UNIVERSITATY **POLITEHNICA** OF BUCHAREST

Faculty of Chemical Engineering and Biotechnologies

Doctoral School of Chemical Engineering and Biotechnologies

Senate Decision No. _____/ _____

ABSTRACT

DOCTORAL THESIS

RADIOPROCESSING OF POLYMERIC MATERIALS

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Supervisor: Prof. dr. eng. Horia IOVU

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Bucharest, 2023

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Key words:

radioprocessing, nanocomposites, stability, radiosterilization, radiochemical recycling, packaging

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CHAPTER 1. OBJECTIVES AND ELEMENTS OF ORIGINALITY OF THE DOCTORAL THESIS

1.1. Aim and objectives of the PhD thesis

Aiming to enhance the benefits of polymer processing technologies using γ-irradiation, the experimental studies upon which this thesis is based are aimed to develop new polymeric materials with improved properties for special applications. In this respect, **the overall puprose** is to obtain novel polymeric and composite materials based on PLA biopolymer and EPDM synthetic polymer, with specific characteristics and performances that are suitable for applications including food, pharmaceutical, cosmetic and medical packaging, radioprocessing, space and nuclear applications, as well as waste elastomer recycling. A modern, efficient and versatile processing technique of exposing macromolecular compounds to γ-radiation has been used to develop the materials.

The **specific objectives** of the thesis are described below:

- Safe implementation of modern and efficient technologies for obtaining and processing new composite and polymeric materials with ionising radiation, with characteristics and features appropriate to the targeted applications;
- Assessment of physico-chemical changes induced by γ-radiation in complex, multicomponent polymeric systems;
- Identification of the interaction mode under γ-irradiation of the component materials in the studied polymeric compositions, in order to extend the applications in the field of industrial radioprocessing of macromolecular compounds;
- Functionality characterization and performance evaluation of the materials obtained by determining thermal and radiation stability, mechanical strength, water vapour transmission rate, gel fraction, as well as physicochemical and morphological properties;
- Kinetic study of oxidation reactions and determination of resistance to oxidative ageing of polymeric materials under the action of stress factors such as thermal energy and gamma irradiation;

- Improving the thermal and radiation stability of PLA/SIS blends and EPDM-based blends for packaging and radiosterilisation applications;
- Extending the durability and functional limits of materials investigated under accelerated degradation conditions to produce durable products for space applications and those requiring radiosterilisation or increased wear resistance;
- Integrating biodegradable materials such as PLA biopolymer and natural additives (caffeic acid, vanillic acid, gallic acid, rosmarinic acid) into the studied formulations for packaging and medical applications for supporting eco-industrial development;
- Evaluating the efficacy of stabilising compounds as antioxidants, nano-fillers and functional additives by analysing their contribution to the stability of the studied formulations and systems using advanced chemiluminescence technique;
- Developing an optimal γ-ray processing technology for EPDM/TMPTA systems to extend EPDM applications in space or nuclear fields;
- Evaluation of the radiochemical recycling potential of waste elastomers exemplified by the EPDM/IIR system.

1.2. Structure of the PhD thesis

The doctoral thesis, "RADIOPROCESSING OF POLYMERIC MATERIALS" is structured in four main chapters (parts):

- **Chapter 1** of the doctoral thesis, entitled *"Objectives and elements of originality of the doctoral thesis"* presents the general aim of the thesis in accordance with the main objectives followed in the experimental research focusing on extending the applications of the radioprocessing technique in the field of polymeric materials.
- **Chapter 2** of the paper, *"The state of the art in radioprocessing of macromolecular compounds"* is divided into three subchapters. The first sub-chapter presents recent information on the importance in the development of polymeric and composite materials with special applications, with reference to PLA biopolymer and synthetic polymer based materials, EPDM, but also significant aspects on strategies to improve or modify their functional properties, and therefore their quality and performance, by combining processing and compounding techniques, leading to diversifying and improving applications in the field of special polymeric materials with important pre-economic benefits. The second sub-chapter describes various aspects of radiochemical modifications

produced in polymeric materials, including presentation of irradiation technologies and the advantages of γ-irradiation processing, detailed explanation and identification of competitive and antagonistic radiolytic effects induced by γ-irradiation in polymeric materials, and presentation of the state-of-the-art of radioprocessing applications. Highlighting the importance of the processing technique of macromolecular compounds upon their stability, the third sub-chapter focuses on describing the possibilities of polymeric materials stabilization under accelerated degradation conditions and describes the techniques for thermal and radiation stability optimization according to the applications proposed in the experimental study.

- **Chapter 3** entitled *"Original contributions"* is devoted to own original research and is structured in six sub-chapters, covering three main research directions involving the development of novel polymeric and composite materials designed for the use in: a) the packaging industry, b) the space or nuclear industry and c) the recycling of polymeric products. The chapter includes the objectives, methodology, investigation techniques used, experimental results obtained, discussions regarding the data obtained and conclusions for each of the six experimental studies:
  1. Thermal qualification study of PLA/SIS-based blends for packaging and medical applications
  2. Contribution of stabilizers agents on the availability of PLA/SIS blends for packaging and medical applications
  3. Thermal and radiation stability study of PLA/SIS-based polymer nanocomposites reinforced with silica nanoparticles
  4. Contribution of ecological oxidation protectors in the stability of EPDM-based packaging materials
  5. Improvement of thermal stability of EPDM by radiation crosslinking for space applications
  6. Degradability characterization of EPDM/IIR blends by γ-irradiation

The study “Contribution of ecological oxidation protectors in the stability of EPDM-based packaging materials and the „Thermal and radiation stability study of PLA/SIS-based polymer nanocomposites reinforced with silica nanoparticles” aim to improve PLA/SIS-based polymer blends, obtained in the first study, for packaging and medical applications, using a novel

processing technique, consisting of additivation of the blends with stabilising compounds and nanofillers, followed by the fabrication of composite or nanocomposite materials by radioprocessing. All four studies are focused on the enhancement of biodegradable or environmentally friendly materials, either by using PLA biopolymer or by using natural antioxidants such as rosmarinic acid, gallic acid, vanillic acid and caffeic acid as additives, which have high *anti-radical* efficacy, and which meet the requirements of ensuring public health and safety by fulfilling restrictive environmental regulations.

Chapter 4, *"General conclusions and perspectives for further research"*, presents the main conclusions of the theoretical and experimental studies, including perspectives for further research related to the development of new polymeric and composite materials by radioprocessing technique with targeted properties for special applications.

1.3. Elements of originality of the PhD thesis

The elements of originality of the doctoral thesis consist of:

- Approaching complex polymer blends/systems that have not been previously studied in the literature;
- Approaching an innovative strategy to optimise the thermal and radiation stability of newly obtained polymeric and composite materials;
- Integrating biodegradable materials in applications requiring long-term durability or high oxidation resistance under intensive stress conditions (radiosterilisation, packaging applications);
- Proposing a novel technology for γ-irradiation processing of EPDM-based materials for space and nuclear applications;
- Proposing advantageous alternatives for radiochemical recycling of EPDM and IIR (butyl rubber) elastomer waste.

CHAPTER 2. THE STATE OF THE ART IN RADIOPROCESSING OF MACROMOLECULAR COMPOUNDS

2.1. The importance of developing polymer and composite materials with special applications

2.1.1. Polymers and composites used in special applications

The polymer and composite materials industry is a key area of industrial development requiring constant innovation to the continuously changing market demands.

2.1.1.1. Polymeric and composite materials based on polylactic acid

2.1.1.2. Polymeric and composite materials based on ethylene-propylene-diene terpolymer

2.1.2. Obtaining and processing materials in relation to their final properties

Materials processing techniques allow the properties of macromolecular compounds to be varied in order to extend their current applications or to achieve a new target application.

2.2. Relevant aspects of radiochemical modifications induced in polymeric materials

2.2.1. Irradiation technologies and the advantages of γ radioprocessing

In the past decades, the exploitation of the industrial γ-irradiation process to obtain new characteristics and features, specific and targeted to commercial applications for regular or special use, has gained a major interest.

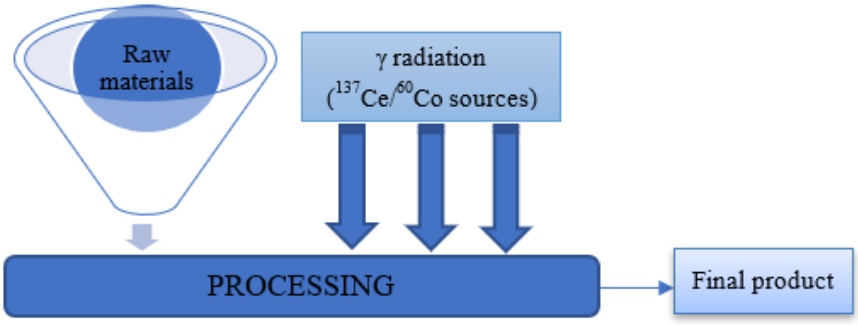


Figure 2.3. Simplified representation of the steps in the radioprocessing of polymeric materials

Among many technical and economic advantages of radioprocessing are its low environmental impact, effectiveness, precise control of processing parameters, versatility in terms of changes in materials and exposure conditions, diversity of application areas and last but not least, the ease of achieving pre-defined functionality characteristics.

2.2.2. Effects induced by γ-ray irradiation in polymeric materials

The study of the effects of γ-ionising radiation on polymers has become an area of great interest, especially because of the significant changes it produces on the structure and physicochemical as well as biological properties of polymers. These changes are mostly due to the large difference between the energy transferred to the material and the bond energy that characterizes the stability of the compound (Zaharescu and Jipa, 2013a; Zaharescu and Podină, 2003).

During γ-ray irradiation, the material gains a significant amount of energy per unit time and mass which is absorbed by the most vulnerable positions (quaternary carbon atoms, π-bonds, etc.), leading to the formation of free radicals. Thus, following the interaction of high-energy radiation with polymeric materials, two antagonistic processes take place simultaneously at relatively different rates, i.e. degradation and crosslinking, where free radicals are the initiation centres for the changes induced in the macromolecular compound. Radiooxidative degradation causes irreversible loss of functional characteristics and shortening of life time, while radiocrosslinking produces favourable changes.

In order to understand the radiolytic effects found in polymeric materials, it is necessary to have a detailed understanding of the chemical mechanisms of modification as well as the stabilisation or degradation processes.

Overall, the consequences of γ-irradiation on materials can be considered as a sum of the simultaneous and concurrent scission and crosslinking effects occurring during exposure.

2.2.2.1. Radiooxidative degradation of polymers

2.2.2.2. Radiation crosslinking of polymeric materials

2.2.2.3. The main factors influencing the degradation/crosslinking ratio

The ratio between the degradation and crosslinking process is strongly influenced by a series of factors such as the molecular structure and nature of the polymer, the absorbed irradiation dose, exposure time, dose rate and other irradiation conditions.

2.2.2.4. Influence of scission and crosslinking competitive effects on the functional properties of polymeric materials

The molecular modifications induced by competitive cleavage and crosslinking effects change the functional properties of polymers, leading to changes in the thermal behaviour and mechanical or electrical properties of the polymeric materials.

2.2.2.5. Radiochemical yield of scission and crosslinking

It is very important to know the formation yields for the radiolysis products of polymers as a result of the chemical structure involved.

The present doctoral thesis has a complex character, the experimental studies carried out following radiochemical changes in multicomponent polymeric systems, including constituents with antagonistic tendencies under γ-irradiation, for crosslinking or degradation.

2.2.3. Applications of radioprocessing

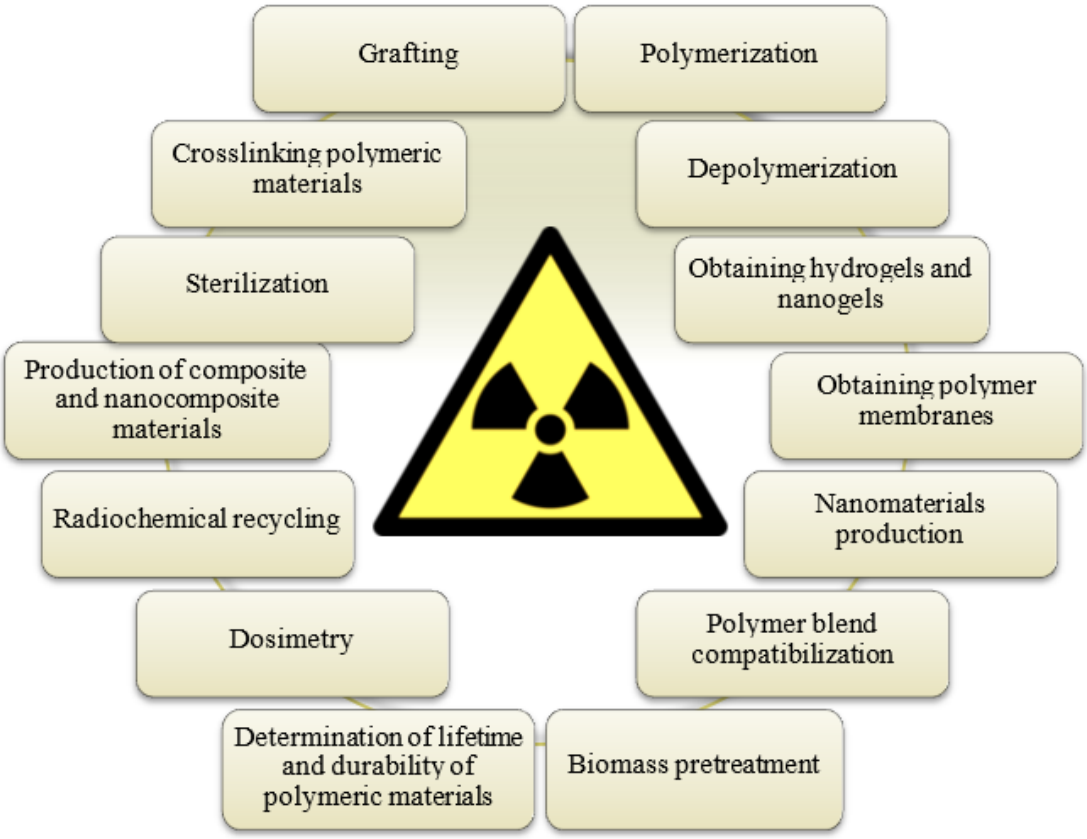


Figure 2.11. Applications of ionizing radiation in materials processing (Zaharescu, 1999 ; Lungulescu, 2014; Zaharescu și Jipa, 2013a; Zaharescu și Jipa, 2013b; Przybytniak, 2017; Torun, 2017; Lungulescu et al., 2018; Kornacka, 201 ; Spadaro et al., 2017; Silvestre et al., 2017; Sonnier et al., 2017)

2.2.3.1. Applications of irradiation technology in product packaging

2.2.3.2. Industrial applications based on the γ-irradiation crosslinking process

2.2.3.3. Applications based on the degradation process

2.2.3.4. Other applications of radioprocessing

2.3. Stabilisation of polymeric materials to radio-oxidative degradation

Durability of material represents a major issue in many areas of applications.

The strategy adopted for increasing the stability of radiochemically processed materials involves controlling the overall degradation rate generated by the diffusion of oxygen into the material. The strategy is based on the mechanism of decreasing the competition between degradation and crosslinking in favour of crosslinking. Thus, the oxidation rate and the amount of free radicals can be varied in three different and complementary ways (Zaharescu et al., 2016a) which include:

- Obtaining crosslinked polymer blends under gamma irradiation; (Abdel-Hakim et al., 2019; Nagasawa et al., 2011; Blanco et al., 2017);
- Additivation of polymers with stabilizing compounds; (Boersma, 2006; Jeon et al., 2007; Kirschweng et al., 2017b; Rivaton et al., 2006; Zaharescu et al., 2019; Zaharescu et al., 2020a);
- Irradiation at high dose rate. (Gillen and Clough, 1989; Baccaro and Buontempo, 1992; Zaharescu et al., 2000).

2.3.1. Obtaining crosslinked polymer blends by γ-irradiation

Polymer blending followed by radioprocessing is a useful technique for obtaining novel polymeric and composite materials with predefined properties (Malinowski et al., 2011; Sonnier et al., 2017; Zaharescu et al., 2018a). Obtaining crosslinked blends under γ-irradiation is based on the formation of some new covalent bonds at the interface between the blending components.

2.3.2. Additivation of polymeric materials with stabilizing agents

Additivation of low-stability polymeric materials or blends with stabilising compounds is one of the main techniques to improve oxidation resistance, leading to new composite or nanocomposite materials by gamma irradiation.

2.3.2.1. Radiooxidative stabilisation effect of antioxidants on materials

The present study reveals the stabilizing effect of primary antioxidants under accelerated degradation conditions initiated by heat and γ-ray treatment on the polymeric materials.

The mechanism of radiooxidative stabilization of polymers in the presence of air and of primary antioxidants is a complex one. Antioxidants of this type react by donating a reactive hydrogen atom to the free radical (alkyl or peroxyl). Thus, they interrupt the oxidation propagation chain by scavenging free radicals from the system, blocking their reactivity, followed by their deactivation.

2.3.2.2. Functional additives

The stabilization mechanism of the functional additives on polymers is based on the simultaneous scission of the double bonds in the monomer and those belonging to the polymer phases and their use as a main source of radicals for radical recombination in order to create intermolecular bridges between macromolecular chains, ensuring a significant decrease in the oxygen penetration rate and contributing to an increase in the content of the resistant phase.

2.3.2.3. Nanoparticles or nanofillers

The protective efficacy of the nanoparticles is based on a favorable interaction between the inorganic phase (nanoparticles) and the organic phase (polymer substrate), by creating new covalent bonds established at the interface, which leads to improved thermooxidative and radiooxidative stability and consequently to the durability of the composite or nanocomposite material under extreme operating conditions (Lungulescu et al., 2014).

2.3.3. Exposure of polymeric materials to high dose rate

The dose rate influences the ratio between the crosslinking and degradation process. A high irradiation dose rate leads to a low oxidation rate, favouring the crosslinking process and thus the radiooxidative stabilisation of the material (Hacıoglu et al. 2013).

CHAPTER 3. ORIGINAL CONTRIBUTIONS

3.1. Thermal qualification study of PLA/SIS-based blends for packaging and medical applications

3.1.1. Objectives

The main objectives of the experimental study were to obtain new PLA/SIS (polylactic acid/styrene-isoprene-styrene copolymer) polymeric materials and to evaluate the influence of the blending ratio of SIS in the biopolymer matrix on their thermal and radiochemical stability for packaging and radiosterilization applications.

3.1.2. Materials and sample preparation

3.1.2.1. Materials

The raw materials for this experimental study were blends of polylactic acid, used as a biopolymer matrix, and styrene-isoprene-styrene copolymer D1165 PT (SIS), used as a thermoplastic to process PLA during melting.

3.1.2.2. Sample preparation

Obtaining the blends

The blends containing 10, 20 and 30 % SIS against PLA were obtained by extrusion at a temperature of 180 °C.

Obtaining specimens

After hardening the melts (both blends and the individual components), they were pressed in order to obtain sheets and films.

Weathering in ionizing radiation environment

The exposure to γ-radiation was performed in air at room temperature in a Sanguis Ob Servo irradiator (Hungary) equipped with a ^{60}Co source at four total absorption doses (D): 0, 10, 25 and 50 kGy and at a high dose rate of 0.8 kGy h^{-1} to promote the crosslinking process.

3.1.3. Investigation techniques

3.1.3.1. Characterisation of thermal behaviour by Chemiluminescence (CL)/differential scanning calorimetry (DSC)

Chemiluminescence (CL)

Differential scanning calorimetry (DSC)

3.1.3.2. Physico-chemical characterisation by FTIR analysis

Results and discussions

3.1.3.3. Thermal and irradiation stability characterisation by chemiluminescence (CL) analysis

The thermal characterization of the components contribution is described in Fig. 3.3. Increasing the fraction of SIS in PLA/SIS blends causes the extent of oxidation. This is demonstrated by the progressive intensification of the CL emission intensity.

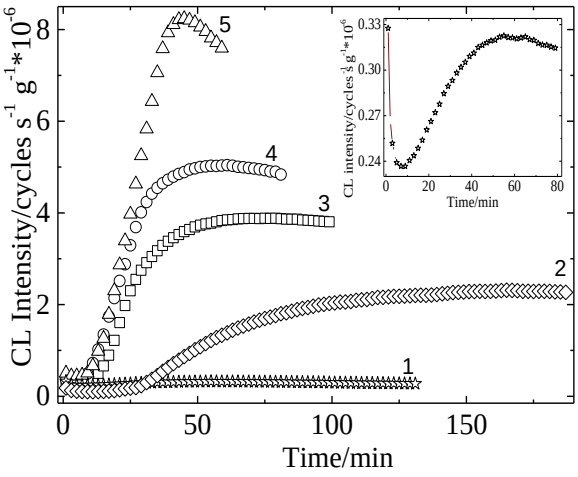


Figure 3.3. Isothermal CL spectra recorded on nonirradiated samples: (1) PLA, (2) PLA/10SIS, (3) PLA/20SIS, (4) PLA/30SIS, (5) SIS. Temperatura de testare: 150 °C

For irradiated samples, the CL emission intensity increases with increasing irradiation dose (Fig. 3.5), with the lowest values for the PLA/10SIS blend. Also, the PLA/10SIS composition (Fig. 3.5.a) shows similar and low degradation times in the 10-50 kGy dose range. The observed effects can be explained by a favourable interaction of SIS molecules with the PLA matrix under gamma irradiation, by the formation of PLA-SIS crosslinks that limit the diffusion of oxygen into the material.

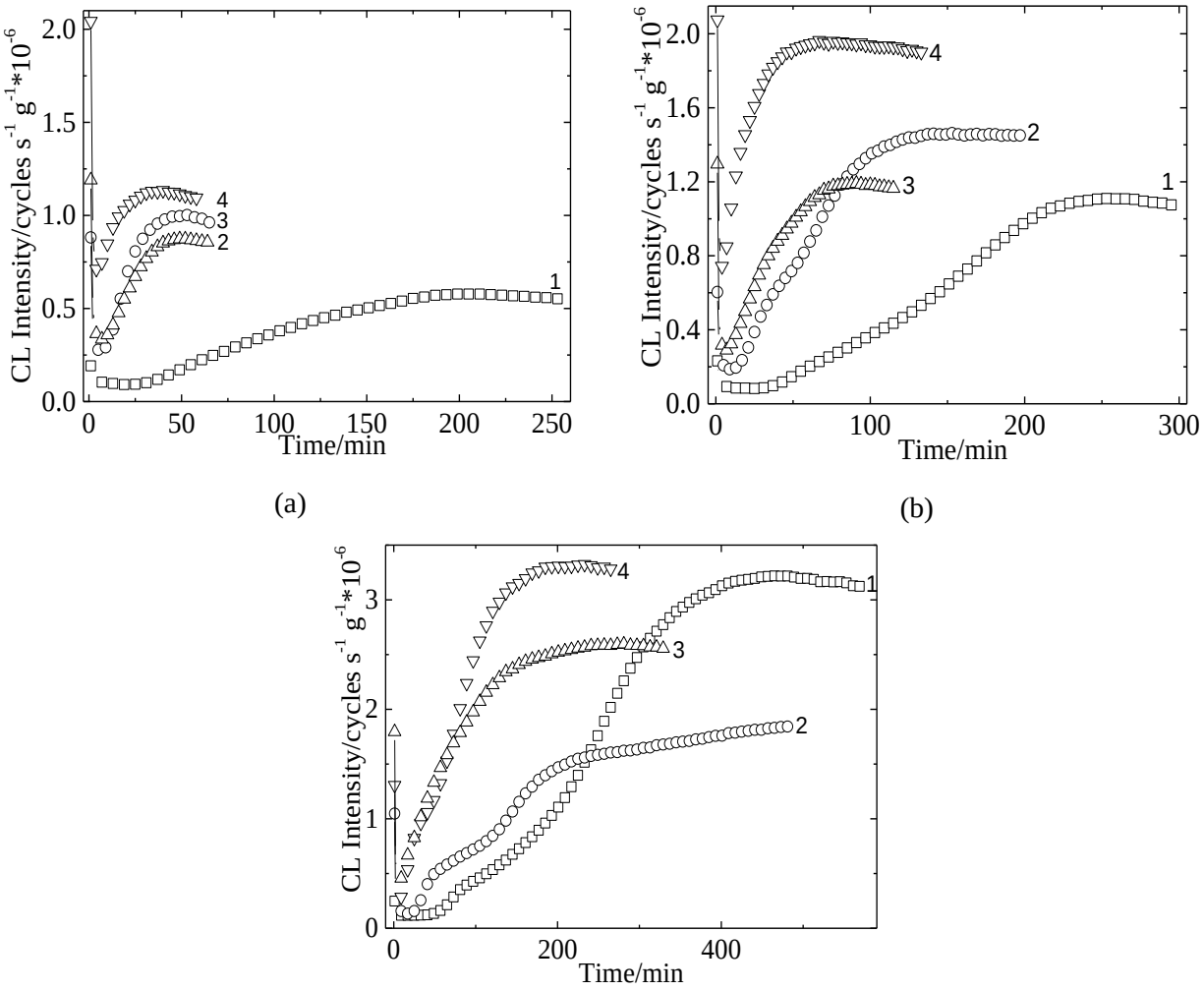


Figure 3.5. Isothermal CL spectra recorded on PLA/SIS blends: (a) PLA/10SIS, (b) PLA/20SIS, (c) PLA/30SIS, irradiated at various doses: (1) 0 kGy, (2) 10 kGy, (3) 25 kGy, (4) 50 kGy. Testing temperature: 150 °C

3.1.3.4. Characterisation of thermal behaviour by differential scanning calorimetry (DSC)

3.1.3.5. Physico-chemical characterisation by infrared spectroscopy (FTIR)

The results obtained from the FTIR analysis are shown in Fig. 3.10, where the accumulation of carbonyl group-containing products is shown. They confirm that a lower elastomer concentration leads to a better oxidation resistance. The constantly low value of the carbonyl index obtained for PLA confirms that this blending component does not follow a radical mechanism leading to oxygen-containing intermediates.

The lower irradiation dose (25 kGy) characterises the sterilisation conditions. It can be related to the exposure of the material to advanced oxidation conditions. The addition of SIS in PLA-based blends is beneficial for the major component as the products show improved processing parameters.

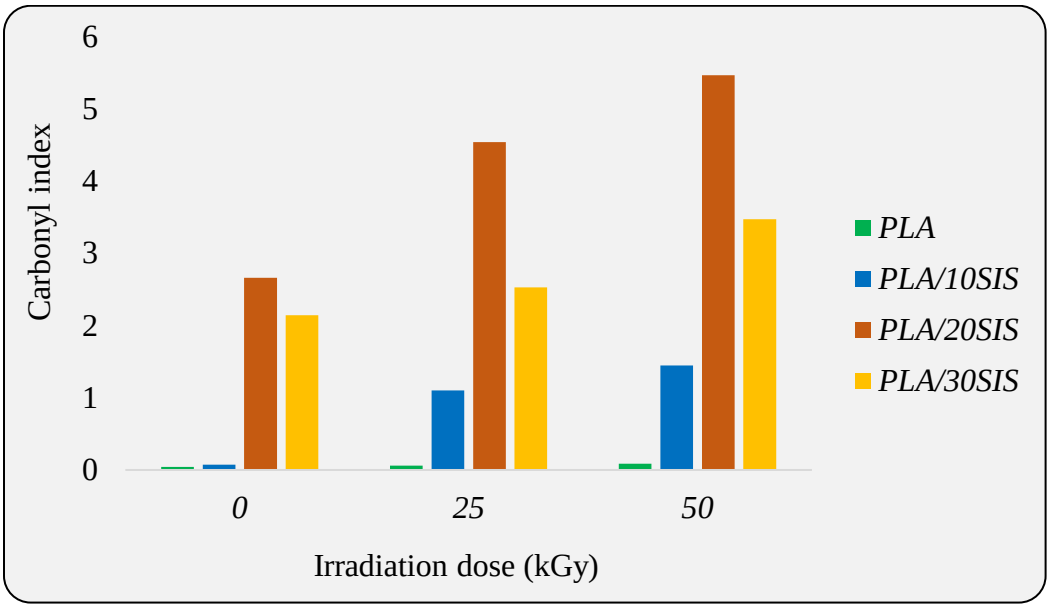


Figure 3.10. Variation of carbonyl index (reference 1452 cm^{-1}) with irradiation dose for neat PLA and PLA/SIS blends

3.1.4. Conclusions

In this research, new PLA/SIS polymeric materials were obtained and the effect of the blending ratio of styrene-isoprene-styrene copolymer in PLA matrix was studied by evaluating their thermal and radiochemical stability. The addition of SIS elastomer in the biopolymer matrix in the ratio of 10% shows optimal thermal and irradiation stability results at the standard radiosterilization dose (25 kGy), as well as improved processing parameters for the manufacture of sterile packaging materials and medical items.

3.2. Contribution of stabilizers agents on the availability of PLA/SIS blends for packaging and medical applications

3.2.1. Objectives

This research aimed to develop new composite materials with biopolymer matrix and environmentally friendly stabilizers and to evaluate the efficiency of natural antioxidants on the thermal and radiation stability of the previously developed PLA/30SIS blend compared to that of a synthetic antioxidant.

3.2.2. Materials and sample preparation

3.2.2.1. Materials

The present study was carried out using composite materials consisting of polylactic acid (PLA), styrene-isoprene-styrene copolymer (SIS), acrylic acid (AA) used as crosslinking agent, natural polyphenolic acids namely caffeic acid (CA) and vanillic acid (VA) as natural stabilizers and Irganox 1076-$C_{35}H_{62}O_3$ as synthetic antioxidant.

3.2.2.2. Sample preparation

Obtaining composite materials

The composites were obtained by melt mixing of PLA, SIS, 0.5% AA and 0.5% antioxidant (CA, VA, Irganox 1076) components, the mixing ratio PLA/SIS/AA/AO being 70/29/0.5/0.5.

Obtaining specimens and preparing samples for investigation

Exposure to ionizing γ radiations

3.2.3. Investigation techniques

3.2.3.1. Characterisation of thermal behaviour by chemiluminescence (CL) and differential scanning calorimetry (DSC)

Chemiluminescence (CL)

Differential scanning calorimetry (DSC)

3.2.3.2. Physico-chemical characterisation by FTIR analysis

3.2.4. Results and discussions

3.2.4.1. Study of thermal and radiation behaviour by chemiluminescence method

Non-isothermal chemiluminescence

The chemiluminescence determinations (Fig. 3.13. and Fig. 3.18) show higher oxidation induction time (OIT) and oxidation onset temperature (OOT) values for the composites with antioxidants, ordering the thermal stability of the composites in the following sequence:

PLA/SIS/AA control < PLA/SIS/AA/VA < PLA/SIS/AA/CA < PLA/SIS/AA/Irganox 1076

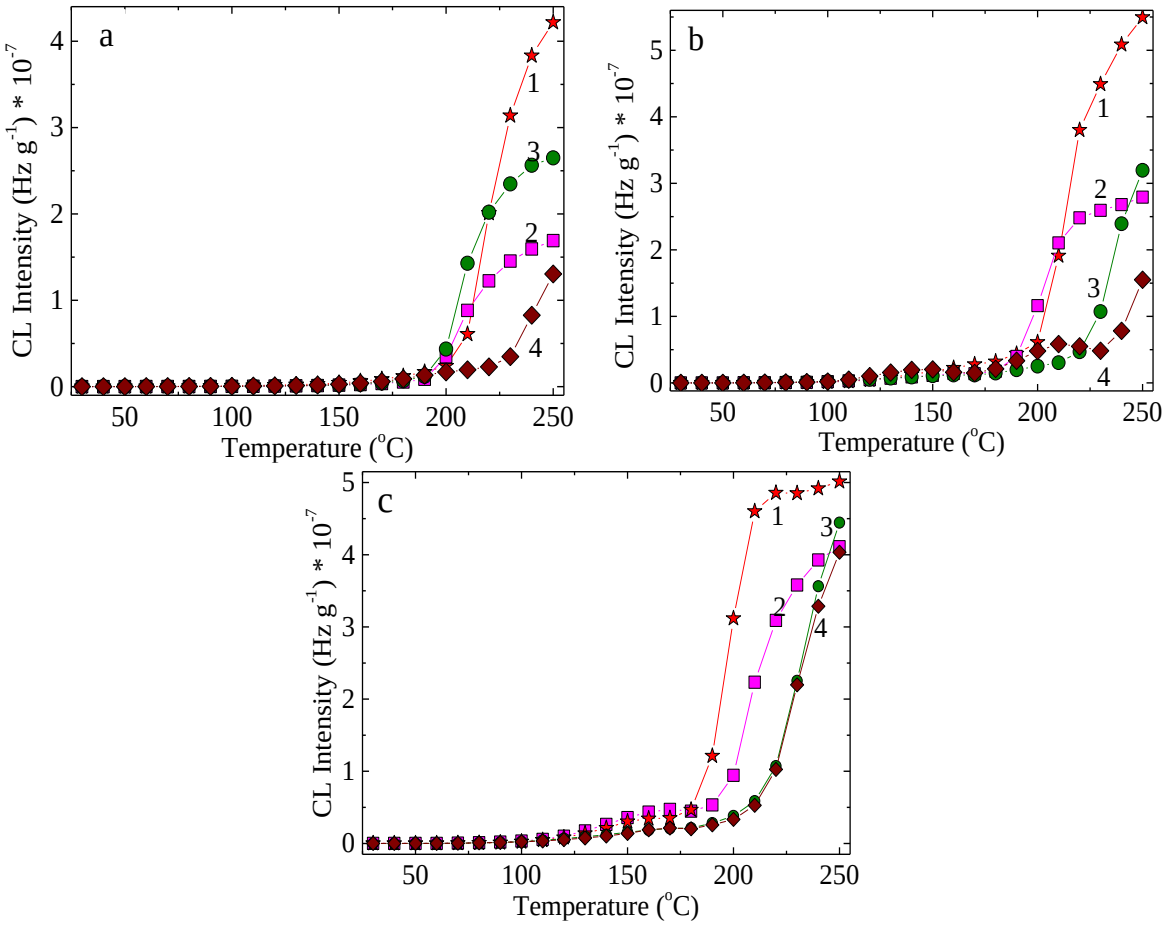


Figure 3.13. Nonisothermal CL spectra recorded on the PLA/SIS blend modified with some antioxidants. Heating rate: 10 ºC min^{-1}. (a) 0 kGy, (b) 25 kGy; (c) 50 kGy. (1) control, (2) vanillic acid, (3) caffeic acid, (4) Irganox 1076

Isothermal chemiluminescence

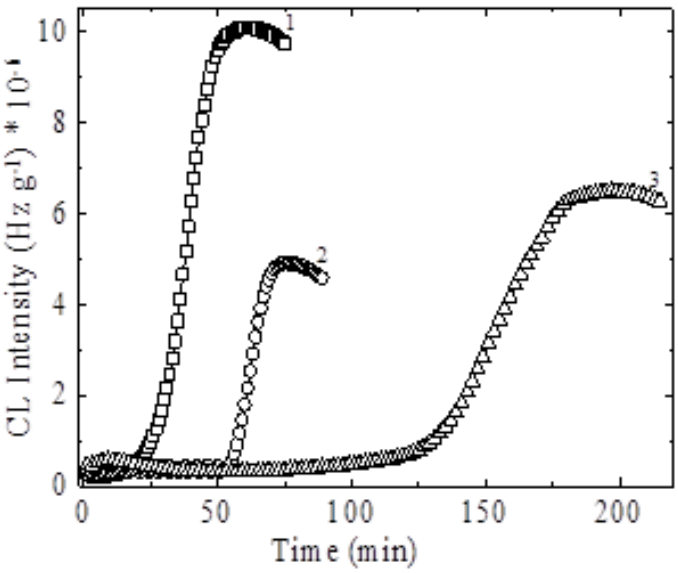
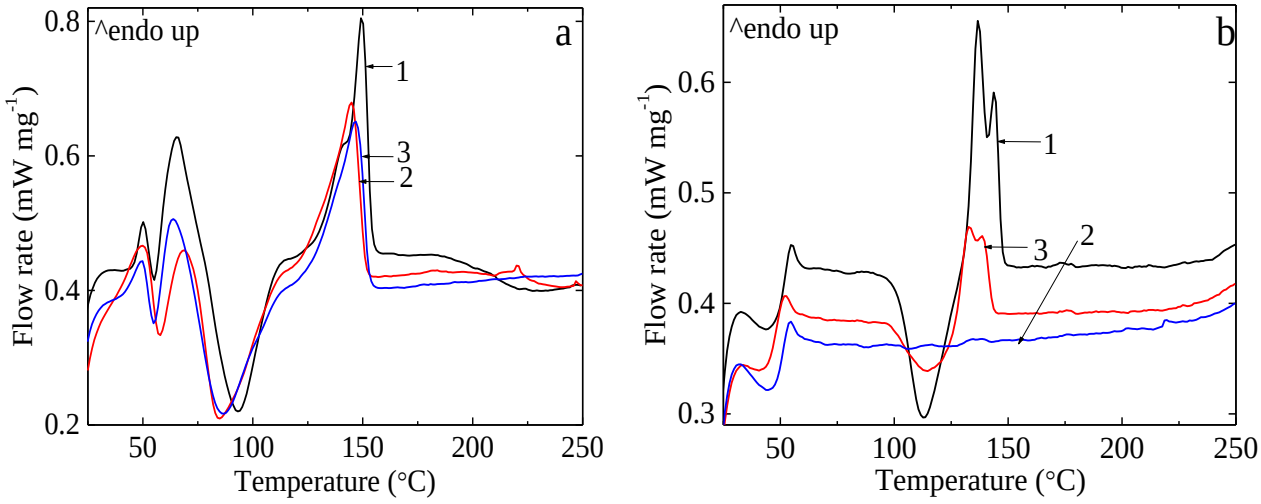


Figure 3.18. Isothermal CL spectra recoded on the PLA/SIS blends with different stabilization states subjected to a dose of 25 kGy. (1) PLA/SIS/AA, (2) PLA/SIS/AA/VA, (3) PLA/SIS/AA/CA. Testing temperature: 140 ºC.

3.2.4.2. Characterisation of thermal behaviour by differential scanning calorimetry (DSC)

DSC investigations highlight the special contributions of vanillic and caffeic acids on the thermal properties, oxidation resistance and crystallinity of the investigated materials (Fig. 3.19).



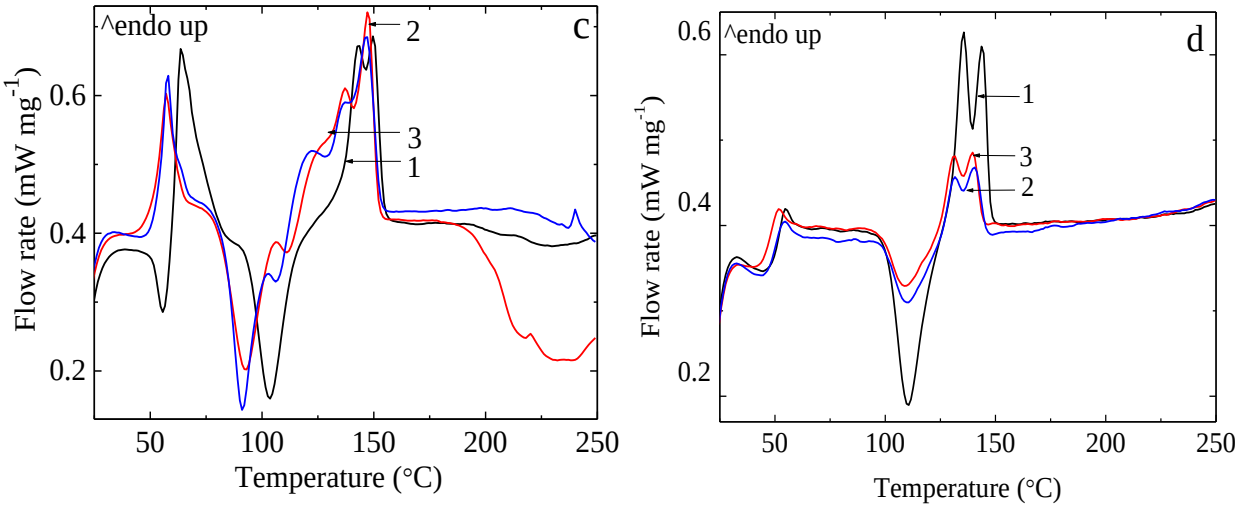


Figure 3.19. DCS curves for PLA/SIS based formulations:(a) dose 0 kGy, first scan; (b) dose 0 kGy, second scan; (c) dose 25 kGy, first scan; (d) dose 25 kGy; second scan. (1) PLA/SIS/AA, (2) PLA/SIS/AA/VA, (3) PLA/SIS/AA/CA. Heating rate: 10 °C/min

3.2.4.3. Physico-chemical characterisation by infrared spectroscopy (FTIR)

FTIR analysis shows the antirad efficiency of caffeic acid compared to vanillic acid. The stabilizing capability of these compounds is related to their ability to capture degradation initiators, mainly occurring through the cleavage of SIS chains.

3.2.5. Conclusions

In this study it was concluded that the selection of the two polyphenols leads to an improved stability of the developed PLA/30SIS blends. The newly obtained composites are stable to accelerated degradation during radioprocessing and post-irradiation and are suitable for the manufacture of environmentally friendly household and medical products (food packaging, beverage bottles, toys or clothing as well as sterile medical products).

3.3. Thermal and radiation stability study of PLA/SIS-based polymer nanocomposites reinforced with silica nanoparticles

3.3.1. Objectives

This study aims to obtain novel nanocomposite materials, PLA/30SIS/n-SiO_2, and to analyze the contribution of silica nanoparticles on the stability of previously developed PLA/30SIS-based polymeric materials under severe environmental conditions for medical, packaging, radiosterilization, or durable materials production applications.

3.3.2. Materials and sample preparation

3.3.2.1. Materials

3.3.2.2. Sample preparation

Obtaining composite materials

The PLA/SIS/n-SiO_2 hybrid nanocomposites were obtained by melt mixing of PLA, 30% SIS and incorporating SiO_2 in four different concentrations (0%, 3%, 5% and 10%).

Obtaining specimens and preparing samples for investigations

Exposure to ionising γ radiation

3.3.3. Investigation techniques

3.3.3.1. Characterisation of thermal behaviour by chemiluminescence (CL)

3.3.3.2. Evaluation of gel fraction by Charlesby-Pinner representation

3.3.3.3. Physico-chemical characterisation by FTIR analysis

3.3.3.4. Morphological characterisation by scanning electron microscopy (SEM)

3.3.3.5. Determination of water vapour transmission rate

3.3.4. Results and discussion

3.3.4.1. Characterisation of thermal stability by chemiluminescence (CL) analysis

Isothermal chemiluminescence

Isothermal CL spectra show the superior thermal performance of SiO_2-reinforced PLA/30SIS materials by increasing the oxidation induction time (OIT) for the PLA/30SIS/10-SiO_2 hybrid by about 9 times compared to the unmodified composition (Fig. 3.23). This proves the ability of the nanoparticles to efficiently capture degradation intermediates before their reaction with free oxygen and to delay the weathering process.

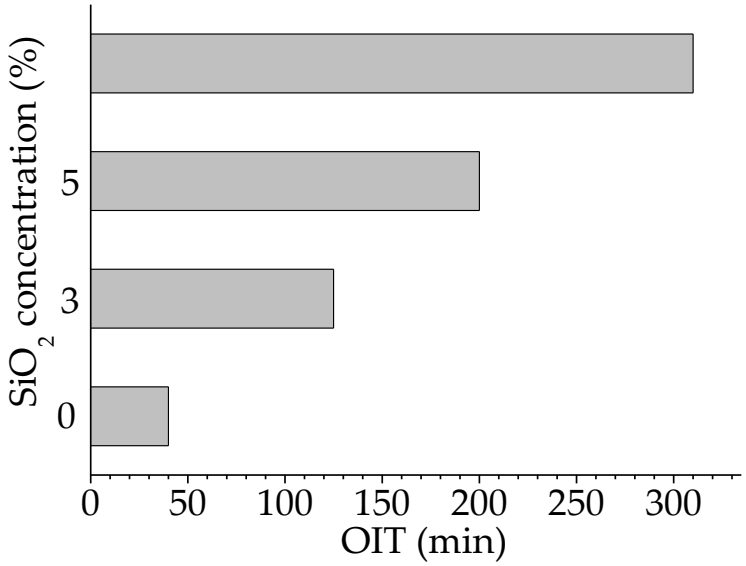


Figure 3.23. The oxidation induction times for PLA/30SIS/n-SiO_2 nanocomposite materials obtained by isothermal CL measurements at 150 °C.

Non-isothermal chemiluminescence

Fig. 3.25 explains the evolution of the oxidative degradation of initial materials in which silica is the stabilising agent.

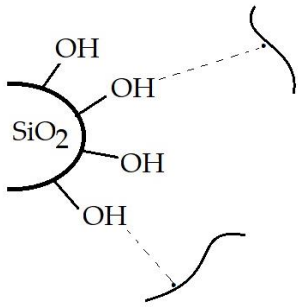


Figure 3.25. The illustration of the basic interaction between silica particles and free radicals from the system

For all heating rates (Fig. 3.27), the CL emission intensity decreases with increasing silica concentration:

0% < 3% < 5% < 10%

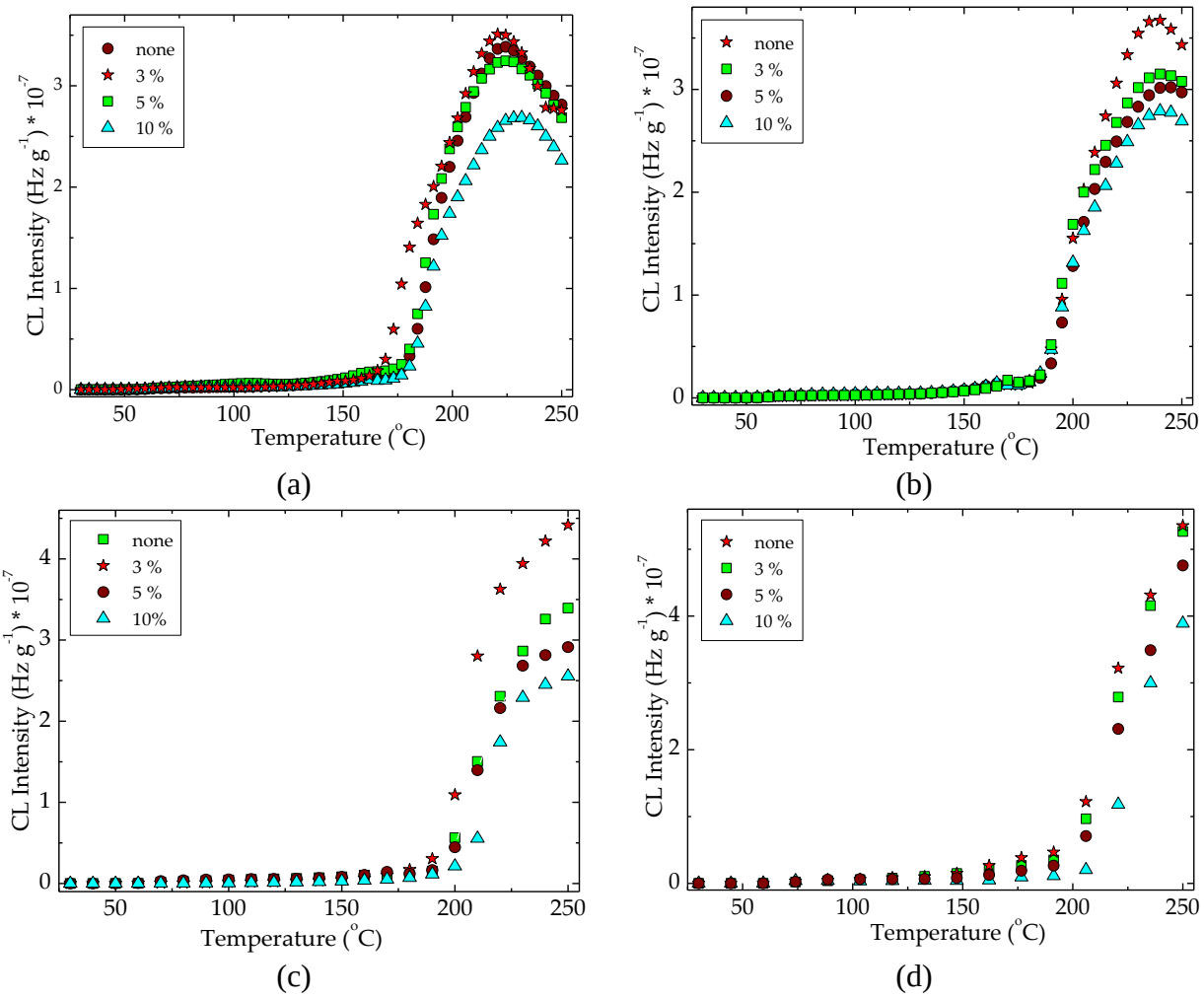


Figure 3.27. Nonisothermal CL spectra drawn for unirradiated PLA/30SIS samples in the presence of silica after receiving 25 kGy. Heating rates: (a) 3,7 °C min^{-1}; (b) 5 °C min^{-1}; (c) 10 °C min^{-1}; (d) 15 °C min^{-1}

Table 3.9. *OOT values for the oxidation of PLA/SIS blends reinforced with SiO_2 nanoparticles obtained by nonisothermal chemiluminescence.*

D (kGy)	**SiO_2 (%)**	**OOT (°C)**			
		3,7 °C min^{-1}	**5,0 °C min^{-1}**	**10,0 °C min^{-1}**	**15,0 °C min^{-1}**
0	0	170	175	177	187
	3	175	190	205	210
	5	177	191	208	215
	10	187	192	210	218
25	0	150	165	184	192
	3	157	168	181	186
	5	162	175	185	192
	10	172	181	195	202

From Table 3.9 it can be noted that increasing the silica content up to 10% induces an increase in OOT values with about 15%.

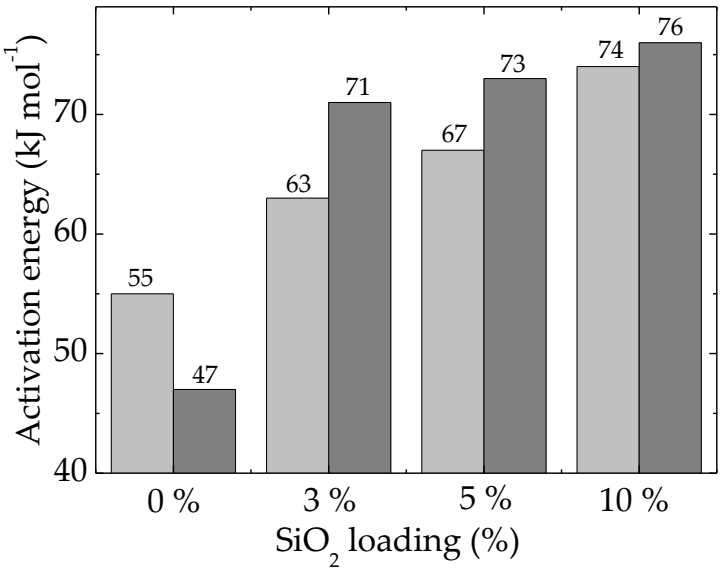


Figure 3.28. Histogram of the activation energies calculated for the oxidation of PLA/30SIS/n-SiO_2. Legend: (light grey): nonirradiated samples; (dark grey): irradiated samples at 25 kGy

The values obtained for the activation energy of thermal degradation (Fig. 3.28) support the idea by which irradiation improves the oxidation resistance. The stabilisation efficiency of nanoparticles can be explained by the formation of new covalent bonds at the interface between the inorganic and organic phases.

3.3.4.2. Evaluation of gel fraction by Charlesby-Pinner representation

3.3.4.3. Physico-chemical characterisation by FTIR analysis

3.3.4.4. Morphological characterisation by scanning electron microscopy (SEM)

Comparing the SEM images shown for irradiated and non-irradiated materials (Fig. 3.32), it can be observed that the presence of silica in PLA/30SIS samples favours the process a slight crosslinking under γ-irradiation, and makes possible the compatibilization between the two polymer phases.

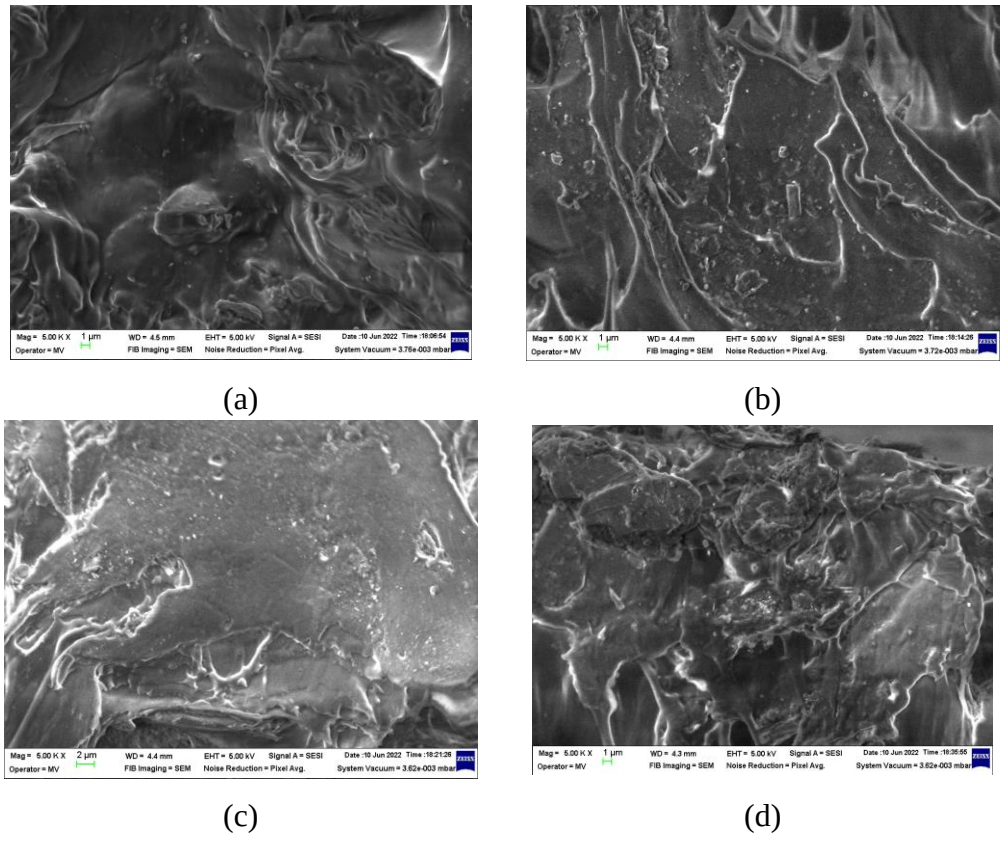


Figure 3.32 The SEM images on PLA/30SIS samples irradiated at 25 kGy. Compositions: (a) control; (b) SiO_2 3 %, (c) SiO_2 5 %, (d) SiO_2 10 %. Magnification: 5,000

3.3.4.5. Determination of water vapour transmission rate

The WVTR values obtained for the investigated systems prove their ability to better resist to moisture transfer when SiO_2 nanoparticles are in high concentration.

3.3.5. Conclusions

In conclusion, the addition of 10% silica represents a convenient solution for extending the durability of PLA/SIS-based materials under accelerated degradation conditions. The resulting nanocomposites can be successfully integrated in the field of radiosterilisation-resistant products (packaging materials, medical wear, containers for the pharmaceutical and cosmetic industry), as well as long-term wear-resistant products (automotive accessories, protective covers, sealing gaskets, wiring components).

3.4. Contribution of ecological oxidation protectors in the stability of EPDM-based packaging materials

3.4.1. Objectives

The main purpose of this study is to obtain new composite materials based on synthetic polymer, EPDM (ethylene-propylene-diene), and natural phenolic-structured antioxidants, gallic acid (GA) and rosemary extract (RE). The study also aimed to evaluate the thermal and radio-oxidative stabilization effect of oxidation protectants on EPDM-based materials for packaging and radiosterilization applications.

3.4.2. Materials and methods

3.4.2.1. Materials

In this experimental study, the raw material used was ethylene-propylene-diene terpolymer, in addition to natural antioxidants such as gallic acid (GA) and rosemary extract (RE).

3.4.2.2. Sample preparation

Obtaining composite materials

Preparation of samples for investigation

For obtaining the polymer films, EPDM solutions in chloroform modified with 1% antioxidant were prepared.

Exposure to γ-ionising radiation and aggressive environmental factors

The samples were weathered in an ionizing radiation environment using the accumulating dose procedure, as well as climatic and UV aged using an artificial xenon weathering chamber.

3.4.3. Investigation techniques

3.4.3.1. Characterisation of thermal behaviour by chemiluminescence (CL)

3.4.3.2. FTIR analysis

3.4.4. Results and discussions

3.4.4.1. Characterisation of thermal behaviour by non-isothermal chemiluminescence analysis

The evolution of the CL curves describes the effect of free radical scavenging by the antioxidants and their blockage, simultaneous with the inhibition of the reaction taking place between free radicals and oxygen. The intensity of CL emission is directly proportional to the concentration of radioinduced oxidised groups and to the concentration of the free radicals in the system.

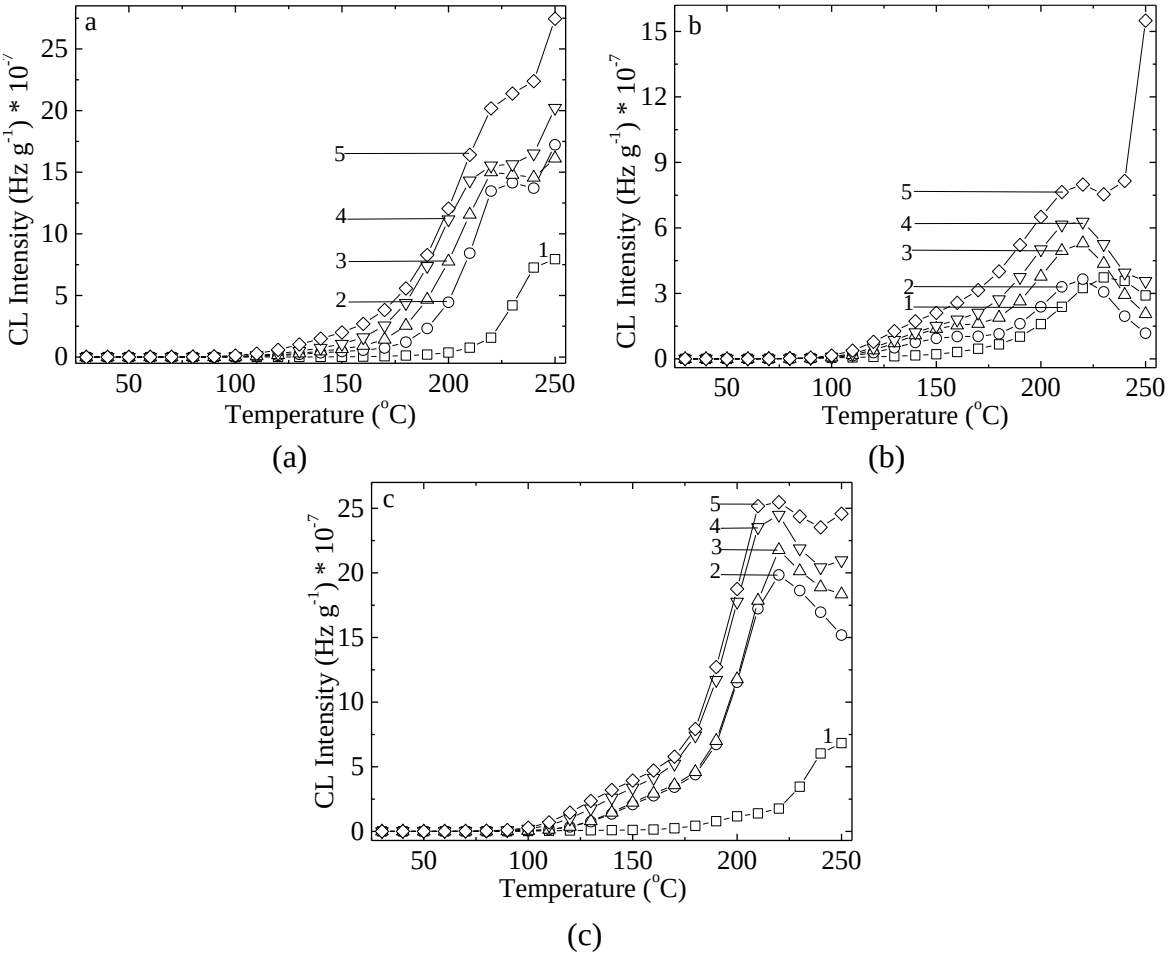


Figure 3.34. Nonisothermal CL spectra at various gamma-doses on EPDM samples. Heating rate: 3,7°C min^{-1}; (a) EPDM, (b) EPDM/GA, (c)EPDM/RE; (1) 0 kGy, (2) 25 kGy, (3) 50 kGy, (4) 100 kGy, (5) 200 kGy

Fig. 3.34 reveals the increased efficiency of antioxidants in stabilizing the EPDM matrix under the action of gamma radiation up to 200 kGy.

The better values of activation energy (Fig. 3.35) and carbonyl and hydroxyl indices (Fig. 3.36) for the EPDM/GA composite compared to the EPDM/RE composite can be explained by the higher content of reactive phenolic protons in the gallic acid structure, capable of trapping the free radicals (alkyl and peroxyl) resulting from the accelerated degradation of EPDM.

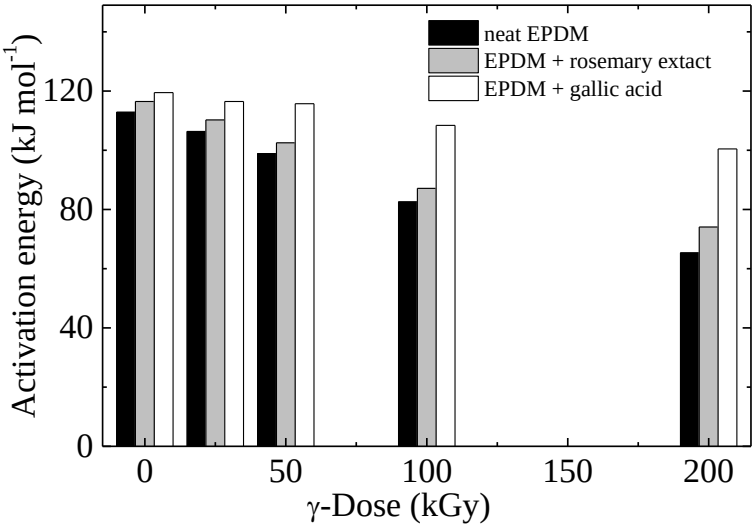
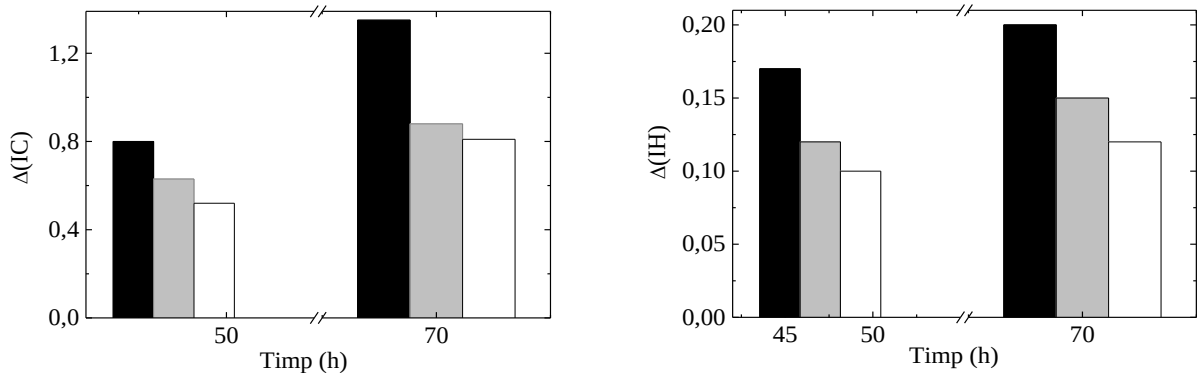


Figure 3.35. Activation energies of nonirradiated/radiation processed EPDM in the presence of the two stabilizers

3.4.4.2. Physico-chemical characterisation by infrared spectroscopy (FTIR)/Determination of carbonyl and hydroxyl indices by FTIR analysis

The gamma irradiation at high dose rate enhances the effect of the stabilisers, limiting the diffusion of oxygen into the material.



Weathering treatment

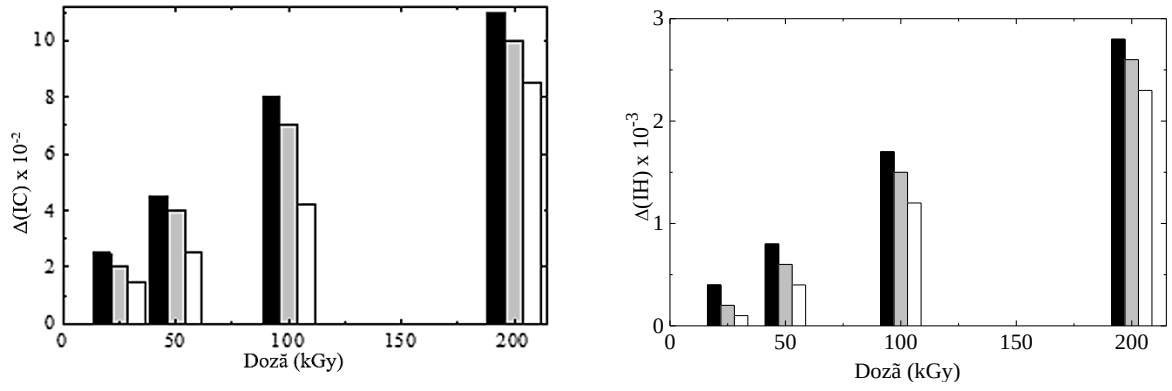


Figure 3.36. The evolution of carbonyl (CI) and hydroxyl (HI) indices in the studied EPDM samples (black- EPDM, grey- EPDM/RE, white- EPDM/GA), subjected to the two different degradation processes

3.4.5. Conclusions

In this study, it was found that in the presence of antioxidants, the oxidation process is reduced. At the same time, the obtained composite materials can be used for applications in food, cosmetic and pharmaceutical packaging, as they prove to be resistant to stressful environmental factors such as UV radiation, humidity and heat, offering the possibility for sterilization by γ-radiation.

3.5. Improvement of thermal stability of EPDM by radiation cross-linking for space applications

3.5.1. Objectives

The experimental study on the research direction for space applications aims to improve the stability and functional characteristics of ethylene-propylene-diene terpolymer by modifying it with an unsaturated additive, trifunctional monomer trimethyl-propane-trimethacrylate (TMPTA), which acts as a crosslinking agent.

The research focuses on the development of an optimal γ-ray processing technology of EPDM/TMPTA systems for the expansion of EPDM applications in the space and nuclear fields.

3.5.2. Materials and sample preparation

3.5.2.1. Materials

The raw material used in this experimental study was ethylene-propylene-diene terpolymer (EPDM). Trimethyl-propane-trimethacrylate (TMPTA) was used as a crosslinking agent to harden the polymer.

3.5.2.2. Sample preparation including preparation for analysis

The materials were prepared by Roseal S.A., obtaining mixtures of various concentrations.

Exposure to γ-ionising radiation

The exposure of the samples to γ-ray irradiation was performed at a high dose rate of 1 kGy h^{-1} favouring the crosslinking process and at total irradiation doses between 50 and 100 kGy.

3.5.3. Investigation techniques

3.5.3.1. Determination of thermal stability by chemiluminescence (CL)

3.5.3.2. Determination of mechanical strength

3.5.3.3. Determination of thermal stability by TG/DSC analysis

3.5.3.4. Morphological characterisation by scanning electron microscopy (SEM)

3.5.4. Results and discussions

3.5.4.1. Determination of thermal stability by chemiluminescence (CL) analysis

Isothermal chemiluminescence

From the isothermal CL analysis, it can be observed that the characteristic photon emission intensities at maximum oxidation times are increasingly lower as the monomer concentration increases (Fig. 3.38).

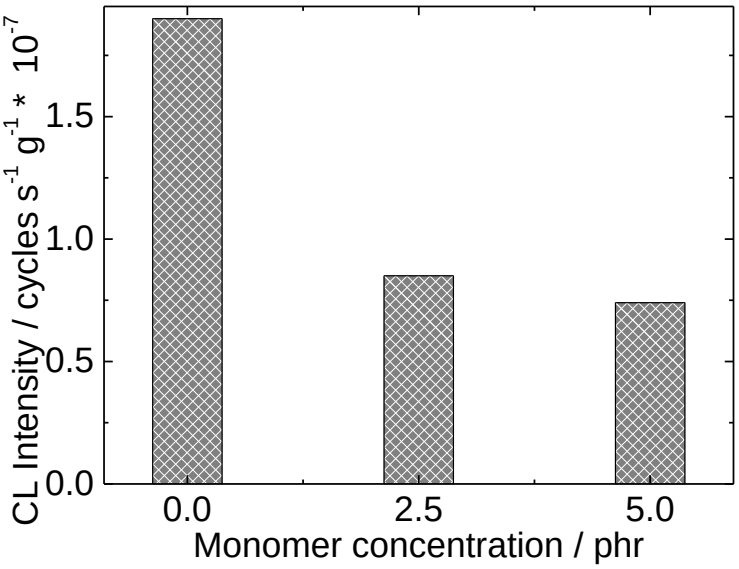
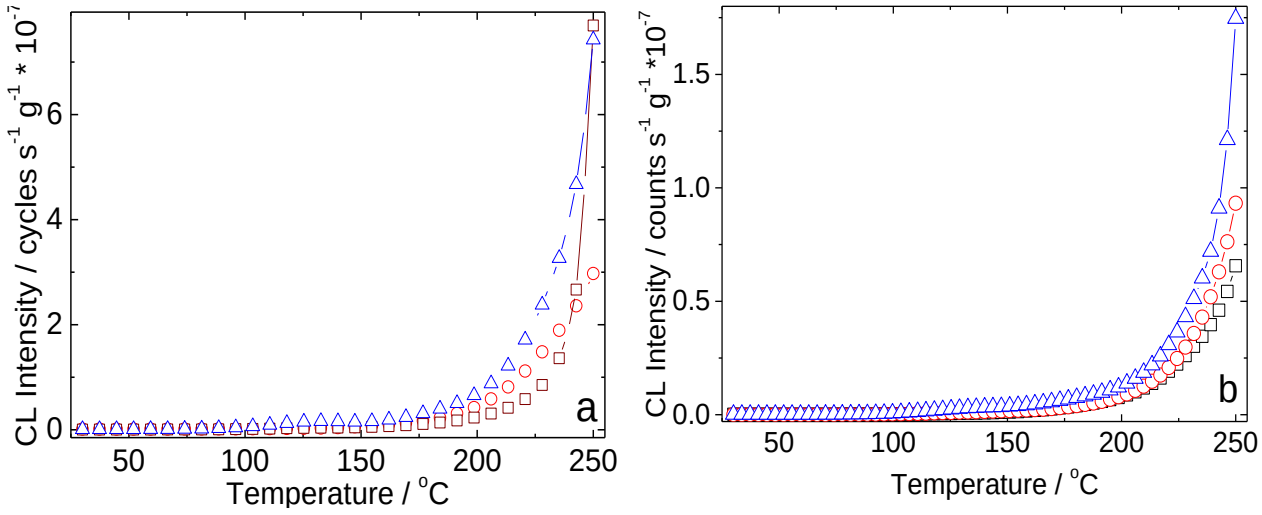


Figure 3.38. CL intensities of studied EPDM samples after 150 min of thermal oxidation at 50 kGy. Testing temperature: 180 °C.

Non-isothermal chemiluminescence

Fig. 3.40 highlights the decrease in degradation rate with increasing crosslinker concentration and irradiation dose, illustrated by the attenuation of CL emission.

The stabilisation mechanism is based on the simultaneous scission of double bonds in the EPDM and TMPTA structure and the establishment of new bond links by radical recombination.

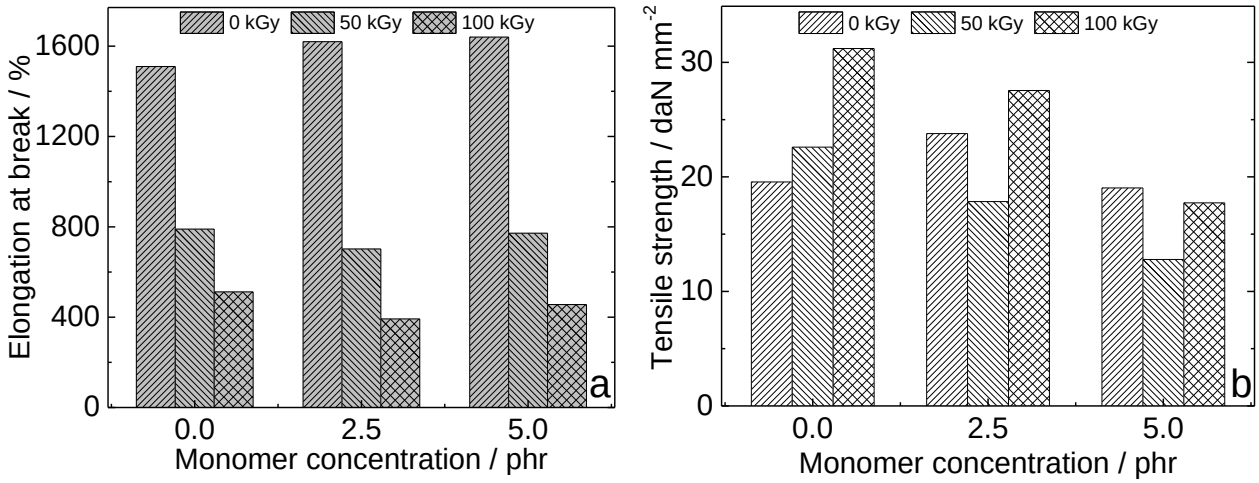


(a) (b)

Figure 3.40. Nonisothermal CL spectra recorded on gamma-irradiated EPDM/TMPTA samples. Heating rate: 3,7 °C min^{-1}. (a) P 2,5; (b) P 5. (△) 0 kGy; (○) 50 kGy; (□) 100 kGy.

3.5.4.2. Determination of mechanical strength

The results reveal the involvement of the monomer in the formation of a structure resistant to oxidation and mechanical stress (Fig. 3.41).



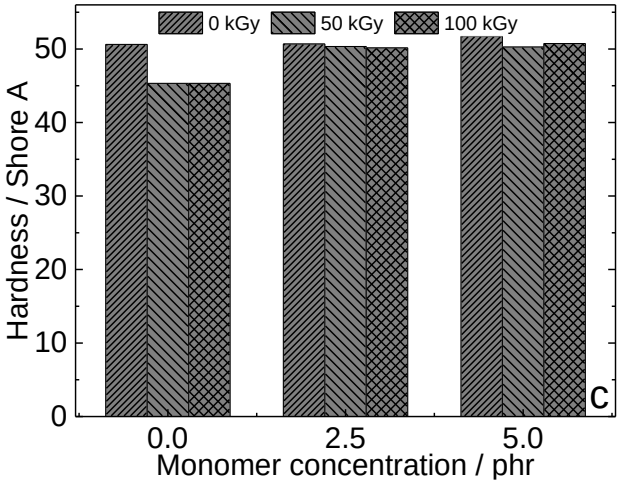


Figure 3.41. Testing the physico-mechanical properties of irradiated EPDM/TMPTA systems: (a) elongation, (b) tensile strength, (c) hardness

3.5.4.3. Determination of thermal resistance by TG/DSC analysis

The DSC analysis recommends EPDM systems loaded with 2.5 phr TMPTA as having the most convenient thermal parameters when radioprocessed at 50 kGy.

3.5.4.4. Morphological characterisation by scanning electron microscopy (SEM)

The SEM analysis demonstrates that TMPTA acts as a proper additive for increasing the degree of crosslinking during radioprocessing at 50 kGy, which directly results in improved stability of the final product.

As a result of the experimental results, an original radioprocessing technology was developed. It consists of an optimal sequence of processing steps (heating of the prepared systems at 150 °C for one hour for pre-initiation of crosslinking, followed by γ-irradiation at 50 kGy to complete the formation of the three-dimensional structure), and appropriate technological parameters to favour the crosslinking process (high dose rate of 1 kGy h^{-1}, loading of EPDM with 2.5 phr TMPTA).

3.5.5. Conclusions

In conclusion, the combination of EPDM and TMPTA leads to materials with improved characteristics. The proposed processing technology also extends EPDM applications in applications involving permanent energy transfer.

3.6. Degradability characterization of EPDM/IIR blends by γ-irradiation

3.6.1. Objectives

The main objective of the work was to evaluate the radiochemical recycling potential of EPDM/IIR-based formulations, on the one hand, by obtaining the degradability profile of EPDM/IIR–X polymer blends subjected to γ irradiation treatment and on the other hand, by evaluation of the effect induced by the addition of the stabilizer Irganox 1010, with the role of initiator of the crosslinking process, on the materials obtained for their conversion into useful products.

3.6.2. Materials and sample preparation

3.6.2.1. Materials

The current study was carried out using ethylene-propylene-diene (EPDM) as the basic polymer and pure butyl rubber (IIR), brominated (IIR–Br), as well as chlorinated butyl rubbers (IIR–Cl).

3.6.2.2. Sample preparation

Obtaining the blends

As a preliminary step for obtaining polymer blends, polymer solutions were prepared in $CHCl_3$ (EPDM, IIR, IIR–Br, IIR–Cl). These were mixed in appropriate proportions to obtain four different concentrations, 0, 5, 10 and 25 phr IIR-X in EPDM. For EPDM/IIR-X/AO blends, 0.5% antioxidant (Irganox 1010) was added.

Preparation of samples for investigation

Exposure to γ-ionising radiation

3.6.3. Investigation techniques

3.6.3.1. Solubility tests

3.6.3.2. FTIR analysis

3.6.3.3. Chemiluminescence determinations (CL)

3.6.4. Results and discussions

a. Evaluation of the radiochemical recycling potential of EPDM-based formulations and butyl rubbers

3.6.4.1. Solubility tests

The solubility tests (Fig. 3.47) rank the γ-irradiation stability of butyl rubbers in the following sequence: IIR > IIR–Cl > IIR–Br.

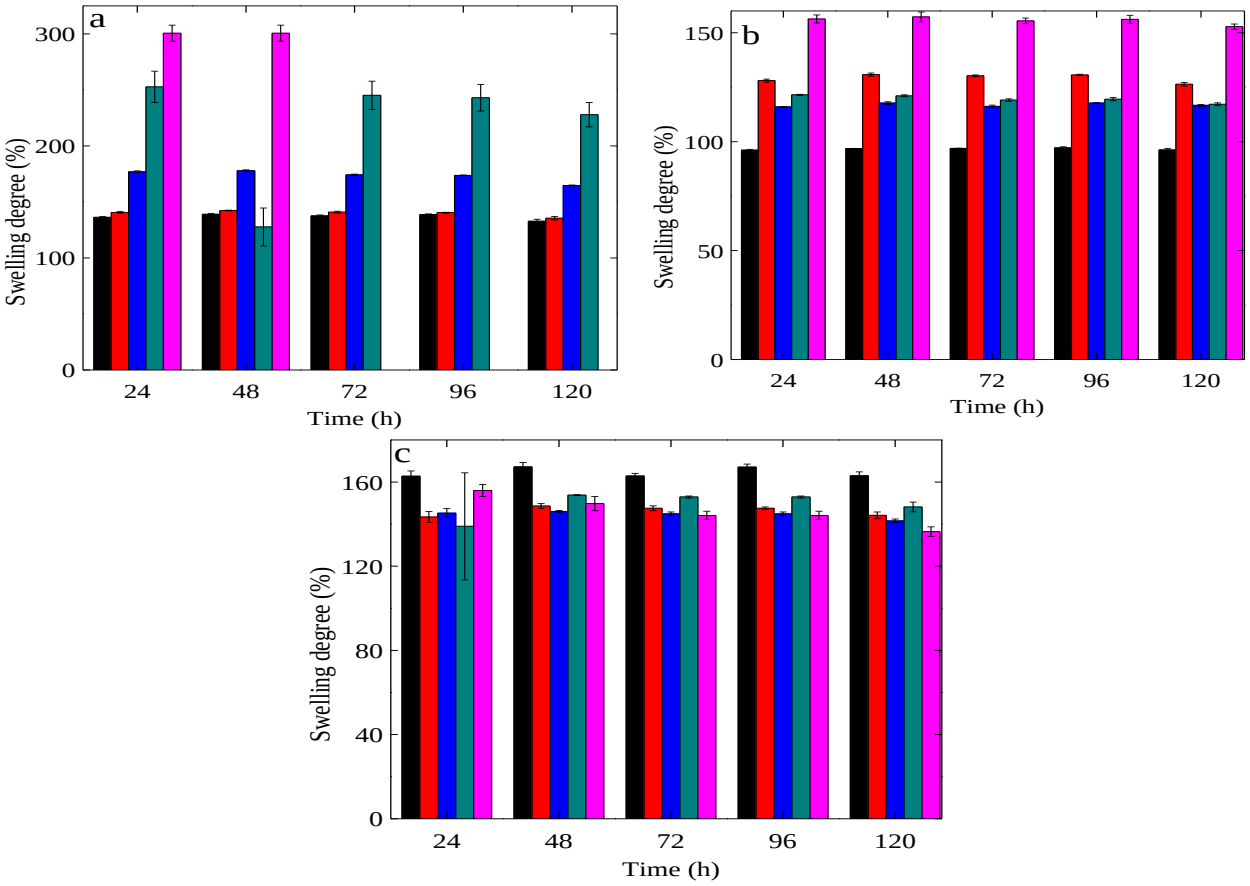


Figure 3.47. Modification of the sweeling degrees of γ-processed samples: (a) IIR, (b) IIR–Cl and (c) IIR–Br. (■) 0 kGy; (■) 5 kGy; (■) 50 kGy; (■) 100 kGy; (■) 200 kGy.

3.6.4.2. Investigation of the oxidation process by FTIR spectroscopy

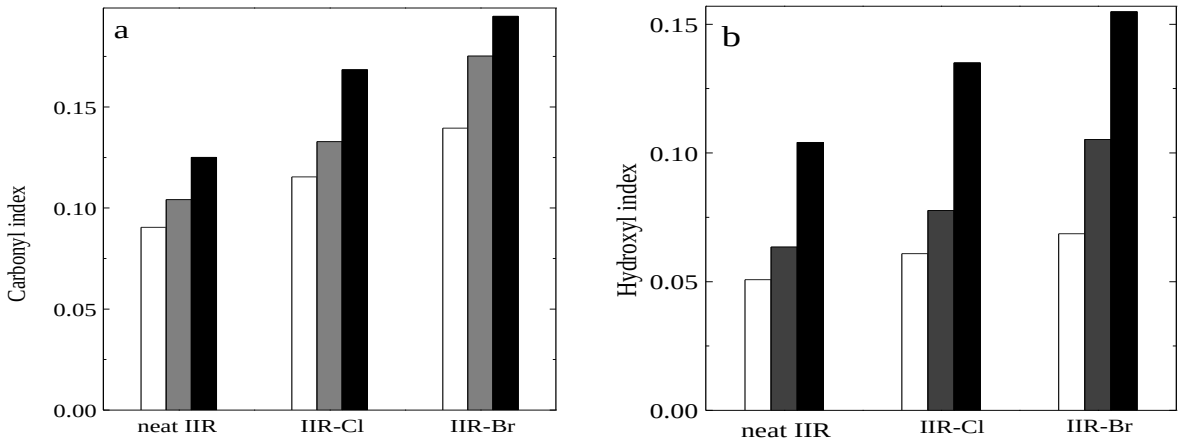


Figure 3.53. Carbonyl and hydroxyl indexes evaluated on EPDM/IIR blends for 100 kGy γ-dose and IIR phase content: (white) 5 phr, (dark grey) 10 phr şi (black) 20 phr

The increased values of the carbonyl and hydroxyl indices for the EPDM/IIR–Br blend resulting from the FTIR analysis (Fig. 3.53), demonstrate that IIR–Br provides the largest amount of free radicals available for oxidation, being the recommended butyl rubber for the procedure of radiochemical recycling by association with EPDM. The optimal parameters of the method involve an exposure dose of less than 100 kGy and a low dose rate of 0.4 kGy h^{-1}.

3.6.4.3. Investigation of the oxidation process by chemiluminescence

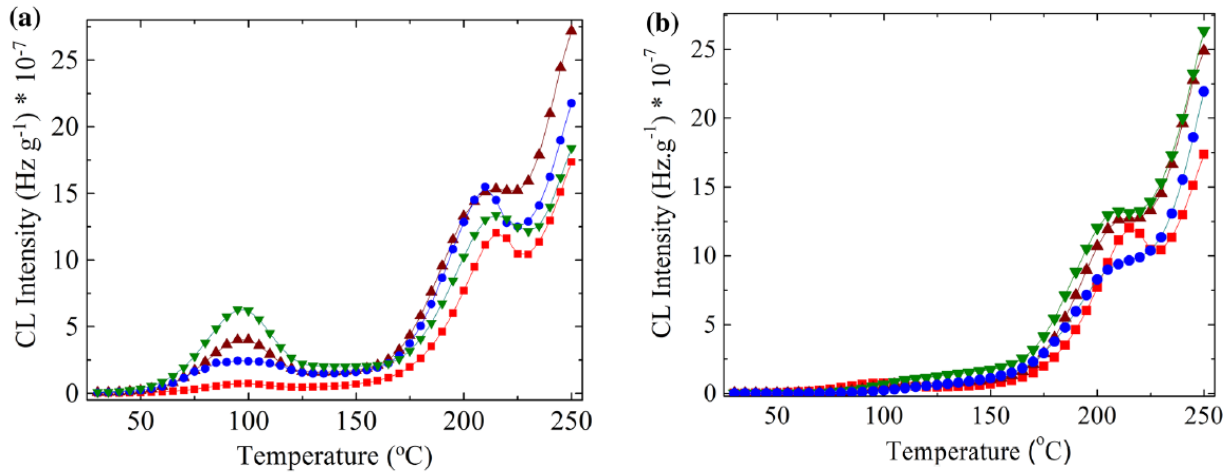


Figure 3.54. Nonisothermal CL spectra recorded for the studied compositions: (a) EPDM/neat IIR and (b) EPDM/IIR–Br irradiated at 100 kGy. (■) EPDM (●) 5 phr (▲) 10 phr şi (▼) 20 phr

The non-isothermal CL investigations recommend efficient processing of the studied systems by γ-irradiation, at exposure doses lower than 100 kGy, because up to this dose, the oxidation of materials reaches a convenient degree (Fig. 3.54).

b. Evaluation of the recycling potential of EPDM/IIR-X blends by conversion into useful products

3.6.4.4. Investigation of the crosslinking process

The variation of the gel content illustrated in Fig. 3.55 describes the evolution of gelation in EPDM/IIR blends, based mainly on EPDM crosslinking.

The addition of a synthetic antioxidant such as Irganox 1010 decreases the oxidation rate and increases the stability of the final product due to the scavenging of the free radicals and to the initiation of the crosslinking process under γ radiation.

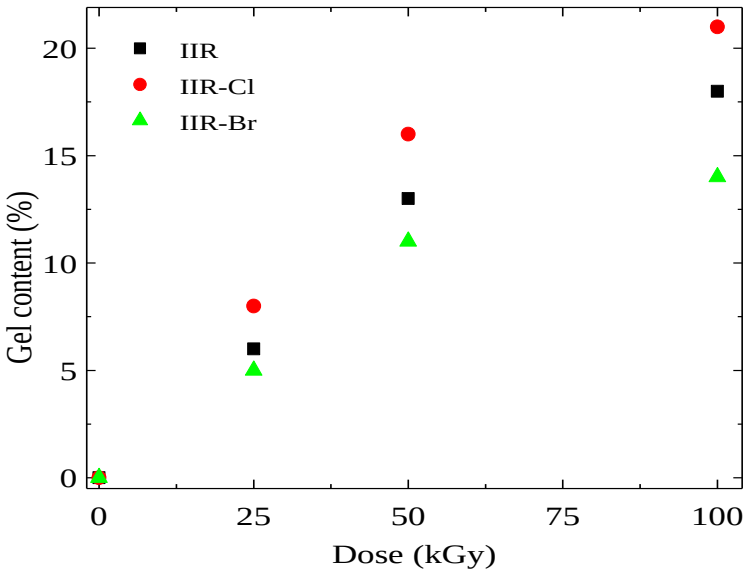


Figure 3.55. Accumulation of gel content in radiation treated EPDM/IIR blends. Butyl rubber concentration: 5 phr; IRGANOX 1010 concentration, 0,5 phr. (■) EPDM/IIR, (●) EPDM/IIR–Cl, (▲) EPDM/IIR–Br

3.6.5. Conclusions

In this experimental study, the radiation processing of butyl rubbers demonstrates the more advantageous recycling possibility of EPDM/IIR–X blends by radiochemical treatment. It depends on the result of the competition between the degradation and crosslinking process, occurring under different processing conditions. Thus, the formulations based on EPDM and IIR-X can be radiochemically recycled by two alternative methods: radiochemical degradation (IIR-X providing the free radicals, initiators of the degradation, dose lower than 100 kGy, dose rate of 0.4 kGy h^{-1}) or stabilization with synthetic antioxidants (Irganox 1010) for obtaining useful products.

CHAPTER 4. GENERAL CONCLUSIONS AND PERSPECTIVES FOR FURTHER RESEARCH

4.1. General conclusions

In this doctoral thesis, several current problems in the polymeric materials industry have been approached, with experimental studies directed towards the development of sustainable packaging and medical materials, radiosterilization, space and nuclear materials and recyclable materials under the influence of ionizing radiation.

The literature review presented was devoted to the state-of-the-art research in the field of radioprocessing of macromolecular compounds, with a focus on the importance of the development of polymeric and composite materials for special applications, relevant aspects of the radiochemical modifications produced in polymeric materials, and the progress of the techniques to optimise and/or improve the thermal and radiation stability.

The main conclusions of the literature review can be summarised as follows:

- there is a growing demand for polymeric products with specific properties and improved long-term performance, but also with a high degree of biodegradability;
- the γ-irradiation processing technique has proved to be one of the most effective methods of sterilisation and of extending the durability of polymeric materials;
- the industrial implementation of irradiation technologies allows for tremendous socio-economic benefits due to the versatility of practical applications;
- the general method of increasing the stability of materials processed by irradiation involves controlling the overall rate of degradation generated by the diffusion of oxygen into the material.

The results presented in the experimental research were mainly focused on the development of novel polymeric materials and composites based on PLA biopolymer and EPDM synthetic polymer, which exhibit pre-defined properties and performance adequate for the use in special applications such as food, pharmaceutical, cosmetic and medical packaging, space, nuclear and aeronautical applications, as well as in the field of elastomer waste recycling, through novel processing techniques using γ-ionizing radiation, additivation with stabilizing compounds or polymer blending. The polymeric and composite materials obtained were

characterized in terms of physicochemical and structural properties, for the evaluation of thermal, radiation, mechanical and morphological resistance, using both usual laboratory techniques and advanced analysis techniques (CL, FT-IR, TG, DSC, SEM). The general conclusions of the experimental studies carried out are presented below.

In *"Thermal qualification study of PLA/SIS-based blends for packaging and medical applications"*, novel PLA/SIS polymeric materials were obtained and the effect of the blending ratio of SIS in the PLA biopolymer matrix was studied by evaluating their thermal and radiochemical stability and investigating the way in which the component materials interact under γ-radiation in order to extend their applications in packaging and radiosterilization. The results demonstrated that the addition of 10% SIS elastomer to the biopolymer matrix (PLA/10SIS) shows optimal thermal and radiation stability results compared to the other blending ratios for the targeted applications. Improved material durability and sterilisation resistance was obtained at the standard dose of 25 kGy. The observed effects are explained by the interruption of the free radical formation process due to the formation of PLA-SIS crosslinks that limit the diffusion of oxygen into the material. The originality of this study consists of the fact that the polymer blends obtained, containing PLA and SIS, have not been previously reported in the literature for the development of packaging materials.

In the study *"Contribution of stabilizers agents on the availability of PLA/SIS blends for packaging and medical applications"* new composite materials were developed by the addition of natural (VA, CA) and synthetic (Irganox 1076) antioxidants to the PLA/30SIS blend investigated in the previous study, followed by radioprocessing. The effectiveness of the antioxidants was evaluated by analysing their contribution to the thermal and radiation stability of the investigated formulations. Chemiluminescence and differential scanning calorimetry determinations for all compositions and doses used demonstrated the higher antirad efficiency of caffeic acid compared to the one of vanillic acid, indicating the thermal stability of the composites obtained in the order: PLA/SIS/AA/control < PLA/SIS/AA/AV < PLA/SIS/AA/AC < PLA/SIS/AA/Irganox 1076. It was also found that the stabilizing ability of these compounds is related to their ability to scavenge free radicals preferentially released by cleavage of SIS chains. The results obtained recommend the selection of the two natural polyphenols for the additivation of low-stability polymer blends, as they prove to be suitable for the manufacture of medical and packaging eco-friendly products resistant to oxidation and ionizing radiation sterilization, which

would allow the sustainable replacement of the synthetic antioxidants. The novelty of the study is the approach of an innovative strategy for optimising the thermal and radiation stability of PLA/SIS-based formulations, which consists of the additivation of polymeric materials with natural stabilising compounds, followed by high dose rate irradiation processing in order to promote the crosslinking process, for applications requiring long durability or high oxidation resistance under high stress conditions.

Further, *"Thermal and radiation stability study of PLA/SIS-based polymer nanocomposites reinforced with silica nanoparticles"* presents own previous research towards the development of novel nanocomposite materials by additivation of PLA/30SIS blend with SiO_2 nanofiller followed by γ-irradiation processing. The contribution of the nanophase to the improvement of the stability of PLA/SIS-based polymeric materials was evaluated for determining the resistance under severe environmental conditions. Thermal (isothermal and non-isothermal regime), physicochemical, morphological and permeability analysis revealed the beneficial influence of SiO_2 on the stability of PLA/SIS/n-SiO_2 composites, which can be explained by a favorable interaction between the inorganic (SiO_2) and organic (PLA/SIS) phases by creating new covalent bonds at the interface between silica nanoparticles and the polymer substrate. The addition of 10% silica (mass percentage) extends the lifetime of the modified material by increasing the oxidation onset temperature value by about 15% and extending the oxidation induction time by about 9 times compared to the unmodified composition. The results underline that increasing the silica content up to 10% can be considered a suitable solution for extending the durability and stability limits of PLA/SIS-based materials under accelerated degradation conditions, in order to obtain environmentally friendly products resistant to radiosterilization (packaging materials, medical clothing, containers for the pharmaceutical and cosmetic industry), but also long-term wear resistance (automotive accessories, protective covers, gasket sealants, wiring components). The original contributions of this research are the identification of a method to stabilize PLA/30SIS polymer matrix by additivation with SiO_2 nanoparticles and irradiation of PLA/30SIS/n-SiO_2 nanocomposites at high dose rate, which decreases the oxidation rate and the amount of free radicals generated during radioprocessing.

In the fourth experimental study, on *"Contribution of ecological oxidation protectors in the stability of EPDM-based packaging materials"*, new composite materials based on synthetic polymer, EPDM, and natural phenolic antioxidants (gallic acid and rosemary extract) were

obtained and their resistance to aggressive environmental factors was investigated. The results obtained from the study of the degradation kinetics conducted by chemiluminescence analysis, and the determination of carbonyl indices and hydroxyl indices by FTIR analysis, reveal the delay of the oxidation process of EPDM in the presence of the two environmental stabilizers. The best results were found for gallic acid, which is more effective in inhibiting the oxidative degradation of EPDM when exposed to both gamma radiation up to 200 kGy and heat and UV treatment up to 70 hours. This effect can be explained by the higher content of reactive phenolic protons in the gallic acid structure capable of scavenging free radicals (alkyl and peroxyl) resulting from the accelerated degradation of EPDM. Due to their resistance to weathering (simultaneous exposure to UV radiation, temperature and humidity), the composite materials obtained are useful in the packaging of food products and pharmaceutical, cosmetic or medical consumables that require sterilisation with γ-radiation for consumer safety. Thus, a novel technology is proposed to manufacture composite materials based on EPDM and natural additives by processing with ionizing γ-radiation, which is sustainable and responds to the environmental restrictions.

Also, new polymeric materials based on EPDM synthetic polymer and TMPTA polyfunctional monomer have been proposed to improve EPDM performance in terms of irradiation and heat treatment stability for long lifetime. The results were presented in the study entitled *"Improvement of thermal stability of EPDM by radiation crosslinking for space applications"*. The materials were investigated by different laboratory techniques, with CL, TG/DSC, mechanical and morphological analysis confirming the research hypothesis. At the same time, from the kinetic study, it was found that the stabilization mechanism was based on the scission of the double bonds in the EPDM and TMPTA structure and the formation of a cross-linked structure by radical recombination, leading to a decrease of the oxygen diffusion rate in the investigated systems. The own contributions are concretised by proposing an original technology for γ-irradiation processing of EPDM/TMPTA systems, in order to achieve satisfactory performance and to extend EPDM applications in fields involving permanent energy transfer and special use conditions, such as space and nuclear fields (seals for space sample container systems, cables or seals for nuclear power plants, exposed materials in nuclear interaction chambers, fine electronics). This consists of determining the sequence of processing steps (heating of prepared systems at 150 °C for one hour for pre-crosslinking, followed by γ-

irradiation at 50 kGy for the completion of the three-dimensional structure formation), but also of selecting the optimal technological parameters to favour the crosslinking process (high dose rate of 1 kGy h^{-1}, EPDM loading with 2.5 phr TMPTA).

The experimental part is concluded by the study *"Degradability characterization of EPDM/IIR blends by γ-irradiation"*, which aimed to evaluate the radiochemical recycling potential of EPDM/IIR based formulations. The experimental results proposed two advantageous alternatives for recycling EPDM and IIR waste elastomers, namely the use of γ-irradiation for the scission of polymer chains, with IIR providing the free radicals initiating the degradation, and the recovery of EPDM/IIR blends by stabilisation with synthetic antioxidant compounds (Irganox 1010) which scavenge free radicals from the system allowing the initiation of the crosslinking process and the conversion of waste elastomers into useful products. Because the influence of several types of halogenated butyl rubbers has been investigated, their comparative analysis allowed ordering the stability in the sequence IIR > IIR-Cl > IIR-Br. Thus, radiochemical recycling is favoured in the case of the association of IIR-Br with EPDM, due to its ability to provide a higher amount of free radicals available for oxidation. The optimal parameters of the method involve exposure dose less than 100 kGy and low dose rate of 0.4 kGy h^{-1}. This study contributes to the development of recycling solutions for butyl rubbers and represents a novel research direction, while contributing to the accumulation of information in the field of radiochemical recycling.

Overall, the experimental studies performed demonstrate the benefits of the radioprocessing technique in the polymer industry. Radioprocessing is proving to be a convenient treatment both for obtaining durable materials resistant to aggressive environmental factors and for modifying difficult-to-recycle materials in order to reduce their environmental impact.

The doctoral thesis *"RADIOPROCESSING OF POLYMERIC MATERIALS"* contains many original elements, the research directions approached having a high degree of novelty. It contributes to the enrichment of the knowledge in the field of polymer radioprocessing and to the extension of the applications in the field of polymer and composite materials.

4.2. Prospects for further research

Considering the results of the conducted experimental studies, the paper provides new perspectives for further research, by the possibility of developing related studies such as:

- further studies on the mechanical, permeability (to H_2O, N_2, O_2, CO_2 vapour), and biodegradability properties of packaging materials developed based on PLA and environmentally friendly additives, in order to facilitate their implementation in the industrial sector;
- approaching physico-chemical and morphological characterisation methods complementary to those used in this paper (Raman spectroscopy, TEM), to further investigate the radiochemical modification mechanisms of the structures of the materials/systems investigated;
- compatibilisation of new polymer blends by radio-induced crosslinking, starting from PLA biopolymer or EPDM synthetic polymer in order to improve their thermal and radiation stability;
- development of materials resistant to conditions specific to space and nuclear environments, starting from EPDM elastomer;
- extending the non-polluting radiochemical recycling process to other types of polymeric materials that cannot be recycled by conventional physical or chemical methods, in order to fulfill the restrictions of environmental protection standards;
- provide relevant information (stability profile of polymer materials, radioprocessing technology parameters, strategies for optimising radiochemical stability) to the economic and industrial environment in order to exploit mature radioprocessing technology.

DISSEMINATION OF RESULTS

The results obtained during the research have been disseminated within the scientific community through publications in peer-reviewed journals, oral presentations and poster presentations.

Articles published in ISI-listed journals

1. **Ana Maria Lupu (Luchian)**, Marius Mariş, Traian Zaharescu, Virgil Emanuel Marinescu, Horia Iovu, *Stability Study of the Irradiated Poly(Lactic Acid)/Styrene Isoprene Styrene Reinforced with Silica Nanoparticles*, Materials, Vol. 15, 2022, 5080.

   https://doi.org/10.3390/ma15145080. **Impact factor 2022: 3,4.**

2. **Ana-Maria Lupu (Luchian)**, Traian Zaharescu, Maria Râpă, Marius Mariș, Horia Iovu,

   Availability of PLA/SIS blends for packaging and medical applications.Part II: Contribution of stabilizer agents, Radiation Physics and Chemistry, Vol. 20, 2022, 110446.

   https://doi.org/10.1016/j.radphyschem.2022.110446. **Impact factor 2022: 2,9.**

3. **Ana-Maria Luchian-Lupu,** Traian Zaharescu, Eduard-Marius Lungulescu, Maria Râpă, Horia Iovu, *Availability of PLA/SIS blends for packaging and medical applications*, Radiation Physics and Chemistry, Vol. 172, 2020, 108696.

   https://doi.org/10.1016/j.radphyschem.2020.108696. **Impact factor 2022: 2,9.**

4. Traian Zaharescu, Tunde Borbath, Virgil Marinescu, **Ana Maria Luchian**, Istvan Borbath, *Improvement of thermal stability of EPDM by radiation cross-linking for space applications*, Journal of Thermal Analysis and Calorimetry, Vol. 138, 2019, 2445–2455.

   https://doi.org/10.1007/s10973-019-08581. **Impact factor 2022: 4,4.**

5. Traian Zaharescu, Sandra R. Scagliusi, **Ana Maria Luchian**, Ademar B. Lugão, *Degradability Characterization of EPDM/IIR Blends by γ-irradiation*, Journal of Polymers and the Environment, Vol. 26, 616.

   DOI10.1007/s10924-017-0966-9. **Impact factor 2022: 5,3.**

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6. **Ana-Maria Lupu**, Traian Zaharescu, Eduard-Marius Lungulescu, Horia Iovu, *Contribution of oxidation protectors in the stability of EPDM-based packaging materials*, University Politehnica of Bucharest Scientific Bulletin Series B, Vol. 82, 2020, 85.

Conferences

1. **Ana-Maria Luchian (Lupu)**, Traian Zaharescu, Horia Iovu, Marius Mariș, *Stabilization effects of natural antioxidants in PLA/SIS blends*, 4th International Conference on Materials: Advanced and emerging materials (ICM2022), 19-21 Octombrie 2022, Barcelona, Spain.
2. **Ana-Maria Lupu**, *Thermal and gamma irradiation qualification of PLA/SIS blends for packaging and medical applications*, Carpathian Summer School of Physics 2020 in 2021 (CSSP 2020), 18-27 August 2021, Sinaia, Romania.
3. **Ana-Maria Luchian**, Traian Zaharescu, Eduard-Marius Lungulescu, Maria Râpă, Gabriela Sbârcea, Horia Iovu, *SIS effects on the radiation processing of PLA*, 2018 Modification, Degradation and Stabilisation of Polymers Conference (2018 MoDeSt Conference), 2-6 Septembrie 2018, Tokyo, Japonia.
4. **Ana-Maria Luchian**, Traian Zaharescu, Eduard-Marius Lungulescu, Maria Râpă, Gabriela Sbârcea, Horia Iovu, *Thermal qualification of PLA/SIS bends for packaging and medical applications*, 12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12), 27-30 August 2018, Brasov, Romania.
5. Traian Zaharescu, Tunde Borbath, **Ana-Maria Luchian**, Istvan Borbath, *Improvement of thermal stability of EPDM by radiation crosslinking for space applications*, 12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12), 27-30 August 2018, Brasov, Romania.
6. **Ana-Maria Luchian**, Traian Zaharescu, Eduard-Marius Lungulescu, Maria Râpă, Gabriela Sbârcea, Horia Iovu, *SIS effects on the radiation processing of PLA*, 18th International Balkan Workshop on Applied Physics and Materials Science (IBWAP 2018), 10-13 Iulie 2018, Constanta, Romania.
7. **Ana-Maria Luchian**, Traian Zaharescu, Eduard-Marius Lungulescu, Nicoleta Butoi, *The differential stabilization effects of some natural antioxidants on γ- irradiated/UV- exposed*

EPDM, International Symposium "PRIORITĂȚILE CHIMIEI PENTRU O DEZVOLTARE DURABILĂ" (PRIOCHEM 13th Edition), 25-27 Octombrie 2017, Bucharest, Romania.

8. **Ana- Maria Luchian**, Traian Zaharescu, Eduard-Marius Lungulescu, *The comparative study on the degradation of EPDM by γ-irradiation and weathering*, 8th International Student Summer School «Nuclear Physics – Science and Applications» (NUCPHYS-SC & APP), 26 Iulie-4 August 2017, Brasov, Romania.

Projects

1. Research project no. 3PS/28.08.2019, entitled *"Research on the hazards of food contact materials by material groups. Harmonization with European legislation"*- **Member** of the research team of the partner INCDIE ICPE-CA
2. Mobility Project No 151/29.11.2017, Mobility Projects for Researchers, PN III-P1-1.1-MC-2017-0944- **Project Manager**
3. Research project no. 132/2017, *"Bio-sealing of container systems for Mars samples",* SealSamCo, Research-Development-Innovation Program for Space Technology and Advanced Research - STAR- **Member** of the research team of the partner INCDIE ICPE-CA
4. Extreme Light Infrastructure- Nuclear Physics (ELI-NP) Project - Project implemented by the Horia Hulubei National Institute of Physics and Nuclear Engineering (IFIN-HH) and co-funded by the Romanian Government and the European Union through the European Regional Development Fund (ERDF) - **Member** of the research team of the Laser Experiments Department.

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