



TE-VSC

TE Technical Note

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Polymeric Materials Review on Oxidation, Stabilization and Evaluation using CL and DSC Methods

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Keywords: Cable insulation, Polymeric materials, Radiation aging, Polymers lifetime.

Summary

Within TE - VSC Group, the Chemistry Laboratory actually works on the project entitled “Studies of Radiation Induced Aging Effects in Polymeric Cable Insulators”.

The aim of the project is the characterization and the evaluation of the aging effects mainly induced by ionizing radiations on the various polymeric materials in cables structure. It is expected, using the accumulated data, to foresee the life-time of these materials in the specific CERN accelerator systems and, also, to assure an acceptance quality control of the supplied cables in CERN.

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Introduction

The present technical note summarizes the theoretical aspects of the polymers degradation mechanisms, the action of chemicals used for their protection and stabilization as well as the analytical capabilities of chemiluminescence (CL) and differential scanning calorimetry (DSC), rapid and cost effective instrumental methods, as resulted from various literature data.

A second technical note should present the experimental data obtained in Chemistry Laboratory on selected cable materials used in CERN.

The life-time of polymeric materials used in the electrical cables as insulators, jackets, etc., is limited; the deterioration of their useful properties induced by a specific environment is known as the "aging" effect.

A number of factors are responsible for the deterioration of the polymer properties, such as: oxidative and thermal degradation, UV irradiation, climate factors, mechanical stresses, etc.; all these factors limit their service life.

Ionizing radiation is one of the main stressors, dose rate dependent, causing age-related degradation of polymer-based cable materials in air. Some degradation mechanisms act synergistically; e.g. the irradiation is known to accelerate the oxidative and the mechanical degradation, as well as the mechanical stress, too. The overall effect of the deteriorating factors acting simultaneously often largely exceeds the simple addition of their separate action.

The commercially available cables and their materials are designed for specific functions and environments; their polymeric insulators contain various organic and/or inorganic additives, such as fillers, plasticisers, stabilizers and colorants, anti UV and/or anti-rad protective substances, etc., which determine their final characteristics. Generally, the compositions of the polymeric insulators are proprietary, due to the high costs for research and development; usually, only the polymeric matrices (LDPE, XLPE, PP, EPDM, etc.) are shown by the cable suppliers.

Three decades ago CERN started an extremely useful program - stopped in late nineties - to test the mechanical behaviour of different irradiated organic materials susceptible to be used for the accelerators and experiments. The published CERN Yellow Reports (H. Schönbacher and co-workers, TIS) were a valuable guide for CERN applications. Presently, new materials, under new trade names are offered on the market and higher irradiation doses levels are expected for certain areas in CERN new machines and experiments.

1. Polymers Oxidation

The degradation processes of the various types of polymer have specific mechanisms and depend on both the main macromolecular chain nature and structure and on the chemical nature of the branched groups. It is well known for the oxidation of polyolefins or rubber (natural and some synthetic types) that hydroperoxides and the peroxy radicals are intermediates in a long kinetic chain mechanism. In the case of the halogenated polymers the dehydrohalogenation is the first reaction step followed by the thermal oxidation, while for the polyamides or cellulose the oxidation occurs by hydroperoxides within a short chain mechanism. [1 - 9].

The polymer degradation is caused by two main classes of factors:

- Physical factors: heat, light, ionizing radiation, mechanical processing, ultrasonic, etc.;
- Chemical factors: oxygen, ozone, chemicals, polymerization catalysts, etc.

Further on these degradation processes will be approached together with the polymer protection methods, as presented in Fig. 1.1.

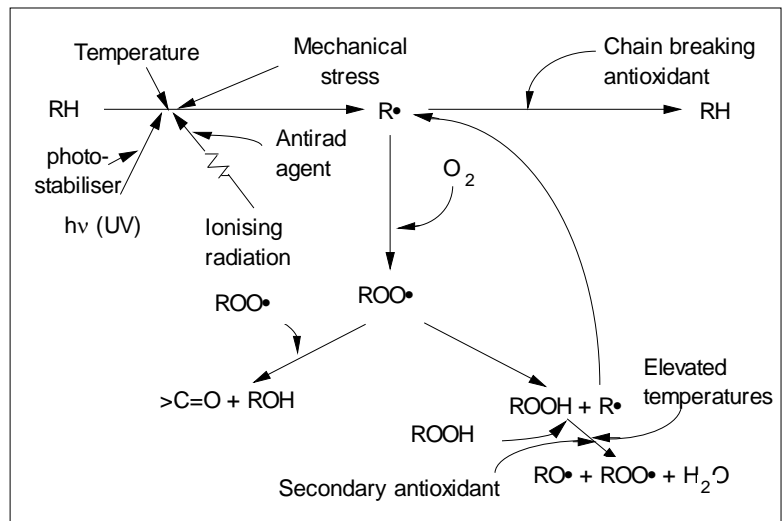


Fig. 1.1 - Oxidation of polymeric materials and ways for their protection

1.1 Thermo-Oxidation

The thermo-oxidation (or thermal-oxidation) of the macromolecular substances is defined as their thermally initiated reaction with the molecular oxygen. The general scheme of the polymers thermo-oxidation indicates the radical character of the process. (Fig. 1.2) [1, 3, 10 - 12].

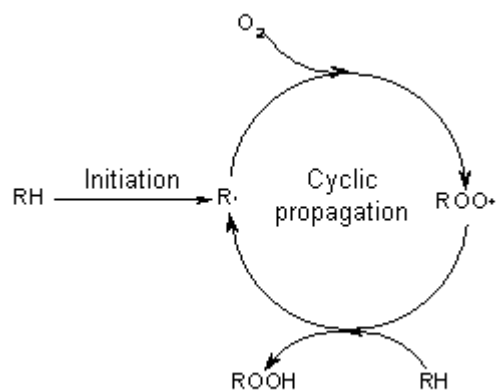
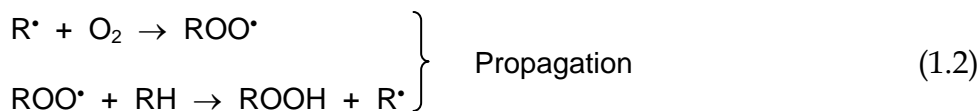


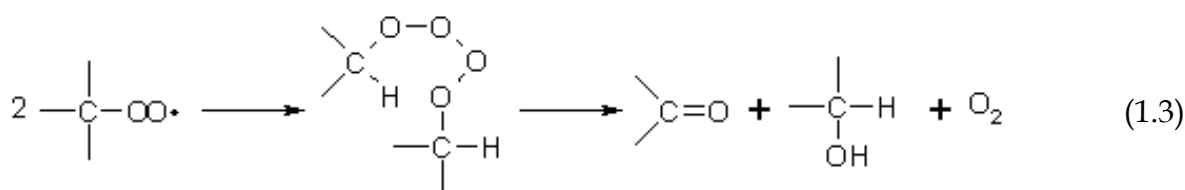
Fig. 1.2 – Thermo-oxidation process in a polymer

The thermo-oxidation of a hydrocarbon polymer starts by an H atom extraction via an excited oxygen or a radical [6, 7]. The organic radical formed reacts

with the polymeric substrate leading to a peroxy radical and further to a hydroperoxide accompanied by a macromolecular radical and thus propagates the chain reaction process:



The main reaction responsible for the chain termination reactions is the peroxy radical recombination:



The unstable hydroperoxides appeared in reaction 1.2 decompose as shown below:



The alkoxy radicals from the reaction step 1.5 may react with the present hydroperoxides leading to alcohols and peroxy radicals:

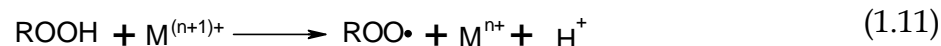
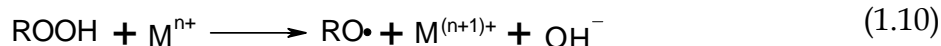
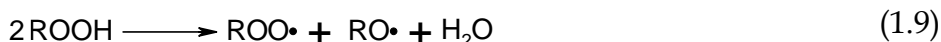


To be noticed that the free radicals R^{\bullet} react in (1.2) and (1.4) with hydroperoxides and/or molecular oxygen thus initiating new reaction chains.

The initiating reaction is extremely important in the thermo-oxidation process. If the H is bonded to a tertiary, benzyl or allyl type carbon atom, its extraction is easier as compared to its bonding to a primary or secondary type atom carbon. This explains the marked tendency towards oxidation of the diene type polymers as well as of the unsaturated polyesters and the higher stability of the linear polyolefins.

The thermo-oxidation at ambient temperature (auto-oxidation) was studied by Bolland and Gee starting from the hydrocarbon oxidation [13, 14] and further extended to polyolefins [13, 14], as shown below (1.7) - (1.19):

Initiation steps:



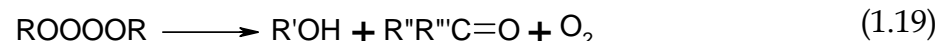
□ **Propagation:**



□ **Transfer:**



□ **Termination:**



The stability of polymers towards thermal oxidation depends on the C-H bonds strength, the crystallinity degree, the presence of substituents including heteroatoms and the catalysts traces, e.g. type Ziegler, etc. [15].

Some general features of the polymer thermo-oxidation process are presented below:

- The oxygen absorption (oxygen uptake) starts after a certain time (*induction time*), followed by an accelerated rise of the peroxy groups concentration, reaching a peak (*autocatalytic stage*), itself followed by peroxy groups depletion (*termination stage*) (Fig. 1.3.) [16];

- The temperature rise determines an accelerated rate of the oxygen absorption;

- The induction time depends on the polymer nature, structure and density, etc.;

- The oxygen absorption is proportional to the polymer open surface;

- The oxygen absorption rate depends on the diffusion coefficient of oxygen (Tab.1.1.);

- The absorbed oxygen mass in the thermal oxidation process is inversely proportional to the crystallinity degree of the polymer. The oxidation process starts within its amorphous phase or interfibrillar areas;

- The stereo regular polymers are less prone to oxidation as compared to the atactic ones;

- A branched polymer is less resistant towards oxidation as compared to a linear polymer. (Tab.1.2.).

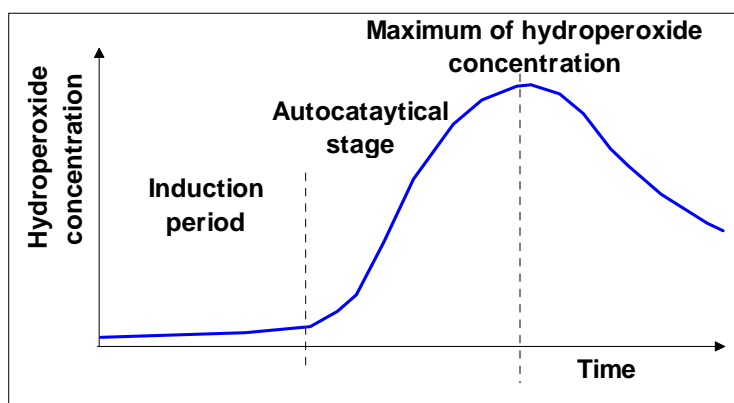


Figure 1.3 The profile of hydroperoxide concentration as a function of oxidation time in isothermal mode.

Table 1.1

Oxygen diffusion coefficient at room temperature for some polymers [16]

Polymer	D (cm ² /s) x 10 ⁶
LDPE ($\rho = 0.914 \text{ g/cm}^3$)	0.46
Polystyrene	0.11
Polymethylmethacrylate	0.034
Natural rubber	1.58
Polybutadiene	1.50
Polyethylene terephthalate	0.0036

Table 1.2
Oxidation induction time for polymers with various structures [17]

Polymer type	Oxidation induction time (hours)	
	at 110 °C	at 80 °C
Polypropylene-atactic	4.5	95
Polypropylene-isotactic	7.5	130
Polyvinile-cyclohexane	300	>500
Polyalyle-cyclohexane	35	700
Polyalyle-cyclopentane	1.5	-
Polystyrene	>10000	-
Poly-3-phenyl-propane-1	1900	>10000
Poly-4-phenyle-butene	30	500
Poly-5-phenyl-pentene -1	23	360
Poly-6-phenyle-hexene-1	13	200
Polyethylene ($\rho = 0.96$ g/cm ³)	70	1300

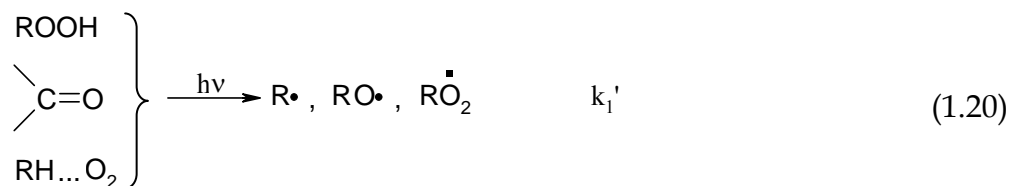
For the low density polyethylene oxidation, the oxygen absorption increases as a function of pressure; a higher temperature reduces the oxidation induction time (OIT); the crosslinking yield exceeds the scission yield; inversely, for the thermo-oxidation of polypropylene the chain scission predominates.

1.2 Photo-Oxidation

The solar energy is an important physical degradation factor for polymers and elastomers due to the presence within their structure of sensitive double bonds, of branched chemical groups, of catalyst traces, etc. [3]. The combined effect of the solar light and of the oxygen is accompanied by properties modification, discoloration, scission and/or crosslinking, appearance of oxygenated chemical groups which diminish the electrical properties, etc. [18 - 25].

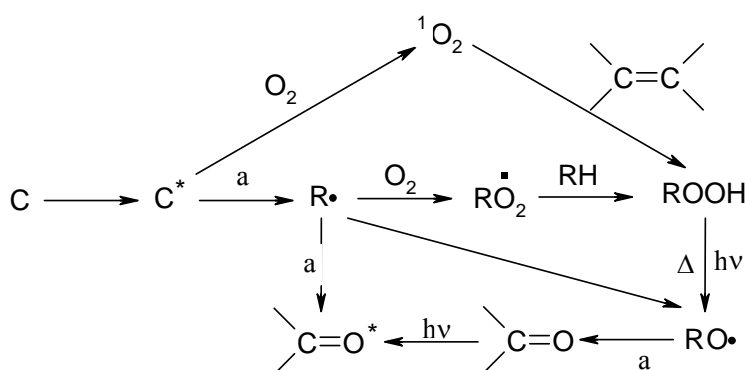
From the point of view of the photo-oxidation mechanisms, the incident photons, in UV - visible spectral range, create excited molecular species, including excited molecular oxygen. The photo-chemical reactions are chain reactions, involving the three stages of such reactions, accompanied by various photo-physical processes: fluorescence, internal energy conversion and intermolecular energy transfer (phosphorescence). The molecular excited oxygen (oxygen singlet, 1O_2) is involved in many reactions due to its high reactivity. The resulted chemical species depend on the chemical nature of the substrate, environmental conditions, temperature, etc.

The initiation reaction rate is higher as compared to the thermal oxidation initiation rate. The general kinetic mechanism is similar to the thermo-oxidation, as developed by Bolland and Gee [13, 14, 26], reactions (1.7) - (1.19). The difference consists in a different mechanism of the initiation stage, as illustrated in the reaction (1.20) [27, 28]:



(k_1' is the global reaction rate constant).

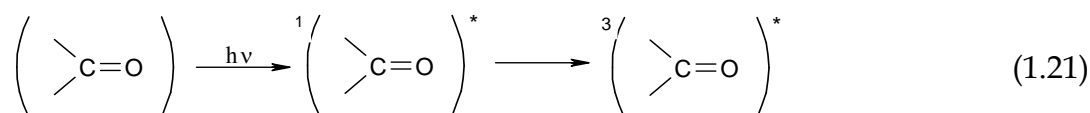
Scheme 1.1 presents the general photo-oxidation mechanism for the hydrocarbon polymers.



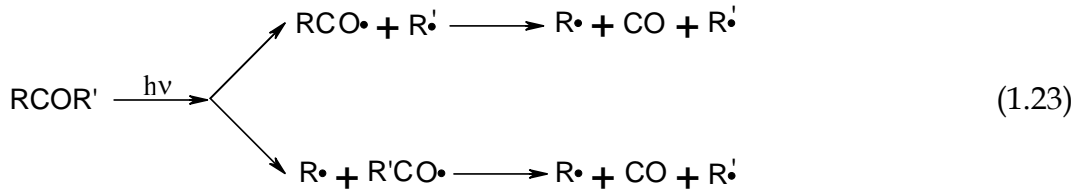
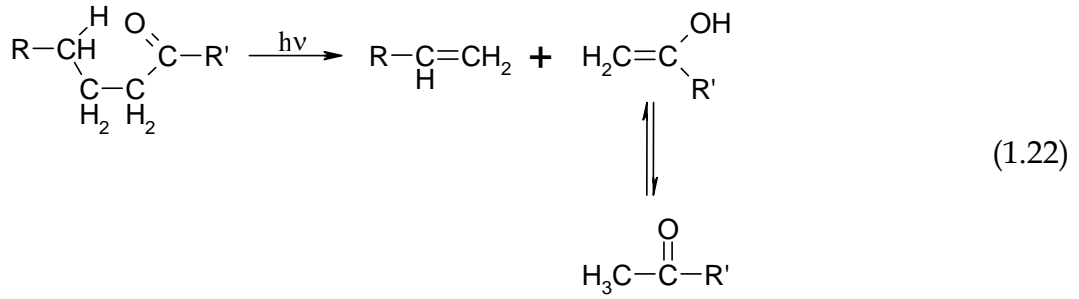
Scheme 1.1 The general photo-oxidation mechanism for the hydrocarbon polymers
(a) –scission processes of the main macromolecular chain

As it is the case for the thermo-oxidation, the photo-oxidation rate depends on the polymer nature, thickness, the diffusion coefficient and the oxygen solubility. The branching and the crystallinity ratios control the photo-oxidation susceptibility. [27]

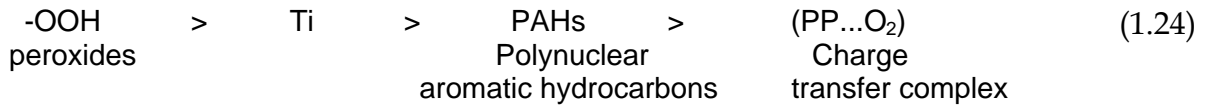
It is by now accepted the initiation role of the carbonyl groups located on the main polymeric chain in the case of UV irradiation [27 - 29]. In the UV light, the carbonyl groups are excited to singlet or triplet states and may initiate Norrish type reactions (1.21), thus leading to the main chain scissions [15].



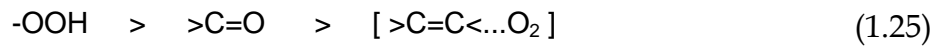
In polyethylene for example, two thirds of the carbonyl groups are photolyzed following a reaction type Norrish II without radicals as intermediates (1.22); only one third follows a reaction type Norrish I having radicals as intermediates (1.23).



The hydroperoxides appeared in the polymers processing play also a role in their sensitivity towards UV [30]. Other impurities, as for example the traces of Ti catalyst decompose the hydroperoxides and influence the thermal and photo-stability of the polymer [31]. The photo-initiating species were ranged, as a function of their degradation efficiency [32] as shown in (1.24):



A similar arrangement was found for LDPE [33]:



1.3. Radio-Oxidation

The literature is relatively rich on the subject; some representative papers can be found in refs. [34 - 57, 67].

The ionizing radiations transfer a huge quantity of energy (which is orders of magnitude higher than the mean chemical bond strength) towards the irradiated material. The energy transfer is not selective and represents a principal difference as compared to the photo-chemical processes [34].

The interaction between the incident radiation particle and the irradiated material is characterized by the Linear Energy Transfer (LET) expressed as keV/ μm (penetration length) [34a]:

$$-\frac{\Delta E}{\Delta x} = \frac{4\pi \cdot e^4 \cdot Z^2}{m \cdot v^2} \cdot \frac{N_A \cdot \rho}{A} \cdot B$$
(1.26)

where: e = electron charge, Z = incident radiation particle charge, m and v the mass and speed.

$N_A \cdot \rho / A$ represents the number of atoms per material volume unit; B = a constant depending on the ionization properties and the nature of the irradiated material. To be noticed that the "slow, cooled" particles have a higher LET.

The electromagnetic radiation loses energy following the equation (1.27).

$$I_x = I_0 \cdot e^{-\mu \cdot x} \quad (1.27)$$

where: I_0 = incident energy flux; I_x = energy flux at depth x ; μ = mass attenuation coefficient.

For electromagnetic radiations having energies between 0.05 and 5 MeV the Compton effect is mainly responsible for their energy losses.

The chain of radiation-induced processes can be divided into three stages:

- (1) the absorption of the radiation energy in the substance (physical stage);
- (2) energy transfer among intermediates (physicochemical stage);
- (3) restoration of the chemical equilibrium (chemical stage).

The succession of the main steps is represented by Fig. 1.4. A time scale of the radiation-induced processes in a substance is shown in Scheme 1.2

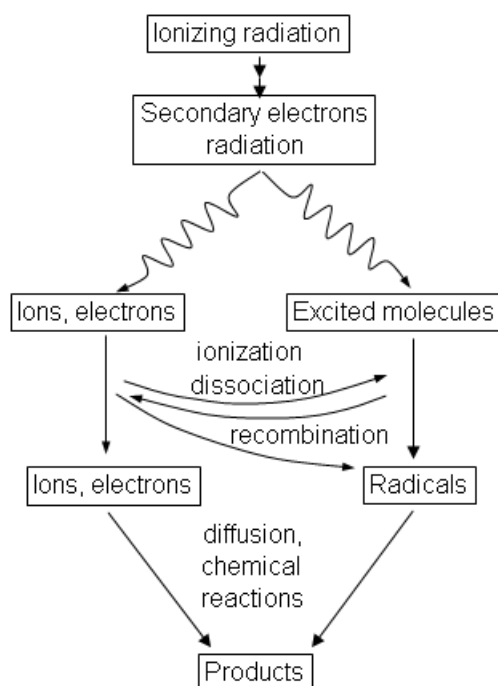


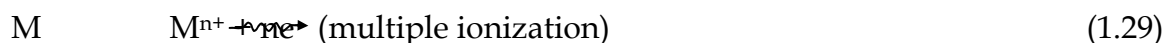
Figure 1.4 The succession of radiation-chemical processes

Scheme 1.2 The time scale for some events in radiation chemistry [67]

Time (s)	Event
10 ⁻¹⁸	Primary electron (1 MeV) traverses molecule
10 ⁻¹⁷	1 MeV α particle traverses molecule
10 ⁻¹⁵	Time interval between successive ionizations
10 ⁻¹⁴	Dissociation of electronically excited species. Free radicals appearance. Energy transfer into vibrational modes
10 ⁻¹³	The electrons are thermalized; electron capture in molecular liquids
10 ⁻¹²	The radicals diffusion
10 ⁻¹⁰	Completion of reactions which depend on very rapid diffusion Dielectric liquids relaxe
10 ⁻⁸	Molecular products formed. Radiative decay of singlet excited states
10 ⁻⁵	Capture of radicals by reactive molecules (oxygen, antioxidants...)
10 ⁻⁴	Radical inter-spur diffusion (1 MeV electron track)
10 ⁻³	Radiative decay of triplet excited states
1	Most of the chemical reactions are finished. Post effects follow

During the *physical stage*, the energy of the radiation is distributed among atoms and molecules through the interaction of the ionizing radiations (α - and β -particles, photons) with the electrons of the substance. Even in the case of γ -absorption, excitation and ionization are caused by high-energy electrons formed through Compton and photoelectric effect. Secondary electron radiation is also called δ -radiation. The interaction time is very short and cannot lead to chemical reactions [53]. A great number of "activated molecules" are formed along the track of the radiation particle. The spatial distribution of the electron-excited or ionized molecules depends on the properties of the irradiated substance and on the radiation type. The excess of energy of the secondary electrons resulted from the primary interaction process is transferred, through ionizations and collisions to the neighboring atoms and electrons thus forming reactive volumes (spurs) which contain ions, radicals and excited atoms and molecules; their spatial distribution depends on the nature and the energy of the incident radiation [34, 37, 38].

The processes of this physical stage (primary processes in radiation chemistry) are characterized by the following general reactions:



The excited molecules may undergo ionization. Most of the ions along the track originate from excited molecules.

The ionization density, i.e., the concentration of the primary products (mainly ions) formed during the physical stage determines the subsequent processes. As the ion density depends to the linear energy transfer, one can say:

1. The ionization density is proportional to the square of the electric charge of the radiation particles (see LET formula). For example, the ion density produced by a α particle is four times higher as compared to that of a proton.
2. In the case of identical incident radiation, the ionization density is inversely proportional to the radiation energy.
3. The high mass particles produce a higher ionization density for the same kinetic energy. The value of the linear energy transfer is 0.2 eV/nm for 1 MeV γ -photons and 190 eV/nm for 1-MeV α -particles (see Table 1.3).
4. The ionization density is also proportional to the electron density of the irradiated substance.

Table 1.3 Initial LET values for various types of radiation [53]

Radiation	Initial LET (J/nm)·10 ¹⁸
$\gamma^{60}\text{Co}$	0.032
250 kV X-rays	0.16
10 kV X-rays	0.32
2 MeV protons	2.7
δ -radiation (Compton and photoelectrons)	1.3-4.8
α -rays of Po	14.1
Recoil Li [$^{10}_5\text{B}(\text{n}, \alpha) ^7_3\text{Li}$]	16-27
Fission fragments	1120

By the end of the physical stage an irradiated molecular system contains ions, electrons radicals and excited molecules. These primary species have a wide spread both in kinetic and internal energies.

During the *physicochemical stage*, the excess of kinetic energies are lost by the interaction with the surrounding molecules. At its final stage (10^{-12} s) the equilibrium energy distribution is reached, accompanied by various chemical transformations, including the free radicals fast reactions.

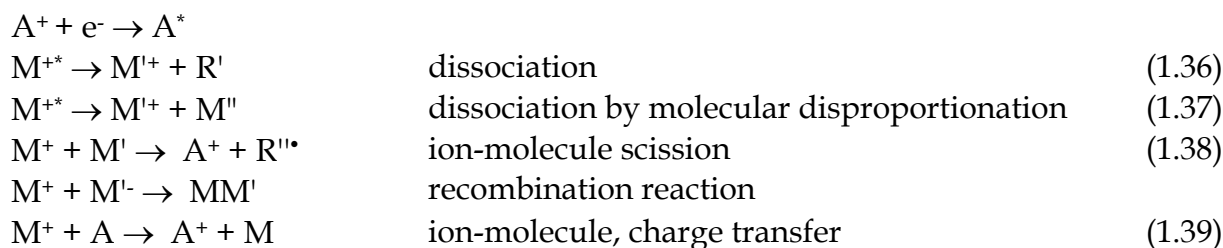
The most important types of reactions of the intermediate species (free radicals, ions, electrons and excited molecules), occurring in the physicochemical stage are presented below (a-c). In the case of the excited molecules (c), the common processes are the luminescence (fluorescence) and the radical dissociation; less common is the ionic dissociation reaction.

a) free radicals reactions

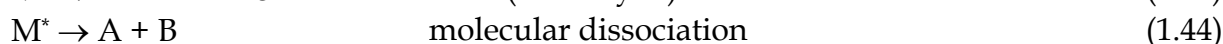
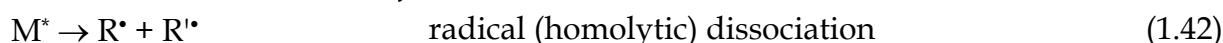
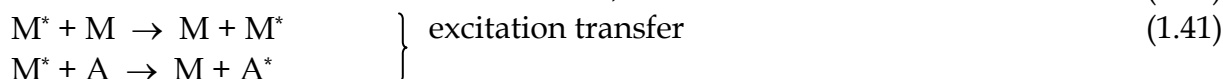
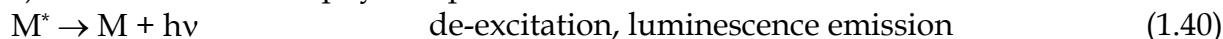


b) ions reactions





c) excited molecules - physical processes and reactions



A measure of the radio induced chemical changes in an irradiated material is the *radiochemical yield* (G), expressed as the number of molecules formed or destroyed per 100 eV absorbed energy in the material. The G value allows the evaluation of the radiation hardness of a chemical substance.

Two main processes occur in an irradiated polymer:

- *Scission* of the main polymeric chain accompanied by the molecular mass diminution and the evolution of small molecular mass products, such as: HCl, CO, CO₂, CH₄ etc.

- *Crosslinking* is accompanied by the molecular mass increase due to transversal chemical bonds created between two or more macromolecular chains.

The free radicals constitute the initiating centers for scissions and/or crosslinking, hence for the induced modifications within the macromolecular chain. According to the predominating processes, the polymers are classified as scission or crosslinking type polymers [54].

In polymers containing mainly $-\text{[CH}_2\text{-CH}_2\text{]}_n\text{-}$ units, the crosslinking predominate.

Within polymers of the $-\text{[CH}_2\text{-CR}_1\text{R}_2\text{]}_n\text{-}$ type, the scission predominate.

For a polymer irradiated in air (or oxygen) the scission ratio increases due to the peroxy radicals which lead to alcohols, aldehydes, ketones, acids, etc.

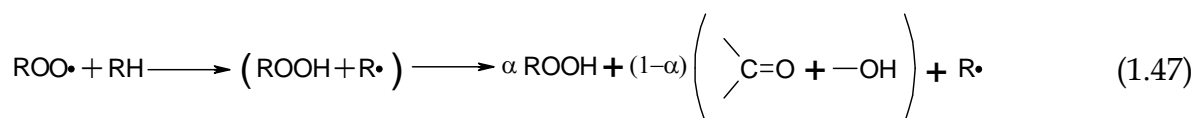
The radio-oxidative degradation of the common PE polymer in air is described by the following chain reactions schemes:

Initiation:

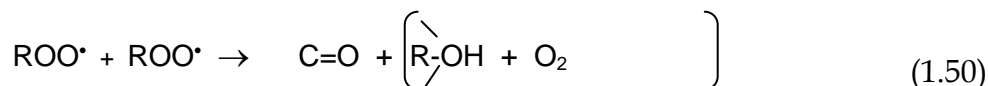


Propagation:





Termination:



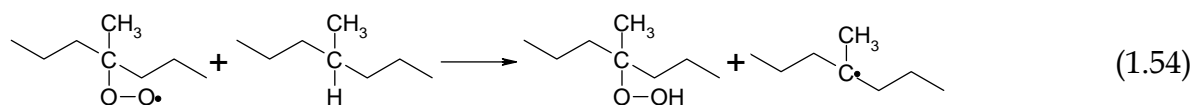
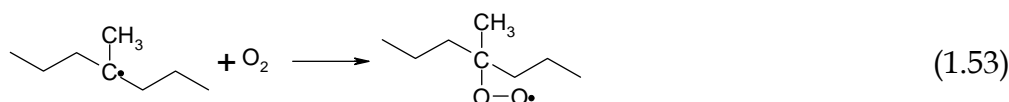
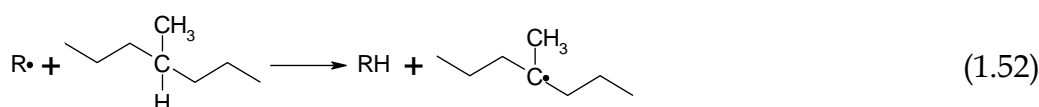
stable products



The differences between the reactions (1.45) - (1.51) and (1.7) - (1.19) illustrate the differences between the thermo-oxidation and the radio-oxidation, mainly within the initiation and termination stages, as well as the role of the trapped peroxy radicals.

Generally, the oxidation processes are located within the amorphous areas of the PE polymer.

Polypropylene (PP) is more sensitive to the oxygen presence than PE: it degrades more rapidly and the dose rate effects are important. Its sensitivity is attributed to the high ratio of the tertiary carbons within the main macromolecular chain [36, 54], as shown in reactions (1.52) - (1.54):



In average, each free trapped radical reacts with five O₂ molecules.

Generally, the physico-mechanical properties of an irradiated polymer are mainly influenced by the radiation-induced hydroperoxides formation rate and by their specific reaction ways. The hydroperoxides formation hinders the free radicals recombination and, consequently, will diminish the average molecular mass of the polymer, its crosslinking degree, its elongation strength, etc.

The three oxidative degradation types (thermal -, photo -, radio-) are studied and their effects evidenced by different physico-chemical methods: mechanical tests [55-57], Differential Thermal Analysis (DTA), Differential Scanning Callorimetry (DSC), Chemiluminescence (CL), IR spectrometry, Electron Spin Resonance (ESR), etc. [58-66]

2. Stabilization of Polymers

2.1 Generalities

To prevent the polymers degradation during their processing and service time, various methods and procedures are employed:

- structural modification of the polymer (removal of the structural non-homogeneities of polymer chains, modification of the terminal groups, copolymerization, internal plasticization etc.);
- improved processing and forming techniques;
- incorporation of small amounts of chemical substances to suppress and/or hinder the degradation processes.

The last method is known as *polymer stabilization*, the chemical substances are named *stabilizers*. This method is applied for most of polymers. In some peculiar cases, to improve the fire resistance or to protect against the micro- and macro-**biological** degradation, the method is usually named *polymer protection*.

It was experimentally proven that an efficient stabilization is achieved through multiple stabilizer types. The stabilization efficiency depends on the following parameters: the polymer type, the processing or molding methods and conditions, the use conditions of the final product.

A suitable antioxidant must satisfy the following conditions:

- good compatibility with the polymer matrix;
- good stabilizer of the polymer in the specified processing and use conditions;
- low volatility and low water extractability;
- not toxic (or low toxicity level) and odorless;
- have a reasonable cost.

The *light stabilizers* used against photo-oxidation must satisfy the following conditions:

- good UV optical absorbers with good energy dissipation properties;
- stable to UV light;
- low optical absorption in the visible spectrum range.

The various mechanical and electrical tests on a stabilized polymeric material characterize in fact the efficiency of its stabilizers content (antioxidants, photo-stabilizers and protection agents) [29].

2.2. Thermo - Oxidative Stabilization

The suppression of the oxidation processes in polymers, by stabilizers or by other ways, is not definitive: it is a retardation of the oxidation process only. The stabilization effect covers both the polymer processing as well as the guaranteed life-time in use - over an as long as possible period [5, 68].

The substances used to retard (inhibit) the thermo-oxidation of the polymers are named *antioxidants*.

The main acting mechanisms of antioxidants [7]:

- *breaking the kinetic oxidation chain* thus obtaining the deactivation of the alkyl and alkyl-peroxy species; this type of antioxidants are classified as **chain breaking antioxidants**;

- *decomposing the appeared hydroperoxides into non-radicalic products* (or inhibiting the hydroperoxides decomposition), thus reducing the formation rate of active free radicals; this type of antioxidants are classified as **preventive antioxidants**.

The antioxidants classification is based on the mechanism of polyolefins auto-oxidation (oxidation at ambient temperature). A suggestive scheme of the antioxidants actions, firstly presented by Scott [1] is shown in Fig. 2.1.

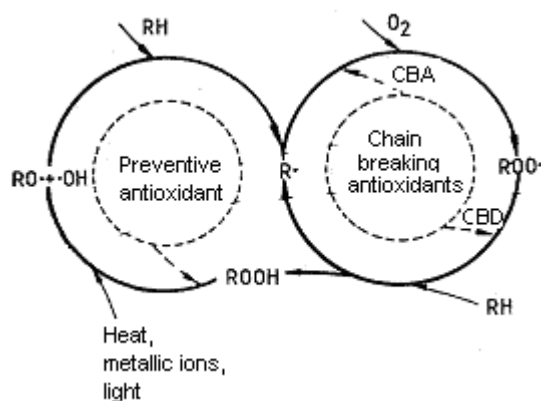


Figure 2.1 The action mechanisms of preventive antioxidants and chain breaking antioxidants in thermo-oxidative stabilization of polyolefins. CBA = chain breaking by acceptor mechanism; CBD = chain breaking by donor mechanism

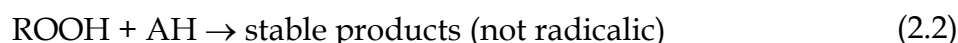
With respect to the thermo-oxidation reactions which occur within a certain polymer (RH), an antioxidant (AH) acts on their specific oxidation stages [17]:

□ **In the initiation phase**

- deactivation of the metal ions catalysts;
- trapping the free radicals R^\bullet (alkyl) or ROO^\bullet (peroxy) to stop the formation of new radicals by chain transfer:



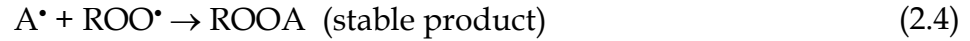
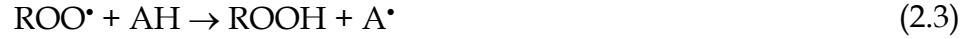
- hydroperoxide polymer conversion in stable products:



These stabilizers are considered as preventive antioxidants.

□ **In the propagation and termination phases**

- blocking the chain transfer processes, thus the propagation of the peroxy radicals:



The following types of antioxidants are used: peroxide decomposers, light absorbers, inhibitors regenerators, free radicals scavengers.

The antioxidative activity [16] represents the capacity of an antioxidant to suppress the oxidation reactions in a certain polymer during its processing, storage and use (service).

The oxidation induction time (OIT) measures the stability of a polymer, hence the antioxidative activity. The relative antioxidative activity is defined in equation (2.5):

$$A_r = \frac{\text{OIT}_i^s - \text{OIT}_i^0}{\text{OIT}_i^e - \text{OIT}_i^0} \quad (2.5)$$

where: A_r is the relative activity, OIT_i^0 is the oxidation induction period of the unstabilized sample, OIT_i^s is the oxidation induction period of the sample stabilized with the studied antioxidant and OIT_i^e is the oxidation induction period of the sample stabilized with an antioxidant selected as an etalon.

The etalon consists usually in a polymer sample stabilized with the simplest antioxidant structure, pending to the analyzed series. The relative activity (A_r) of this antioxidant will equal the unit and the other stabilizers will have supra-unitary or sub-unitary values of A_r depending on their antioxidative efficiency as compared to the etalon.

In some cases, the antioxidative activity can be described also by the oxidation slow-down during the autocatalytic step, using the equation (2.6):

$$S_r = \frac{v_{ox}^0}{v_{ox}^s} \quad (2.6)$$

where: S_r is the relative stability; v_{ox}^0 is the oxidation rate of the un-stabilized polymer sample and v_{ox}^s is the oxidation rate of the stabilized polymer sample.

2.3. Radio-Oxidative Stabilization

Stabilization of the polymers against ionizing radiations can be achieved by the control of the free radicals reactions and by the inhibition (suppression) of oxidation processes. While the free radicals reactions depend on the polymer morphology, the oxidation reactions themselves can be suppressed by stabilizers. This results not only in the radiation protection of the polymer during the irradiation but also in providing long-term stability in storage and use.

Most of the radio-oxidative stabilizers additives (anti-rad) can be grouped in two categories depending on their action mechanism:

- **Radical scavengers** - some substances, such as sterically hindered phenols, amines, quinones, thiols etc., are very effective in free radicals trapping [36, 69], either as single additives or in synergistic mixtures [70, 71].

- **Energy scavengers** - are molecules which can deactivate the polymer excited states during irradiation. The anti-rad efficiency of some aromatic compounds can be explained by such a mechanism [72 - 75]; a charge transfer mechanism can play also an important role in some cases.

For both anti-rad categories, were reported significant changes in radiochemical yields of scission, crosslinking, hydrogen (or other gases) evolution, etc. from the irradiated polymers [74]. A lot of tested commercially antioxidants were found extremely efficient [71, 76 - 79].

2.3.1. Antioxidants types

The efficiency of the radio-oxidative stabilization is controlled, similar to the case of thermo-oxidation stabilization, by the antioxidant type, compatibility and concentration.

A study on post-irradiation thermo-oxidative stability of polyethylene and EVA copolymer stabilized with substituted secondary amines (derivatives of diphenylamine, phenylamine, or p-phenylenediamine) has shown that the highest efficiency was presented by the bis-aryl substituted diamines [80]. Generally, a higher efficiency of aminic antioxidants as compared to the phenols was observed [69].

A point which should be taken into account when the efficiency of various additives in radio-oxidation stabilization is evaluated consists in their radiation stability. It is expected that the molecules with a complex structure, such as Irganox 1010[®] or Irganox 1330[®], will be more susceptible to radiation-induced scission as compared to simpler structure molecules, such as Topanol OC[®]. Gal & coworkers [81] took into account the radiolysis of antioxidants to explain the OIT decrease, as

evidenced by thermo-gravimetric method, of radiation-crosslinked polyethylene. Supplementary proves were obtained by IR spectroscopy and UV spectrophotometry. Chromatographic studies (HPLC, LC-MS) on various polymeric materials stabilized by phenolic antioxidants concluded a different behavior of the antioxidants depending on their chemical structure [79].

The higher efficiency of low molecular weight antioxidants as compared to higher molecular weight antioxidants (with more complicate molecules) was explained in terms of both higher homogeneous repartition and higher mobility in the amorphous phase of polymers [75].

Two examples illustrating the influence of the antioxidant type on the radio-oxidation stabilization efficiency of HDPE and PP are summarized in Tables 2.1 and 2.2; the efficiency is expressed by the dose corresponding to half of the initial elongation at break value [36].

Table 2.1
The effect of various antioxidants on the radio-oxidation stabilization of HDPE (Hostalen GC 6465[®])* [36]

No .	Stabilizer (antioxidant)	Concentration (%)	Dose- (kGy)
1	Without stabilizer	-	6
2	2-Mercaptobenzimidazole	0.5	6
3	Trilaurilphosphite	0.5	6
4	Etanox 330 [®]	0.5	8
5	Mercaptobenzothiazole	0.5	13
6	N,N'-di-β-naphthyl-p-phenylendiamine (DPPD)	0.5	15
7	Santonox R [®]	0.5	23
8	Santowhite Powder [®] refined	0.5	24
9	Phenothiazine / Ionol [®]	0.0075/0.175	36
10	Phenothiazine / Ionol [®]	0.125/0.125	32
11	Carbon black Corax A [®]	0.1 – 2.5	6

* Dose rate: 25 Gy/h, γ⁶⁰Co; thickness: 0.5 mm

Table 2.2
The effect of various antioxidants on the radio-oxidation of PP (Hostalen PPN[®])* [36]

No .	Stabilizer (antioxidant)	Concentration (%)	Dose- (kGy)
1	Without stabilizer	-	5
2	N,N'-di-β-naphthyl-p-phenylendiamine (DPPD)	0.5	6
3	Trilaurilphosphite	0.5	6

No	Stabilizer (antioxidant)	Concentration (%)	Dose- (kGy)
4	Santowhite Powder [®]	0.5	12
5	Irganox-1076 [®]	0.5	14
6	Irganox-1010 [®]	0.5	15
7	Ionox-330 [®]	0.5	27
8	Phenothiazine / Ionol [®]	0.25/0.25	22
9	Ionol [®]	0.5	26

* Dose rate: 25 Gy/h, γ ⁶⁰Co; thickness: 0.5 mm

The crosslinking degree depends both on the concentration and the intrinsic efficiency of the antioxidant. The maximum effect of cross links density decrease is observed in the range of antioxidant concentration of 0.2 - 1 % (Fig. 2.2) [80]. To produce, by irradiation processing, the same crosslinking degree in a stabilizers free polymer and a stabilized material, a higher dose is necessary for the stabilized material. Due to technological reasons, the processing dose should be kept at minimal values; various solutions to compensate the crosslinking decrease are applied, for example the use, in presence of the antioxidants, of some polyfunctional allyl compounds, such as the *triallyl cyanurate* or the *trimethylpropane-trimethylacrylate*. [80]

The increase in antioxidant concentration leads to an increase in stability, proven by the OIT increase during the post-irradiation thermo-oxidation. At higher antioxidant concentrations, the stability vs antioxidant concentration dependence is no longer linear, as shown in Fig. 2.3. [80].

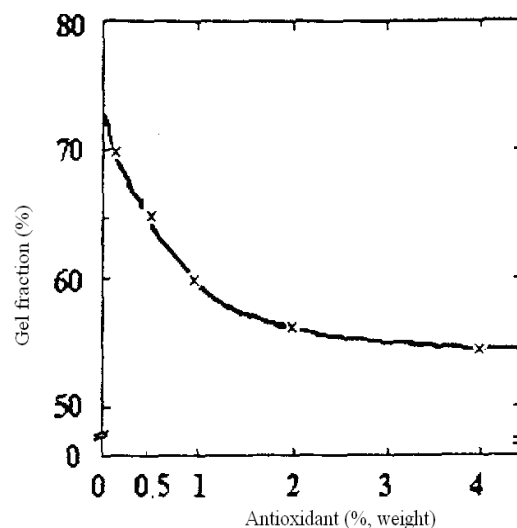


Figure 2.2 Gel fraction related to the initial antioxidant (Agerite Resin D[®]) concentration in radiation-crosslinked polyethylene [80]

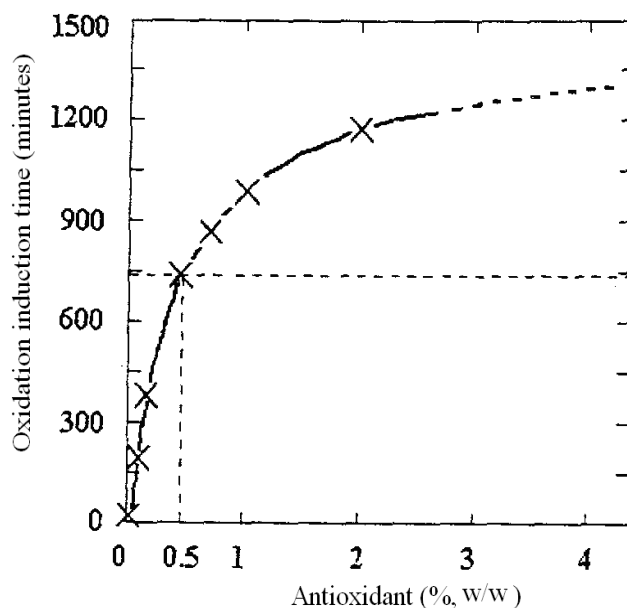


Figure 2.3 The oxidation stability at 135 °C of radiation-crosslinked polyethylene (D = 200 kGy) stabilized with various concentrations of 2,2,4-trimethyl-1,2-dihydroxyquinone (polymeric form); the optimal antioxidant concentration is shown [80].

2.3.2. Energy scavengers

The stabilization effect provided by the aromatic hydrocarbons molecules was observed several decades ago [72 - 75] and studies were carried out on model compounds such as liquid n-hexadecane ($C_{16}H_{34}$) and liquid squalane ($C_{30}H_{62}$) to elucidate the protection mechanism [83 - 85]. In presence of aromatic hydrocarbons was observed a decrease of evolved hydrogen and oligomerization accompanied by the inhibition of additives decomposition. It was observed also that the stabilization efficiency depends on the aromatic character of the hydrocarbons. Thus, the polycyclic aromatic hydrocarbons (PAH) containing several condensed rings in their molecule, such as naphthalene and phenanthrene, are considerably more efficient as the mononuclear aromatic hydrocarbons [83 - 85].

Protection effects were reported for the cases of various polymers and lubricants [74, 75, 82, 85, 86]. For polypropylene stabilized by phenolic antioxidants and PAHs (i.e. propyl-fluoranthene and octahydrophenanthrene) it was observed that the hydrogen evolution is reduced as increases the content in aromatic rings of the stabilizer. The CH_4 yield remains practically unchanged for the two types of stabilizers but smaller than for the un-stabilized polypropylene [75]. In ref. [74] an enhanced stabilization effect provided by the couple of a *radical scavenger* [i.e. 2, 2 methylene-bis(4-methyl-6-tert-butyl)phenol] and an *energy scavenger* (pyrene) is described. The chromatographic analyses of the degraded samples revealed that the PAH provides a protective effect not only on the polymeric material, but also on the phenolic antioxidant.

In ref. [86], were analyzed the stabilizing effects of PAHs as a function of the irradiation dose. The carbonyl group concentration and the OIT were chosen as markers of stability during irradiation and post-irradiation, respectively. It was

evidenced that the pyrene provides a radiation stabilization effect similar to Irganox 1330[®] or Irganox 1010[®], two phenolic antioxidants with good efficiency. The stabilization effect increased when couples of pyrene and phenolic antioxidant were used. The effect was not synergistic for the irradiated PE only, but synergistic effects intensely appeared for the post-irradiation thermo-oxidation. It is considered that both the energy and charge transfer from polymer to stabilizer play an important role [87].

3. Ageing of polymeric materials studied by CL and DSC methods

3.1 Basic Principles and Mechanisms

Relatively recent and young technique, the following text will be mainly focused on CL method. The DSC method is well known and widely used in Chemistry Laboratory [88-90].

Luminescence can be defined as the emission of light by a substance, phenomenon directly related to a molecular excitation process. Different types of luminescence emissions are known, corresponding to various ways of excitation: *radioluminescence* (induced by ionizing radiations), *photoluminescence* (induced by UV radiation), *electroluminescence* (induced by electrical fields), *thermoluminescence* (induced by thermal transitions), *phonoluminescence* (induced by ultrasonic treatments), *chemiluminescence* (induced by a particular chemical reaction).

The **chemiluminescence (CL)** is the object of a special attention in the last years, because the emission mechanism, being closely related to the oxidation processes, provides useful information on such processes.

Chemiluminescence is a luminescence phenomenon; usually, the excess of energy is lost as thermal energy through molecular vibrations or collisions with the surrounding molecules, but often a light emission is observed. The prefix *chemi-* means that the excitation energy is supplied by a chemical reaction (Fig. 3.1).

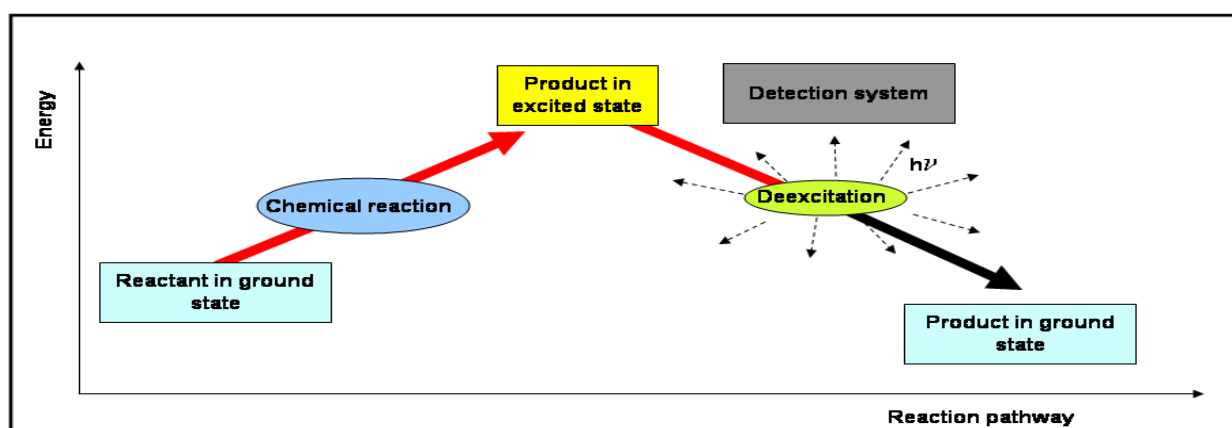


Figure 3.1 Scheme of a chemiluminescence generating process

It is well known also that chemiluminescence (CL) phenomena in nature consist in light emission from glow-worms and fire-flies [91]. In analytical chemistry and in biochemistry, CL is widely used as an indicator in various reactions, for example in titrimetry [92].

The oxidation of low molecular weight hydrocarbons and polyolefins is accompanied by a weak CL emission in UV-visible optical range. The quantum yield of such emission is very low (10^{-9}) as compared to other luminescence phenomena. Despite this fact, the light-detection systems measure such low intensities of CL, thus making possible the oxidation processes observation at various temperatures, even at room temperature.

The CL emission resulted from the oxidation of polymers was firstly reported by Ashby at the beginning of sixties [93]. His pioneering work was soon followed by a study on polymers CL emission performed by Schard and Russell [94, 95].

After a break of more than 10 years, with a few papers published, the studies on CL of polymers were restarted, using the new and sensitive techniques developed meanwhile. Now it is an active field in study of polymeric materials, oils, greases, foods and various stabilizing additives.

Many authors reported correlation between CL and parameters recognized to univocally describe the oxidation state of a polymer. The correlation between CL signal and the carbonyl content of several oxidized samples is presented in Fig. 3.2 [70].

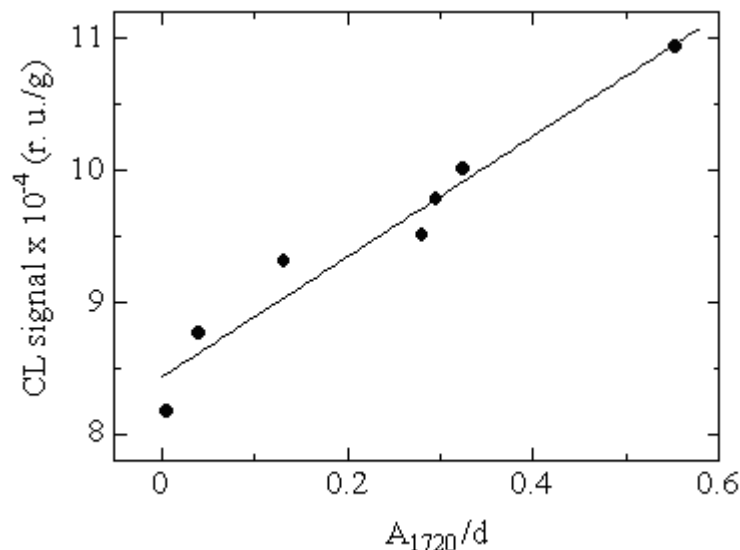


Figure 3.2 Dependence of CL signal on the carbonyl content measured by IR method for oxidized LDPE samples [70]

The CL emission (Fig. 3.3), the oxygen uptake, the concentration of ROOH (Fig. 1.3), and the DSC signal (Fig. 3.4) have the same shape curve for the same isothermal conditions.

A curve exhibiting an initial maximum is observed for polymers containing heteroatoms in the main chain (Fig. 3.5).

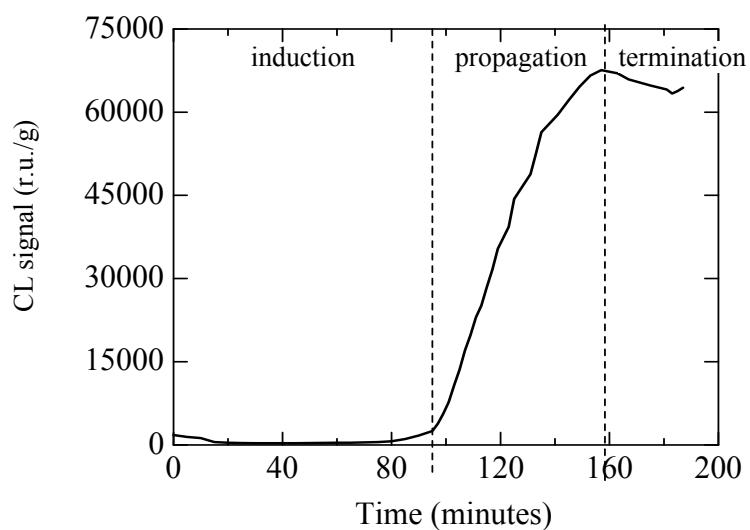


Figure 3.3 Induction, propagation and termination oxidation stages on a CL curve from LDPE stabilized with 0.1% Irganox 1010; T (isothermal) = 190 °C [96]

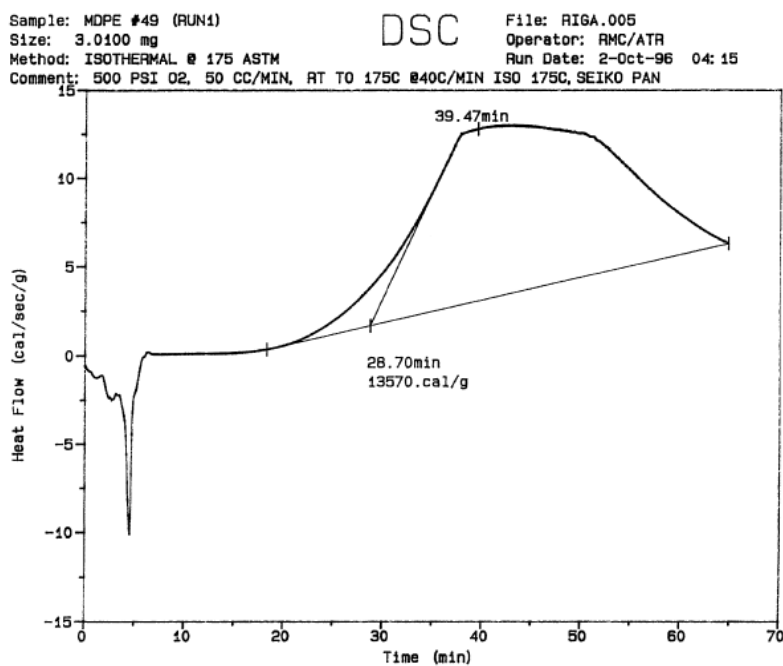


Figure 3.4 PDSC curve of MDPE; T (isothermal) = 175 °C [97]

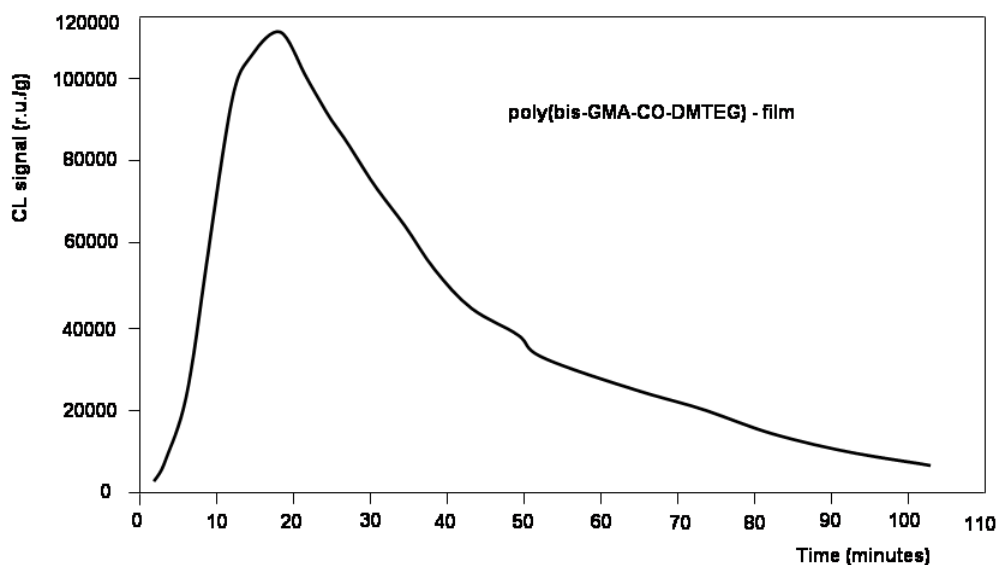
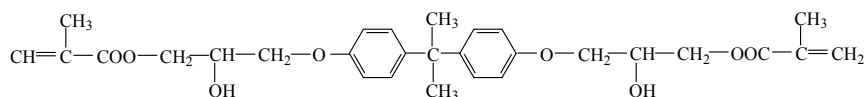
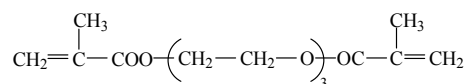


Figure 3.5 CL curve from poly(bis-GMA-co-DMTEG); T (isothermal) =170 °C film [98];

bis-GMA:



DMTEG:



To occur, a CL emission needs an exothermic reaction to provide the necessary energy. CL emission from polyolefins is located around 380 - 500 nm, and several emission peaks may be present [99, 100]. For polypropylene, a peak at 380 nm is the major CL emission early in the oxidation, but later the 460 nm peak starts to predominate: the peak and the decay of isothermal CL are to greater extent made up of 460 nm light (Fig. 3.6) [101]. A possible source of the 460 nm emission is the phosphorescence emission of carbonyl chromophores [102].

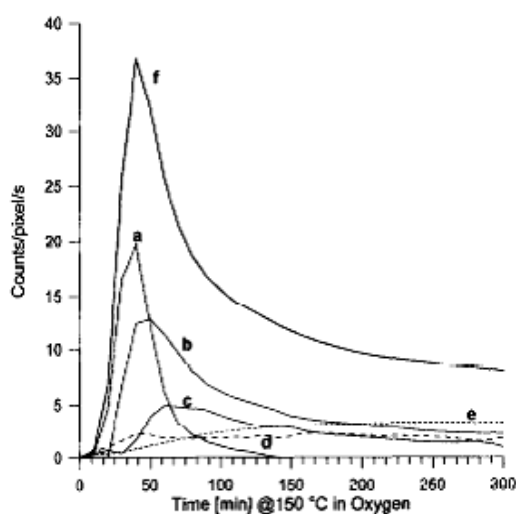
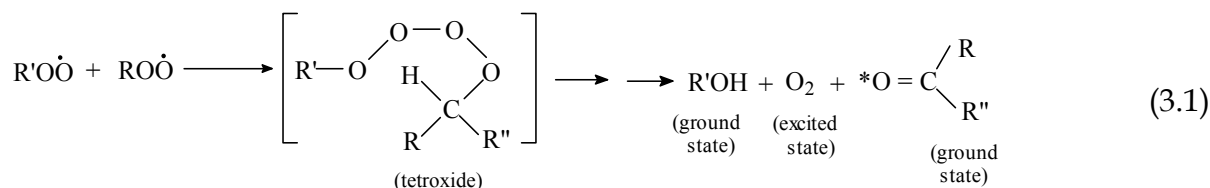


Figure 3.6 CL emission from PP powder, monitored over different wavelength ranges:

(a) <385 nm, (b) 385-475 nm, (c) 475-530 nm, (d) 530-590 nm, (e) >590 nm, (f) unfiltered emission [103]

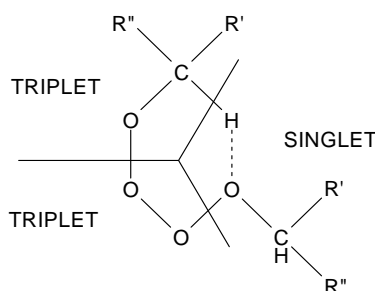
Taking into account that the requested energy to populate a carbonyl triplet state is around 290 - 340 kJ/mol [104], the following reaction mechanisms fulfilling this energetic condition were proposed for the CL emission:

1. *Bimolecular termination of peroxy radicals* [82, 105]. The reaction is highly exothermic, releasing 460 kJ/mol (Russell mechanism [106]).



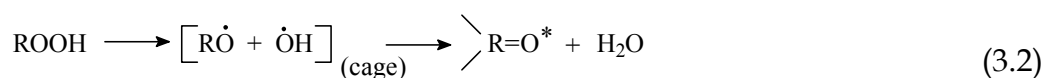
The Russell mechanism consists mainly in the bimolecular recombination of the peroxyalkyl radicals, that is a disproportionation reaction, having the "tetroxide" as an intermediate.

From this fragmentation (Scheme 3.1) results an alcohol in a singlet ground state and an oxygen in a triplet state:

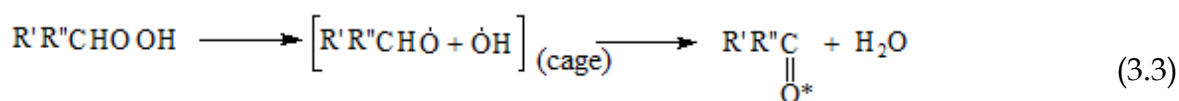


Scheme 3.1 – Russell mechanism having the tetroxide as intermediate

2. *Direct homolysis of hydroperoxides, followed by a cage reaction.* It leads to an excited carbonyl and water [107, 108]. Exothermic reaction: 315 kJ/mol.

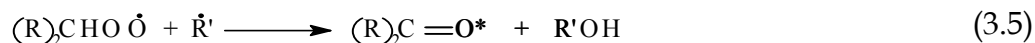


Thermolysis of peroxides (dioxyethanes) [109] or of hydroperoxides with an alkyl group having an H atom in α position [108] also leads to an excited carbonyl and thus, to CL:



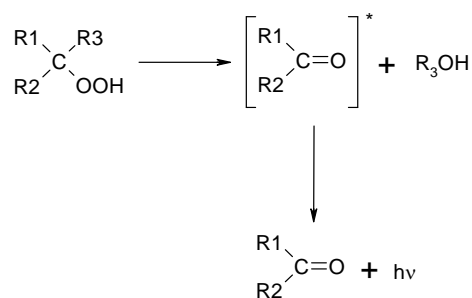
Thermolysis of hydroperoxides already existing in the polymer was considered to explain the CL emission of polymers in absence of oxygen [111].

3. *Methathesis of alkoxy or peroxy radicals* provides 374 kJ/mol and 323 kJ/mol, respectively [101, 110]:



Kellog's studies [112] performed in solution, other experiments on solid materials as well as some observations concerning the effect of temperature and crosslinking on CL in epoxy resins [104], are important arguments that Russell type mechanism is reasonable. In addition, Billingham et al. underlined that antioxidants stop the CL emission when the experiment is performed in nitrogen atmosphere [113].

The high oxidation rate of i-PP is attributed to its chemical structure that contains tertiary H atoms and frequent CH₃ groups on the side chain, as explained in Scheme 3.2. [2].



Scheme 3.2 Reich & Stivala mechanism for PP chemiluminescence

Based on evidences that the CL emission is related to the oxidative degradation of polymers via peroxy radicals and hydroperoxides, CL technique is a very useful method in the investigation of the aging processes in various organic materials such as polymers, oils, greases, foods or additives.

The CL experiments can be performed in *non-isothermal* and *isothermal* mode, in inert atmosphere or in the presence of oxygen.

The CL experiments in non-isothermal mode and inert atmosphere give information on the hydroperoxides content within the polymer sample (Lloyd CL type mechanism [108]) and show "*the oxidation history*" of the material. The CL curve integral value reflects the oxidation degree of the same material.

The same oxidation degree is obtained in isothermal mode and inert atmosphere, from the CL peak height, too. Higher the oxidation degree, higher the peak height (or the curve integral, see Fig. 3.7).

The integral and the peak height can be directly converted to hydroperoxide concentration or to any physical property related to the polymer degradation.

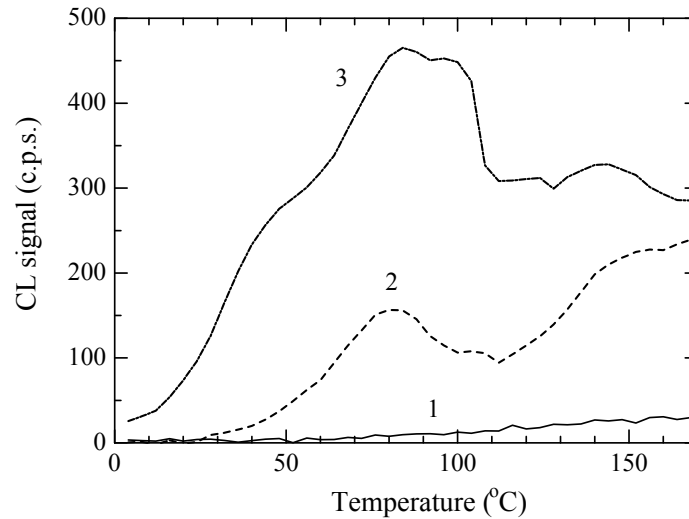


Figure 3.7 CL curves in nitrogen atmosphere from γ -irradiated LLDPE: 1 - initial (un-irradiated); 2 - 50 kGy; 3 - 240 kGy. Heating rate: 4°C / min; N₂ flow: 90 ml/min. [41]

The CL experiments in oxygen atmosphere, both in non-isothermal mode and isothermal mode, give information on the oxidation rate and, important for practical applications, on the anti-oxidative stabilization properties of the polymeric material.

The CL experiments in *isothermal* mode and in the presence of oxygen or air atmosphere were extensively studied and are often applied for the evaluation of the oxidation state and/or the stabilization degree of various polymeric materials in different fields of use.

Figure 3.8 presents the typical oxidation steps i.e. induction, propagation and termination for an ideal sigmoidal shape CL curve recorded in isothermal mode in oxidizing atmosphere.

The kinetic parameters for polymers oxidizing following a Bolland - Gee type mechanism chain, are listed in Table 3.1.

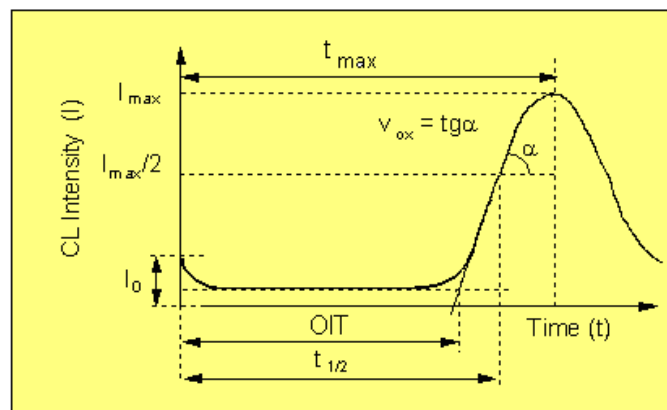


Figure 3.8 A typical CL curve recorded in isothermal mode and oxidizing atmosphere

Table 3.1
The kinetic parameters of a CL curve in isothermal mode
and oxidizing atmosphere

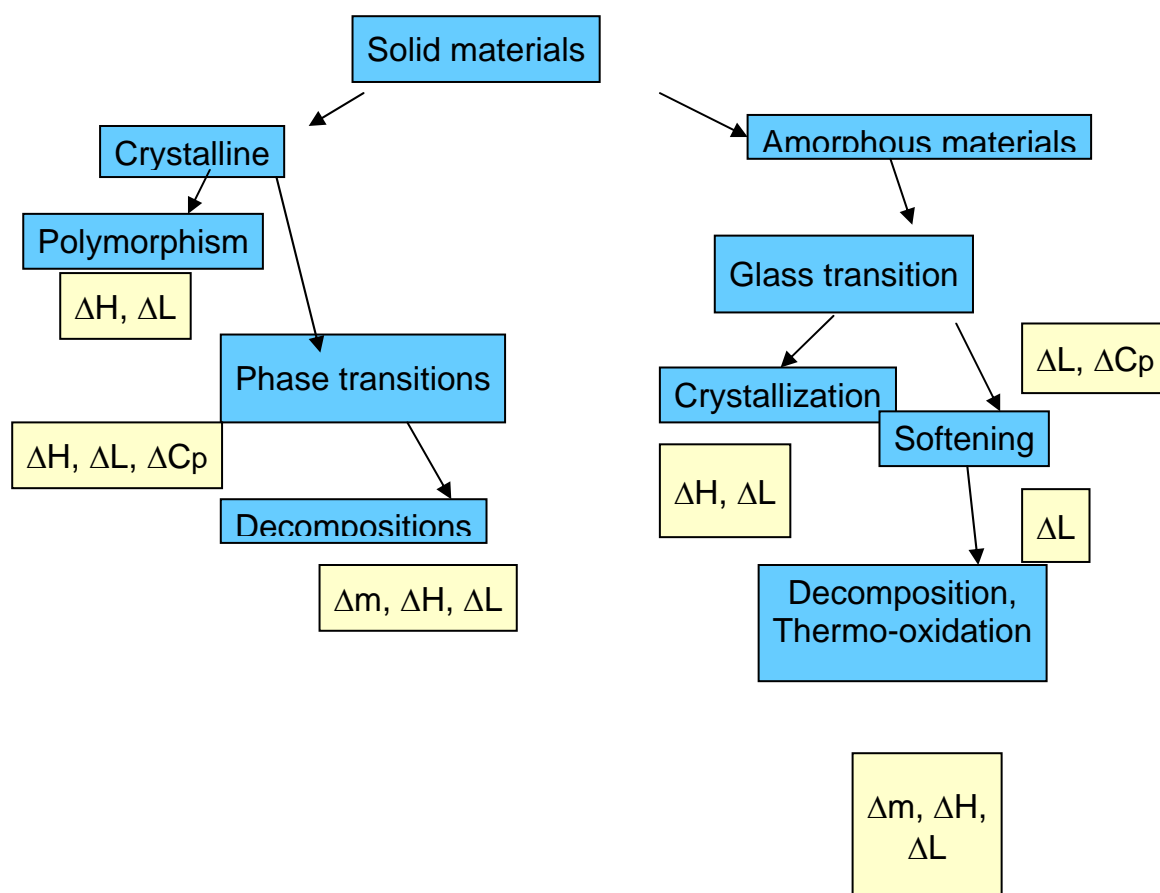
Parameter	Significance
OIT	Oxidation induction time
$t_{1/2}$	Time to reach half of maximum CL intensity
V_{ox}	Oxidation rate
t_{max}	Time to reach the maximum of CL intensity
I_{max}	Maximum of CL intensity
I_0	Initial CL intensity

The same mechanisms and parameters are involved in Differential Scanning Callorimetry (DSC) method, accompanied by various other thermal transitions. It turned out that the CL and DSC methods are similar from the point of view of the characterization of the oxidation processes in polymeric materials. The data obtained using the DSC method are not disturbed by the optical transmission properties of the probe, which constitutes its advantage.

The term thermal analysis (TA) is frequently used to describe the analytical experimental techniques which investigate the behavior of a sample as a function of temperature (Scheme 3.3). The CL is also a thermal analysis method. However, generally TA refers to conventional TA techniques such as DSC, differential thermal analysis (DTA), thermogravimetry (TG), dilatometry, thermomechanical analysis (TMA), dynamic mechanical analysis (DMA) [88].

The advantages of TA over other analytical methods can be summarized as follows:

- (i) the sample can be studied over a wide temperature range using various temperature programs;
- (ii) almost any physical form of sample (solid, liquid or gel) can be accommodated using a variety of sample vessels or attachments;
- (iii) a small amount of sample (1 mg -10 mg) is required;
- (iv) the surrounding atmosphere of the sample can be precisely controlled;
- (v) the time required to complete an experiment ranges from several minutes to several hours;
- (vi) TA instruments are reasonably affordable



Scheme 3.3 The general use of TA methods for solid materials investigation

In polymer research, preliminary investigation of the samples transition temperatures and decomposition characteristics is routinely performed using TA before the spectroscopic analysis is begun (Scheme 3.3).

3.2 Experimental Techniques

The CL equipment for polymers investigation generally contains the main parts presented in Fig. 3.9. (a DSC instrument replaces the light detector with a specific micro calorimetric system):

- a light tight box which encloses the furnace measuring cell jointed to a light detector - PM or CCD camera;
- a stable HV supply for PM;
- a furnace temperature controller;
- an electronic amplifier of the PM signal;
- a data acquisition system;
- a sample compartment with controlled atmosphere (gas type, pressure, flow rate).

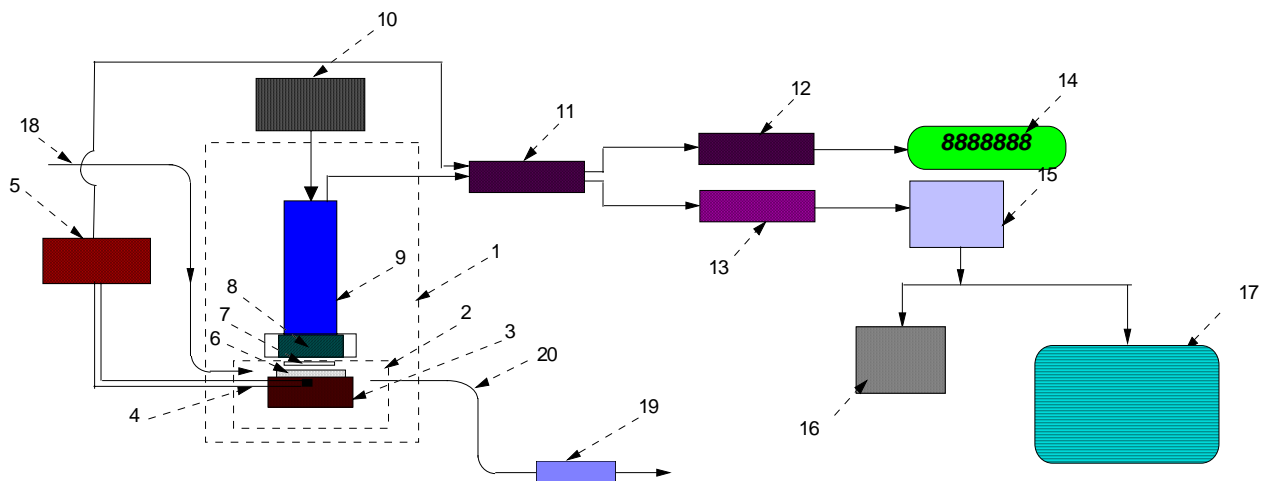


Figure 3.9
temperature
voltage
data
inlet;

Chemiluminescence instrument scheme:
 1 - light tight box; 2 - oven; 3 - heater; 4 - thermocouple; 5 -
 temperature controller; 6 - sample; 7 - lens; 8 - shutter; 9 - PM tube; 10 - high
 voltage supply; 11- amplifier; 12- A/D converter; 13 - interface; 14 - digital
 display; 15 - computer; 16 - printer; 17 - computer display; 18 - gas
 inlet;
 19 - flowmeter; 20 - gas exit



Figure 3.10 A CL instrument Lumipol 3 type

If a CCD camera is used as a detector, a chemiluminescence image of oxidation can be provided [114, 115]. The technique, called *imaging CL*, detects the distribution of early oxidation stages on the sample surface.

3.3. Polymers oxidation studied by chemiluminescence (CL) method

3.3.1. Characterization of the oxidation process and mechanism

CL in isothermal mode can be used to study the oxidation process of various polymers. An illustration is given in Fig. 3.11. The maxima observed in CL curves from PE can be related to the stability of various fragments of the polymer chain. The changes observed in IR spectra of the sample oxidized till the first CL peak suggests that oxidation occurs in the amorphous part of the polymer. The polymer oxidized up to the second CL peak appears like a yellowish resin. This CL peak can be assigned to the oxidation of the chain fragments, initially present in the crystalline part, because the absorption bands at 888 cm^{-1} (vinylidene double bond) and 1894 cm^{-1} disappeared almost completely (Fig. 3.12) [116].

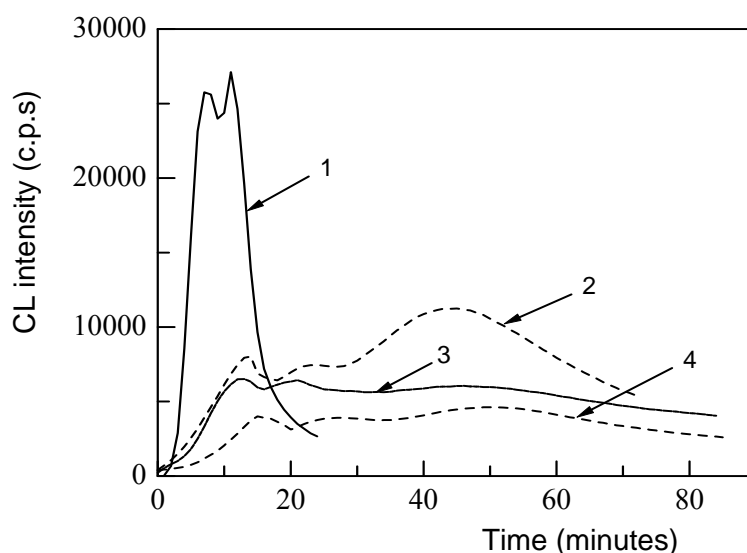


Figure 3.11 CL curves from polyolefin samples: 1- i-PP (I/4); 2 - LDPE; 3 - LLDPE; 4 - HDPE oxidation (170 °C, oxygen atmosphere) [116]

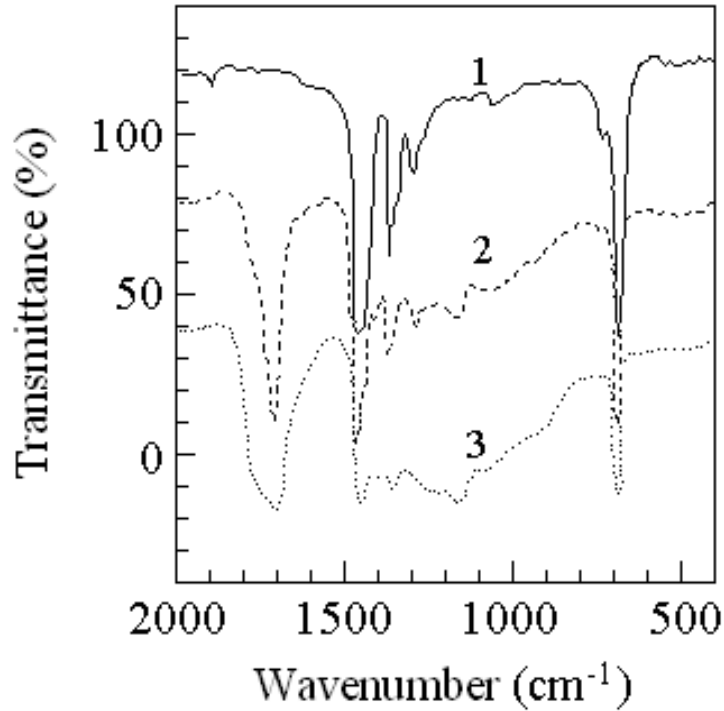


Figure 3.12 IR spectra in the 2000 cm^{-1} - 400 cm^{-1} region of LLDPE oxidized in oxygen ($T_{\text{iso}} = 170\text{ }^{\circ}\text{C}$): 1 - un-oxidized; 2 - 14 min (first CL peak); 3 - 19 min (second CL peak) [116]

Osawa and coworkers used CL to prove the higher stability to thermo-oxidation of syndiotactic polypropylene (s-PP) as compared to isotactic polypropylene (i-PP) and high-density polyethylene (Fig. 3.13) and assigned this high stability to the helicoidal structure of s-PP [117].

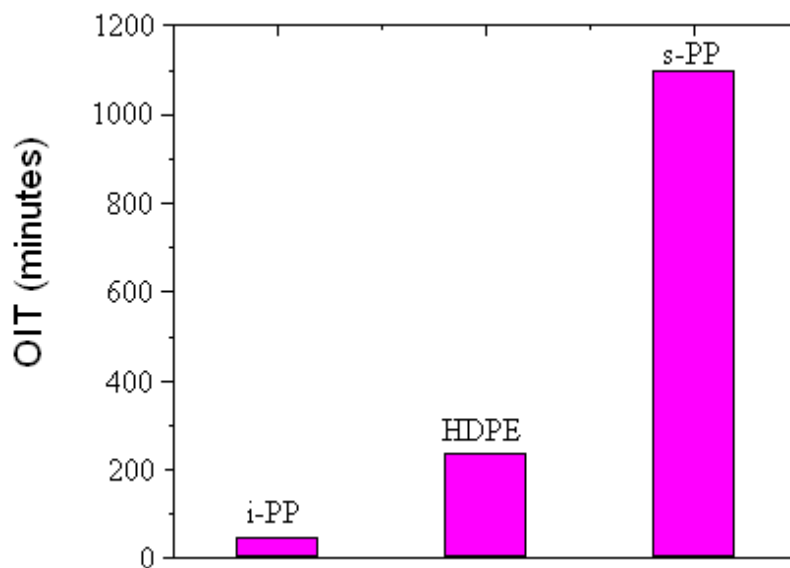
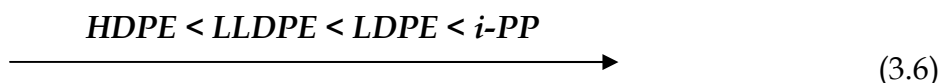


Figure 3.13 Representation of CL data on the oxidation at 140 $^{\circ}\text{C}$ in oxygen of HDPE, i-PP and s-PP [117].

The role of branched structure in oxidation susceptibility is evidenced in Figs. 3.14 and 3.15 for PE. The correlations between CH₃ content and the intensity of the CL signal recorded in nitrogen and respectively in oxygen atmosphere are shown. It can be observed an increase in CL intensity as increases the content in CH₃ groups. Taking into account the significance of CL emission, a branched polymer is more susceptible to oxidation both in moderate stress conditions (manufacture, storage) and accelerated conditions (in oxygen at 170 °C):



The oxidation susceptibility increases together with the CL signal [41]

The influence of the temperature on oxidation process can be studied by isothermal CL in oxidized atmosphere as presented in Fig. 3.16 and Table 3.2. Using CL parameters, the apparent activation energy values for oxidation are calculated, depending on the particular oxidation stage. The most useful for the life-time evaluation is E_a calculated from OIT which represents the apparent activation energy of the inhibited oxidation. E_a values calculated from OIT are higher than those from v_{ox} due to the influence of the polymer structure (the intrinsic resistance of the polymer - branching and crystallinity - if the oxidation occurs in solid state) or to the antioxidant type. The E_a value calculated from I_{max} can be related to the influence of temperature on CL emission, that is the increase in concentration of the active oxidation centers.

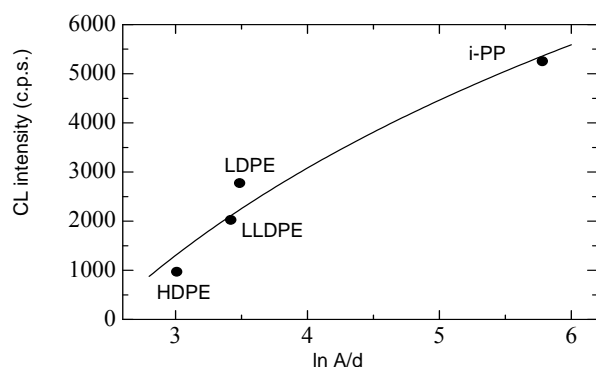


Figure 3.14 - The dependence of the integrated CL emission (0-30 minutes) in nitrogen on CH₃ content of some polyolefin samples (A = abs. at 1378 cm⁻¹; d = sample thickness) [41]

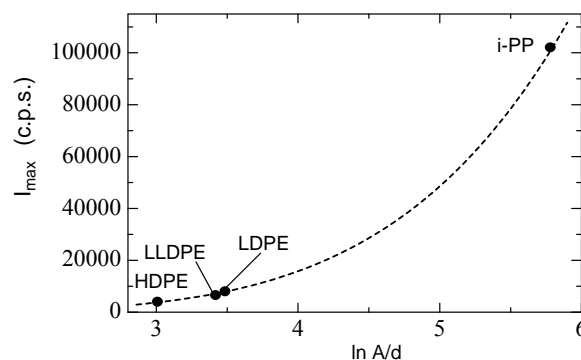


Figure 3.15 - The dependence of the maximum CL emission in oxygen on CH₃ content of some polyolefin samples (A = abs. at 1378 cm⁻¹; d = sample thickness) [41]

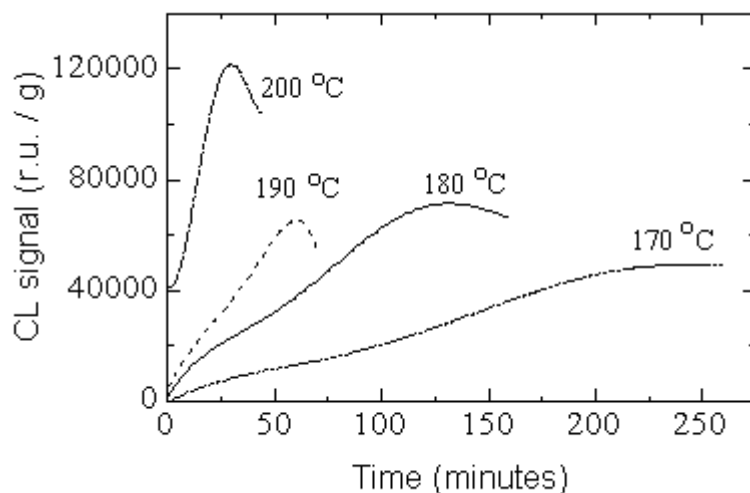


Figure 3.16 Isothermal CL curves for the oxidation of LDPE (in air) at various temperatures [118]

Table 3.2
CL parameters for oxidation of LDPE (in air) at various temperatures and Arrhenius parameters [118]

T (°C)	$t_{1/2}$ (min.)	t_{max} (min.)	v_{ox} (%/min.)	I_{max} (r.u./g)
170	118	226	0.43	49 024
180	65	122	0.85	71 643
190	26	58	1.43	68 614
200	14	29	3.62	125 797
intercept (lnA)	-29.77	-27.18	31.76	23.92
slope	15325.4	14464.9	-14468.2	-5815.02
E_a (kJ/mol)	127.6	120.4	120.5	48.4
Correlation	0.9964	0.9990	0.9921	0.9168

The E_a value calculated from OIT is higher for the stabilized samples as compared to those non-stabilized, due to the antioxidant influence (Fig. 3.17, Tab. 3.3) [119]. The activation E_a values of the samples exposed to various stress conditions were found to be lower than in the case of initially un-exposed sample (Fig. 3.18). Similar results were obtained for i-PP, PE and EPR copolymer. Compensation effects were also observed in these cases, as shown in Fig. 3.19.

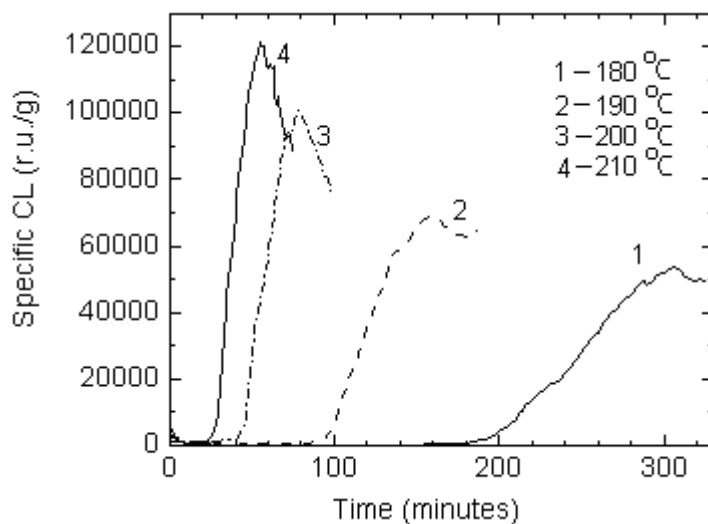


Figure 3.17 CL curves for the oxidation of LDPE + 0.1% Irganox 1010[®] (in air) at various temperatures [119].

Table 3.3

CL parameters for oxidation of LDPE + 0.1% Irganox 1010[®] (in air) at various temperatures and Arrhenius parameters [119].

T (°C)	OIT (min.)	t _{1/2} (min.)	t _{max} (min.)	v _{ox} (%/min.)	I _{max} (r.u./g)
180	190	206	308	1.13	53564
190	96	92	165	1.76	75550
200	43	50	80	3.57	100777
210	20.5	26	55	5.65	117767
Intercept = lnA	-30.61	-27.46	-22.62	26.64	23.69
Slope	16255.7	14833.1	12828.1	-12028.3	-5780.6
E _a (kJ/mol)	135	123.5	107	100	48
Correlation	0.9990	0.9989	0.9943	0.9954	0.9901

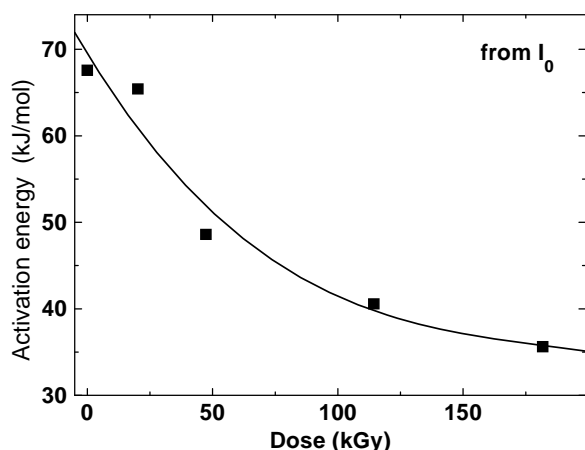


Figure 3.18 - Variation of E_a for oxidation of EPR as a function of stress factor duration (irradiation dose) [118]

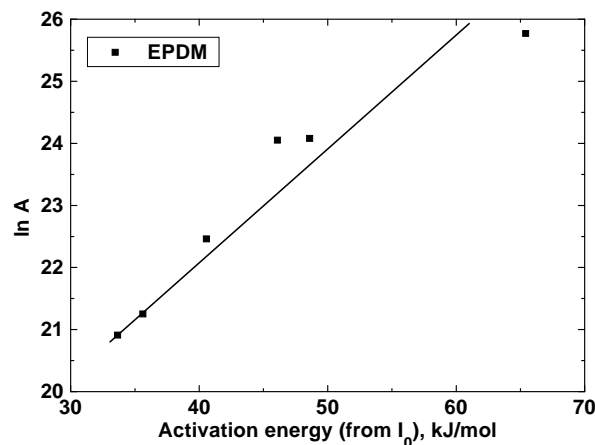


Figure 3.19 - Compensation effect of E_a and $\ln A$ for irradiated EPR [118]

3.3.2. Antioxidants efficiency and stabilization mechanisms

The antioxidants increase the OIT values by the control of the competition between the oxidation and the deactivation of free radicals and peroxy species. CL curves in Fig. 3.20 illustrate this effect for a commercially LDPE sample as received and after antioxidant extraction [116].

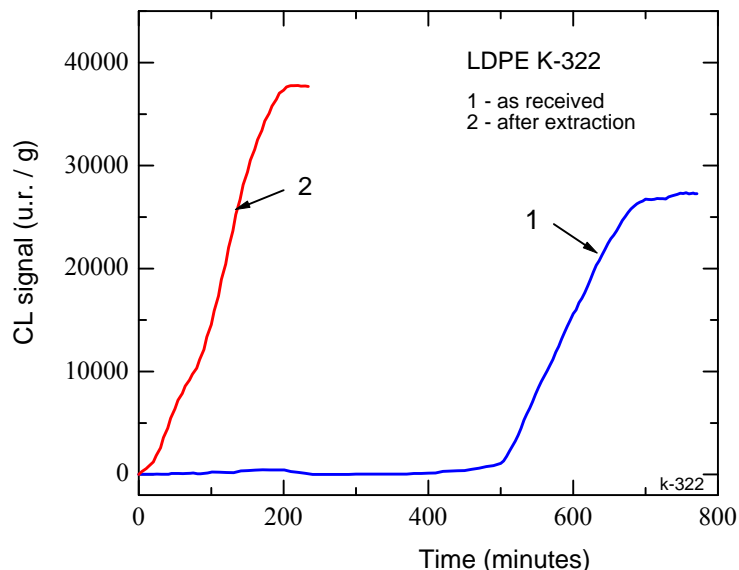


Figure 3.20 Isothermal CL curves from oxidation of LDPE K322 in air at 180 °C, as received and after antioxidant extraction [116]

The effect of antioxidant structure for *i*-PP is shown in Fig. 3.21.

The kinetic parameters (OIT, $t_{1/2}$, v_{ox}) derived from CL data can be used to characterize the efficiency of the antioxidants (Table 3.4, Fig. 3.22, 3.23), directly or using the formulae already presented for the relative activity and relative stability (see Ch. 2).

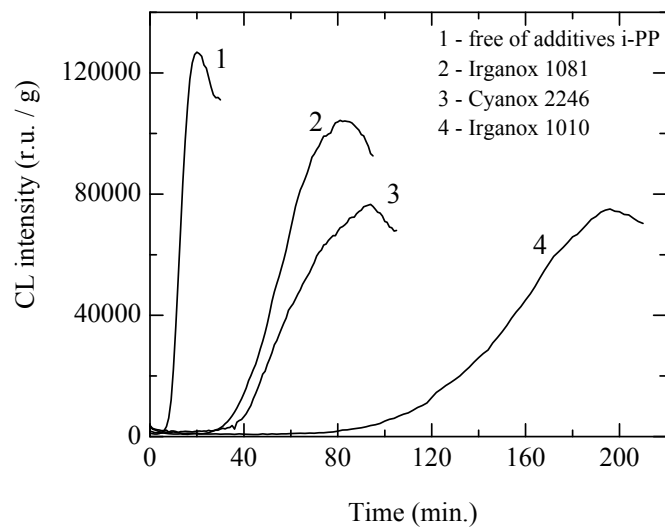


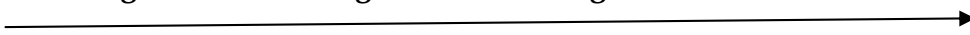
Figure 3.21 Isothermal CL curves from oxidation of i-PP stabilized with 0.1 % different antioxidants (in air; 180 °C) [118]

Table 3.4

CL parameters for oxidation of LLDPE stabilized with various antioxidants. (170 °C, oxygen atmosphere, $C_{\text{antioxidant}} = 0.25 \%$) [118]

Antioxidant	OIT (min.)	$t_{1/2}$ (min.)	t_{max} (min.)	v_{ox} (%/min.)	I_{max} (c.p.s.)
none	0	7.5	14	11.61	6 583
Irganox 1222 [®]	27	40	50	4.76	10 931
Irganox 1330 [®]	150	212	224	4.59	8 921
Irganox 1010 [®]	260	327	341	3.85	3 264

$$Irganox\ 1010^{\text{®}} > Irganox\ 1330^{\text{®}} > Irganox\ 1222^{\text{®}} > none$$



OIT decreases together with the antioxidant efficiency

(3.7)

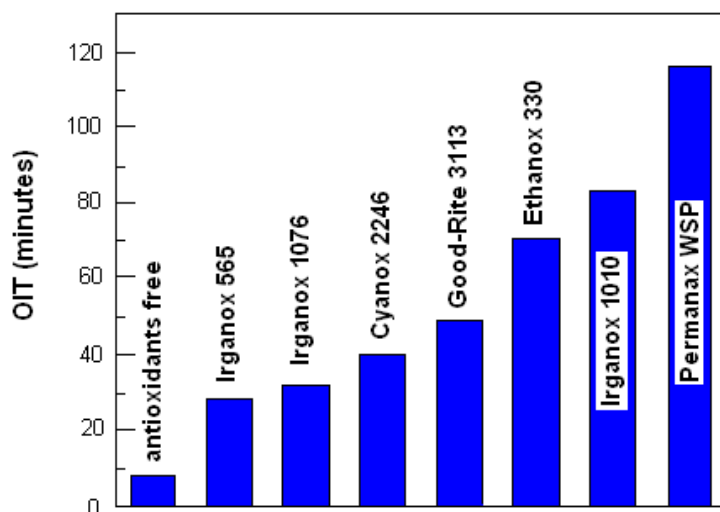


Figure 3.22 Ranking of several antioxidants for the oxidation of i-PP at 180 °C in air atmosphere based on OIT parameter [120]

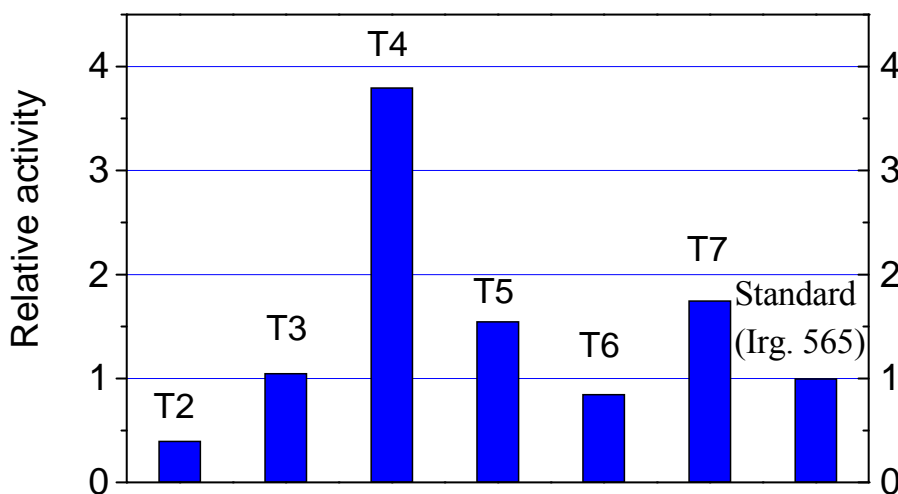


Figure 3.23 Relative antioxidant activity of some triazine based compounds [121]

The effect of antioxidant concentration is presented in Fig. 3.24, 3.25 and in Table 3.5. The stability increases as a function of the antioxidant concentration. The calibration curves presented in Fig. 3.25 are used for quality control in plastic production processes (stabilization level and uniformity).

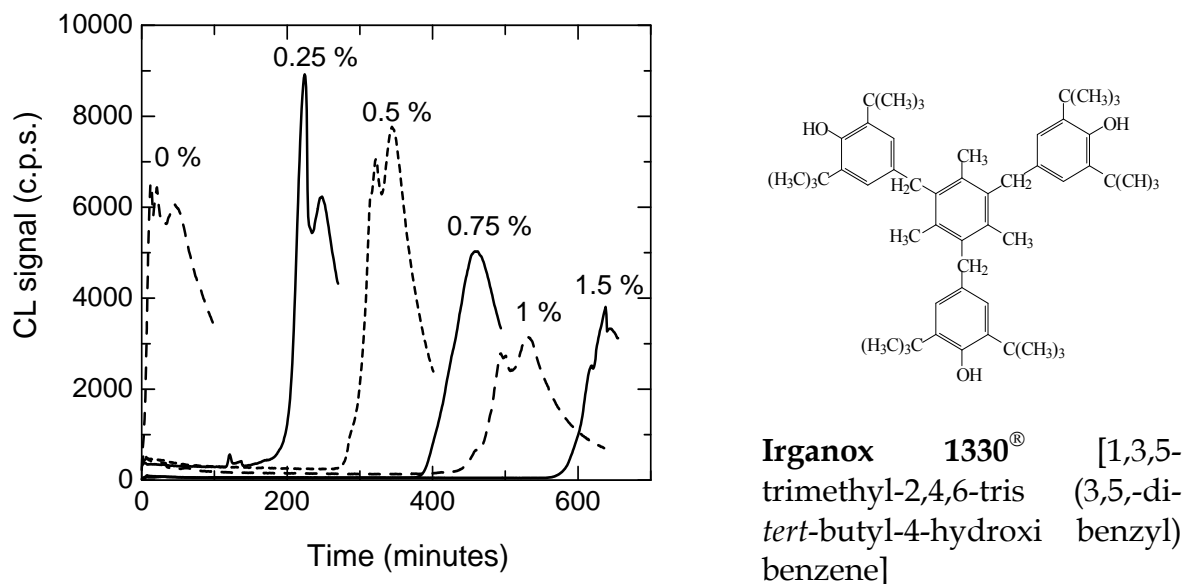


Figure 3.24 - Isothermal CL curves from oxidation (at 170 °C in oxygen) of LLDPE stabilized with various percent of Irganox 1330[®] [122]

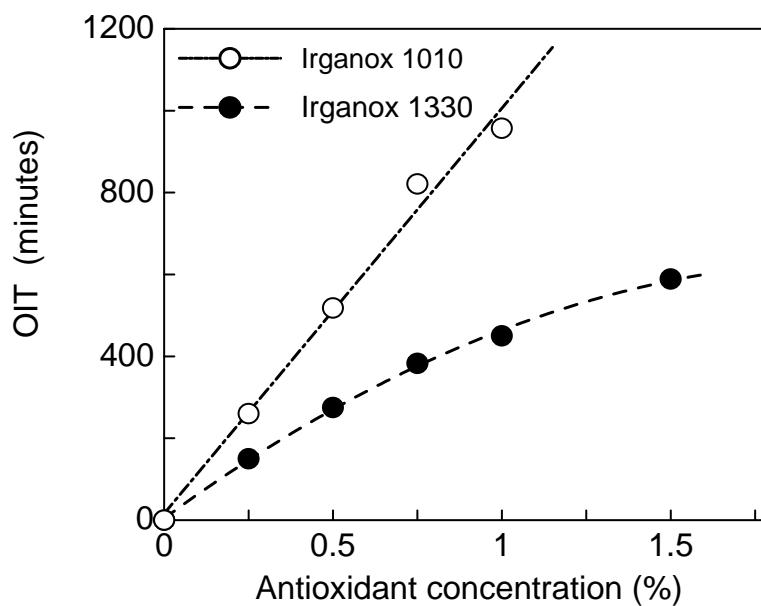


Figure 3.25 OIT as a function of concentration for LLDPE stabilized with Irganox 1330[®] and Irganox 1010[®] thermally oxidized at 170°C in oxygen [122]

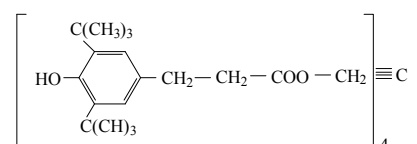
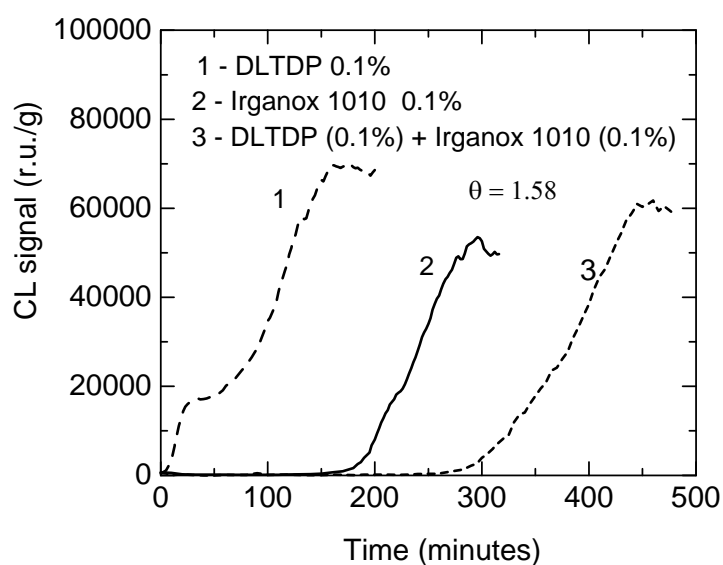
Table 3.5
Isothermal CL parameters for the oxidation of LLDPE containing various percent of Irganox 1330[®] (170 °C, in oxygen) [122]

Irganox 1330 [®] (%)	OIT (min.)	t _{1/2} (min.)	t _{max} (min.)	I _{max} (c.p.s.)	v _{ox} (%/min.)
0	0	8	14	6 533	11.61
0.25	150	212	224	8 921	4.59
0.50	275	305	345	7 767	3.61
0.75	383	437	472	5 030	1.65
1.00	450	471	500	3 148	2.19
1.50	589	638	671	3 871	2.99

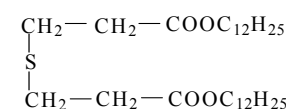
Mixtures of antioxidants are frequently used in polymers stabilization for a better protection using their synergistic effects. Isothermal CL in oxidative atmosphere is applied to characterize these effects, as illustrated in Fig. 3.26 for a couple of a phenolic antioxidant (Irganox 1010[®]) and a substituted sulphide (DLTDP) [70]. The intensity of the synergistic effect is characterized by the cooperative factor:

$$\theta = \frac{OIT_{(mixture)}}{OIT_{(1)} + OIT_{(2)}} \quad (3.8)$$

CL in isothermal mode measured at various temperatures on samples stabilized using couples of additives can be also used for the thermal behavior evaluation of the synergistic effects. In the case of Irganox 1010[®]/DLTDP couple, it can be observed the increase of this effect as the temperature decreases (Fig. 3.27) [70].



Tetrakis [methylene -3-(3',5'-di-*tert*-butyl-4'-hydroxy phenyl) propionat]metan
Irganox 1010[®]



Dilauroil-tio-dipropionat (DLTDP)

Figure 3.26 CL curves from LDPE stabilized with

DLTDP, Irganox 1010[®] and their mixture[70]

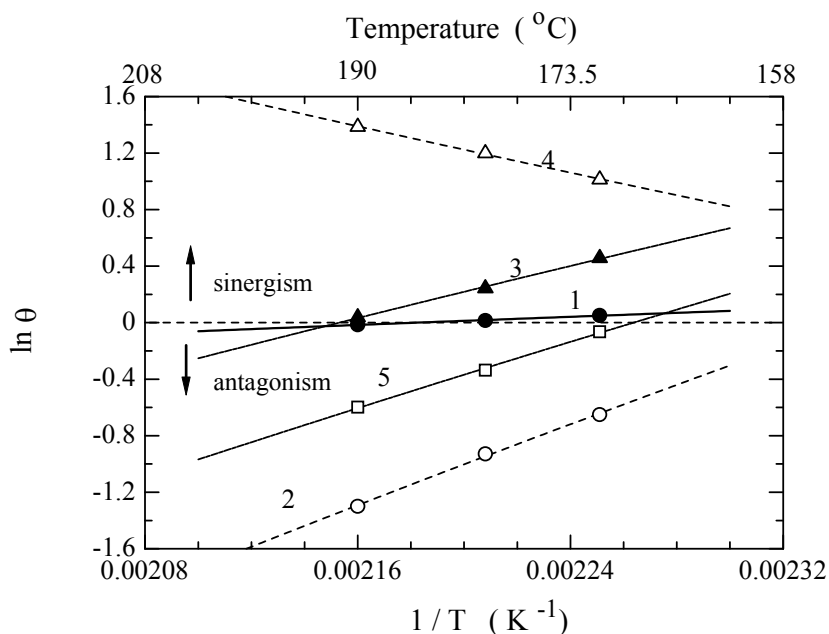


Figure 3.27 The temperature influence on the cooperative factor θ , for LDPE stabilized with different antioxidant couples: 1-Irganox 1010[®] (0.1%) + Santonox R[®] (0.1%); 2-Irganox 1076[®] (0.1%) + Santonox R[®] (0.1%); 3-Irganox 1010[®] (0.1%) + DLTDP (0.1%); 4- Irganox 1076[®] (0.1%) + DLTP (0.1%); 5- Santonox R[®] (0.1%) + DLTDP (0.1%) [70]

Antioxidative effects of various substances, such as selenium [123 - 125], triazines [121, 125], vitamins E, C [126], fullerenes [127 - 129], calixarenes [129, 130], thiosemicarbazides [66], metallic complexes [131], secondary amines from dehydroabiatic acid [132], sterically hindered amines (HALS) [137] and derivatives from 3,5-di-*tert*-butyl-4-hidroxy ethane or ethylene [133] were also evidenced and studied by isothermal CL.

Selenium exhibits a relative high antioxidative activity, which increases linearly with selenium concentration (Fig. 3.28).

Synergistic effect with several antioxidants, such as triazines (Fig. 3.29) [123] or hindered phenols were also observed. A dependence was found for phenols between the intensity of the synergistic effect and the antioxidant nature, as shown in Fig. 3.30 [120].

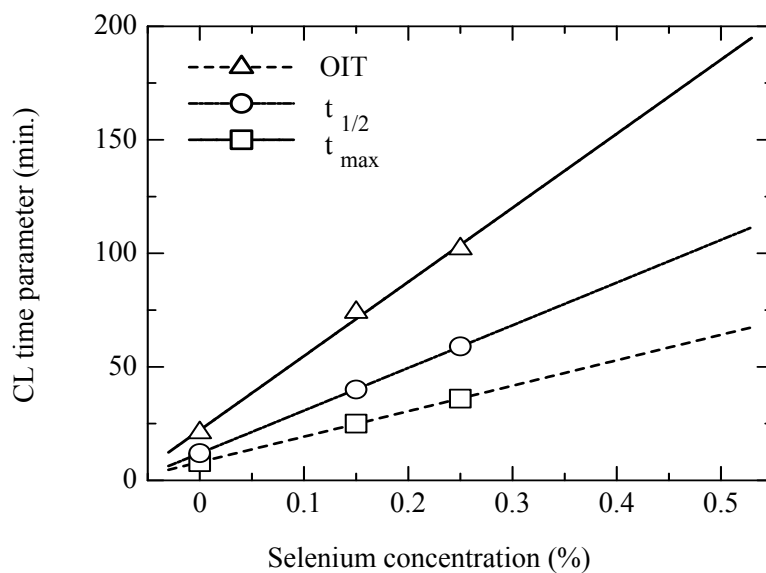


Figure 3.28 Dependence of some kinetic parameters of LDPE oxidation on selenium concentration [123]

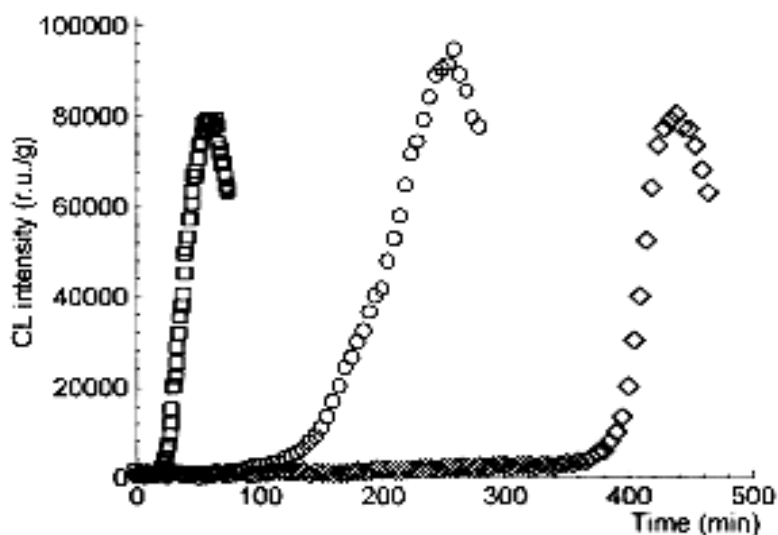


Figure 3.29 CL curves from oxidation at 180°C of i-PP stabilized with 0.15% Se (□) 0.50% triazine T7 (○) and their mixture (◇) [123]

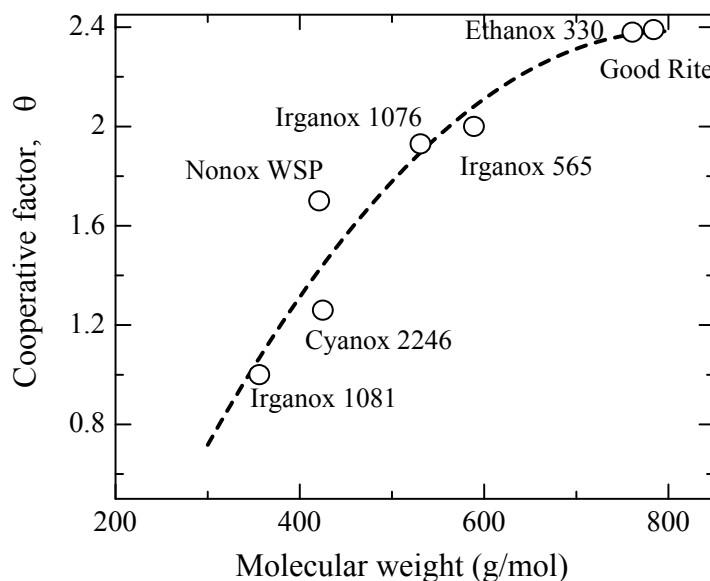


Figure 3.30 Dependence of the cooperative factor (θ) on the antioxidants molecular weight in i-PP stabilization at 180°C using binary mixtures of Se and phenolic antioxidants [120]

3.3.3 Radiation-induced effects studied by the CL method

CL in isothermal mode is applied for the evaluation of the anti-rad efficiency when these additives exhibit an antioxidant function. Thus, phenol or amine type antioxidants used as anti-rad agents can be evaluated using initial and irradiated samples (Fig 3.31 - 3.34). The stability of the polymer submitted to thermo-oxidation post-irradiation is measured and applied for the life-time evaluation both in storage and use.

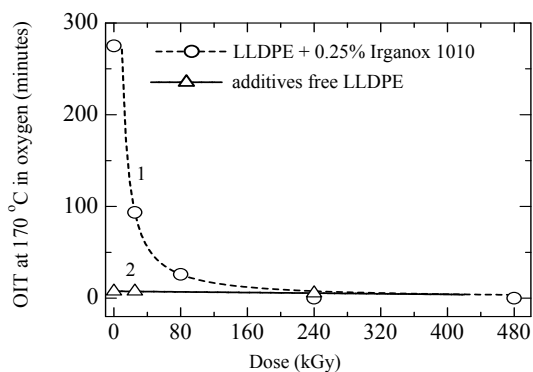


Figure 3.31 - Decrease of OIT values for oxidation at 170 °C in oxygen of γ -irradiated LLDPE [122]

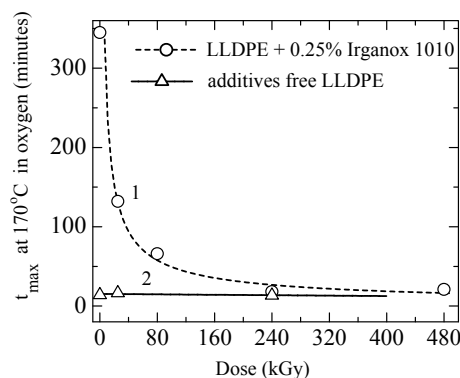


Figure 3.32 - Decrease of t_{\max} values for oxidation at 170 °C in oxygen of γ -irradiated LLDPE [122]

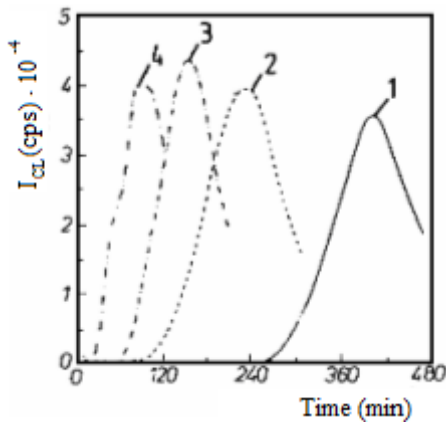


Figure 3.33 – CL curves at 170 °C in air of γ - irradiated LDPE stabilized with 2 % of Irganox 1330[®] [134]: (1) 0 kGy; (2) 100 kGy; (3) 200 kGy; (4) 400 kGy

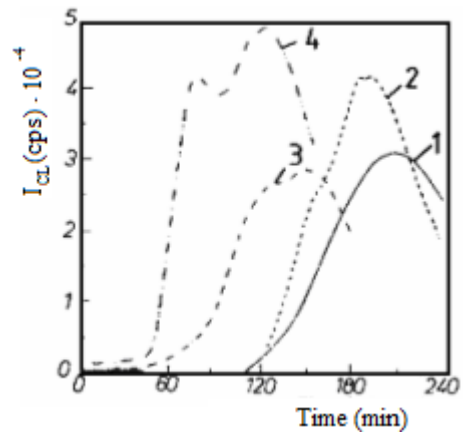


Figure 3.34 – CL curves at 170 °C in air of γ -irradiated LDPE stabilized with 2 % of Sumilizer MDP-S[®] [134]: (1) 0 kGy; (2) 100 kGy; (3) 200 kGy; (4) 400 kGy

The efficiency of anti-rad and of other stabilizers designed to protect the polymer against low-temperature oxidation, is controlled not only by the capacity to trap the radiation-induced free radicals, but also by their mobility, facilitating the active species contact - Fig. 3.35 [122]. As an example, Irganox 1010[®] or Irganox 1330[®] protect the polymer against the post-irradiation oxidation, but their anti-rad protection (evidenced by carbonyl groups concentration) is lower as compared to Irganox 1222[®], a low molecular weight antioxidant [122].

As shown in Fig. 3.36, the isothermal CL is used to establish the stabilizer optimal concentration for the required stabilization level [124]. Using the measurements of carbonyl concentration as a function of antioxidant concentration, shown in Fig. 3.37, an optimal antioxidant concentration of 0.5% is found. After irradiation, all the stabilized samples showed a carbonyl concentration under the limit of 0.5 % generally accepted as the end-life criterion for PE electro-insulating materials [135].

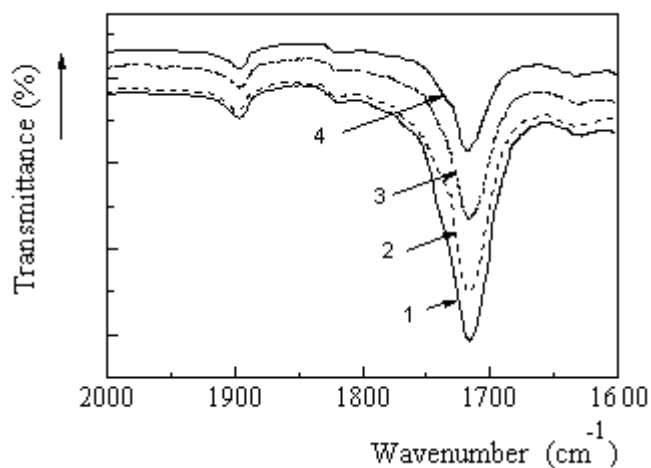


Figure 3.35 FT-IR spectra in region 2000 - 1600 cm^{-1} of some stabilized LLDPE γ -irradiated samples (240 kGy): 1 - free of additives; 2 - 0.25% Irganox 1010[®]; 3 - 0.25% Irganox 1330[®]; 4 - 0,25% Irganox 1222[®] [122]

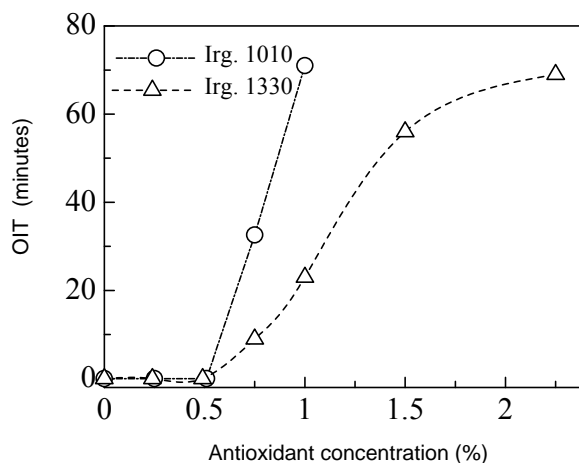


Figure 3.36 Dependence of OIT parameter for γ -irradiated LLDPE oxidation (at 170°C in oxygen) on the initial concentration of antioxidant [122]

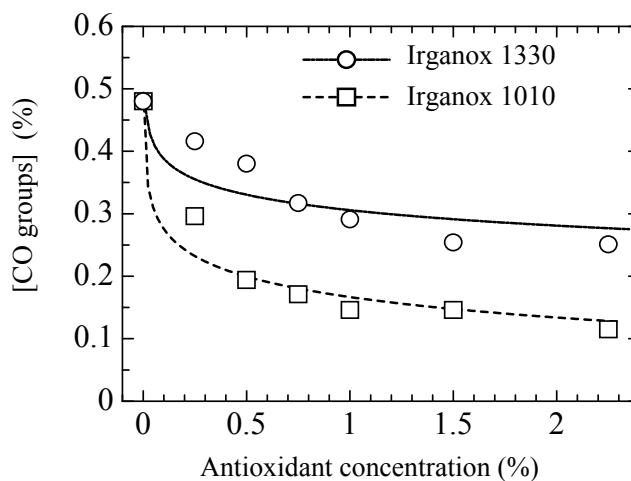


Figure 3.37 Carbonyl concentration vs. antioxidant concentration for γ -irradiated LLDPE (240 kGy) [122]

Better results are obtained using a couple of an efficient radical scavenger and an energy scavenger (see Ch. 2). CL and FT-IR measurements characterized the efficiency of several polynuclear aromatic hydrocarbons (PAH): anthracene, phenanthrene, pyrene, perylene and coronene as well as their couples with phenolic antioxidants. All PAH had a negligible stabilization effect against thermo-oxidation, but were very effective as anti-rad in PE - Fig. 3.38 [86]. The most efficient was the couple pyrene/phenolic antioxidant. The studied couples exhibited synergistic effects for both pure thermal oxidation and for the post-irradiation oxidation for a PE material (Fig. 3.39) [86]. CL in isothermal mode was also applied to establish the optimal ratios in the synergistic couples (Fig. 3.40) [86].

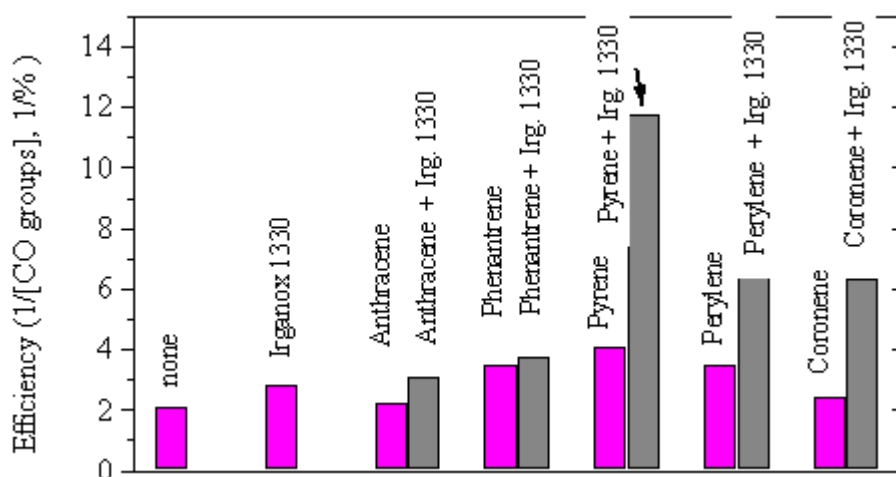


Figure 3.38 Comparative values of various additives efficiency in PE stabilization against radiation induced oxidation [86]

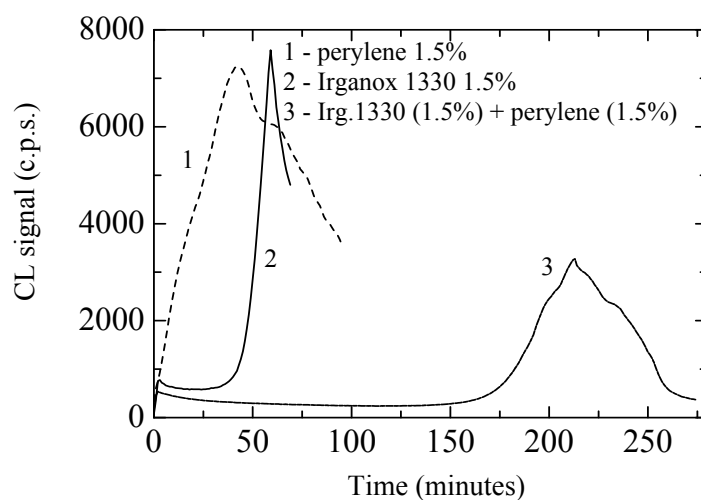


Figure 3.39 CL curves at 170°C in oxygen of stabilized and γ - irradiated LLDPE (240 kGy) [86]

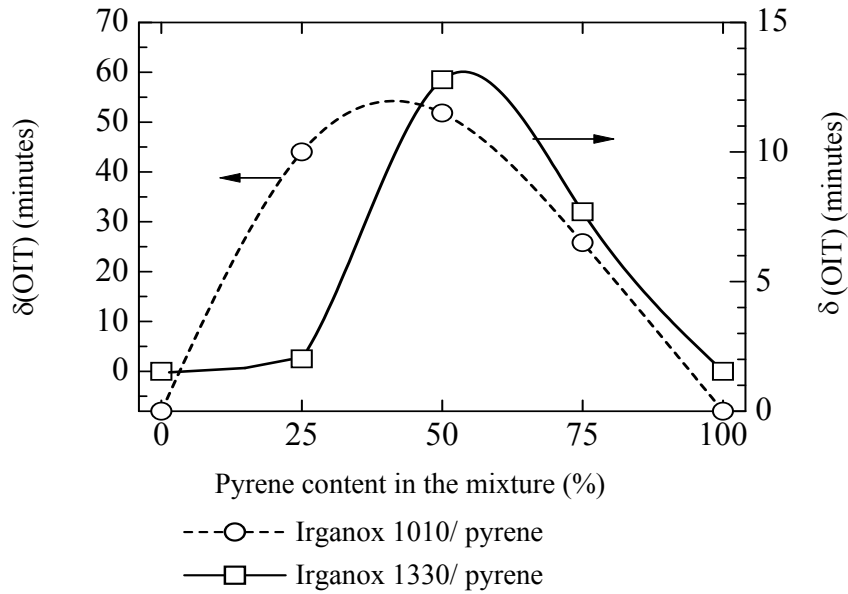


Figure 3.40 The dependence of the synergistic effect intensity of the phenolic antioxidant type on the mixture composition; thermo-oxidation of irradiated LLDPE (240 kGy); the total concentration of additives: 1%; $\delta(OIT) = OIT_{couple} - (OIT_{pyrene} + OIT_{antioxidant})$ [86, 136]

3.3.4. Life - time estimation by CL method

A steep rise of the CL emission indicates the antioxidant consumption and the start of the polymer oxidation, followed by the deterioration of the polymer properties. Hence, **the OIT measured in specific conditions represents the life-time of the material in the same specific conditions.**

The thermally oxidized PP films in solid state become brittle after their **OIT was over-passed** because the chain breaking processes starts together with the polymer oxidation. Therefore, the life-time of PP is equal to the time needed for the antioxidant consumption. Hence, the **OIT** measured on an initial, un-aged, sample and on a thermally oxidized sample enables the rough life-time evaluation using the formula based on the stress effects addition hypothesis, as proposed by Shlyapnikov et al. [138]:

$$\sum \frac{t_i}{\tau_i} = 1 \quad (3.9)$$

where t_i is the exposure time in certain conditions and τ_i is the **OIT** in the same conditions.

In the case of PE, no brittleness is observed immediately at the end of the induction period, and the useful properties remain unchanged for a certain time after the **OIT** reaches a zero value. This effect is related to crosslinking processes dominant in PE. In such cases, the parameter $t_{1/2}$ may be more appropriate for the life-time

evaluations. In Fig. 3.41 is shown an example of the Shlyapnikov [138] formula applied for a rough life-time evaluation of PE thermally oxidized.

For the oxidation processes at lower temperatures and high dose rates carbonyl group appears, but the OIT is still measurable, indicating the antioxidant traces presence in certain zones (Figs. 3.36 and 3.37). The effect is a consequence of the antioxidant limited diffusion and of radical migration, resulting in inhomogeneous oxidation [99].

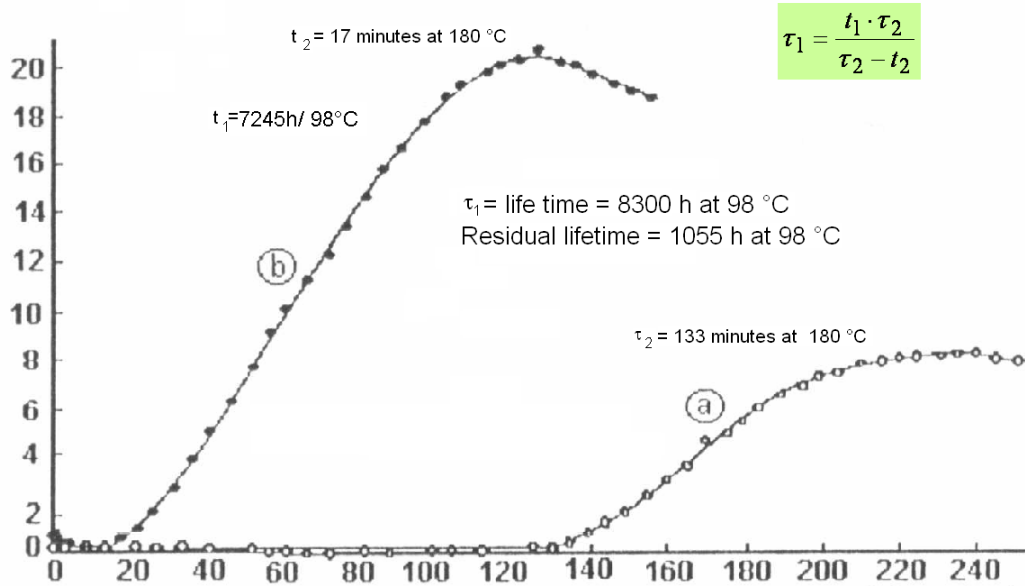


Figure 3.41 Example of the life-time evaluation for LDPE using isothermal CL (180°C in air) [86]

a): un-aged; b): aged

For the poly-isoprene rubber (Fig. 3.42) the decrease of the induction period vs. irradiation dose fulfills the equation [140]:

$$\frac{1}{t_i} = k \cdot D^{0.3} + \frac{1}{(t_i)_0} \quad (3.10)$$

Where:

t_i = the OIT at D dose
 $(t_i)_0$ = the OIT at $D = 0$;
 k = a proportionality constant

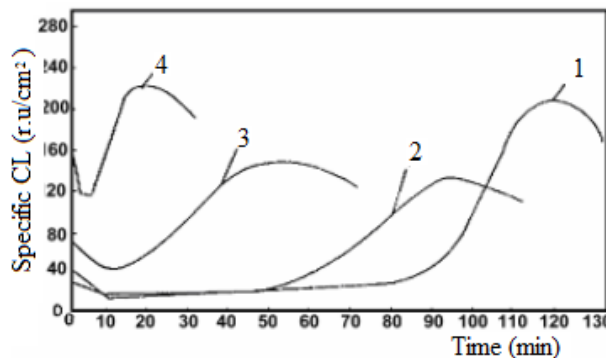


Figure 3.42 Isothermal CL (air, 140 °C) from poly-isoprene rubber irradiated γ ^{60}Co : (1) 0 kGy; (2) 7 kGy; (3) 22 kGy; (4) 95 kGy [140]

Kron [101] proposed a multistep method for the luminescent emission measurement from an irradiated polymer (Fig. 3.43). Such measurements give information on thermoluminescence (TL), the oxidation and the crosslinking processes occurring in an irradiated polymeric material:

I. Heating in nitrogen atmosphere the freshly irradiated polymer sample to 150 °C and simultaneously recording the integrated luminescence signal. Knowing that TL and CL emissions are located in different spectral ranges i.e. CL: 350 - 500 nm, TL: 500 - 600 nm, their contribution is estimated.

II. Measuring the CL at 120 °C in oxygen atmosphere. The CL intensity gives the sample stability to oxidation [113].

III Non-isothermal CL measurement from 120 °C to 170 °C in oxygen. The slope of the CL emission is smaller if crosslinking effects are present [20]: the slope of the CL curve correctly describes the crosslinking process.

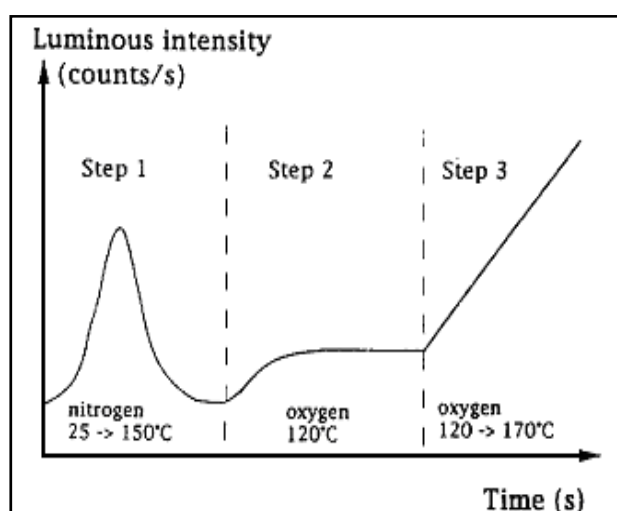


Figure 3.43 An ideal curve describing Kron model for the luminescence emission from irradiated polymers [101]

3.4 Criteria for the evaluation of polymers stability from thermal analysis data - For materials which decompose in volatile products

The non-isothermal data obtained by TG, DTA techniques are used. The corresponding stability criteria are:

1. $T_{x\%}$ - temperature corresponding to $x\%$ weight loss
2. $\% \Delta m_T$ - weight loss at a given temperature T .

The increasing order of $T_{x\%}$ or the decreasing order of $\% \Delta m_T$ is the increasing order of the thermal stability (see, for example, the recent references [141-143]).

- For materials which degrade in non-volatile compounds

a) Use of the data from non-isothermal DTA or DSC or chemiluminescence (CL)

The stability criterion in this case: the onset (OOT) or the corresponding thermal peak (T_m) of the initial oxidation process *accompanied by the formation of solid, non-volatile compounds*. The increasing order of the onset (OOT) or the thermal peak from DTA, DSC or CL is the order of increasing the thermo-oxidative stability.

b) Use of the data from isothermal DTA, DSC or chemiluminescence (CL)

In order to evaluate the oxidative stability of some polymeric materials and the corresponding kinetic parameters, the following isothermal thermal analysis methods are used: DTA [144], DSC [145] and CL [146]. In all these techniques, the polymeric sample, encapsulated in a metallic can, is rapidly heated in an inert atmosphere (argon or nitrogen flow) up to the programmed constant temperature. As soon as this temperature is reached, oxygen replaces the inert gas and the effect of the interaction between oxygen and the investigated material is measured. Figure 3.44 illustrates a typical thermogram obtained by all these techniques. There is an induction time during which no heat (for DTA and DSC) or no light (for CL) is emitted from the sample. After the induction time, follows an autocatalytic stage characterized by an exothermal peak in DTA and DSC curves, or an increase of the emitted light intensity in CL curve, reaches a maximum and finally decreases towards the terminal stage.

The OIT is defined as the time between the introduction of oxygen and the intersection of the base-line extension with the main oxidation peak slope.

The t_{max} , called the oxidation maximum time, is defined as the time between the introduction of oxygen and the time to reach the signal maximum.

Stability criterion: OIT or t_{max} .

The increasing order of OIT or t_{max} obtained for a same temperature is the order of the thermo-oxidative stability increase.

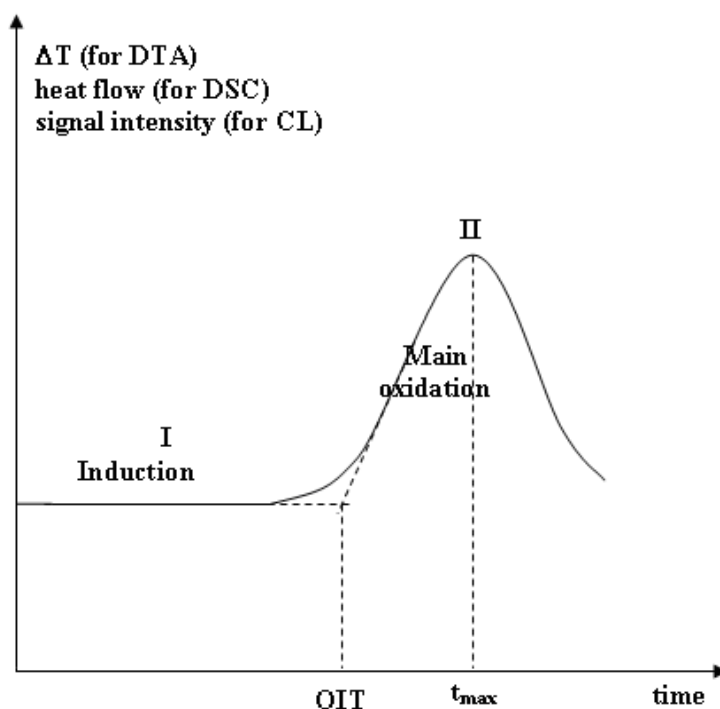


Figure 3.44 DTA, DSC or CL typical thermogram for the isothermal oxidation of a polymeric material

3.5 Examples of radiation-induced effects studied by thermal analysis methods

The following two examples concerning the changes in the thermal behavior of polymeric materials will be discussed:

a) γ -irradiated EPDM - PP mixtures [147]

Ethylene-propylene-diene terpolymer (EPDM, 3.5 % ethylidene norbornene, Terpit C[®]) and polypropylene (injection type, flow index 3.5 g/10 min at 230 °C and 2.16 kg load, F 401[®]) were provided by ARPECHIM Pitești (Romania).

Mixture plates in various percentages (100/0, 80/20, 60/40, 40/60, 20/80 and 0/100 w/w) were pressed at 180 °C and 150 bar; small and uniform chips were cut from these specimens.

γ -irradiation was performed in air and room temperature in a GAMMACELL (USA) irradiation machinery using a ¹³⁷Cs source at a dose rate of 0.54 kGy/h. Portions were taken off when certain doses were attained (6, 12, 30, 50, 105, 160, 250 kGy). The radiation processed specimens were investigated immediately after irradiation.

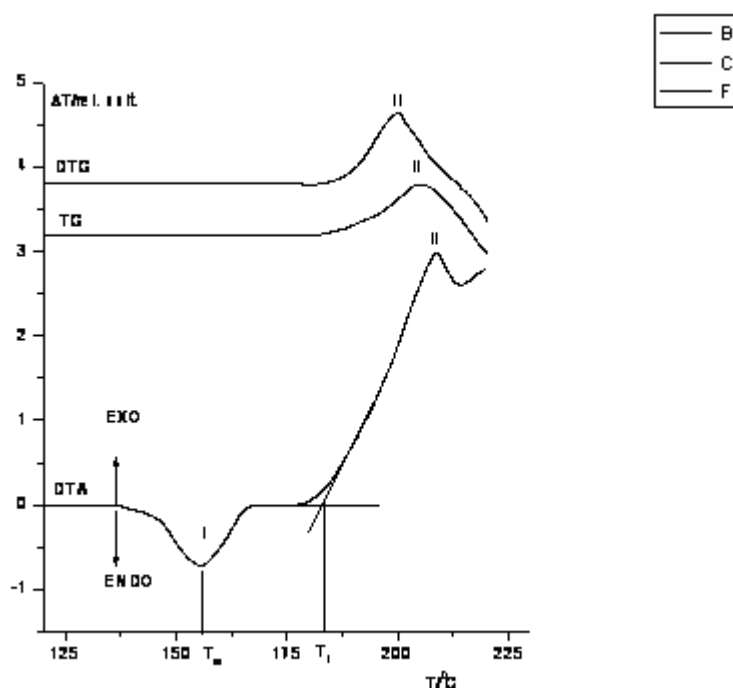


Figure 3.45 TG, DTG and DTA curves recorded for unirradiated polymer mixture EPDM/ PP = 40/60 (w/w)

Thermal analyses: TG, DTG and DTA curves were obtained from the polymeric blends. Fig. 3.45 shows the curves obtained for the unirradiated sample containing 40 % EPDM. The DTA curve displays a first-order phase change (melting or softening) at minimum point I characterized by the temperature T_m . At higher temperatures, the sample presents an exothermal change (peak II on the DTA curve) accompanied by a slight weight increase. This process starts at the temperature (OOT) T_i . The exothermal peak corresponds to

the thermo-oxidation of sample and the apparition of some non-volatile products. Hydroperoxides and the subsequent hydroperoxide reaction products are formed probably, due to the attack of oxygen on the active carbon sites of the macromolecular chains. Increased temperatures will further promote a progressive degradation accompanied by the generation of volatile products.

Fig. 3.46 shows the modification of the characteristic temperatures for two randomly selected samples, namely EPDM 100 % and EPDM/PP = 20/80. The analysis of all thermograms recorded for these samples reveals a sharp decrease in T_i and T_m values.

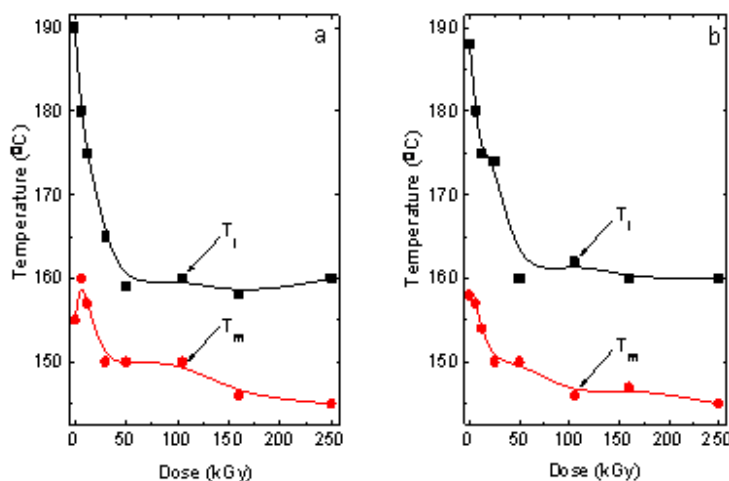


Figure 3.46 T_i (OOT) and T_m values for (a) EPDM/PP = 100/0 and (b) EPDM/PP = 20/80 specimens vs. irradiation doses.

b. Electron beams effects on EVA based compound [148]

The investigation was carried out on FRAGOM P/1, a compound based on EVA polymer containing magnesium hydroxide, antioxidants and anti-aging additives, supplied by SACOM-Parma-Italy.

This polymeric material has the following initial characteristics: density: 1.50 g.cm⁻³; melt flow index (21.8 kg at 190 °C): 20 g/10 min; tensile strength: 9 N.mm⁻²; elongation at break: 500 %; temperature index (21 % O₂): 360 °C. Sample plates were obtained by press molding of the polymeric material pellets for 10 min, at 130 °C.

FRAGOM P/1 samples were irradiated in air, at room temperature, using electron beams from an accelerator ILU 6M (Budker-Institute of Nuclear Physics, Novosibirsk, Russia).

Were chosen the following absorbed doses: 12; 30; 60; 90; 120; 120; 150; 180 and 240 kGy. Unirradiated samples were investigated for control purposes.

Fig. 3.47 shows the TG, DTG and DTA curves of the initial polymeric material, in static air atmosphere, at a heating rate of 2.5 K.min⁻¹.

The thermo-oxidative degradation occurs through four main processes, noted as I, II, III and IV regions. The exothermic change I, evidenced by the DTA curve,

occurs without any detectable weight change in TG curve. The real modification consists of polymeric material thermo-oxidation that generates non-volatile products via peroxy radicals and hydroperoxides. In the investigated cases the corresponding increases of the samples weight were not detected because the change I is immediately followed by the change II in which some volatile compounds are generated. At higher temperatures, three thermo-oxidative degradations steps (II, III and IV) accompanied by volatile products generation occur.

The DTG peaks corresponding to the processes II and IV are well separated only for the unirradiated sample case. For each irradiated sample, the process IV is characterized in DTG curve by a "shoulder" of the main peak corresponding to process III.

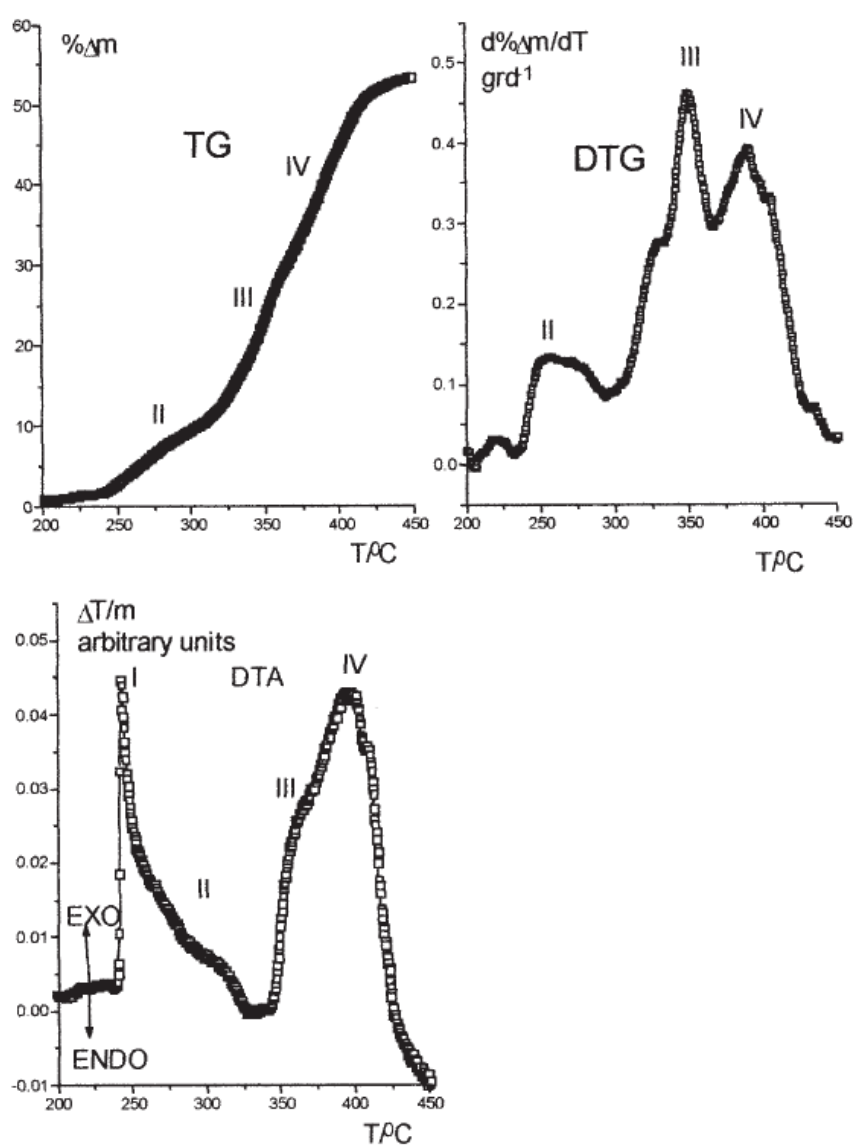


Figure 3.47 TG, DTG and DTA curves of the initial polymeric material, in static air atmosphere, at a heating rate of 2.5 K.min⁻¹.

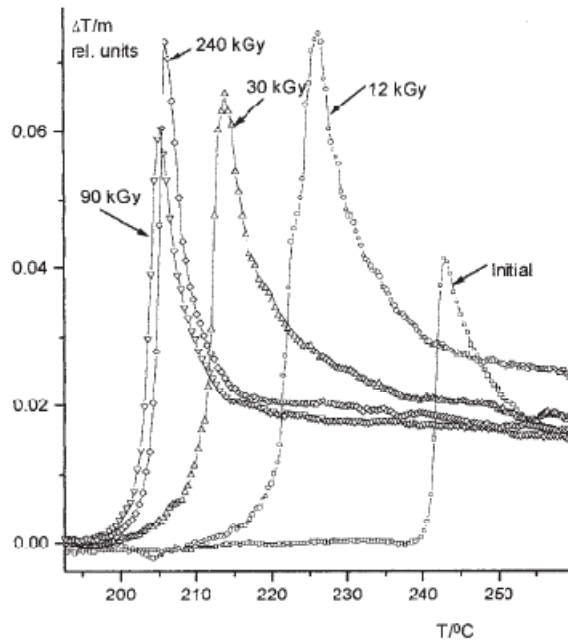


Figure 3.48 The DTA curves characteristic for the process I, for the initial and the irradiated samples

As observed in Figures 3.48 and 3.49, the irradiation of the EVA compound leads to the modifications of the following characteristic parameters:

- (a) the height of the DTA curve, which is proportional to the reaction rate;
- (b) the temperature of oxidation onset (OOT) and the temperature corresponding to the maximum of the DTA peak (T_{max}).

The minimum height of the DTA curve belongs to the initial sample, and both OOT and T_{max} display a sharp decrease over the dose range of 0 -60 kGy. If the dose exceeds 60 kGy, OOT and T_{max} are practically constant. Consequently, the main structural modifications of the material occur on the first 60 kGy.

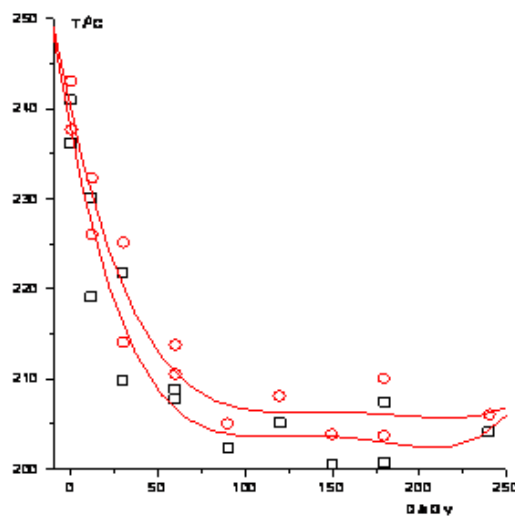


Figure 3.49 The changes in the characteristic temperatures of the process I: (□) OOT; (○) T_{max} with the irradiation dose for thermal oxidation of the EVA compound at a heating rate of 2.5 K.min⁻¹.

3.6 Rapid life-time estimation by thermal analysis

Considering that the thermal degradation of a polymeric material results from a single main chemical reaction, and the change of the critical material property is dependent on the degree of conversion (quasi-chemical approximation), Dakin [149, 150] derived the following kinetic equation:

$$-\frac{d\varepsilon}{dt} = Af(\varepsilon)\exp\left(-\frac{E}{RT}\right) \quad (3.11)$$

where ε is the critical property (mechanical property, electrical property, weight loss), $f(\varepsilon)$ is the differential function of degradation, A is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

If the activation parameters do not depend on ε , the integration of eqn. (3.11) leads to:

$$F(\varepsilon) = At \exp\left(-\frac{E}{RT}\right) \quad (3.12)$$

where: $F(\varepsilon) = -\int_{\varepsilon_0}^{\varepsilon} \frac{d\varepsilon}{f(\varepsilon)}$; ε_0 is the initial value of ε ; t is the time.

The logarithmic form of eqn. (3.12) is:

$$\ln t = a + \frac{b}{T} \quad (3.13)$$

where:

$$a = \ln F(\varepsilon) - \ln A \quad (3.14)$$

$$b = \frac{E}{R} \quad (3.15)$$

A polymeric material can be used until the relative value $\frac{\varepsilon_L}{\varepsilon_0}$ of the critical property decreases at a certain value, called end-point criterion, when $t = L = \text{thermal life-time}$.

Thus, according to eqn. (3.13):

$$\ln L = a_L + \frac{b}{T} \quad (3.16)$$

Equation (3.16) is the thermal life-time equation, and the corresponding straight line $\ln L$ vs. $(1/T)$, for a certain end-point criterion, is the thermal life-time line [151]. Through extrapolation of this straight line at the temperature of use, T_U , the thermal life-time is evaluated. In some cases [151], the thermal life-time of a polymeric material is abbreviated using the temperature index, TI, which is the temperature, in $^{\circ}\text{C}$, at which the end-point criterion is reached in 20000 h. From the equation (3.16), results the following formula for TI calculation:

$$TI = \frac{b}{-a_L + \ln 20000} - 273 \quad (3.17)$$

For a certain end-point criterion, it is also possible to use the following formula in order to calculate the life-time of the polymeric material:

$$\ln L_u = \ln L_a + b \left(\frac{1}{T_u} - \frac{1}{T_a} \right) \equiv \ln L_a + \frac{E}{R} \left(\frac{1}{T_u} - \frac{1}{T_a} \right) \quad (3.18)$$

where the subscripts u and a correspond to the aging value at the temperature of use and at the temperature of the accelerated aging, respectively. Thus, in order to determine the thermal life-time, L_a and E should be known.

The main assumption in the analytical test methods for the thermal life-time evaluation is that the activation energy of the degradation process can be derived in a short time using appropriate techniques. The thermal endurance line slope is given by an experimentally point, obtained from a conventional life test, corresponding to ≈ 300 h at the maximum admitted temperature for accelerated aging.

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