

Article

The Stability Consequences Promoted by Doping Metallic Atoms on the Degradation of Poly (ϵ -Caprolactone)

Traian Zaharescu ^{1,2,*} , Tunde Borbath ^{2,*}, Marius Mariş ^{3,*}, Istvan Borbath ² and Mihaela Mariş ⁴¹ INC DIE ICPE CA, Radiochemistry Center, 131 Splaiul Unirii, 030138 Bucharest, Romania² ROSEAL SA, 5A Nicolae Balcescu, Harghita District, 535600 Oorheiu Secuiesc, Romania³ Dental Medicine Faculty, University "Titu Maiorescu", 22 Dâmbovnicului Tineretului St., 040441 Bucharest, Romania⁴ Medicine and Pharmacy Faculty, University "Dunarea de Jos", 35 Al. I. Cuza, 800216 Galati, Romania

* Correspondence: traian.zaharescu@icpe-ca.ro (T.Z.); borbath.tunde@g-mail.com (T.B.);

marius@drmaris.ro (M.M.)

Abstract: The stability of polymer materials is essentially determined by the molecular structure and the presence of additives and impurities. When a polymer substrate is subjected to vigorous damage by an energetic treatment, the molecular scission generates fragments, which may be oxidized by the diffused oxygen. The traces of oxide catalysts that may be accidentally incorporated into the polymer materials initiate a faster oxidation that influences the material durability. This study presents the behavior of poly (ϵ -caprolactone) (PCL) loaded with 2 wt% PbZrO_3 previously doped with foreign atoms (Cr, Nd, Mg, Mn, Ti) at the concentration of 0.1 mol%. The investigation procedure, chemiluminescence, reveals the acceleration of the degradation of PCL. The contribution of the metallic traces existing in the structure of PbTiO_3 powder is characterized by the activation energies (E_a) involved in the propagation of oxidation. The free radicals are involved in a faster oxidation, when the polymer substrate is heated at superior rates. The comparison of the oxidation levels at the extended period of heating and irradiation indicates the sustained activities of metallic traces acting in oxide powder fillers, especially at temperatures exceeding 150 °C. The essential considerations on material strength against oxidation are presented.

Keywords: oxidative degradation; poly (ϵ -caprolactone); chemiluminescence; γ -irradiation



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1. Introduction

The durability of any polymer material is determined by the molecular configuration and the existence of various compounds that are accidentally or permanently present in the material composition. The progress of oxidative degradation depends on the chemical nature of these components, even though the concentration is at the trace level. This is the situation of oxide catalysts, whose existence brings about the progressive oxidation [1]. The pro-oxidant contributions of organic compounds are often characterized [2,3] in the degradation of polymer materials, but the effects of oxide traces were never analyzed. On the other side, the damaging activities of antioxidants were seldom reported [4,5] in spite of the protective actions of this category of compounds [6,7]. The detailed aspects of stabilization related to the low concentration of metallic atoms were not published, because the doped fillers were not taken into consideration. This is a novelty approach to material ageing starting from the manufacturing stage.

While the main targets of additives are related to the improvement in polymer stabilities [8,9], inorganic structures may promote the efficient protection of polymer substrates [10]. The consequence of the interaction between the host polymer and filler is strongly influenced by the degradation mechanism, by which the scission fragments are converted into oxygen-containing structures. Accordingly, our previous investigations on the effects of oxides on the stability of polymers reveal an improved strength during

thermal and radiation degradation [11]. The protective activity of the doped inorganic structures is ascribed to the electronic interaction between the traps with electron deficit placed on the particle surface and the free radicals that possess an unpaired available electron. This behavior is valid for the polymers degrading by the Boland and Gee mechanism [12]. The free radicals appearing by the scission of polymer macromolecular chains are subjected to oxidation via hydroperoxides [13]. The different behavior under oxidation is shown by the macromolecules degraded by the various reactions of splitting fragments, depolymerization in the case of poly (lactic acid) [14], or hydrogen abstraction on α -carbons in the case of poly (ϵ -caprolactone) [15]. The chemiluminescence investigation method, which may discriminate the oxidation behavior of these classes of polymers (Figure 1), is a proper tool for the qualification of the material response to the oxidative degradation.

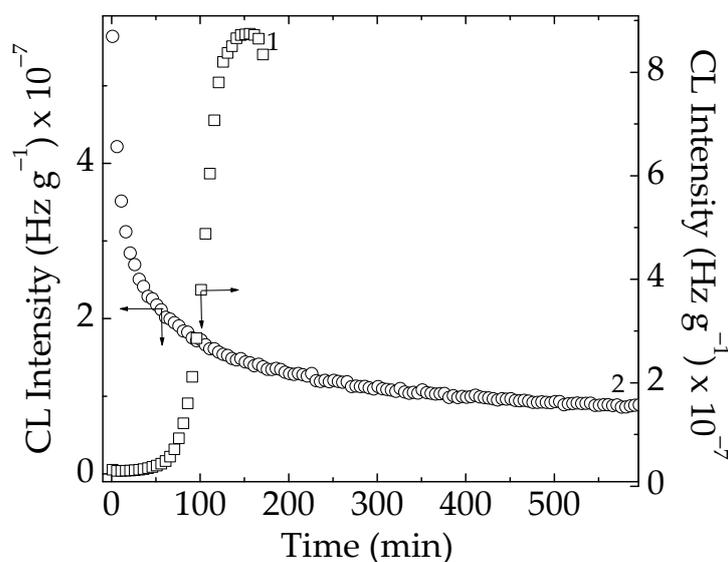


Figure 1. The isothermal chemiluminescence spectra recorded on two polymers with different degradation mechanisms. (1) Styrene–isoprene–styrene block copolymer (SIS); (2) poly (lactic acid) (PLA).

The stability of polymer matrices is an essential feature that characterizes the product life, and the items operate in hard conditions described by the action of heating, photo-exposure, electrical field, and ionizing radiation. The investigations into the evolution of oxidation indicate the appropriate operation regimes, where the materials may function under high warranty parameters. The pro-oxidant effects are often discarded when the commercial reasons have a certain priority.

The degree of stability is not only correlated with the molecular structure, but it is also influenced by the applied technologies that define the property ranges and the resistance against oxidation [16]. The ranking of polymers by thermal characteristics takes into consideration all features that converge onto the stability requirements inside the ranges of presumable applications. The pristine materials are usually modified with proper compounds like antioxidants, softeners, crosslinking, or grafting agents. They effectively screen the negative effects of catalyst traces and extend the material durability according to the interaction strengths.

The trace nature raises the problem of how deeply they influence the material failure. The uncontrollable levels of oxide traces impose the evaluation of oxidability for each technology by statistical determination of product stability. In spite of it being impossible to eliminate the action of metallic traces, their effects can be easily quantified for the determination of the stability periods in relation to the thermal regimes of applications.

The stability of polymers with respect to the presence of metals in direct contact was reported previously [17]. The evidence of the initiation of oxidation is provided for several polyolefins. The kinetic parameters that describe the acceleration of oxidative

degradation for the contributions of metals on the damaging promotion in polymers characterize the influence of metallic atoms in the intimate contact with polymer surfaces. The catalytic activities of metals included in polymer materials were reported [18,19], where the oxidation activators are the degradation factors in macromolecular materials. Other types of investigations into the role of metallic compounds upon the stability of polymers by their inclusion into the matrix as fillers were reported for the certification of their ageing effects on polymer composites [20]. Unfortunately, the amounts of these compounds are far from trace amounts, as in polymer materials manufactured by means of catalysts.

The present investigation presents the influence of traps existing naturally in the inorganic fillers that may play the role of scavenging spots with respect to the free radicals. This work provides evidence for the action of metallic traces existing in the polymer materials manufactured by means of catalysts. Their effects on the progress of oxidative degradation are analyzed and the consequences on the material durabilities are discussed. Unfortunately, the investigation into the effects of all metallic materials that are components of catalysts is impossible to achieve. Our experimental results provide examples for any other researchers that want to drill deeply into this subject as an area of interest.

This paper presents the results of chemiluminescence investigation achieved on the basic polymer, styrene–isoprene–styrene (SIS), modified with PbTiO₃ loaded with traces of metallic oxides. The differences between the thermal behaviors of SIS hybrids reflect the different contributions of metals that doped the lattice of titanate. This polymer may be considered as an example for any other materials that follow a similar mechanism of degradation. In addition, the present results illustrate the reason for the differences that exist between various sorts of the same material.

2. Materials and Methods

Poly (ϵ -caprolactone) was manufactured by Sigma Aldrich (Saint Louis, MO, USA), as a polymer material with average $M_w \sim 14,000 \text{ g mol}^{-1}$ and average $M_n \sim 10 \text{ kDa}$. It was used as received. The pristine powder of lead zirconate was provided by Sigma Aldrich (purity > 95%) and was terminally treated together with some oxides (Cr₂O₃, Nd₂O₃, MgO, MnO₂ and TiO₂), whose loading in the neat zirconate was 0.1 mol%. They were heated at 1150 °C for 2 h. The resulting materials were individually milled to an average size of 100 μm . These inorganic components were added to the polymer mother solution (solvent CHCl₃) at the appropriate amounts. From these new solutions, aliquots of 50 μL were transferred into aluminum caps. These samples were evaporated at room temperature, when thin films were obtained. The dried samples were placed in a desiccator, where keeping their weights and structures constant. The elimination of solvent does not affect any molecular changes, because it does not carry any volatile component and does not interfere between the polymer substrate and surface of additional filler particles. This procedure is appropriate for our investigation, because it allows the fast preparation of samples without the action of any damaging factor [21].

The γ -exposure of the pans containing dried films was accomplished in an irradiation machinery (Ob Servo Sanguis, Budapest, Hungary), where the samples received 25 or 100 kGy of γ -dose. This value of 100 kGy was selected for the illustration of the medium treatment condition applied in radiation processing of polymers, while 25 kGy is the characteristic dose for radiation sterilization.

The thermal stability of patterns was characterized by isothermal and nonisothermal chemiluminescence (CL) methods [22]. The isothermal CL measurements were conducted at 140 °C, while nonisothermal CL assays of nonirradiated samples were carried out at four heating rates (5, 10, 15 and 20 °C min⁻¹) and at 10 °C min⁻¹ for all other irradiated specimens. These measurements provide characteristic chemiluminescence spectra from which the kinetic parameters were obtained. The values of activation energies required for the oxidative degradation of studied systems were calculated by the application of Kissinger procedure [23].

3. Results

The evolution of oxidative degradation in poly (ϵ -caprolactone), PCL, occurs by the random chain scission following the breaking probability according to the bond energy values (Table 1).

Table 1. The energies involved in the PCL chains [24].

Bond	Energy (kJ mol ⁻¹)
C-H	413
C-C	348
C-O	358
C=O	799

The scission event with the highest probability is the splitting C-C bond places in the neighborhood of an oxygen atom existing in the molecular chain from the initial monomer. The further process in the oxygen attack creates either hydroperoxyl intermediates or alkoxide on the chain end [15]. A previous FTIR study on the thermal degradation of PCL by pyrolysis at high temperatures reports the scission of PCL chains on the α -position with respect to ester moieties [25].

3.1. Isothermal Chemiluminescence Assay

The chemiluminescence procedure is an accurate method by which the initiation, progress, and termination can be evaluated. It follows the progress of oxidative degradation, when the intermediates, peroxy radicals, are formed and decayed simultaneously. The measurement of emitted photons shows the evolution of conversion that occurred during the achievement of material deterioration. The isothermal investigation is an appropriate way through which evolution to the oxidation state is achieved when the materials are subjected to an accelerated process of oxidation.

The different oxidation rates that can be observed from the isothermal CL spectra (Figure 2) illustrate the discrepancies that characterize the pro-oxidant effects of studied filler structures. The steady states are reached after several hundreds of minutes, when the major fractions of molecular fragments are completely oxidized and the light of the photon emission increases following the depletion of reactive radicals.

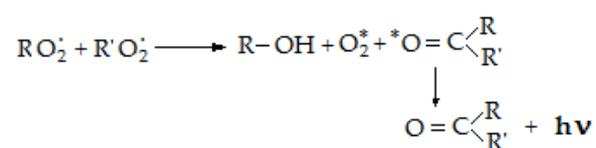


Figure 2. The principle scheme for the chemiluminescence emission in oxidizing polymers.

The sharp decrease in emission confirms the greater proportion of radicals that end with carbon atoms compared with the intermediates having oxygen atoms at their head. The consumption of free radicals transformed in hydroperoxides occurs over the first 20 min, but the accumulation of ketones (Figure 3), the photon emitters, progresses very slowly.

The contribution of doped PbZrO₃ develops differently for each doping atom and, consequently, the degradation proceeds.

As may be noticed from Figure 4, the pristine PCL with neat PbZrO₃ shows the smallest intensity values either at the beginning or at the end of measurement, in contrast with similar compositions in the presence of doped zirconate, whose particle surfaces are modified by foreign metallic atoms. They change the superficial electron densities, causing differences in the interaction strengths.

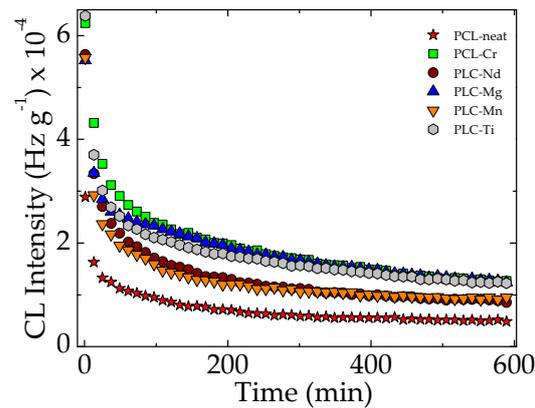


Figure 3. The isothermal CL spectra recorded on the pristine PCL-based samples containing PbZrO_3 doped with various metallic atoms. Testing temperature: 140°C .

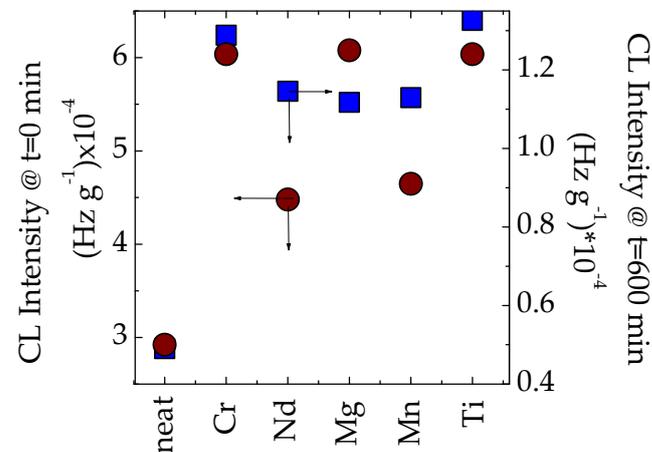


Figure 4. The CL intensities recorded at the starts and the ends of isothermal measurements on unirradiated PbZrO_3 doped with various metallic atoms. The degradation time is expressed in minutes. Testing temperature: 140°C .

The progress of degradation is effectively accelerated more or less by the doping atoms, which represent the reaction centers for the propagation of oxidation. The direct effect of radiation processing is the increase in defect numbers, which will enhance the probability of interactions with oxidation consequences. On the particle surface, the closing fragments are trapped with a certain strength. This scavenging action is controlled by the local density of electrons on the inorganic particle surface, when the availability of electrons of free radicals is the attraction reason for the charge carriers. The trap depth that characterizes the interaction amplitude is roughly evaluated at the values of 1 eV [26], much smaller than the energy of a covalent bond, but enough strong to catch free radicals.

The γ -exposure of PCL-based hybrids does not modify the curve shapes (Figure 5), but the CL intensities obtained for long-term oxidation are closer to each other. The activity of magnesium atoms is substantial. This concern is related to the degrees of degradation, which is reflected in the fluence of photon emission.

Figure 6 illustrates the differences between the degradation effects caused by the unlike contribution levels on the PCL products when they have metallic traces incorporated into the polymer matrices. The pro-oxidant character is also present in the irradiated polymer, because the particle lattices are not damaged by the incidental high energy radiation.

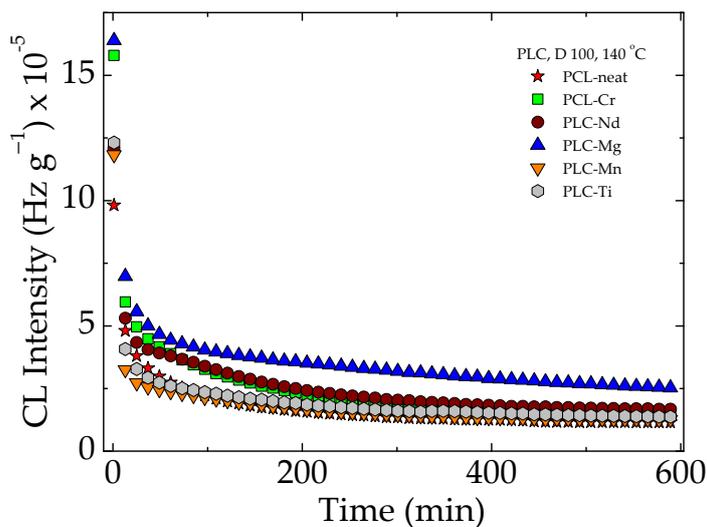


Figure 5. The isothermal CL spectra recorded on the pristine PCL-based samples containing PbZrO_3 doped with various metallic atoms after receiving a γ -dose of 100 kGy. Testing temperature: 140 °C.

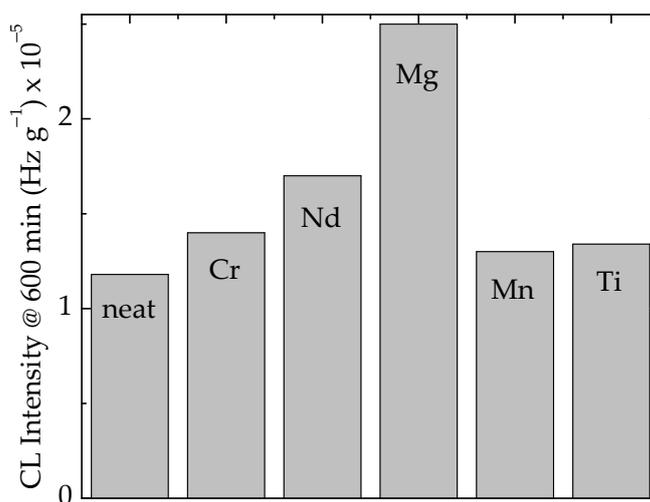


Figure 6. The CL intensities obtained at the ends of isothermal measurements on PbZrO_3 doped with various metallic atoms after the γ -irradiation of samples by an exposure of 100 kGy. Testing temperature: 140 °C.

3.2. Nonisothermal Chemiluminescence Assay

The evolution of oxidation as the temperature increases (nonisothermal determinations, Figure 7) advances differently, when the heating rate increases. The PCL substrate containing non-doped filler is oxidized more easily. This characteristic feature sustains the basic idea that the presence of doped oxides would be an appropriate solution for an improvement in the stability of polymer materials without classical antioxidants, either synthesis or natural protectors, for a lower temperature usage.

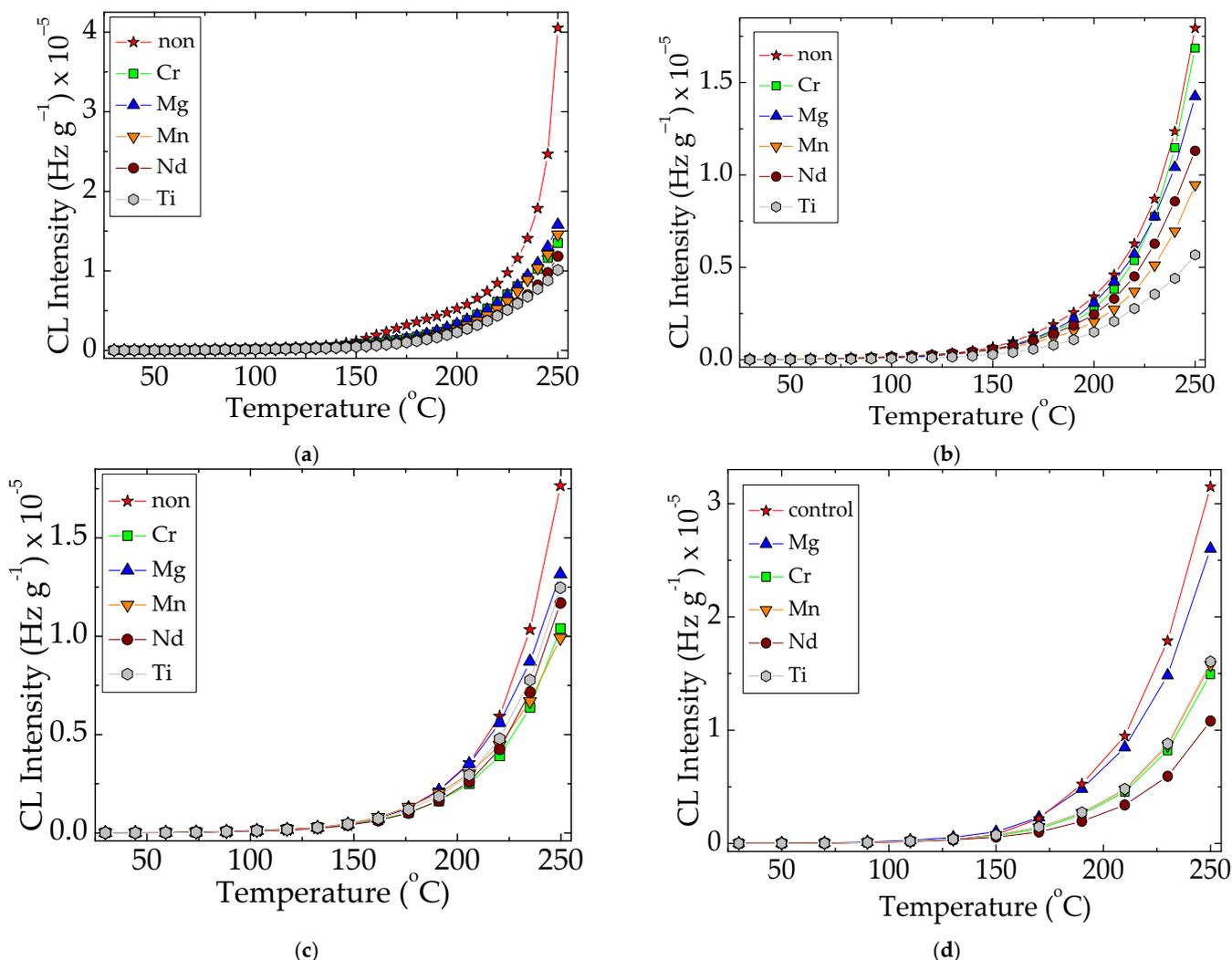


Figure 7. Nonisothermal CL spectra recorded on the PCL samples containing PbZrO_3 doped with various metallic atoms at different heating rates: (a) $5\text{ }^\circ\text{C min}^{-1}$, (b) $10\text{ }^\circ\text{C min}^{-1}$, (c) $15\text{ }^\circ\text{C min}^{-1}$, and (d) $20\text{ }^\circ\text{C min}^{-1}$.

The exposure of PCL samples containing doped inorganic oxide filler to γ -radiation reveals the radiolysis effect of degradation on the organic component. The oxidation peak at $120\text{ }^\circ\text{C}$ is absent in pristine polymers, and a whole broad maximum appears in the CL spectra recorded on the samples subjected to an irradiation dose of 25 kGy (Figure 8). It is somewhat strange that this peak is not present in the spectra or irradiated samples at 100 kGy , a severe level of exposure for this relatively unstable polymer. It may be supposed that the slowing down effect of fillers becomes effective when the concentration of degradation intermediates is sufficiently high. At the higher dose (100 kGy), the difference between pristine PCL and PCL modified with doped oxide is large enough that it concerns the proper activities of doped PbZrO_3 . The nature of the dopant is essential for the development of oxidation. The irradiated PCL samples modified with doped inorganic filler show similar profiles, but the ascendant parts start on different temperatures. The longer irradiation processing (100 kGy), regarding the advanced fragmentation, initiates an early oxidation even at lower temperatures ($75\text{ }^\circ\text{C}$), but the increase in CL intensities that demonstrates the thermal resistance during degradation grows smoothly near $150\text{ }^\circ\text{C}$. This behavior may be a good feature for the PCL-based products that are subjected to sustained energy transfers during their sunlight photodegradation.

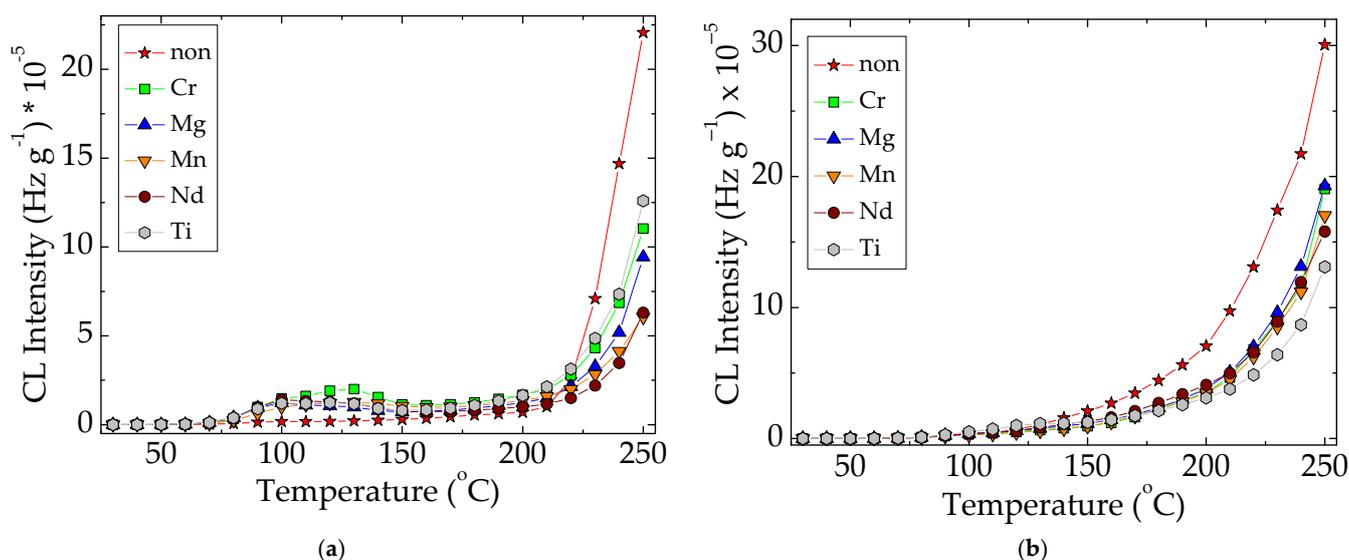


Figure 8. Nonisothermal CL spectra recorded on the PCL samples containing PbZrO_3 doped with various metallic atoms γ -irradiated at (a) 25 kGy and (b) 100 kGy. Heating rate: $10^\circ\text{C min}^{-1}$.

In Table 2, the values of onset oxidation temperatures (OOTs) allow the calculation, with good accuracy of the thresholds of energetic limitation involved in degradation, of the values of activation energies. In spite of the lower positions of nonisothermal CL curves with respect to pristine material, the E_a values are inferior in comparison with the corresponding figure of neat polymer material.

Table 2. Activation energy values of the degradation of PCL PbZrO_3 samples loaded with various metallic atoms.

Doping Atoms	OOT ($^\circ\text{C}$)				Correlation Factor	Activation Energy (kJ mol^{-1})
	5°C min^{-1}	$10^\circ\text{C min}^{-1}$	$15^\circ\text{C min}^{-1}$	$20^\circ\text{C min}^{-1}$		
Dose 0 kGy						
none	201	212	225	230	0.98832	82
Cr	195	208	220	232	0.98423	65
Nd	194	203	215	231	0.98423	62
Mg	192	199	210	224	0.95331	70
Mn	198	210	226	235	0.98115	63
Ti	195	209	222	229	0.99539	70
Dose 100 kGy						
none	190	210	215	223	0.98591	72
Cr	190	202	215	229	0.97172	60
Nd	183	190	208	220	0.93735	56
Mg	186	210	218	225	0.98663	58
Mn	183	190	205	220	0.92973	57
Ti	180	195	210	218	0.99339	58

The detailed analysis of these results reveals the correlation between the accumulation of carbonyl intermediates and the activity upon the early scavenging of free radicals [27] on the surface of filler particles, where the traps are organized.

4. Discussion

The progress of degradation is assured by the conversion of hydroperoxides into oxygen-containing stable structures [13], which represents the propagation step of degradation. This consideration leads us to assume that the inorganic filler scavenges hydroper-

oxides rather than the free radicals ended by carbon atoms. This assessment may be supported by the electronic interactions between the trapping defects existing on the surface of filler particles.

The oxidative degradation mechanisms of various polymers influence the activities of superficial traps. In a previous paper describing the effects of doped lead titanate [28], the clear stabilization activity of doping metals was demonstrated. Starting from the mechanistic considerations, it can be stated that the chain sequence initiated by the scission followed by the oxidation reactions of hydrocarbon intermediates is efficiently broken by the lattice traps existing on the surface of particles. In contrast, when the degradation takes place through the fragmentation of macromolecules followed by the molecular rearrangements, as occurs in poly (lactic acid), PLA, or ϵ -polycaprolactone (PCL), these traps have catalyst activity causing oxidation. The combination of intermediates on the traps of dopant atoms eliminates the protection barrier. The conversion of free radicals provided by the thermal decomposition of PCL [29] into final degradation products is conducted by the positioning of the unpaired electron on the breaking macromolecules. However, from Table 1, it may be noticed that the bonds with the most susceptible probability of scission are C–C and C–O. Accordingly, the proposed mechanism for the radiochemical degradation of PCL is presented in Figure 9.

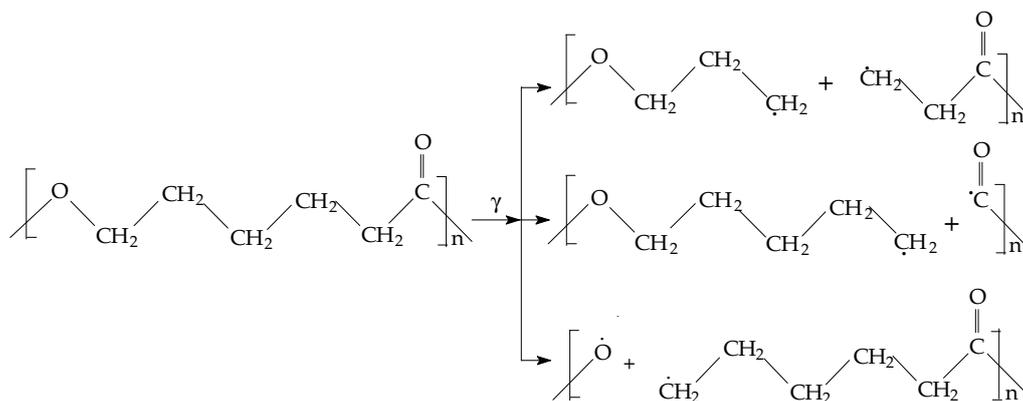


Figure 9. The proposed methods for the formation of free radicals by γ -irradiation.

As can be noticed, a great proportion of radicals have the unpaired electron near oxygen atoms, the electronegative element. This condition influences the electron availability to fill the trap, such that these entities do not entirely fill the electron trap. Therefore, a large part of the fragments remain unlinked by the particles and may become available for oxidation. Furthermore, the stabilization function is not fulfilled and, consequently, the degradation progresses.

The explanation for the lack of improvement in stability is correlated with the degradation of poly (ϵ -caprolactone) [30,31]. According to the fragmentation process that occurs when degrading PCL [15], the decrease in molecular weight is promoted by the scission of high energy transfer and the radicals cannot be associated with the particle surface, because they are decayed into superoxide radicals [24] by oxidation before being cached.

The exposure of PCL to the action of ionizing radiation conducts polymer to higher crosslinking degrees [32], when the free radicals are generated during γ -irradiation. The assumed mechanism involves the intermediates with unpaired electrons, which may delay this curing through their blocking on the surface of the particles of the doping spots, thus the local concentration is diminished and the crosslinking probability declines. This behavior is confirmed by the results presented in Figure 4, where the CL intensities for the unmodified PCL maintain the lowest values. The radical traps that act on the particle surface have different scavenging activities, which place the CL emission intensities on various levels of oxidation. When the oxidation reached the steady state, the lowest intensity was measured for pristine material. The composition including PbZrO_3 doped with magnesium atoms

(Figure 6) shows the most advanced degradation, which indicates the lowest resistance against oxidation.

Starting from the EPR (electron paramagnetic resonance) studies of the radiation effects on PCL [33], the free radicals (hydroperoxyl, hydroxyl, or carbonyl structures) formed during the radiolysis of PCL undergo conversions into oxidation-stable products even at $-79\text{ }^{\circ}\text{C}$, if the populations of radicals are somewhat increased or if they are spread after their early formation at $120\text{ }^{\circ}\text{C}$ (Figure 8a). For the extrapolation of these circumstances to any other concern, the progress in the degradation of PCL/PbZrO₃ doped with various metallic atoms is also related to the loss of crystallinity accompanied by the sharp fragmentation [34], allowing easier penetration of oxygen.

The most plausible arguments for the pro-oxidant effects of PbZrO₃ containing trace concentrations of various metallic atoms are the values of activation energies (Table 2). The significant decrease demonstrates the indirect effect of radical scavenging, which changes the fates of radicals from stabilization to oxidation. It is possible to initiate oxidation by withdrawing a fraction of radicals with an immediate consequence on the diminution of recombination.

During the degradation of PCL materials, the fillers are the inactivation blending component for the promotion of stabilization. If the PCL hybrid materials are subjected to a sustained scission process, as occurs during γ -treatment, the contribution of doped PbZrO₃ hinders the progress of crosslinking through their expected catching on the inorganic particle surface.

5. Conclusions

This study presents the promotion of oxidation in PCL substrates containing PbZrO₃ doped with various metallic atoms, when the polymer matrix is subjected to oxidative ageing. The γ -exposure, which is a proper procedure to cause molecular scissions in the polymer component, initiates oxidative degradation. The rates of oxidation depend on the nature of the dopant, whose catching activity differs from one type of atom to another. The chemiluminescence spectra demonstrate the concern of the defects in the doped inorganic materials by trapping free radicals from their recombination. In opposition to polyolefins, where these structures offer an increase in the stability level during degradation, PCL gains a higher oxidation rate. The traces of metallic atoms are not real promoters of oxidation through their catalytic contribution, but they become blocking agents whose scavenging surface is the essential factor for the extension of oxidative degradation.

This study intends to indicate the effect of metallic traces that remain after the manufacturing of several polymer materials. They act as oxidation initiators, which shorten the lifetime of products. The addition of a foreign atom into a crystalline lattice generates the formation of traps, which determine a modification in the electron distribution. A related consequence is the possibility to scavenge free radicals that have an unpaired electron. This process takes place on the particle surface, where the oxygen molecules can be easily associated. Accordingly, oxidation is promoted, depending on the electron density, the valence, and the radius of the interstitial atom, which disturbs the local electron density. The degradation rates are different from one atom to another, because the joint strength is based on the difference between the valence band of the doping atom and the conduction band of the crystal. Because the degradation intensity depends on the nature and level of impurity contents, the stability characterization must take into account the history of material and the storage/handling conditions.

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Abbreviations

CL	chemiluminescence
EPR	electron paramagnetic resonance
FTIR	infrared spectroscopy
OOT	onset oxidation temperature
PCL	poly (ϵ -caprolactone)
PLA	poly (lactic acid)
SIS	styrene–isoprene–styrene triblock copolymer

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