UNIVERSITY OF BUCHAREST
CHEMISTRY FACULTY
DOCTORAL SCHOOL IN CHEMISTRY

PhD THESIS SUMMARY

CONTRIBUTIONS TO THE STUDY AND CHARACTERIZATION OF DEGRADATION PROCESSES OF THE INSULATING POLYMERIC MATERIALS IN HIGH-ENERGY RADIATION FIELDS

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SUMMARY

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It was kept the numbering of figures and tables from PhD thesis

1. INTRODUCTION

The polymeric materials durability is an important area for various applications such as construction, aerospace, automotive or distribution of electricity from conventional or unconventional sources, geology, etc. The important position of the polymeric materials among the conventional and advanced materials for various applications is widely recognized.

The main goal of the PhD thesis is to study the aging of insulating polymeric materials of cables used in the CERN particle accelerator systems and the elaboration of a simple kinetic model, applicable to the specific operating conditions, characterized by the presence of highly non-uniform ionizing radiation field in terms of view of the intensity (energy and dose rate, variations over a cable may be of several orders of magnitude) as well as over time.

Practical applicability of such a model in diagnosis degradation and subsequent evaluation of the remaining life-time is even greater as it can be adapted to a wider range of operating conditions and materials.

Part I – STATE OF THE ART

In the first part of the thesis (Chapters 2-4) is presented a synthesis of the most important scientific papers related to the addressed research topics.

In Chapter 2 is realised a synthesis of the main types of polymeric materials used in the manufacture of lectrical cables (both as insulating and jacketing materials) such as: various types of polyethylene (LDPE; XLPE, HDPE, PE foam), ethylene-propylene and ethylene-vinyl acetate copolymers, PVC, etc.. Their chemical and physical characteristics are also presented.

It is also carried out a study of literature on the degradation and stability of polymeric materials in different stress conditions (thermal, thermooxidative and photooxidative) being presented the main degradation mechanisms and mechanisms of action of stabilization systems to slow down the aging process of these materials.

The Chapter 3 is dedicated to the state of the art regarding the degradation and stabilisation of insulationg polymeric materials in radiation fields.

În the Chapter 4 is carried-out a synthesis of the main methods of the degradation state diagnosis and of the durability evaluation of insulationg materials:

- Spectroscopic methods (Infrared spectroscopy, measuring the propagation velocity of acoustic waves, NMR relaxation time);
- thermal analysis methods (TG analysis, Differential Scanning Calorimetry-DSC, chemiluminescence-CL);
- Mechanical testing of materials.

PART II - EXPERIMENTAL PART

5. EXPERIMENTAL TECHNIQUE

5.1 Materials

The polymeric materials studied in the chapters 6 and 7 (LDPE, HDPE, XPE, EVA and EPR copolymers are intended for use as dielectrics in various application, of which the most important is halogen-free electrical cables.

The studied cables were classified in following classes: high voltage cables (HV), signal cables (S) and instrumentation and control cables (IC, Fig. 5.1). The nature of the base polymer of these materials was established by ATR-FTIR spectroscopy and DSC, the experimental information being corroborated with data from spectral libraries, literature as well as with the technical specifications (if were available). The studied materials for cables with identical names are different in terms of composition and of the nature of the base polymer.

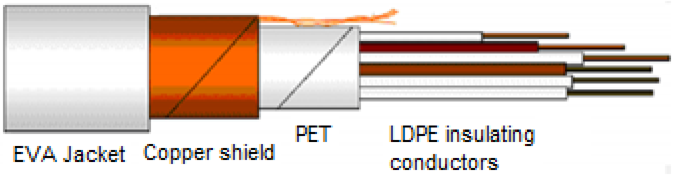


Fig. 5.1 *– The Schema of an IC cable*

To the carrying-out

To the achievement of the experiments regarding the irradiation behavior of nanocomposite materials with nanosilica (Cap. 8) were used the following materials:

- low density polyethylene (LDPE) B21/2 type, produced by Rompetrol Petrochemicals (Romania) with the following characteristics: density – 0.9077 g/cm^3, crystallinity – 42 %, MI – 3.25 g/10 min (190°C/2.16 kg), CH_3 numbers/100 Carbon atoms – 3.05.

- Isotactic polypropylene (i-PP), type TATREN HG 10.07 produced by Rompetrol Petrochemicals (Romania) with the following characteristics: density 0.8994 g/cm^3, MI – 1.498 g/10 min (190°C/2,16 kg).

- EPDM provided by Arpechim Pitești (Romania). The ratio ethylene/polypropilene was 3/2, and the initial amount of diene (ethylidene norbornene – ENB) was 3.5 phr.

- SiO_2 nanoparticles, Aerosil 380 type, provided by Degussa, as fumed silica with a specific surface of 380 m^2/g and a diameter between 3 and 15 nm.

In the case of blends of EPDM and butyric rubber the used polymeric materials were:

- EPDM with a content of 29 % polypropylene and 3.5 % ethylidene norbornene provided by Arpechim Pitești;

- Butyric rubber, BK2045 type (Russia) with an unsaturation degree of 2%.

The materials used for the achievement of experiments regarding the modification of a PA6 matrix and various types of elastomers (Chap. 9) were:

- EPDM Nordel IP 3745IP type, unfunctionalized. The blends were irradiated at different irradiation doses (up to 160 kGy) at various PA6 concentrations: PA6:EPDM – 100:0, 90:10, 80:20, 70:30. These samples were characterized in terms of the influence of the elastomer content and of the irradiation behavior by ATR/FTIR Spectroscopy;

- Exxelor VA 1801 functionalized cu maleic anhydride in order to obtain a chemical compatibility between two immiscible polymers. The blends in the following concentration of elastomers 0, 5, 10 and 20% were irradiated at different doses (up to 800 kGy). These materials were characterized by ATR/FTIR spectroscopy.

In the experiments regarding the use of antioxidants to the stabilization of an organic substrate (Chap. 10) were used the following materials:

- pure flavonoids commercially available: Naringenin (5,7,4’-trihydroxyflavonone), Hesperetin (5,7,3’-trihydroxy - 4’metoxyflavonone), Epicatechin (3,5,7,4’,5’-pentahydroxyflavan), Epigallocatechin (3,5,7,3’,4’,5’-hexahydroxyflavan), Quercitine (3,5,7,3’,4’-pentahydroxyflavone), Morin (3,5,7,2’,4’-pentahydroxyflavone);
- Phenolic acids (chemical reagents): m-hydroxybenzoic; chlorogenic; galic; sinapic; cafeic, carnosic;
- BHT - Butylated hydroxytoluene - 2,6-bis(1,1-dimethylethyl)-4-methylphenol)
- Plant extracts obtained from Apiaceae family (celery, lovage, dill and parsley) and Labiatae family (sage, rosemary, thyme and oregano).

5.2 Samples aging

The studied polymeric materials were aged in various stress conditions such as:

5.2.1 Thermal aging, in air-circulation oven

In a series of experiments was proceeded according to IEC60811-408 standard, the samples being thermo oxidative aged (at 100°C for 1008 h). For kinetic studies samples were extracted and characterized at intermediate times.

In other series of experiments was studied the influence of temperature in the range of 70-100°C.

5.2.2 Photooxidative aging

The aging of the samples used to realize the experiments from Chapter 7 was carried-out in the following conditions:

- Inside conditions, at visible light emitted by fluorescent lamp (2x18W), in circulating air;
- Outdoor conditions by direct exposure to the solar light.

5.2.3 Ionizing radiation aging

The radiative stress represented the main form of aging of studied polymeric materials, the experiment being classified in two categories, namely aging in controlled conditions of dose rate and aging in real conditions of exploitation in particles accelerator systems at CERN (SPS – Super Proto Synchrotron).

The polymeric materials from cables were irradiated with gamma irradiation in controlled conditions of temperature and dose rate:

- ^{137}Cs, at room temperature, D_r = 0,4 kGy/h, (University of Bucharest);
- ^{60}Co, D_r = 1,5 kGy/h (Ionisos, Dagneaux, France);
- ^{60}Co, D_r = 21,1 kGy/h (Wiehl, BGS - Beta-Gamma-Service, Germany);
- SPS (Super Proton Synchrotron) particles accelerator systems at CERN (Tab.5.6).

Table 5.6 *– Irradiation dose of SPS irradiated cables*

Hot Spot	**Dose (kGy)/Averaged dose rate (kGy/an)**	
	2 ani	**3 ani**
P1-MSE	22/10,5	24/8
P2-EMSE	11/5,3	14/4,6
P3-MST	6/2,9	11/2,6
P4-ZS	105/50,4	144/48
P5-EZS	26/12,4	31/10,3

5.3 Preparation of polymeric samples for irradiation

The samples subjected to irradiation (Fig.5.2) were in the form of strips (obtained by the lathing of the massive insulation of HV cables) or fragments of cables with the free ends (samples V_1) or air limited access (the ends being encapsulated in paraffinic wax over a distance of 10 cm, samples V_2). In the case of **HV2** cable the wax encapsulating was inefficient due to the high diameter of cable, so that, instead of samples of type V2, fragments of insulating materials were irradiated in inert atmosphere (Nitrogen) in glass ampoules (samples type V3, Fig. 5.2-3)

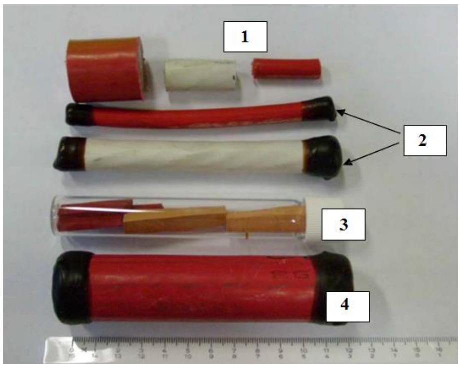


Fig. 5.2 – Cable samples prepared for irradiation: 1 - cable fragments with free ends (free air access, Type V_1); 2,4 – cable fragments with was encapsulated ends (Type V_2);3 – samples irradiated in an inert atmosphere

5.4 Instruments

In order to characterize the studied polymeric materials were used different techniques such as: Differential Scanning Calorimetry - DSC (isothermal and non-isothermal), Chemiluminescence – CL, Infrared spectroscopy, Shore D Hardness, Dielectric spectroscopy and Scanning Electron Microscopy – SEM.

6. CONTRIBUTION TO THE CHARACTERISATION OF THE DEGRADATION STATE AND DURABILITY ASSESSMENT OF INSULATING POLYMERIC MATERIALS

The purpose of the work carried-out in this chapter was to propose and verify a simple kinetic model for assessing the life-time of insulating polymeric materials in radiation environment, both in controlled and in service conditions.

This model is based on following premises:

- the effect of the stress factors, irrespective of their nature, consists in molecular scissions which lead to free radicals; these species reacts rapidly with the surrounding oxygen in air and trigger the oxidation chain reactions, thus leading to the material deterioration and failure;

- even in the absence of oxygen, the radiation-induced free radicals produce the polymer degradation (scission) or crosslinking; the subsequent air exposure of such a material will result in its oxidation due to the reactions of the trapped free radicals;

- the introduction of an antioxidant additive (or of several types) in the polymer matrix increases its oxidative resistance (life-time), due to the competition between the degradation reactions via the free radicals and the neutralization of these free radicals by the antioxidant;

- the antioxidants (together with other additives) are consumed in the reactions with the free radicals: hence a continuous depletion of the antioxidant content initially introduced in the polymer occurs during the service time of the material;
- when the antioxidant is completely consumed, the chemical protective barrier no longer exists, the polymer remains unprotected, and the oxidation spreads;
- the life-time of the material can be considered as the antioxidant consumption time in the specific operation conditions; the kinetics of the material residual life-time decrease coincides, practically, with the kinetics of the antioxidant depletion;
- the degradation diagnosis can be obtained from the analysis of the thermal stability, i.e. by the determination of OIT (Oxidation Induction Time) or OOT (Oxidation Onset Temperature); an aged sample shows lower values of OIT or OOT.

Generally, the stability of polymeric materials subjected to irradiation (Fig. 6.1) decrease progressively with irradiation dose. The kinetic parameters values (OIT and t_{max} – isothermal measurements; OOT and T_{max} – nonisothermal measurements) depend on the antioxidant amount into the sample and they decrease with the increase of dose (Fig. 6.2) due to progressively consumption of antioxidants by reactions with free radicals induced by irradiation.

The value of oxidation induction time (OIT), related to the amount of antioxidants, decrease exponentially with irradiation dose (or with irradiation time) (Fig. 6.2).

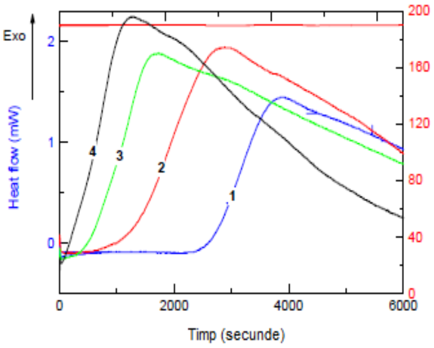


***Fig. 6.1** – DSC curves (190°C, air) obtained on LDPE insulation (strap) of cable HV1: 1 - 0 kGy (initial); 2 – 9,6 kGy; 3 – 28,8 kGy; 4 - 96 kGy*

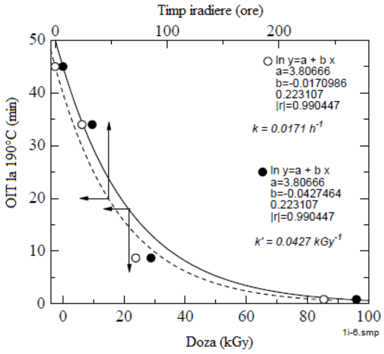


***Fig. 6.2** - OIT (la 190 °C, aer) vs. irradiation dose (γ^{137}Cs, D_d = 0.4 kGy/h) for LDPE insulation of cable HV1 (irradiated as strap)*

Based on these experimental data, the equations of the kinetic model proposed for life-time and maximum supportable dose evaluation of polymeric materials, are:

$$OIT = OIT_0 \cdot e^{-kt} \tag{1}$$

$$OIT = OIT_0 \cdot e^{-k'D} \tag{2}$$

Where: OIT – Oxidation Induction Time at time “t”; OIT_0 – OIT of unaged material; k, k’ – oxidation rate constants which depend on material structure and irradiation conditions (time, dese); t - irradiation time, D – absorbed dose.

The proposed kinetic model was verified on the main insulating polymeric materials used in cable production as: LDPE, XLPE, PE foam, HDPE, EPR and EVA.

The procedure of life-time and maximum supportable dose evaluation is similar for all types of polyethylene, the OIT values being directly obtained by isothermal DSC measurements. However, the PE foam presented a different oxidation behavior, DSC curve presenting more oxidation maxima (probable due to swelling agents), making difficult the precisely determination of OIT values. For this type of material were developed a method to obtain OIT values from OOT values (Oxidation Onset Temperature) based on non-isothermal DSC measurements and unconversional methods.

The obtaining methodology for life-time evaluation for a cable insulation based on high density polyethylene is presented in table 6.4, being evidenced the exponential decrease of OIT values with irradiation dose rate and the influence of type of sample subjected to irradiation (encapsulated or with free access of oxygen) (Fig. 6.11, 6.12)

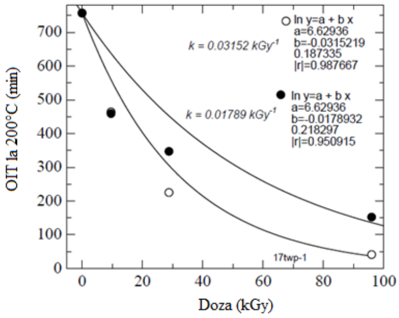


Fig. 6.11 *- OIT (at 200 °C in air) vs. dose (γ ^{137}Cs, D_d = 0.4 kGy/h) for HDPE insulation of cable S1, irradiated as V1 (○) and V2 (●)*

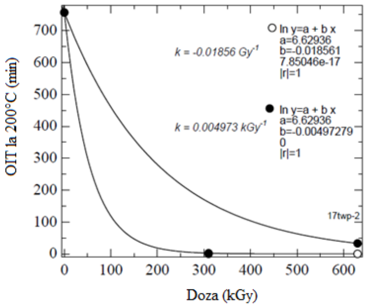


Fig. 6.12 *- OIT (at 200 °C in air) vs. dose (γ ^{60}Co, D_d = 1.5 kGy/h) for HDPE insulation of cable S1, irradiated as V1 (○) and V2 (●)*

Table 6.4 *– Life-time evaluation of HDPE insulations of cable S1 (Isothermal, T=200°C, air)*

Irradiation conditions	**Dose (kGy)**	**Dose rate (kGy/h)**	**OIT (min.)**	**k' (kGy^{-1})**	**D_x (kGy)**	**RI**	**t_x (hours)**
V1	0 9.6 28.8 96	0.4 0.4 0.4	757 464 225 41	$3.152 \cdot 10^{-2}$	267	5.4	668
V2	0 9.6 28.8 96	0.4 0.4 0.4	757 459 347 152	$1.789 \cdot 10^{-2}$	471	5.7	1178
V1	0 310 630	1.5 1.5	757 2.4 0*	$1.856 \cdot 10^{-2}$	454	5.7	303
V2	0 310 630	1.5 1.5	757 1.9 33	$4.973 \cdot 10^{-3}$	1693	6.2	1129

* Breakable

In the case of PE foam the OIT values were determined by using the Gimzewski equation:

$$e^{-\frac{E_a}{RT_{iso}}} \int_0^{t_{ind}} dt = \frac{1}{\beta} \int_0^{T_{ind}} e^{-\frac{E_a}{RT}} dT \qquad (20)$$

Where: E_a – activation energy, T - temperature; T_{iso} – temperature of isothermal experiment; T_{ind} – the value of OOT; R – gas constant; t - time; β – heating rate; t_{ind} – induction time. The defined integral $\int_0^{t\ ind} dt$ represents the value of OIT (obtained from isothermal measurements). The defined integral $\int_0^{T\ ind} e(-\frac{Ea}{RT})\, dT$ is numerically solvable.

The oxidation activation energy E_a (in fact E_a/R; R = gas constant) was determined by Kissinger method [254], being the slope of $\ln(OOT^2/\beta)$ vs. 1/OOT, where β is heating rate (Fig. 6.18). In order to obtain the E_a are necessary 4 different heating rates (2.5, 5, 10, 15 °C/min)

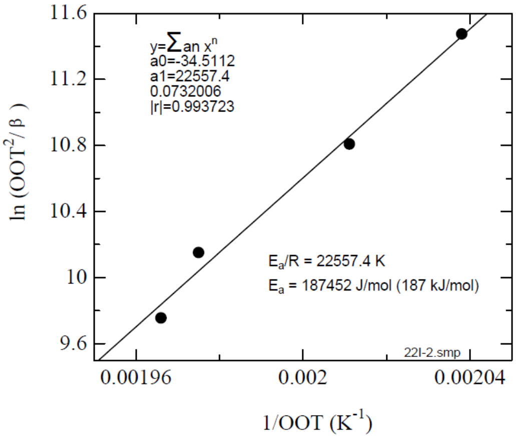


Fig. 6.18 *– E_a determination from OOT values using Kissinger method for PE foam insulation of cable S3 irradiated encapsulated (V_2) at 310 kGy*

In table 6.9 is presented an example of obtaining OIT values from OOT values for a PE foam aged in various conditions. With these OIT values was possible to evaluate the life-tim and maximum supportable dose, using the same procedure as for LDPE.

The DSC analyses carried-out on insulating polymeric materials based on ethylene-vinyl acetate copolymer evidenced a different oxidation behavior of those materials as a function of vinyl acetate concentration into the polymeric system. Thus, these materials were classified in two classes:

- Type I EVA: with small values of ΔH_D (decomposition enthalpy related to acetic acid elimination) (<200 J/g) and OOT: <275 °C
- Type II EVA: with higher values of ΔH_D (>300 J/g) and OOT: >300 °C.

In the case of type I materials the OIT values can be directly determined by isothermal DSC measurements, and the evaluation of life-time and maximum supportable dose methodology is similar to polyethylene. In the case of type II materials (with very high OIT values) the OIT values were determined from OOT values using a procedure similar to PE foam.

***Table 6.9** – OIT values evaluation at 200°C from OOT values for PE foam insulation of cable S2*

Dose (kGy)/ Irradiation conditions	**β (K/min)**	**OOT (K)**	**1/OOT** (K^{-1})	OOT^2/β **(K·min)**	**ln** (OOT^2/β)	E_a/R	$T_{iso}(K)/T_{iso}(°C)$	$e^{-\frac{E_a}{RT_{iso}}}$	T_0 **(K)**	$\int_{T_0}^{T_{ind}} e^{-\frac{E_a}{RT}}$	**OIT calc. (min)**	**OIT Avg. (min)**
0 /inițial	2.5	511.4	0.0019	104592	11.55782	28961.6	473.15/200	$2.61\cdot10^{-27}$	303	$2.22\cdot10^{-24}$	340	335
	5	521.2	0.0019	54319	10.90264					$6.68\cdot10^{-24}$	335	
	10	523.5	0.00191	27400	10.21830					$8.60\cdot10^{-24}$	330	
	15	527.4	0.001893	18540	9.82768					$13.1\cdot10^{-14}$	335	
310 /V2	2.5	490.7	0.002038	96250	11.47517	22557.4	473.15/200	$1.97\cdot10^{-21}$	303	$1.11\cdot10^{-19}$	22.5	22
	5	497.3	0.002011	49452	10.80875					$2.10\cdot10^{-19}$	21.3	
	10	506.4	0.001975	25639	10.15187					$4.91\cdot10^{-19}$	24.9	
	15	508.7	0.001966	17248	9.75547					$7.26\cdot10^{-19}$	20.5	
310 /V1	2.5	481.0	0.002079	92525	11.43524	18918.1	473.15/200	$4.32\cdot10^{-18}$	303	$9.67\cdot10^{-17}$	9.0	9.5
	5	491.8	0.002033	48364	10.78650					$23.1\cdot10^{-17}$	10.7	
	10	497.9	0.002008	24785	10.11801					$39.3\cdot10^{-17}$	9.1	
	15	503.1	0.001987	16871	9.73333					$59.4\cdot10^{-17}$	9.2	
630 /V2	2.5	481.1	0.002078	92564	11.43565	18945.9	473.15/200	$4.07\cdot10^{-18}$	303	$9.19\cdot10^{-17}$	9.0	9.1
	5	489.9	0.002041	47991	10.77876					$19.3\cdot10^{-17}$	9.5	
	10	496.8	0.002013	24676	10.11359					$34.0\cdot10^{-17}$	8.4	
	15	503.4	0.001986	16891	9.73452					$57.5\cdot10^{-17}$	9.4	

7. CONTRIBUTION TO THE CHARACTERISATION OF DEGRADATION IN DIFFERENT CONDITIONS OF INSULATING COMPOSITE MATERIALS BASED ON LDPE MATRIX

Within this chapter are presented the experimental results obtained on insulating polymeric materials of some instrumentation and control (IC) cables. These, though exposed on less severe exploitation conditions [room temperature, the absence of UV light, low intensity of natural light, low intensity of electric current (order of mA) and low voltage (<100 V)], unexpectedly showed signs of intense degradation, manifested by the appearance of cracks specific to photooxidative degradation.

Insulation materials had different colors (white, brown, red, yellow and orange), suggesting different materials (at least as regards the type of dye), but the appearance of cracks was observed always on white material, the phenomenon occurring after 5 -7 years of use, and only in the unprotected external jacket of the cable (Fig. 7.1).

The ATR/FTIR analysis (Fig. 7.2) of white insulating materials, showed clearly in both cases (1) and (2), the presence of oxidation groups, such as those at 1770 cm^{-1} (peroxyester), 1749 cm^{-1} (possibly esters) or 1715 cm^{-1} (carboxylic acids).

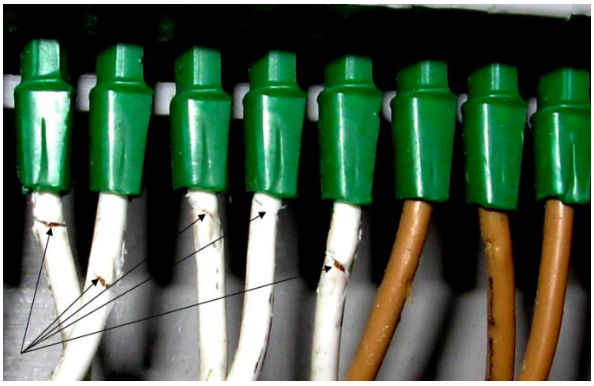


Fig. 7.1 *– The effect of aging in less severe exploitation conditions. All conductors from the image are part of one and the same cable; white colored materials show crack (marked by arrows)*

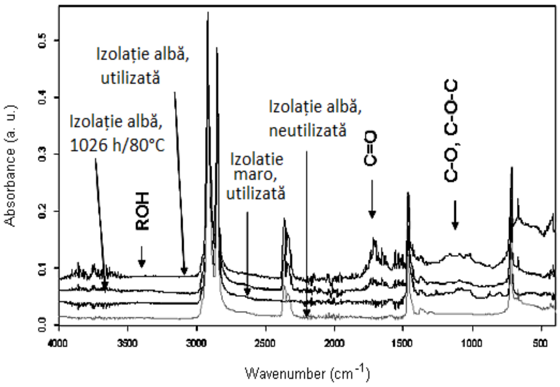


Fig. 7.2*– Oxidation Groups evidenced by ATR-FTIR spectroscopy: relatively intense bands for OH and CO on white aged insulation; less intense or even absent bands for brown insulation, as well as for white thermally aged insulation.*

The stability to oxidation was assessed by isothermal DSC measurements (200°C, in air) and nonisothermal DSC measurements (with a constant heating rate, 10°C/min, in air), both on used and unused cables (Tab. 7.2).

With obtained data from Tab. 7.2 and using the proposed kinetic model it can be evaluated the storage life-time of these cables using:

- For white insulating material: OIT after 1 year of storage: 59 minutes; OIT after 5 years of storage: 25 minutes. The estimated life time is about 27 years, and the remaining life time is 22 years;

- For brown insulation material: OIT after 1 year of storage: 60 minutes, OIT after 5 years of storage: 28 minutes. The estimated life time is about 31 years, and the remaining life time is 26 years.

***Table 7.2** – DSC parameters on initial, used and stored cable insulations*

Insulating material	Age of cable (years from production date)	State of the cable	OIT (minutes)	t_{max} (minutes)	ΔH_h (J/g)
White	1	unused	59	71	0
	5	unused	25	43	-0.9
	5	Aged in service (used without jacket, sample 1)	0	3.7	-19.6
	7	Aged in service (used without jacket, sample 2)	0	3.1	-28
Brown	1	unused	60	70	0
	5	unused	28	39	-0.75
	5	Aged in service (used without jacket, sample 1)	4.6	13.4	-3.8

The protective role of the external jacket has been illustrated by plotting an oxidation profile along of an aged service conditions cable (Table 7.3). The cable sample used for this study had the following characteristics: the length of the zone protected by jacket 112 cm; one cable end was not protected by jacket, and the other one ends with a semi-air-tight connection. The obtained results also support the hypothesis of physical loss of the antioxidant.

***Table 7.3** – Stability and oxidation profile for used white insulation, described by DSC parameters. Age of the cable: 7 years.*

Sampling position	**OIT (minute)**	**t_{max} (minute)**	**ΔH_h (J/g)**
No jacket	0	4.1	-12.3
Under jacket, 2 cm from unprotected cable end	3.4	14.4	-5.0
Under jacket, 30 cm from unprotected cable end	5.6	16.0	-2.2
Under jacket, 60 cm from unprotected cable end	13.3	20.9	-2.1
Under jacket, 90 cm from unprotected cable end	8.8	17.1	-1.3
Under jacket, 100 cm from unprotected cable end and 2 cm from connector	6.4	14.4	-2.1
No jacket, into the connector	2.1	9.4	-7.9

The stability decrease over time was observed, also, on the stored cables (as described above), in outdoor conditions (the each cable end being encapsulated): the OIT values decrease with the age of the cable (Fig. 7.6). In each case, insulating samples were taken under the jacket, at 30 cm from the free to air end cable. Under these conditions, were obtained low ΔH_h values, suggesting rather a physical loss of antioxidant than the antioxidant consumption by chemical reactions (by oxidation).

Evidence to the decreasing of the concentration of antioxidants and for the instability of antioxidant-polymer mixture has also been brought by various laboratory aging tests. Results from these tests showed the following behavior of the studied materials:

- In all cases, OIT decreased with the increasing of the aging time;

- In dark conditions, at room temperature, the base polyethylene loses much faster its stability than insulation material: after less than two years of laboratory storage (in dark) a strap of polyethylene presents an OIT of 24 minutes, the initial OIT values being of 116 minutes; this behavior illustrates clearly the instability of the antioxidant into the polymer matrix: the antioxidant is quickly lost by migration and volatilization mechanisms at room temperature;

- a greater retention of the antioxidant in some insulating materials may be due the interactions between antioxidant and other components such as pigments in the case of masterbaches;
- in dark, the decreasing of OIT value (the decrease of the antioxidant concentration) is comparable or even lower for the white insulation compared to the brown one (table 7.4); this behavior can be attributed to the TiO_2 influence which can fix the antioxidant molecules by adsorption or barrier mechanisms; the differences between OIT values of white and brown insulations are higher when the aging takes place at room temperatures, and lower when the aging is performed at higher temperatures, when, probably, the contribution of adsorption and barrier mechanisms decreases;
- the presence of light lead to the accelerated decrease of the antioxidant concentration for the white insulating material. The process is much faster than that of brown insulation and even of base polyethylene, suggesting a photochemical destruction mechanism induced by the photocatalytic effect of TiO_2 particles.

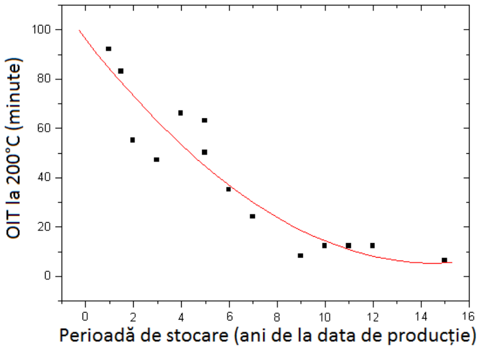


Fig. 7.6 – OIT at 200°C as a function of the age of the cable for white insulating material

The elemental analysis of the residue of calcination of white insulating material indicated that TiO2 is the major component (about 95%). The SEM micrograph showed round TiO2 particles greater than 300 nm. It is known that the incorporation of TiO2 fine powders in polyethylene gives white bright color materials and determines the improvement of certain properties such as abrasion resistance and flame behavior. It is also known that TiO2 particles may play a complex role in the photodegradation of polyethylene: on the one hand has a shielding effect, light being absorbed and dispersed, thus protecting the polymer from photooxidation. On the other hand, the particles of TiO2 catalyzes the oxidation by a mechanism which involve the photo-induced electrons, the generation of voids and the formation of reactive free radicals (OH) by interaction with adsorbed water molecules. These free radicals being highly mobile and reactive can initiate the oxidation of polymer matrix.

DSC analysis of the raw materials used for coloring (masterbatches), showed that they have different degrees of stability, reflected by the different values of OOT and OIT (Fig. 7.8 and 7.9), the brown masterbatch seems very stabilized, while the white masterbatch is substantially non-stabilized (OIT = 0 at 200 ° C); other masterbatches used for similar cables showed intermediate values of stability (Fig. 7.9). The stability of masterbatches varies, and thus their contribution to the stability of insulation should be different: the white masterbatch will bring additional stability and insulation material will not be protected after the consumption of initial concentration of antioxidant. Stabilizers used for masterbatches are probably different and less volatile than those used to stabilize the LDPE. Due to the additional contribution of these stabilizers and low levels of Ti (or TiO 2), insulating materials of different colors present a better aging behavior, in particular to the photodegradation. This process being responsible for the lowering of the molecular weight and the appearance of cracks.

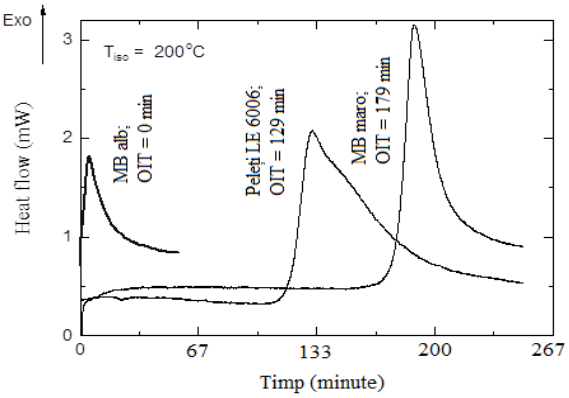


Fig. 7.8 *– Isothermal DSC curves for the base LDPE and masterbaches used to manufacture the studied insulating materials (T_{iso} = 200 °C, air)*

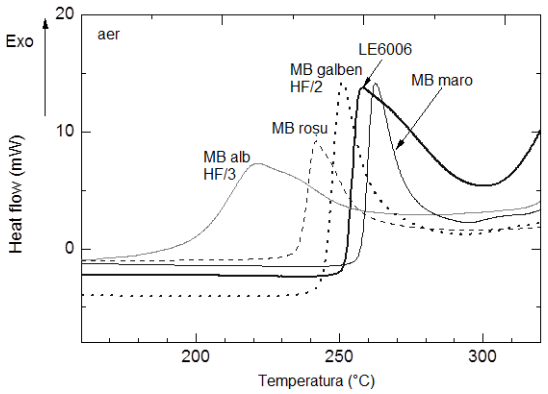


Fig. 7.9 *– Nonisothermal DSC curves for masterbaches used to manufacture the studied cable IC2 and similar (heating rate: 10 °C/min., air)*

8. IRRADIATION BEHAVIOR STUDY OF SOME NANOCOMPOSITE AND POLYMERIC BLENDS BASED ON EPDM MATRIX

The using potential of polymeric materials and their applications within the fields of ionizing radiation are related to their structural characteristics, defined by changes in the level of degradation. In the case of favorable interactions between the polymer matrix and the reinforcing element, composite materials may have a considerably higher radiation resistance than pure polymers, which considerably broadens the field of application of polymeric materials in the nuclear industry.

Within this chapter has been studied by different methods of analysis, the thermal and radiation stability of some nanocomposite materials based on EPDM and nano-silica and of EPDM/IIR rubber blends.

Comparative studies of radiooxidative stability between nanocomposites based on EPDM / nano-SiO2 and nanocomposites based on LDPE / nano-SiO2 and PP / nano-SiO2 have been performed.

CL curves (Fig. 8.1-8.3) recorded on EPDM materials without additives and additivated with nano silica revealed, after irradiation, the existence of a maximum at low temperatures (approx. 100 ° C) due to the formation of a significant amount of peroxy radicals due to radiation induced scissions of the double bond of the diene component. The low temperature maximum temperature appears increasingly lower with increasing radiation dose while the maximum intensity values of CL moves towards higher values and seems to be influenced by the presence of mineral batch, so we can conclude that inorganic filler has a low influence on the formation of peroxy radicals.

A greater stability was observed on the 5% nanosilica sample compared to the sample without filler, which can be explained by the fact that the thermooxidation stability after irradiation of the polyolefin composite is determined not only by the presence of the antioxidant, radical scavenger or a hydroperoxide decomposer, but also by the presence of mineral batch. In the case of a favorable interaction with the polymer matrix, it can cause a high percentage of termination reactions at the interface polymer-mineral particle and an important reduction of oxygen diffusion into the material, both processes contributing to the lowering of the oxidation rate.

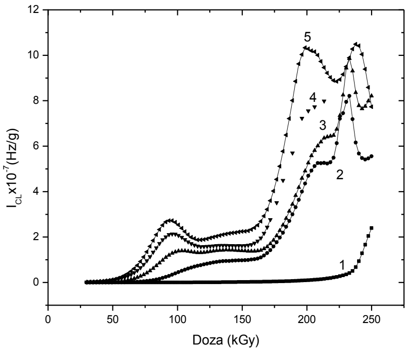


__Fig. 8.1__ – CL curves recorded on initial EPDM: 1 – 0 kGy; 2 – 10 kGy;, 3 – 20 kGy; 4 – 50 kGy; 5 – 100 kGy

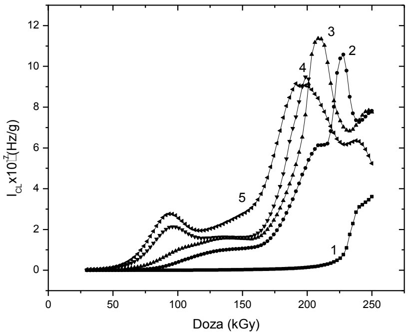


__Fig. 8.2__ – CL curves recorded on EPDM modified with 2% nanosilica: 1 – 0 kGy; 2 – 10 kGy; 3 – 20 kGy; 4 – 50 kGy; 5 – 100 kGy

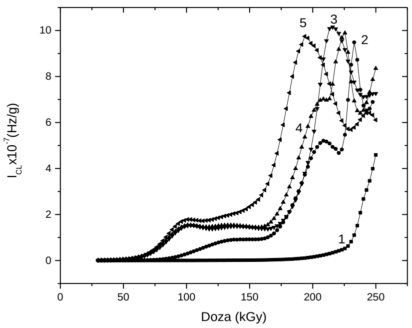


__Fig. 8.3__ – CL curves recorded on EPDM modified with 5% nanosilica: 1 – 0 kGy; 2 – 10 kGy; 3 – 20 kGy; 4 – 50 kGy; 5 – 100 kGy

The FTIR analysis showed an increase in absorbance with the time of irradiation, so with the irradiation dose, of the main oxygenated groups (hydroxyl and carbonyl). The band corresponding to the diene double bond was identified at ~ 810 cm^{-1}, its intensity decreasing with the increasing of irradiation time due to consumption of this component.

The analysis of carbonyl and hydroxyl indices revealed two effects:

- A strong increase at the same rate (based on dose) of the degree of oxidation for EPDM and LDPE and surprisingly low increase for PP, all materials being unmodified with nano particles. This behavior can be explained by the contribution of the factory stabilization systems, polymeric materials were used as received, except the compounding with silica;
- Increase in carbonyl index follows a similar trend for the PE and EPDM, suggesting that interaction with SiO2 particles is small; in the case of polypropylene, it is noted that the carbonyl index tends to remain constant, even though it is known that PP susceptibility to irradiation is considerably higher than that of PE. This behavior can be attributed to a favorable interaction of the free radicals induced of PP and SiO2 nanoparticles, and possibly, to the original stabilizing system, which results in a more efficient radio-stabilization of polypropylene matrix material.

Dielectric spectroscopy analysis of the data revealed an increase in electrical resistivity, at higher doses of radiation for the EPDM modified with different concentrations of nanosilica, suggesting that the EPDM nanocompozite materials exhibit better insulating properties. Electrical resistivity of the nanocomposite materials based on LDPE and PP is low.

In the case of EPDM / IIR polymeric blends, the obtained CL data (Fig. 8.14-8.16) suggests that the blend has a better radiation stability than individual EPDM polymer, both on irradiated and unirradiated samples. This may be due to the free radicals produced by the butyl rubber (which is more susceptible to radiation than EPDM) grafted on the EPDM macromolecules or their recombination to restore the original structure.

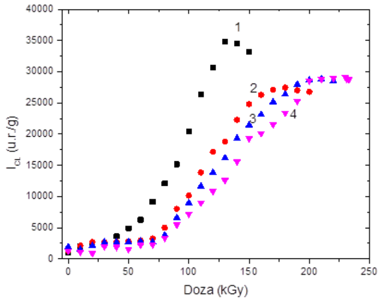


***Fig. 8.14** – CL curves (200°C, air) recorded on unirradiated EPDM/IIR blends at various EPDM/IIR concentrations: 1 – 100:0; 2 – 25:75; 3 – 50:50; 4 – 75:20*

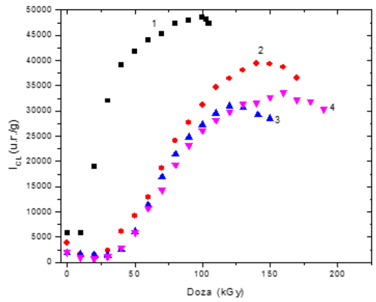


***Fig. 8.15** – CL curves (200°C, air) recorded on air irradiated EPDM/IIR blends (**dose = 10 kGy**) at various concentrations EPDM/IIR: 1 – 100:0; 2 – 25:75; 3 – 50:50; 4 – 75:20*

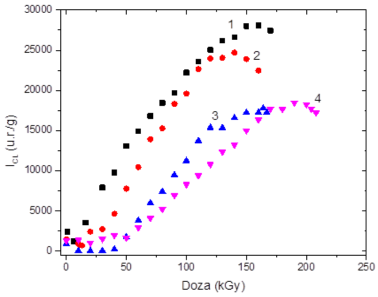


***Fig. 8.16** – CL curves (200°C, air) recorded on air irradiated EPDM/IIR blends (**dose = 20 kGy**) at various concentrations of EPDM/IIR: 1 – 100:0; 2 – 25:75; 3 – 50:50; 4 – 75:20*

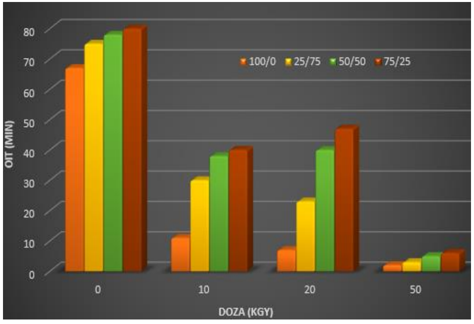


Fig. 8.17 –The dependence of OIT values on both dose and IIR concentration in EPDM/IIR blends

Within this study it was also evidenced the effect of irradiation environment on oxidation stability of EPDM/IIR polymeric blends.

The propagation rate of oxidation reaction at the thermo oxidation of EPDM/IIR blend in aqueous and saline environment shows higher values than samples irradiated in air. Depending on the environment type, the propagation rate of oxidation characterizes the material's ability to resist to the simultaneously attack of the temperature, ionizing radiation and oxidizing agents (oxygen, radiolysis products of water).

The exposure to γ radiation of the polymeric blend in saline solution lead to close to each other OIT values, because of chlorine ions which can facilitate crosslinking reaction into the EPDM phase.

During to the irradiation process, the formed free radicals are in completion with reactions with molecular oxygen. The different amount of IIR component in studied blends determines the obtaining of different propagation rates of oxidation for each macromolecule type. Thermal degradation of unirradiated or γ-irradiated blends follows a Bolland-Gee type mechanism.

Interactions between the two components of polymeric blends are evidenced by differences between obtained kinetic parameters. The oxidation susceptibility of those components increases due to the increasing irradiation dose and depends on irradiation environment.

The irradiation of EPDM/IIR blends leads to the obtaining of a new materials with better properties than individual polymers such as: thermal and radiation stability, especially at low irradiation doses. The obtaining of EPDM/IIR blends can be also a recycling efficient method of isobutyl rubber residues.

9. IRRADIATION BEHAVIOR STUDY OF SOME PA6/ELASTOMER COMPOSITE MATERIALS

Within this chapter was carried-out a study of the radiation stability of PA-6 / elastomer polymeric blends: PA-6/EPDM and PA-6/Exxelor (EPDM functionalized with maleic anhydride).

The irradiation behavior study of PA-6 without additives, performed by FTIR and DSC analyses, showed:

- the existence of some crosslinking processes due to changes of the absorption bands 1100 and 1118 cm^{-1};

- the increasing of the concentration of carbonyl compounds, due to radio-induced oxidation, occurs up to about 600 kGy, when it becomes saturated due to the consumption of oxygen in the material

- the increasing of the concentrations of γ crystalline form.

In the case of PA-6/EPDM blend it was observed, on the irradiated samples, that the carbonyl index values decrease with the increasing of EPDM concentration, while on the unirradiated samples the effect is opposite (Fig. 9.9). This particular behavior can be explained by the appearance of some radio-induced crosslinking processes in the structure of PA-6/EPDM blends and leads to the obtaining of a new materials with improved radiation resistance. This fact have been evidenced by stability tests peroformed by Chemiluminescence, being observed a decrease of the propagation rate of oxidation and of hydroperoxides concentration from 30% to 10 % of EPDM in polyamide blends.

In the case of PA-6/Exxelor blends it can be observed, from the analysis of carbonyl indexes (Fig. 9.16), a decrease of oxidation stability of the blend from 5% to 20% Exxelor up to irradiation doses of about 100 kGy. At higher doses, the sense of stability is reversed, i.e. a higher concentration of Exxelor (functionalized with maleic anhydride) induces higher stability than at small Exxelor concentrations, even at very high irradiation doses (800 kGy).

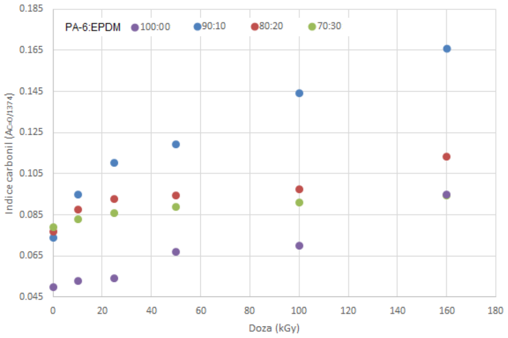


Fig. 9.9 – *Carbonyl indexes variation with irradiation dose and EPDM concentration*

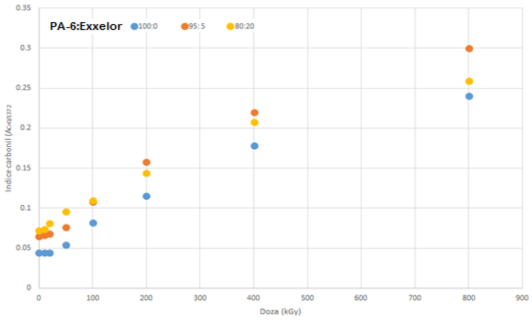


Fig. 9.16 – *Carbonyl indexes variation with irradiation dose and Exxelor concentration*

This study evidenced the possibility of using some radio-processed PA-6/elastomer blends to obtain new insulating materials with high radio-oxidation stability, even at high irradiation doses, and improved mechanical properties such as flexibility of blend, induced by elastomeric component.

10. STUDY OF THE ANTIOXIDATIVE CAPACITY OF SOME NATURAL COMPOUNDS

Within this chapter has put into evidence the possibility of using the natural compounds derived from plants to stabilize a polyolefin type organic substrate to thermooxidation, the antioxidant activity of these compounds is due to a high content of flavonoids. These flavonoids contain highly reactive hydroxyl that interact with free radicals forme in different degradation processes according to the following mechanism:

$$\text{Flavonoide (OH)} + RO_2^{\bullet} \longrightarrow \text{Flavonoide}(O^{\bullet}) + ROOH$$

The technique of chemiluminescence has been used to study the effectiveness of antioxidant of some commercially available natural compounds (Fig. 10.2) and extracted in laboratory from plant of the family Apiaceae (parsley, dill, lovage, celery) (Fig. 10.4) and of the family Labiatae (Sage, rosemary, thyme, oregano) (Fig. 10.5).

The antioxidant capacity of these plant extracts is due to the existence in their structure of two classes of phenolic compunds: phenolic acids (Hydrocinnamic acids: caffeic acid, chlorogenic acid, sinapic acid; hydroxybenzoic acids: gallic acid, o- and m hydroxybenzoic acids) and phenolic diterpenes (carnosic acid). Among these compounds the highest antioxidant activity present caffeic acid and carnosic acid. The antioxidant activity of carnosic acid is due to the possibility of oxidation of this compound in cascade, each intermediate being in turn an effective antioxidant.

The polyphenolic antioxidants obtained from plants may be an alternative to synthetic antioxidants as BHT (Fig. 10.11) to delay the start of the oxidation process, their presence in organic substrate being shown to contribute to the expansion of the oxidation induction time (OIT).

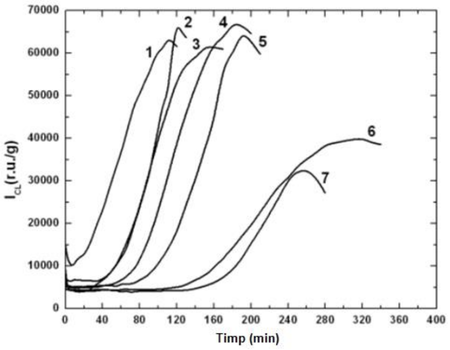


Fig. 10.2 *– Isothermal CL curves (150°C, air) recorded on unstabilized (1) and stabilized paraffin with 0,25% flavonoids: (2) – Naringenin; (3) – Hesperidin; (4) – Epicatechin; (5) – Epigallocatechin; (6) – Morin; (7) - Quercitine*

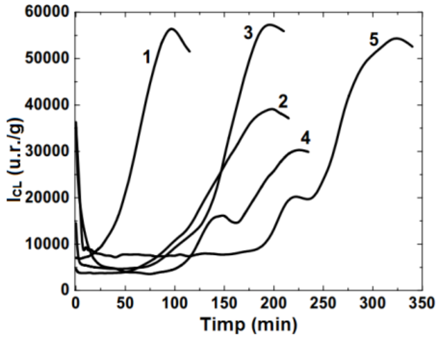


Fig. 10.4 *– Isothermal Cl curves (150°C, air) recorded on stabilized paraffin (0,25% w/w) with different plant extracts from Apiaceae family: 1 – unstabilized; 2 – celery; 3 – lovage; 4 – dill; 5 – parsley*

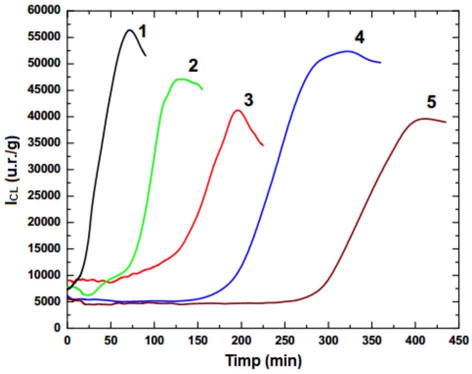


Fig. 10.7 *– Isothermal Cl curves (150°C, air) recorded on stabilized paraffin (0,25% w/w) with different plant extracts from Labiatae family:1 – unstabilized; 2 – Oregano; 3 – Thyme; 4 – Rosemary; 5 – Sage*

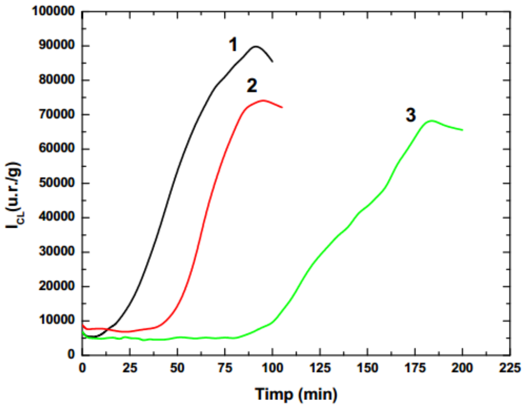


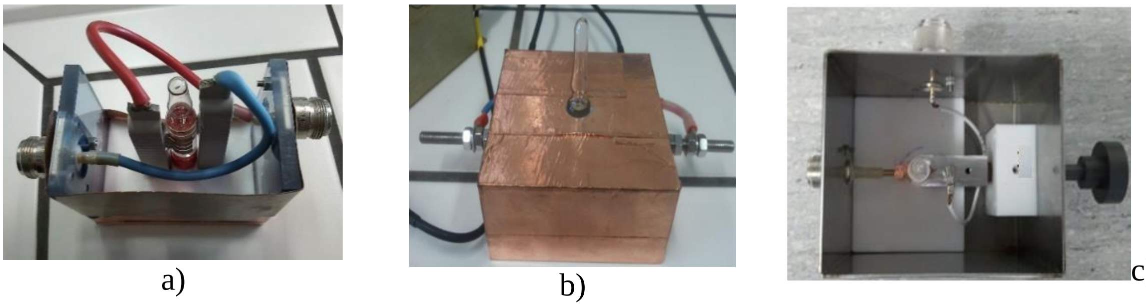
Fig. 10.11 *– Isothermal CL curves (168°C, air) recorded on unstabilized paraffin (1) and stabilized (0,25% w/w) with BHT (2) and carnosic acid (3)*

11. DOSIMETRY MEASUREMENTS ON ECB SYSTEMS BY HIGH FREQUENCY OSCILLOMETRY

To evaluate the life-time of insulating polymeric materials used in radiation environment, by applying the proposed simple kinetic model (see Chap. 6) is necessary to know the irradiation aging conditions, such total dose absorbed by these materials.

For this purpose was developed a method of determining the dose absorbed by a dosimeter based on ethanol-monochlorobenzene (ECB) using a high frequency oscilometry method. The methodology to determine the dose absorbed by the system is based on the HCl concentration in ECB produced during irradiation as a measurement of the absorbed dose.

Within this work were used the three types of cells (Fig. 11.1) designed and constructed at CERN, and measurements were made using a device formed of a signal generator and a vector analyzer.



a) b) c)

Fig. 11.1 *– Measurement cells: a) semi-shielded cells with Copper electrodes; b) MACOR cell shielded with Copper foil; c) metal cell with lid, completely shielded*

The steps for obtaining the dose absorbed by the dosimeter ECB system can be summarized as follows:

- Determination of the frequency at which the oscillometric measurement can be made. This is achieved by sweeping the frequency and by choosing the frequency at which the response of the analyzer is maximum (200 MHz in our case);

- Performing the calibration curve using known dose ECB vials (Fig. 11.2)

- Performing measurements on systems ECB with unknown doses.

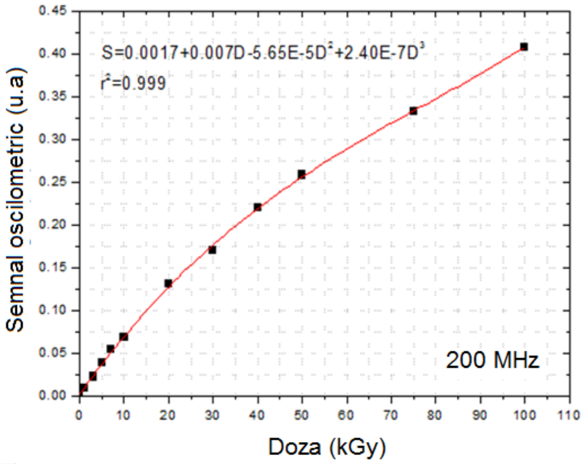


***Fig. 11.2** – Oscillometric signal variation with irradiation dose. Calibration curve determination*

The main advantage of this method is the lack of contact between the cell electrodes and the ECB solution, being non-destructive, thus contributing to the possibility of performing dosimetry measurements at any time after radiation. This is possible due to stability over time of the ECB dosimetry solution. Dose range in which the ECB solution is effective can go up to 300 kGy.

The reliability of proposed oscillometric method applied on ECB solutions was evidenced by comparing the results obtained on ECB systems with those obtained on alanine base dosimeters, the correlation being 0.99.

GENERAL CONCLUSIONS. ORIGINAL CONTRIBUTIONS

A first research direction was to propose and verify a simple kinetic model in order to evaluate the life-time and the residual life-time of of materials exposed to radiation fields, and in various other conditions (non-nuclear environments), directly on the materials exposed to the operating conditions, without having to carry-out accelerated tests under simulated conditions.

Although simple, the model takes into account the combined effect of all factors acting in service conditions.

The proposed method is based on the determination (by the DSC technique or CL) of OIT values of small samples and allows the highlighting and monitoring of hot spots along the cable in service.

Because the influence of environment factors, such as humidity or temperature, is reflected in the general degradation level of the material, the influence of these factors on the result of prognosis is insignificant.

The proposed method is applicable to any polymeric insulating material (based on LDPE, HDPE, XLPE, EPR copolymer, etc.) whose stability is controlled by the use of radical scavengers such as hindered phenols and secondary amines. A specific behavior was observed for expanded polymeric materials (such as expanded PE) for which investigation of the oxidation behavior was more appropriate by non-isothermal measurements. Within the thesis has been developed a methodology for conversion of data from non-isothermal measurements (OOT) into data of oxidation induction time (OIT) for any temperature measurement.

The kinetic model can be applied also an EVA copolymers, being identified in this case two types of EVA, as a function of oxidation parameters obtained by DSC measurements. A first category (type I materials), characterized by smaller ΔH_D (< 200 J/g) and OOT (≤ 275 °C) values, for these is applicable the direct determination of OIT by isothermal measurements. For the materials of the second category (type II materials), characterized by higher ΔH_D (> 300 J/g) and OOT (≥ 300 °C), is applicable the determination of OIT by nonisothermal measurement, followed by the conversion of OOT to OIT, mentioned above.

The second research direction consisted in the characterization to degradation, in various conditions, of some insulating polymeric materials with composite structure based on LDPE by using the DSC technique.

The DSC method was applied to the degradation prognosis and to the investigation of the differences between various insulating composites with LDPE matrix, aged in service in indoor conditions or in various conditions in laboratory. It has been evidenced a greater susceptibility to degradation of white insulating material, which contains a large amount of TiO_2 compared to the colored ones.

In order to evaluate the life-time of these materials in non-nuclear environments, without directly exposure to solar light, it was applied the kinetic model proposed within this thesis, being obtained a life-time of about 11 years for the brown insulation and 5 years smaller for the white one. These values are well correlated with the direct observations on these cables, being observed cracks on the white insulation, after 5 years in service. The behavior differences were attributed to the presence of TiO_2 particles, with an intense photo catalytic effect, even in the case of weak light intensity conditions. The decisively influence of TiO_2 on the life-time of white insulation is proved by the fact, that when the insulation is protected by external jacket, the life-time is higher than 25 years, like as the other colored materials. The presence of small amount of Titan in the other insulations, evidenced by elemental analysis, can explains the life-time decreasing of those insulations, when they are in free air access (no jacket), compared to the state completely protected from the action of light (under jacket).

Besides preventing the effect of light on the insulating material, jacket appears to contribute to limiting the loss of antioxidant at ambient temperature through physical processes. The life-time of insulating material located in the open air atmosphere (in the case of the unprotected sectors of multiconductors cable - in the connections area) will therefore be lower due to the gradual decrease of the concentration of the stabilizer.

Differences in behavior between the materials studied have their origin in significant differences between masterbatches used for the additivation of LDPE matrix. White insulation masterbatch composition's is significantly different from the other, from the point of view of the basic polymer and the chemical composition (the level of stability, the nature of dye, the nature of the inorganic component) resulting from this significant differences in aging behavior.

Experimental studies proved that the DSC technique is a useful tool in characterizing the qualitative and quantitative differences between polymeric materials used in the construction of the cable, and to the study of differences in their aging behavior under laboratory conditions, in storage or in use.

Another research direction consisted in the study of the oxidation behavior of some polymeric materials based on EPDM, modified with nano-silica particles (compared with LDPE and PP) and isobutyl rubber (IIR), and of the blends of the PA-6 with 2 elastomer types (EPDM and Exxelor – functionalized with maleic anhydride).

The CL curves recorded on the EPDM unmodified and modified with nano-silica, evidenced, after irradiation, of a peak at lower temperatures (100°C) due to the peroxy radicals formed by radio induced scission of the double bond of the diene component. This peak seems not to be influenced by the presence of mineral particles, so it may be concluded that the inorganic filler has a low influence on the formation of peroxy radicals.

A greater stability was observed on the 5% nanosilica sample compared to the sample without filler, which can be explained by the fact that the thermooxidation stability after irradiation of the polyolefin composite is determined not only by the presence of the antioxidant, radical scavenger or a hydroperoxide decomposer, but also by the presence of mineral batch.

The analysis of carbonyl and hydroxyl indices revealed two effects:

- A strong increase at the same rate (based on dose) of the degree of oxidation for EPDM and LDPE and surprisingly low increase for PP, all materials being unmodified with nano particles;
- Increase in carbonyl index follows a similar trend for the PE and EPDM, suggesting that interaction with SiO2 particles is small; in the case of polypropylene, it is noted that the carbonyl index tends to remain constant, even though it is known that PP susceptibility to irradiation is considerably higher than that of PE.

Dielectric spectroscopy analysis of the data revealed an increase in electrical resistivity, at higher doses of radiation for the EPDM modified with different concentrations of nanosilica, suggesting that the EPDM nanocomposite materials exhibit better insulating properties. Electrical resistivity of the nanocomposite materials based on LDPE and PP is low.

In the case of EPDM / IIR polymeric blends, the obtained CL data suggests that the blend has a better radiation stability than individual EPDM polymer, both on irradiated and unirradiated samples, especially at low irradiation doses.

In the case of PA-6/EPDM blend it was observed, on the irradiated samples, that the carbonyl index values decrease with the increasing of EPDM concentration, while on the unirradiated samples the effect is opposite.

In the case of PA-6/Exxelor blends it can be observed, from the analysis of carbonyl indexes, a decrease of oxidation stability of the blend from 5% to 20% Exxelor up to irradiation doses of about 100 kGy. At higher doses, the sense of stability is reversed, i.e. a higher concentration of Exxelor (functionalized with maleic anhydride) induces higher stability than at small Exxelor concentrations, even at very high irradiation doses (800 kGy)

In the last part of the thesis was analyzed by CL, the antioxidant efficiency of some natural antioxidant extracted in laboratory from plant of the family Apiaceae (parsley, dill, lovage, celery) and of the family Labiatae (Sage, rosemary, thyme, oregano).

These polyphenolic antioxidants obtained from plants may be an alternative to synthetic antioxidants as BHT to delay the start of the oxidation process, not only for the stabilization of some alimentary products (oils for frying), and of packaging for food and pharmaceutical products as well as less aggressive polymeric materials to the environment. Their presence in organic substrate being shown to contribute to the expansion of the oxidation induction time (OIT).

Also, it is presented an oscillometric method developed in laboratory, in order to determine the absorbed dose by an ECB solution. This method is based on the increasing of the ECB conductivity with dose.

The main advantage of the method is given by the contactless of the cells electrodes with de ECB solution, being a nondestructive method.

The original contributions can be summarized as follows**:**

- The development and testing on a large number of cables and in a wide variety of stress conditions of a simple kinetic model of degradation, which allows the evaluation of residual life of cables in the conditions of very small amounts of sample (of the order of milligrams) without being absolutely necessary to have the reference data (initial values) of the material under evaluation;

- Compared with the classical methods used to evaluate the status of cables, the proposed method allows an accurate assessment of their state of degradation and of the remaining life-time based on the thermo-oxidative stability, obtained from DSC and CL measurements;
- The proposed method is applicable for the cable management in irradiation facilities, facilitating the decision of replacing the used cables, based on the assessment of their remaining life-time from data obtained on real cables or witness (control) cables.
- Is proposed an original way of measuring the absorbed dose by the irradiated material using an ethanol-monochlorobenzene system (ECB) and oscillometric detection by spectroscopy at high frequencies;
- The obtaining of new materials (like polymer blends of PA6 / elastomer and EPDM / isobutyl rubber) with improved physical and chemical properties by radiochemical processing of them;
- The obtained original results were the subject of technical reports (elaborated at CERN), 5 papers published in ISI journals and 6 papers submitted in international conferences. A number of papers are currently in advanced elaboration stage or already submitted for review for publication.

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