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Insulation properties of degrading LDPE modified with metallic oxides

E. D. POPESCU, T. ZAHARESCU[a,*], G. GAVRILĂ
Military Academy, 81-83 G. Coşbuc, Bucharest 050141, Romania
[a]INCDIE ICPE CA, 313 Splaiul Unirii P. O. Box 149, Bucharest 030138, Romania

The degradation resistance of LDPE electrical insulations is qualified under accelerated ageing by the exposure gamma radiation. LDPE compounded samples contain FeO, Fe_2O_3,, CrO_3, or TiO_2 in the concentration of 1 %. The effect of compounding upon the stability of LDPE insulations is discussed based on structural modifications revealed by FTIR spectroscopy and electrical resistivities pointed out by volume and surface conduction measurements. The considerations concerning the role of metallic impurities are presented for the evaluation of long term stability of electrical cables insulated with LDPE.

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The interaction between central wire and cable insulation may generate several problems related to the long term stability especially when they are subjected to overcharge regime. The water tree presence in polymer electrical insulation leads to the increase in the humidity level in the neighborhood of central wire [1, 2]. The direct consequence is the oxidation of central wire surface, which generates oxides capable to interact with polymer interface. The self oxidation of polymer layer during its water treeing deterioration may provide oxygen for further material damage [3]. The existence of an outer electrical field causes the polarization of oxygen bonds [4], which can become a source of degradation as well as the presence of metallic oxides [5] even for medium voltage cables. Because of the variation in electrical permittivity, the local deposit of energy becomes significant for the acceleration of degradation [2]. The electret effect of polymer interface is the cause of start of degradation [6] simultaneously with the action of effect of oxides formed on the external surface of metallic wire.

The stability of polyethylene jackets is influenced by the diffusion of gases through which oxygen is the most aggressive. The permeability of oxygen into polyethylene under various procedures of fabrication brings about an oxidation environment for degradation promotion.

The accelerated oxidative degradation can be energetically sustained by electrical discharge [8, 9] or the exposure to high intensity radiation beam [10, 11]. The oxidation that results from the various reactions of free radicals with oxygen generates oxygen-containing final products which modify the electrical behavior of LDPE. The dielectric response of materials can be used as an indicator of ageing processes occurring in insulating polymer samples. The general description of γ-irradiation consequences in polyethylene is already reported earlier [12].

The most of primary processes involve the expelling of electrons, which will be trapped on electronegative sites after thermalisation. This aspect will influence the conductivity of polymer samples, when they are subjected to the action of an external electrical field.

The post-irradiation characteristics of polyethylene dielectric samples are influenced by the former structure of material [13], irradiation dose rate [14], formulation [15, 16].

This paper provides information on the stability of γ-irradiated low density polyethylene samples, which covers usually metallic central wire. The presence of metallic oxides simulates the effects of impurities contained in metallic cable component, which are subjected to oxidation during degradation. The consequences of oxidation are envisaged by the modifications occurred in chemical structures and in electrical properties.

1. Experimental

Low density polyethylene (LDPE) was provided by ARPECHIM Piteşti (Romania) as A23 BP085 type. Neat material was inserted in an electrically heated plate press and it was maintained at 150 °C and 180 bars for 10 minutes. Sheets of 150 μm thickness were obtained. The oxide powders (TiO_2, FeO, Fe_2O_3, and CrO_3) were separately added before pressing at the concentration of 1 % for each sample preparation. For spectral investigation films of 100 μm thickness were prepared and for electrical measurements plaques with the thickness of 1mm were processed.

The obtained samples 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 on the same film, which avoid increased errors.

Spectral measurements were carried out with JASCO 4200A (Japan) FTIR spectrophotometer. Electrical investigations were performed with Keithley 6517A (USA) electrometer.

2. Results and discussion

The influence of degradation conditions namely dose rate, chemical formulation, exposure environment on aging processes of polymeric insulating materials may be revealed by the modification in material properties. In the case of γ-irradiation a charge accumulation is possible because of δ electrons which are expelled during radiation treatment. This charge accumulation will effectively contribute to the breakdown of materials by water treeing in correlation with metal/polymer interface [17].

The progress in the oxidation degradation of basic polymer, LDPE, is illustrated in Fig. 1, where the vibration bands of carbonyl and bonded hydroxyl units can be easy noticed. The changes in the prominent peaks of FTIR spectra on the regions of 3450 cm^{-1} and 1720 cm^{-1} indicate respectively the increase in the amounts of oxygenated products, hydroperoxides and carbonyls.

The recorded FTIR spectra reveal the differences that exist between LDPE compounded with various oxides. On the first analysis, the LDPE control samples exhibits the fastest oxidation process, which progresses with a rate characteristic for neat material. The spread of oxidation precursors, peroxyl radicals, induces a vigorous attack on the propagation stage. The presence of oxide filler causes a delay in the reaction of oxidation intermediates with reactive sites on polyethylene backbones. These components slow also down the diffusion of oxygen which feeds the degradation process. The early step of oxidation runs quicker for all studied compositions. This aspect may be correlated with the consumption of reactive places in the polymer matrix, which is accompanied by the coupling of hydrocarbon free radicals on filler particles.

The contributions of different incorporated fillers on the advance in oxidative degradation of low density polyethylene are illustrated in Fig. 2, which proves the influence of electronic configuration of metal on the accumulation of the main oxygenated products, ketones and alcohols. The most stabile LDPE formulation was obtained in the presence of ferrous oxide, FeO. The other ferric oxide, Fe_2O_3, became a more efficient oxidation promoter. TiO_2 and CrO_3 present similar behavior related to the initiation of oxidative degradation of polyethylene.

As it can be remarked from Fig. 1, the oxidation of basic material, LDPE, takes place either through the reaction of molecular oxygen with free radicals (Bolland and Gee's mechanism) or by oxidation of unsaturation formed by disproportionation occurred during polymer radiolysis.

However, the reactive fillers TiO_2 and CrO_3, catalyze the formation of carbonyl units. Their concentration in the compositions containing these oxides exceeds the similar concentration measured in control sample subjected to higher γ-doses surpassing 100 kGy. Although the oxide fillers would be a source of oxidation, the formation of bonds between metal and oxygen atoms belonging to oxidized macromolecules was previously demonstrated [18]. These bridges may stabilize the new formed structures, which promote a chemical reactionlessness.

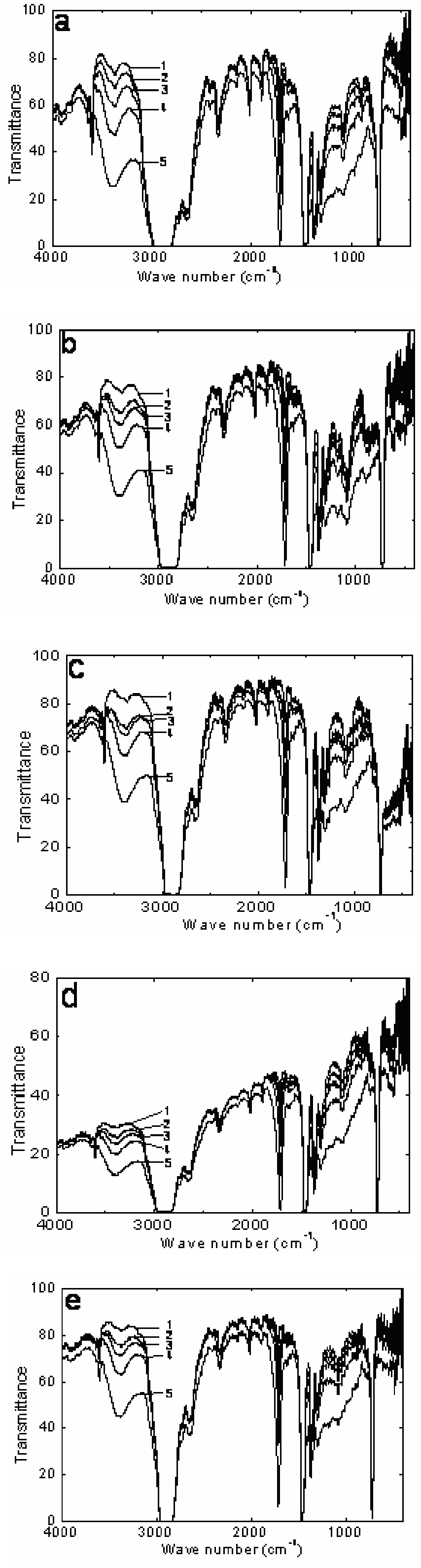

Fig. 1. FTIR spectra recorded on LDPE under different compounding states.(a) control LDPE; (b) LDPE/CrO_3; (c) LDPE/TiO_2; (d) LDPE/FeO; (e) LDPE/Fe_2O_3. (1) 0 kGy; (2) 20 kGy; (3) 50 kGy; (4) 100 kGy; (5) 250 kGy.

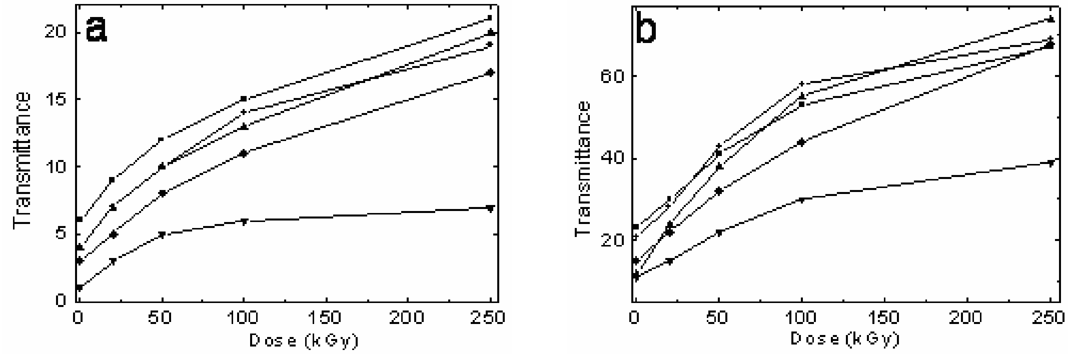

Fig. 2. Changes in hydroxyl (a) and carbonyl (b) accumulations in LDPE formulations subjected toγ- irradiation (■) LDPE control; ●) LDPE/CrO_3;(▲) LDPE/TiO; (▼) LDPE/FeO; (◆) LDPE/FeO_3.

The achievement of high performance dielectrics with long term durability requires detailed studies on the modifications occurred inside material during over regime practice [19]. The breakdown of cable insulation has multiple reasons [20], through which the presence of impurities plays an important role.

The investigations on polyethylene conductivity under different conditions infer the contribution of new dipoles that appear during degradation [21].

The presence of various oxides that may be provided during material fabrications of insulations around the oxidation of metallic central wire modifies the resistivity of insulator (Fig. 3).

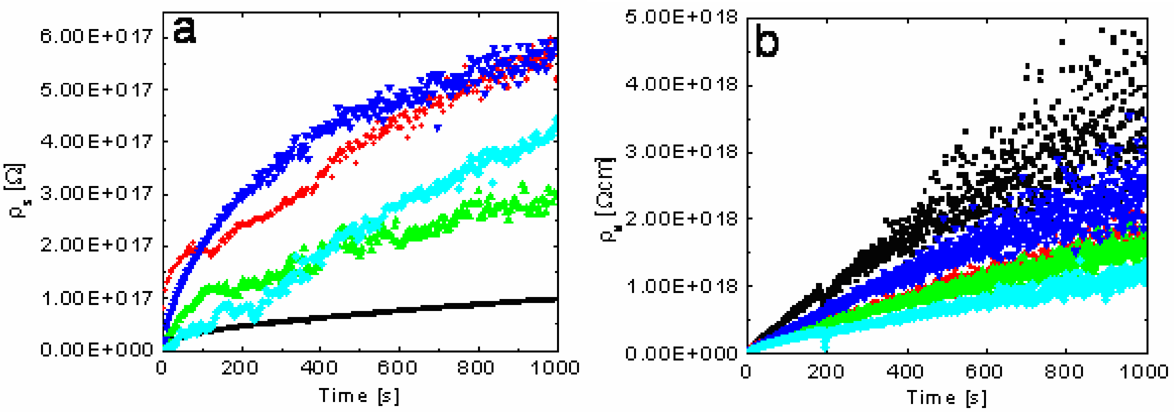

Fig. 3. Modification occurred in surface resistivity (a) and volume resistivity (b) for LDPE samples. (■) control; (●) LDPE/CrO_3; (▲) LDPE/TiO_2; (▼) LDPE/FeO; (◆)LDPE/Fe_2O_3.

The values of surface resistivities increase from the unmodified polyethylene to ferrous oxide based on the susceptivity of filler for scavenging water from environment. This series of ρ_s is: control LDPE < LDPE/TiO_2 < LDPE/Fe_2O_3 < LDPE/CrO_3 < LDPE/FeO while the order of increase in ρ_v is:

LDPE/Fe_2O_3 < LDPE/TiO_2 < LDPE/CrO_3 < LDPE/FeO < control LDPE

These sequences reflect the contribution of electronic configuration of metal, which are related with the occupation levels of electron orbitals.

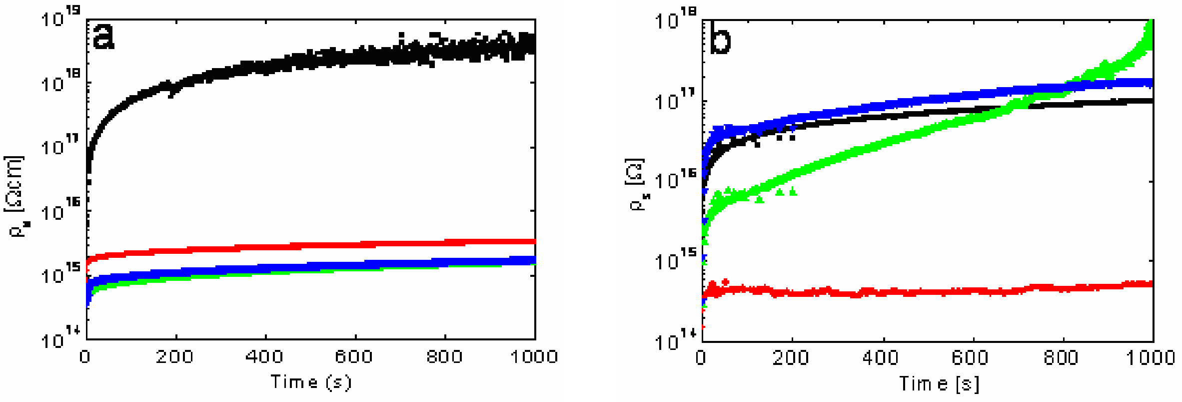

Fig. 4. Changes in volume resistivity (a) and surface resistivity (b) of neat LDPE at various doses (■) 0 kGy; (●) 8 kGy; (▲) 15 kGy;(▼) 25 kGy.

The degradation of LDPE under γ-irradiation leads to the decrease in the both types of resistivities because the escape of trapped electrons takes place by the application of measurement tension. The sharp decrease in ρ_v can be observed over the dose interval of the first 8 kGy due to the fast consumption of dissolved oxygen for the oxidation reactions of free radicals. The low ρ_s values in the case of 8 kGy irradiation dose can be explained by the high accumulation of dipoles on the first stage of irradiation. At higher doses the radiolysis of oxygenated products diminishes the concentration of dipoles by their partial decay.

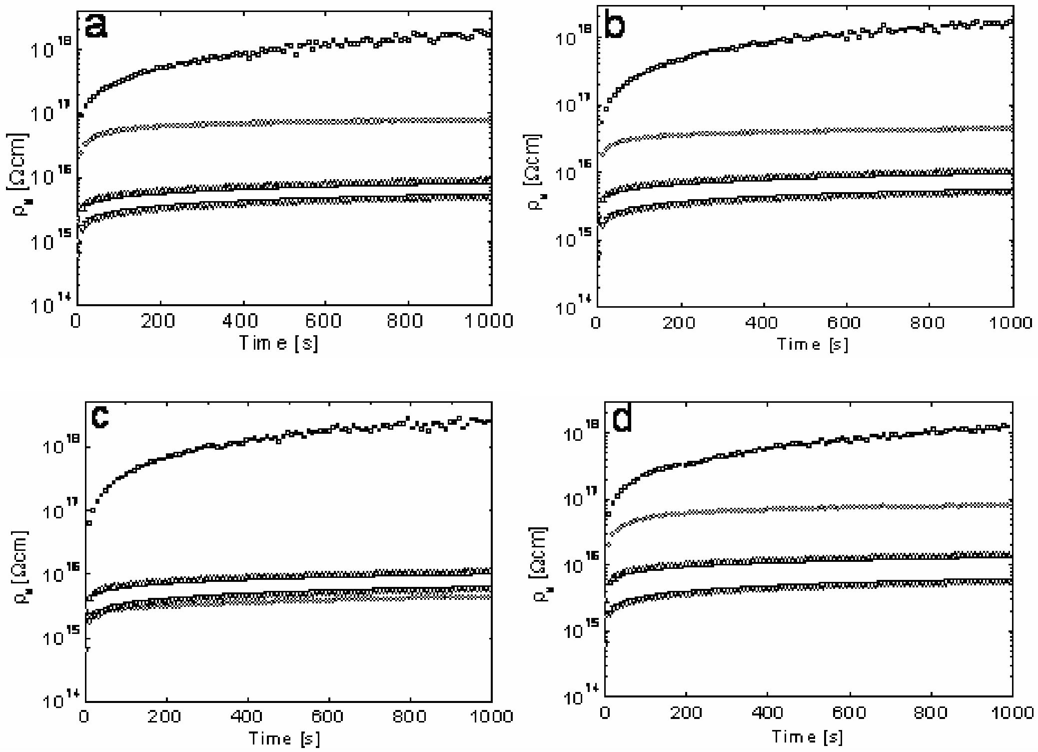

Fig. 5. Changes in volume resistivity of irradiated LDPE modified samples (a) CrO$_3$; (b) TiO$_2$; (c) Fe$_2$O$_3$; (d) FeO. (□) 0 kGy; (○) 8 kGy; (△) 15 kGy; (▽) 25 kGy.

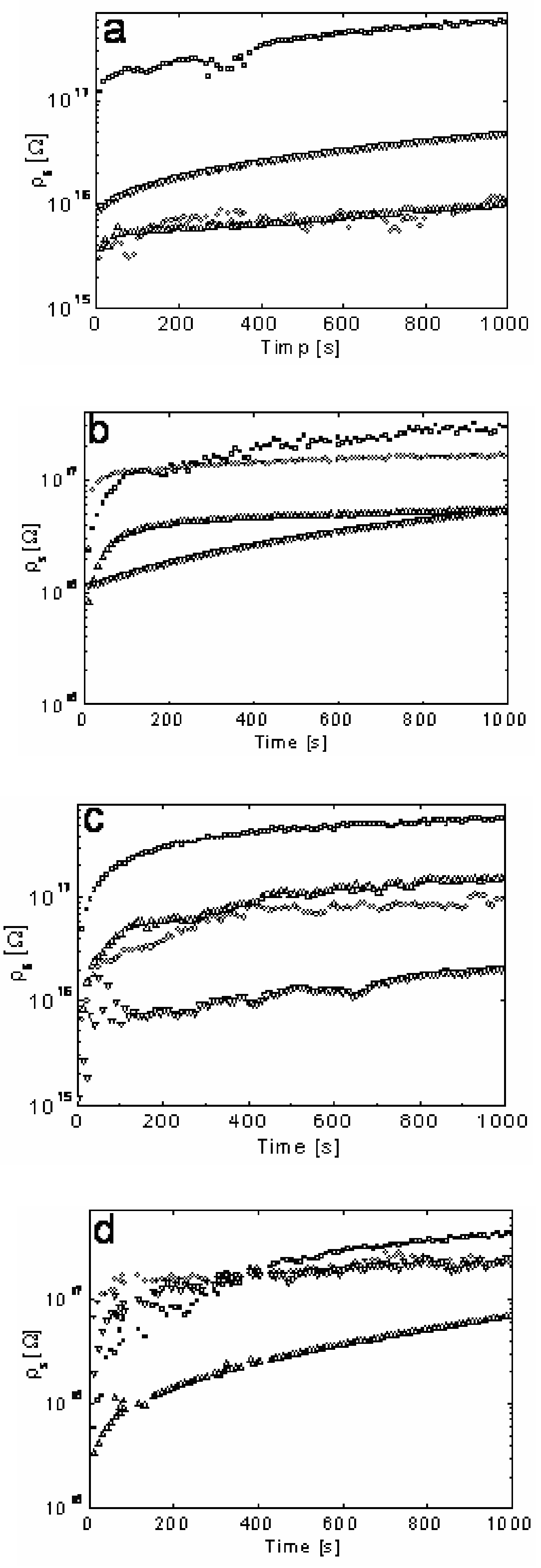

Fig. 6. Changes in surface resistivity of irradiated LDPE modified samples(a) CrO_3; (b) TiO_2; (c) Fe_2O_3; (d) FeO. (□) 0 kGy; (○) 8 kGy; (△) 15 kGy; (▽) 25 kGy.

The volume resistivity (Fig. 5) reveals small differences between the electrical behaviors of oxide-modified low density polyethylene. The accumulation of dipoles in polyethylene represents the effect of molecular scission that takes place on the most instable sides on macromolecules. Simultaneously, the electrons that were rejected from molecules become more dynamic and their movement feeds the measured current. The promotion of oxidation provided by fillers is connected to the reactivity of oxide which can accelerates the oxidation rate by direct interaction between metal atoms and polymer molecules in the presence of molecular oxygen. It may be considered as a catalytic effect of metallic oxide filler contained in LDPE.

The surface resistivity (Fig. 6) presents a larger increase over the first kGy, which may be explained by the accumulation of water molecules that exist in the irradiation environment. Further γ-exposure produces an advanced radiolysis of polymers and the oxidized products interact more or less strong with adsorbed water molecules.

3. Conclusion

The oxidation degradation of low density polyethylene is catalyzed by metallic oxide filler which promote the formation of dipoles in host polymer. The radiolysis of macromolecular component is significant in relation with filler reactivity. The decrease in the oxygen diffusion during γ-irradiation induces a slight increase in structural stability which is revealed by the lower accumulation of oxygenated products. The conduction of oxide-modified LDPE is enhanced by the formation of dipoles even on sample surface or in polymer bulk. The modifications occurred on the early stage of γ-irradiation are more evident because of the availability of reactive places on polyethylene macromolecules.

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[*] Corresponding author: traian_zaharescu@yahoo.com