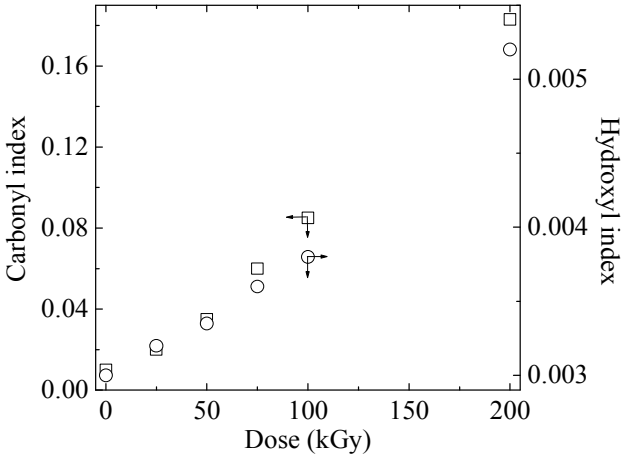

Fig. 2. Carbonyl and hydroxyl indexes calculated for different irradiation doses received by EPDM sample.

B. Chemiluminescence Spectroscopy Investigation

The isothermal chemiluminescence spectra (Fig. 3) present different shapes that prove the involvement of formulation components in the reactivity of peroxyl radicals. If the unirradiated material has a large loop with a oxidation induction time of minutes, followed by a sharp increase in the CL intensity (a very high oxidation rate) and a long period of slow oxidation, the increasing dose shortens the induction time followed by other short periods of fast oxidation. However, the periods defined by slow oxidation rate exist and they are enough long to assume that the RO_2 radicals are inhibited against the propagation of oxidation.

The nonisothermal chemiluminescence spectra (Figs. 4 and 5) illustrate the small differences that exist between the oxidation strengths of EPDM samples with our formulation. The onset oxidation temperatures decrease slowly due to the effect of antioxidant, Irganox 1010, a very efficient stabilizer. These long durations of pseudo-constant CL intensities are the useful information of proper stability of material.

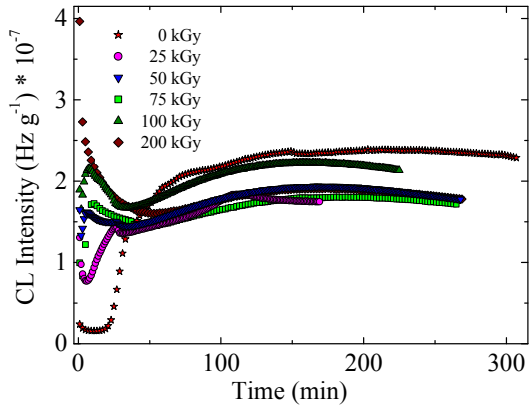

Fig. 3. Isothermal chemiluminescence spectra recorded on the EPDM-based samples.

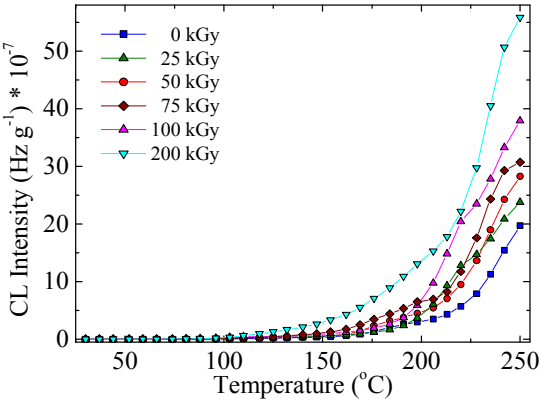

Fig. 4. Nonisothermal chemiluminescence spectra recorded on the EPDM-based samples.

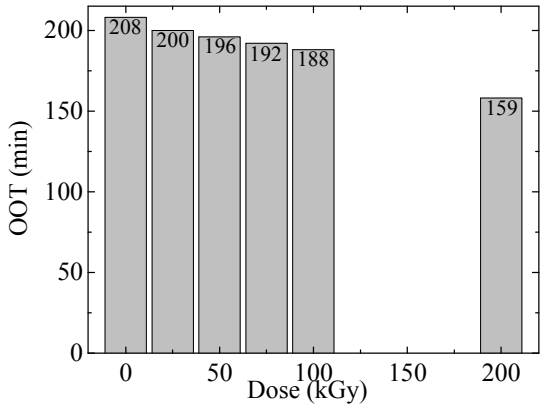

Fig. 5. Onset oxidation temperature obtained from nonisothermal chemiluminescence spectra recorded on the EPDM-based samples.

C. *Electrical Conduction Investigation*

The electrical conduction of polymers is a complex process in which charge carriers appear and move away after the application of electrical field. The asymptotic decrease of current on time illustrates the decay of distributed charge. The structural characteristics, i.e. crosslinking degree, determine either the level of constant current or the maximum absorption current. The applied doses are specific for slight crosslinking of EPDM and it is seldom accompanied by an oxidative degradation as the result of scission/crosslinking competition [37]. The modification of material behavior in high energy radiation field is caused by the unlike distributions of trapped electrons and by the number of intermolecular bridges. Because EPDM belongs to the class of crosslinkable polymers [37], γ-irradiation creates three dimension networks, which slows down the movement of electrical charge. The free electrons removed from molecule by the interaction between photons and polymer material are scavenged by various sites being released in electrical field.

Fig. 6 presents the absorption/resorption currents measured in EPDM samples subjected to different γ-irradiation doses. The lower values of current in irradiated polymer in respect with pristine material can be ascribed to slowing down the speed of electron escaped from the less and less deep traps and to the formation of polar entities containing oxygen. However, the diminution of current, when exposure dose is higher can be explained by the crosslinking of material in which the most sensitive sites are unsaturation (ethylidene norbornene) and tertiary or quaternary carbon atoms. The volume resitivities corresponding to the peculiar currents become higher and the larger polymer backbones prevent the movement of charge. The generation of degradation products changes the energy distribution in molecules. Consequently, the jump of electrons in strongly influenced by the molecular orbital distribution and the delocalization of energy becomes an important factor influencing electrical conduction [38].

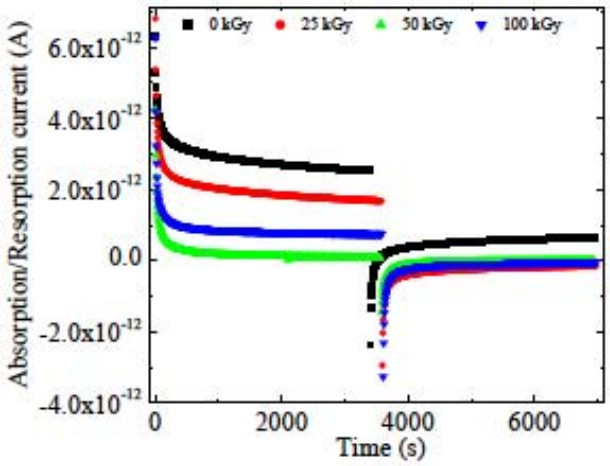

Fig. 6. Absorption/resorption curves recorded on some EPDM-based samples.

The degradation mechanism is based on the formation of radicals which react further with oxygen [39]. The accumulation of oxygenated products changes the polarizability of material inducing a certain level of the interaction between moving charge and chemically modified polymer.

IV. Conclusions

Our EPDM-based samples prove their high chemical stability against oxidation that demonstrates the possible application on the manufacture of electrical insulations. The slight variation of carbonyl and hydroxyl indexes

demonstrates the satisfactory chemical stability in radiation fields. The radiation processing of EPDM reveals a certain level of crosslinking which increases the volume resistivity. The absorption/resorption currents are diminished by irradiation indicating a certain crosslinking during radiation exposure. The chemiluminescence and FTIR investigations proved the good structural and strength of EPDM, which is slowly oxidized by γ-treatment. The γ-exposure of EPDM is a proper procedure for the manufacture and performance evaluation of cable insulations.

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