Comparative Qualification Assessment of Polyethylenes under γ-Irradiation

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The structure of dielectric materials is one of the main important parameter, which determines the durability of products. The degradation process runs differently in various types of polyethylene, because the macromolecules present different level of branching, different crystallinity grades, different chemical resistance. The dissimilarities between the resistance on ageing of different sorts of polyethylene are depicted by FTIR analysis, chemiluminescence determinations and the measurement on electrical resistivity. The consequences on the long term service under γ-irradiation degradation are discussed.

Keywords: polyethylene materials, degradation, FTIR, chemiluminescence, electrical properties

Polyethylene is an essential plastic whose manufacture places it on the first position through engineering plastic materials. The several areas of applications (cables and wires, automotive, medical wear, packaging, pipes, miscellaneous) consume enormous amounts of polyethylene due to its excellent features like flexibility, toughness, barrier for gas diffusion, easy of fabrication, low cost. The polyethylene type determines the peculiar use. The dissimilarities between their structural characteristics (branching, crystallinity, physical properties, chemical resistance) are the criteria on which the praxis of polyethylene is based.

A large amount of work can be found in literature, which is devoted to the depiction of material behaviour under certain working conditions [1-6]. Polyethylene blends have received special attention due to the alternative possibility of suitable formulation for certain applications [7-11].

The accelerated degradation promoted by ionizing radiation is an appropriate procedure for characterization of the effects induced by the long term utilization under oxidative environments. The qualification of materials performances directs the customers on the correct way of implementation. The tests performed by the degradation of polyethylene in the ionizing radiation field represent the fast evaluation of material quality in the direct connection with the endurance for peculiar applications [12-21].

The concomitant reactions occurred during endurance testing run to the modifications in the chemical state of material, which determines the warranty period for hazardous applications like nuclear power stations, aircraft, automotives, electrical cables, gaskets, and many other key items.

The present investigation presents a comparative study on the polyethylene answer to the degradative action of γ-radiation as the carrier and donor of energy.

Experimental part

Three kinds of polyethylene (two types of HDPE (named HDPE 1 and HDPE 2) and one sort of LDPE) were selected for the characterization of resistance on the hard conditions of usage. These materials were investigated as received products supplied by ARPECHIM Piteşti (Romania). Table 1 presents the main features of raw materials.

Each polyethylene sheet (thickness: 0.3 mm) was obtained in an electrical heated press at 150 atm for 10 min. The polyethylene films were also processed by pressing under similar conditions.

The exposure in high energy radiation field was done using an irradiator GAMMATOR M-38-2 (USA) provided with ^{137}Cs source in air at room temperature. Dose rate was 0.4 kGy/h. This low dose rate simulates the accidental conditions that are really met when electrical and thermal overcharges are attended.

For the characterization of chemical modifications two sensitive procedures were applied:

-chemiluminescence (equipment: LUMIPOL 3 – SAS, Slovakia). The procedure and data interpretation for chemiluminescence results have been previously reported [22];

-FTIR and UV-Viz spectrometric records were carried out on JASCO 4200 with 20 scans and 4 cm^{-1} resolution and JASCO V 570 Japan, respectively.

Electrical measurements were assured by Keithley 7600A (USA) multimeter coupled with a resistivity test chamber 8009 (Agilent, USA).

Carbonyl and hydroxyl indexes were calculated as the ratios of the absorptions at 1720 cm^{-1} and 3350 cm^{-1}, respectively, and the absorption at 1475 cm^{-1} [23]. The values for number of CH$_3$/100 carbon atoms were calculated according with ASTM 2238-68. The radiochemical yield, expressed as mol/J, was evaluated by the expression [24]:

$$G = \frac{\Delta A}{D.\varepsilon.\rho.l}$$

where:

ΔA means the change in the absorbance at 1720 cm^{-1}, D denotes the absorbed dose (Gy), ε is the linear molar extinction coefficient at 1720 cm^{-1}, (220 L mol^{-1} cm^{-1} [25, 26]), ρ is the material density (g.cm^{-3}) and l represents the optical path (cm).

The samples were subjected to investigations immediately after the end of irradiations.

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Results and discussion

The polymers exposed to the action of ionizing radiation are profoundly modified as the consequence of energy transfer onto macromolecules. The random scissions of weaker bonds of macromolecules creating free radicals are the primary chemical events [10, 27]. The subsequent reactions in which free radicals are involved become the competitive processes. During γ-exposure to applied low dose rate oxidative degradation is the main process that depletes free radicals. The mechanism of radiation induced oxidation of polymers may be found elsewhere [28, 29].

The dissimilar susceptibility of tested polyethylenes to oxidation is described by the evolution in UV-Viz spectra (fig. 1). The maxima placed at 220 and 270 nm in the UV spectra of LDPE are ascribed to the presence of ketonic carbonyl groups and conjugated double bonds in polyene structures, respectively [24]. These peaks are shifted towards higher wavelengths in tested HDPEs. This difference arises from the discrepancy in the polymer matrixes. The augmentation in the absorption of carbonyl components is faster than the enhance in the absorption depicting the accumulation of double bonds. The former oxygenated function is the result of the reactions of free radicals with the molecular oxygen diffused from the outer layers of polypropylene and the later peak absorption for unsaturation increases due to the disproportionation reactions. The advance in the – C = C – absorption is smoother than the accumulation of carbonyl moieties because double bonds are consumed by addition or oxidation.

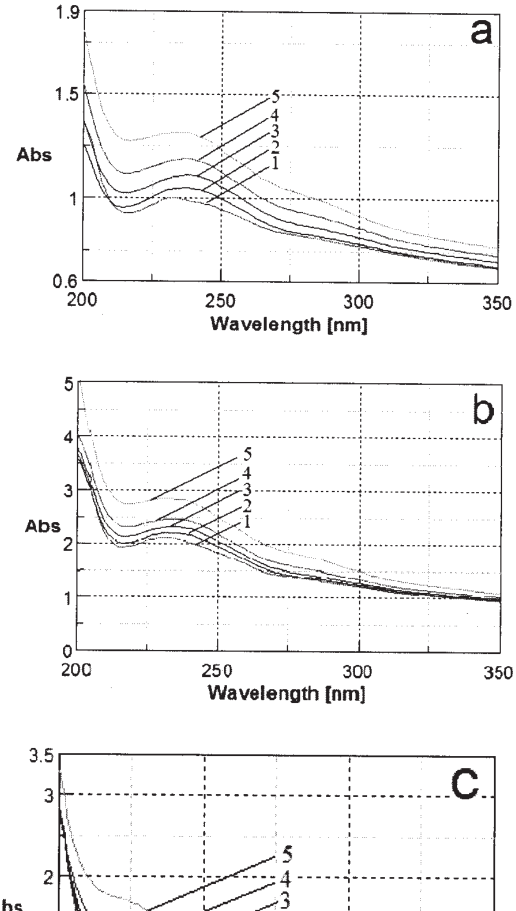

Fig. 1. UV-Viz spectra of different kinds of polyethylene: (a) HDPE 1; (b) HDPE 2; (c) LDPE. (1) 0 kGy; (2) 20 kGy; (3) 40 kGy; (4) 70 kGy; (5) 100 kGy.

The comparison of UV recorded spectra for the three polyethylenes reveals the faster development in the degradation process in LDPE than it occurs in HDPE. The explanation is the branching level of each material, which is directly related to the higher number of tertiary carbon atoms in low density polyethylene. The early start of oxidation in LDPE is concerned either by the direct attack of molecular oxygen on the tertiary carbon positions, or by the formation of peroxyl radicals, the promoters of chain process of oxidation, as the intermediates resulting from the reactions $R^{\cdot} + O_2$. The present results are in a good agreement with other previous information [1, 30-32]. The exposure to high energy radiation accelerates causes the formation of free radicals by the generation of *trans*-vinylene structures [33].

The influence of branching on the evolution in the amounts of oxidation products can be explained by the different values in Nr. CH_3/100 C. The highest figure for this property (3.55, table 1) for LDPE illustrates the material tendency to oxidation, because the probability of the scission or oxygen attack on tertiary carbon positions is higher in comparison with HDPEs. The radiation stability order of tested polyethylenes:

HDPE 1 > HDPE 2 >> LDPE

is the opposite sequence of the increase in the number of CH_3 per100 carbon atoms. The relative increases in the absorbance at 220 nm, ($A_{D=100}/A_{D=0}$) are 0.62, 0.75 and 3.4 for HDPE 1, HDPE 2 and LDPE, respectively. It defines the corresponding augmentation in the oxidation availability on polyethylene macromolecules.

The susceptibility of polyethylene to generate of unsaturation (absorption at 270 nm) follows the same order as the sequence of oxidation instability. The lower – branched polyethylene withstands better on the low irradiation dose range, which may be assimilated with the condition of accident. Because 1 kGy is equivalent to 10^3 J/kg, the radiation – induced modifications occurred for each 1 kGy involves high amount of energy transferred onto material on a short time interval. This energy is enough for the induction of degradation during the encroaching technological limits.

FTIR spectra (fig. 2) describe more detailed the structural modifications occurred in irradiated polyethylenes. The absorption of several peaks is modified displaying the contribution of various reactions of free radicals during the competition between the formation and the decay of these reactive intermediates.

There are three important spectral regions: below 1000 cm^{-1}, where several unsaturated structures like *trans*-vinylene (965 cm^{-1}), vinyl (909 cm^{-1}) and vinylidene (888 cm^{-1}) appear [34]; the peak around 1720 cm^{-1} (1716 cm^{-1} for acids, 1722 cm^{-1} for ketones, 1735 cm^{-1} for aldehydes [35] and 1746 cm^{-1} for esters [36]) and the last range around 3350 cm^{-1}, where the hydroperoxides can be determined. All these functions appear as the result of degradation mechanism through which free radicals react with oxygen forming peroxyl intermediates further subjected to intramolecular rearrangements or with macromolecules abstracting proton. These reactions occur predominantly in the amorphous zones, where the movement of reacting

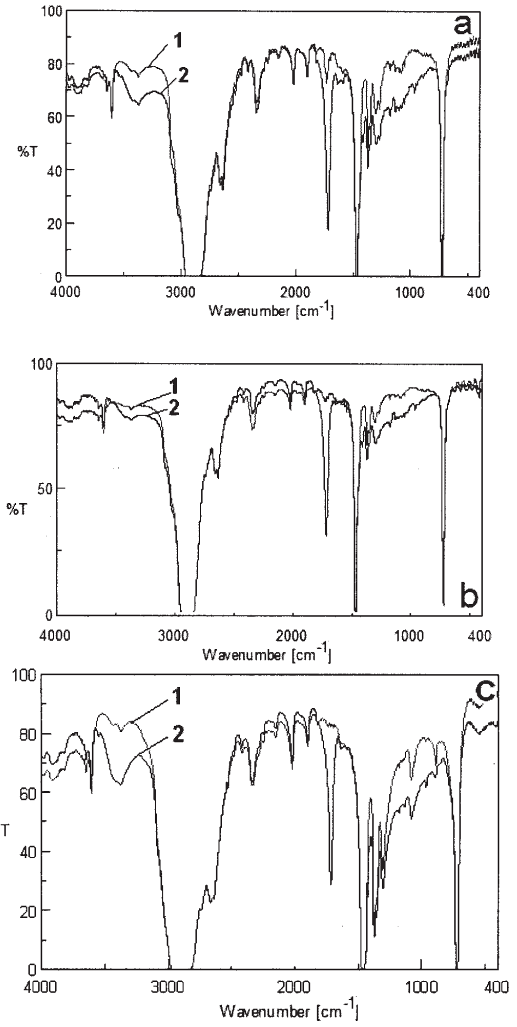

Fig. 2. FTIR spectra of different kinds of polyethylene.
(a) HDPE 1; (b) HDPE 2; (c) LDPE.
(1) 0 kGy; (2) 100 kGy.

entities is much less restricted than it is happened inside the ordered phase (crystalline component).

The enhance in the generated carbonyl amount is directly related by the simultaneous processes: the reaction of free radicals with O_2 and the conversion of other intermediates, hydroperoxyl entities. The accumulation of ketonic functions is described by carbonyl index (fig. 3a) and radiochemical yield (table 2). Our results are in a good accordance with the other previously reported values [37]. They depict the increasing contribution of the later manner of C = O buildup, when the accumulation of hydroperoxyl moieties attends enough high concentration. The simultaneous formation and depletion processes decide the growth in hydroperoxyl function. Figure 3b presents comparatively the progress in the oxidation state based on the formation of ROOH structures. From figures 3a and 3b it can be noticed that the accumulation of carbonyl functions is faster than it is happened with hydroperoxides.

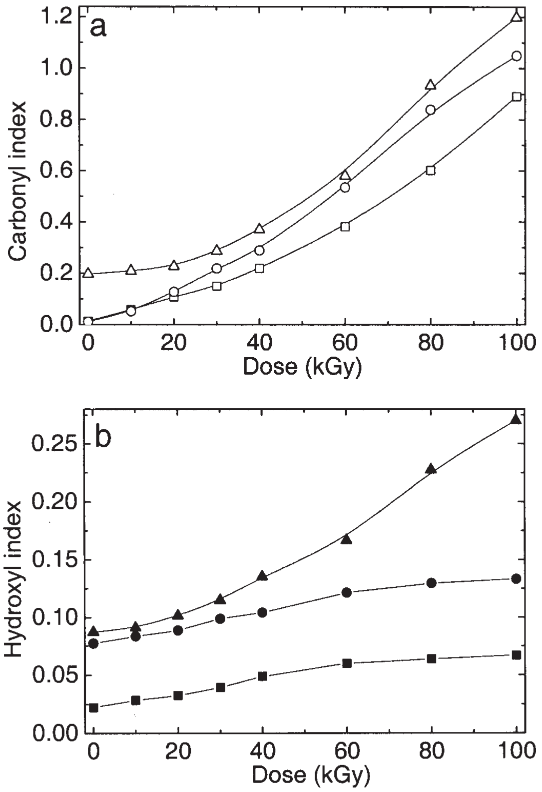

Fig. 3. Modifications in carbonyl (a) and hydroxyl (b) indexes
(■,□) HDPE 1; (●,o) HDPE 2; (▲,△) LDPE

The collection of oxygenated products by migration brings about major defects, which allow the breakdown of materials as mechanical and/or electrical overcharge is accidentally applied.

The differences between these kinds of polyethylenes reflect the tendencies towards oxidation. If HDPE 1, which presents higher initial crystallinity, starts smoothly oxidative degradation, the other two polyethylenes exhibiting lower crystalline phase display constant of radiochemical yields for C = O. This feature is also related to the mobility of intermediates, which is determined by the level of toughness (table 1, MFR values).

The progress in the oxidative degradation of different sorts of polyethylene is well depicted like a self catalyzed process (fig. 4). The most important kinetic characteristics are oxidation induction time and rate of oxidation. The chemiluminescence investigation for the qualification of the resistance to oxidation has revealed the specific oxidation rate for each material. The higher concentration of free radicals generated by radiolysis in the higher dose irradiated polyethylenes allows the recombination of radicals in a larger extent than in the same material subjected to low irradiation dose.

The oxidation induction time is 52 min. for LDPE, while the same parameter attends 154 min. and 188 min. for HDPE 1 and HDPE 2, respectively. Due to the high percentage of crystalline phase, the propagation of

Property	HDPE 1	HDPE 2	LDPE
Density @ 23^{0}C (g.cm^{-3})	0.964	0.963	0.925
Melting flow rate (190^{0}C/2.16 kg) (g/10 min)	5.5	0.33	1.63
Crystallinity (%)	68.60	65.07	48.75
Nr. CH_3/100 C	1.17	0.91	3.55

Table 1
MATERIAL INPUT DATA

Table 2
EVOLUTION OF RADIOCHEMICAL YIELD FOR THE FORMATION OF C = O

Dose (kGy)	HDPE 1	HDPE 2	LDPE
0	0.68	0.71	0.75
25	0.69	0.70	0.73
50	0.65	0.71	0.76
75	0.68	0.68	0.74
100	0.64	0.70	0.72
Average	**0.67**	**0.70**	**0.74**

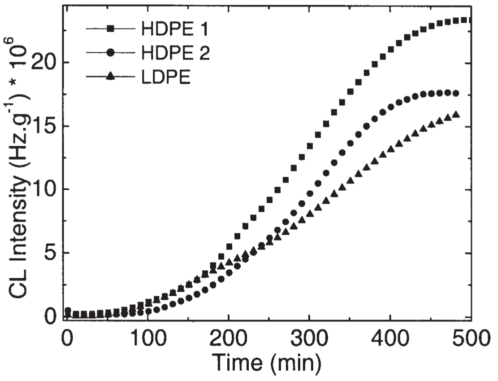

Fig.4. Dependences of CL intensity on time for non irradiated polyethylenes evaluated at 170^{0}C.

oxidation takes place somewhat slower than it was expected for a branched molecule materials.

The advanced degradation obtained in γ-radiation field brought about significant cropping of oxidation induction time (fig. 5) anticipated by the higher amount of free radicals formed during irradiation. The medallion inserted in figure 5 depicts the tendency for oxidation in the case of low density polyethylene. The same order of radiation resistance is pointed out:

HDPE 1 > HDPE 2 > LDPE

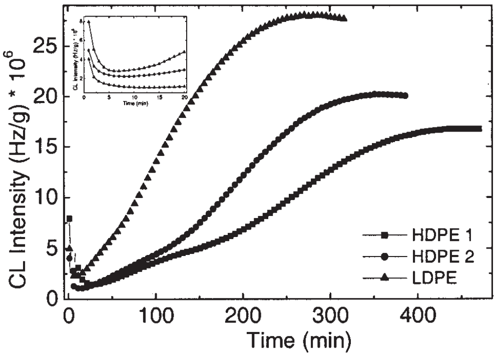

Fig. 5. CL curves for polyethylenes irradiated at 100 kGy (measurement temperature: 170^{0}C).

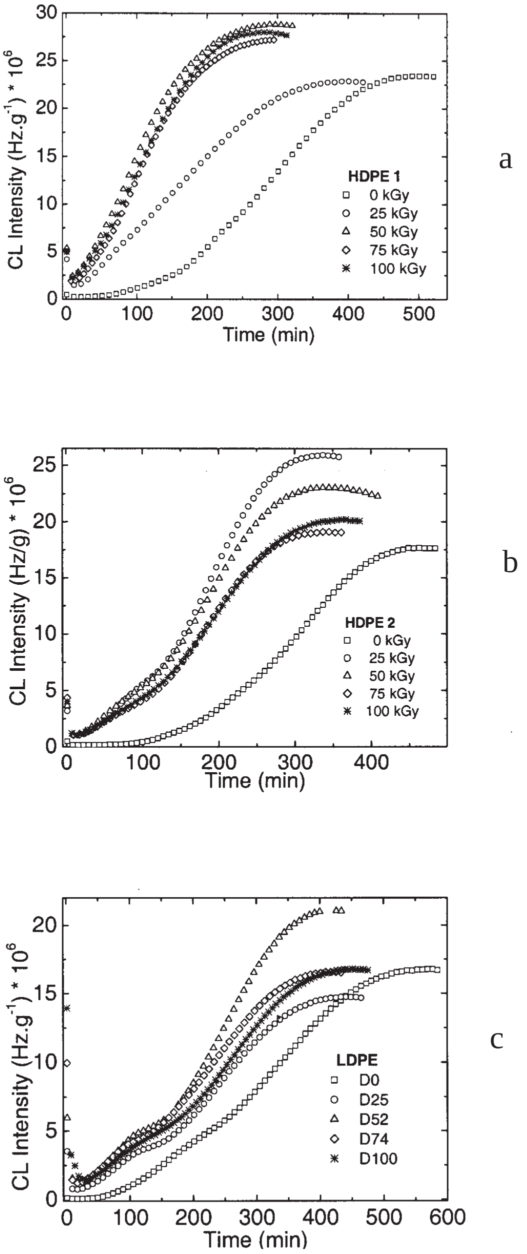

Fig. 6. CL curves recorded for HDPE 1 sample irradiated at various doses

Figure 6 illustrates the results of the competition between degradation and crosslinking. If at the first applied dose (25 kGy) a sharp alteration in the oxidation resistance can be noticed. For higher doses (50, 75 and 100 kGy) a slight amelioration in the oxidation rate may be obtained passing from LDPE onto HDPE 1, but the thermal stability of all irradiated samples is far from the behavior of pristine material. The higher concentration of free radicals generates by radiolysis in the higher dose irradiated polyethylenes allows the recombination of radicals in a larger extent than in the same material subjected to low irradiation dose. This comportment was observed for all three types of polyethylene However, there is difference between the intake levels of recombination. The scission mechanism and the processes in which radical intermediates are involved have been previously reported [38].

The effect of oxidative degradation can be described by the evaluation in electrical properties, because the oxygenated products act as electrical dipoles. If the high energy radiation passes the testing polymer samples, δ electrons appear. These charge carriers may be trapped onto electronegative sites like oxygen atoms, double bonds, or even some molecular defects acting as gaps in entanglement configurations [39].

The excellent electrical insulation properties of polyethylene are the result of the constitution of polyethylene molecule exclusively by non-polar atoms (carbon and hydrogen). The residual conduction measured on pristine samples is the consequence of random scissions which take naturally place by the attack of moderate stressors during handling.

In figure 7a (dose 0 kGy) there may be noticed some definable remarks:

·the different values for volume resistivity are obtained characterizing the peculiarity of each type of polyethylene; the most conductive type is low density polyethylene, which is the most susceptible to scission and oxidation; the order based on the increase in the conductivity:

HDPE 2 < HDPE 1 < LDPE

is the same sequence that defines the increase in the values of CH_3 number per 100 carbon atoms, i. e. the order of the increasing in branching level.

HDPE 2 presents an ascendant manner in the resistivity values. It may be considered that the electron traps are successively released in the succession of increasing their depths.

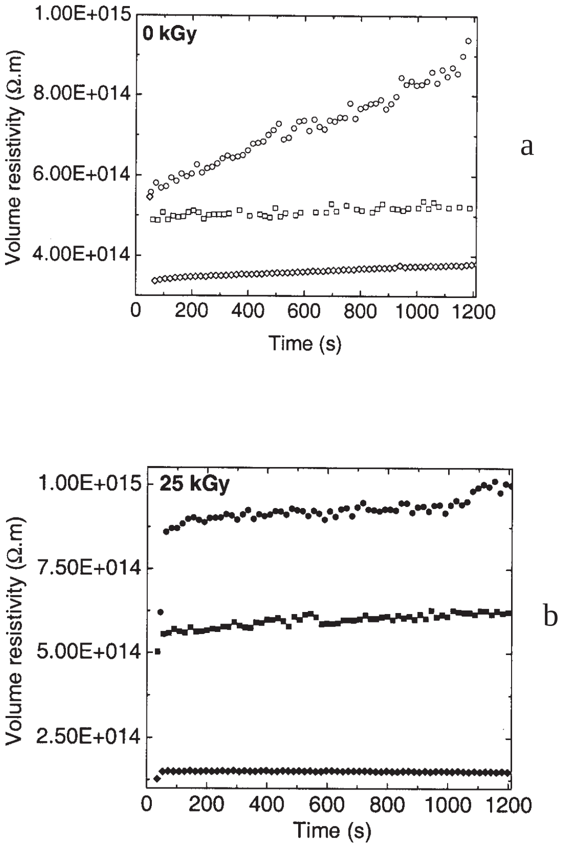

Fig.7. Evolution of volume resistivity on time (applied tension 50 V)
(■,□) HDPE 1; (o, •) HDPE 2; (◇, ♦) LDPE

In figure 6b (dose 25 kGy) the contribution of dipole structures simultaneously with the trapped electrons alters the insulation performances of polyethylenes. The largest difference in resistivity values is displayed by low density polyethylene, due to its noticeable availability for oxidation.

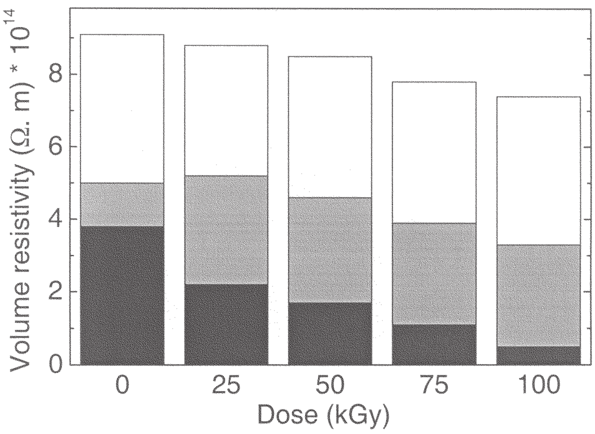

Fig. 8. Change in volume resistivity for different irradiation doses. (black) HDPE1; (gray)HDPE 2; (white) LDPE

Different dipoles containing oxygen presenting their specific dipole moments are accumulated during γ-exposure and oxygen diffusion [40], whose presence leads to the depreciation of insulating features of PEs (fig. 8).

Conclusion

The comparative study on the modification in chemical and electrical resistances of three sorts of polyethylene emphasizes the higher susceptibility of low density polyethylene to oxidation due to the lower content of crystalline phase and higher value of CH_3 number per 100 carbon atoms. The contribution of various physical factors are demonstrated by the unlike evolution of chemical modifications (hydroxyl and carbonyl indexes, rates on propagation stage of oxidation), by the changes in electrical properties caused by the different evolution in the formation of dipoles).

The applications of polyethylene must take into account the type of material, because the action of various stressors reduces the life time of products. On the other side, the customers have to choose the type of polyethylene in connection with the stability threshold, which imposes the limit of warranty under the circumstances of synergistic effect of degrading agents (heat, oxygen, water vapors, light, mechanical and electrical overcharges).

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