

The stabilization assisted by POSS nanoparticles embedded in styrene-isoprene-styrene triblock copolymer

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ABSTRACT

Various substituents ($-\text{CH}_3$, $-\text{OCH}_3$, $-\text{F}$, $-\text{Cl}$) placed in polyhedral oligomeric silsequioxane (POSS) structure influence the stability of styrene-isoprene-styrene block copolymer (SIS) hybrids by the electronic interaction on the surface of the particle. The chemiluminescence investigation on the oxidability of these samples allows the characterization of the interaction between the radiolysis polymer fragments and the tetrahedral configuration broken by γ -irradiation. The modified POSS structures mitigate the evolution of oxidation, because the penetration of free radicals is controlled by the substituent action on the penetration of radical into the free space of POSS structures rather than their oxidation. In the degrading polymer material. The evaluated protection activities of modified POSS structures are characterized by the values of the activation energies required for the improvement in the extended stability based on the oxidation induction times, as well as the slowing down of the oxidation rates at the degradation temperature exceeding 170°C . The substituents play the role of moderators in the scavenging of polymer fragments by their ability to influence the efficiency of cage withdrawing of free radicals from the degradation chain. These SIS hybrids represent the appropriate versions of fillers that may minimize the development of ageing in degrading products and waste recycling. The study intends to demonstrate that a crystalline compound can extend material durability simultaneously with the improvement of functional ability due to the interaction on the particle surface.

1. Introduction

The great interest paid to the polyhedral oligomeric silsequioxane (POSS) composites, whose application range is extended continuously, is demonstrated by the large number of reviews and reports that are published over the last years (Zhang et al., 2017; Mohamed et al., 2020; Liu et al., 2021; Wang et al., 2021; Zhou et al., 2021). The structures of POSSs are appropriate for the promotion of the stabilization for polymers and their nanocomposites (Wanke et al., 2016; Zaharescu et al., 2017; Radaelli et al., 2018; Kuo, 2022; Kuan et al., 2023), when the cage effect controls the progress of the oxidative degradation. The involvement of POSS filler in the diminution of the oxidation rate during the polymer ageing is ascribed to the opening of the tetrahedral configuration by the scission of $-\text{O}-\text{Si}-$ moieties belonging to the general structure $(\text{RSiO}_{1.5})_n$ (Takahashi et al., 2021; Shi et al., 2022). It may be assumed that the protection activity of the different substituted POSS

concerns the superficial interaction between the newly appeared free radicals from the scission of polymer macro chains and the holes in the tetrahedral lattice construction that is broken during thermal or radiation degradation (Ozimek et al., 2021).

The stability of polymer matrices in which these compounds are added may be modified by the filler structures that allow molecular fragments to penetrate the damaged tetrahedral edge (Choi et al., 2009). This stabilization step is driven by the electronic distribution established by the substitutions placed at the corners of the POSS geometry (Zaharescu et al., 2020). The incorporation of modified POSS in various polymer composites determines a significant improvement in the functional properties associated with the material strengths, especially in the thermal stability (Jiao et al., 2015; Blanco et al., 2020; Fan et al., 2021). The mitigation of oxidation induces the auspicious adjustment of mechanical resistance (Jung et al., 2014; Lu et al., 2019), flame retardancy (Chua et al., 2021), stability for several medical applications (John et al.,

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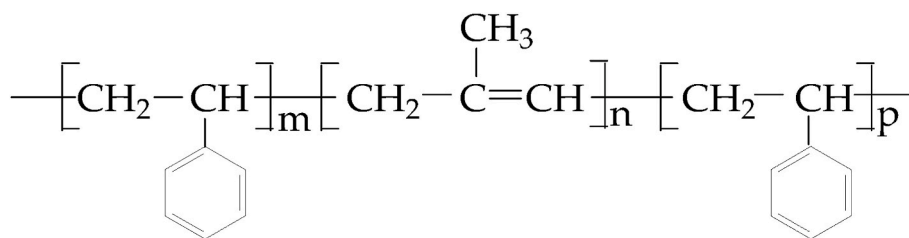


Fig. 1. The structure SIS where the susceptible positions for molecular damaging are shown.

2018; Ozimek and Pielichowski, 2022), their implementation in seawater desalination (Moon et al., 2014), and many other targets.

The importance of POSS hybrids consists of the stabilization consequences (Kuo and Chang, 2011) on the host materials, which become suitable for unexpected fields. The designed functionalities are related to the available potential of participation due to the inner free space and the possibility of structural opening during processing. The modification of polymer matrices with filler like POSS opens new ways in the preparation of stabilized and the manufacture of high-tech materials with satisfactory durability.

The stabilization mechanism through which POSS structures act during the oxidation of polymers differs essentially from the activities of synthetic antioxidants (Rychlý et al., 2015; Xu et al., 2020), natural extracts (Mohanta et al., 2022), or inorganic oxides (Zaharescu et al., 2016). The inhibition of oxidation is controlled by the different electron density, which is determined by the interaction between the structural cells of POSS and the substituents. In essence, the POSS filler subtracts polymer radicals from their oxidation by diffusing into the silicon structure after breaking an edge of the lattice unit.

According to the SIS structure (Fig. 1), the weakest positions available for scission are placed in the isoprene moieties, because the styrene units are generally nominated as the hard segment, while the median part, isoprene, is named soft fragment (Han et al., 2020). The unsaturation and the presence of quaternary carbon atoms are the most reactive positions that allow fragmentation are illustrated during the energetic exposures: thermolysis, photolysis, and radiolysis.

The oxidative degradation of the host polymer (SIS) occurs by the formation of hydroperoxides as a result of the oxygen attack on the isoprene units. This linear block copolymer does not appear as vulnerable material due to the presence of styrene parts, because the π -electron delocalization in benzene rings maintains the stability of block macromolecules (Getlichermann et al., 1994). The involvement of unsaturation belonging to the isoprene segments into the slight crosslinking of SIS was already demonstrated (Menga et al., 2005), which is a competitive process that simultaneously happens with the oxidation of triblock polymer material. During the environmental degradation, the styrene-isoprene triblock copolymer is degraded faster than the second component of blends, because it shows more evident oxidation instability in respect with the behavior of other structures (Ghioca et al., 2013). The reactivity of SIS was proved by the epoxidation of this substrate (Li et al., 2010), when the attack on the macromolecules occurred on the position of double bonds.

The necessity of the material stabilization against oxidation during its long term service is due to the problem of inhibition with respect to the accumulation of hydroperoxides, which may be achieved by the addition of appropriate compounds. Based on the previous results obtained by the stability investigations of an elastomer (Zaharescu et al., 2020), the present information can be considered as the starting background in the evaluation of material lifespan, though the lack of similar details represents an important shortcoming related to the identification of a reliable alternative for the ecological procedure of the improvement of product life time.

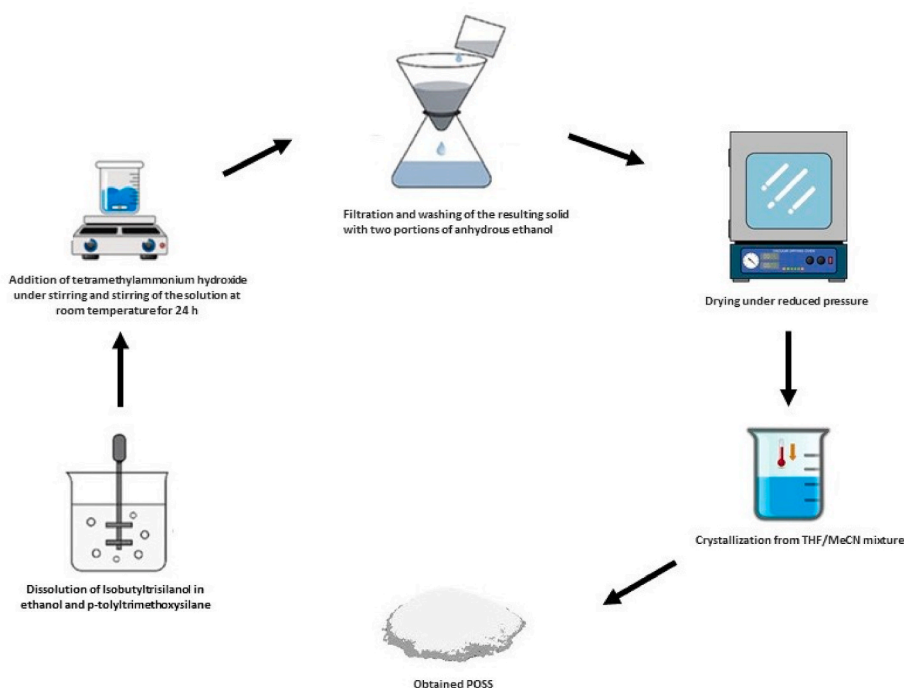


Fig. 2. The synthesis procedure for studied POSS structures.

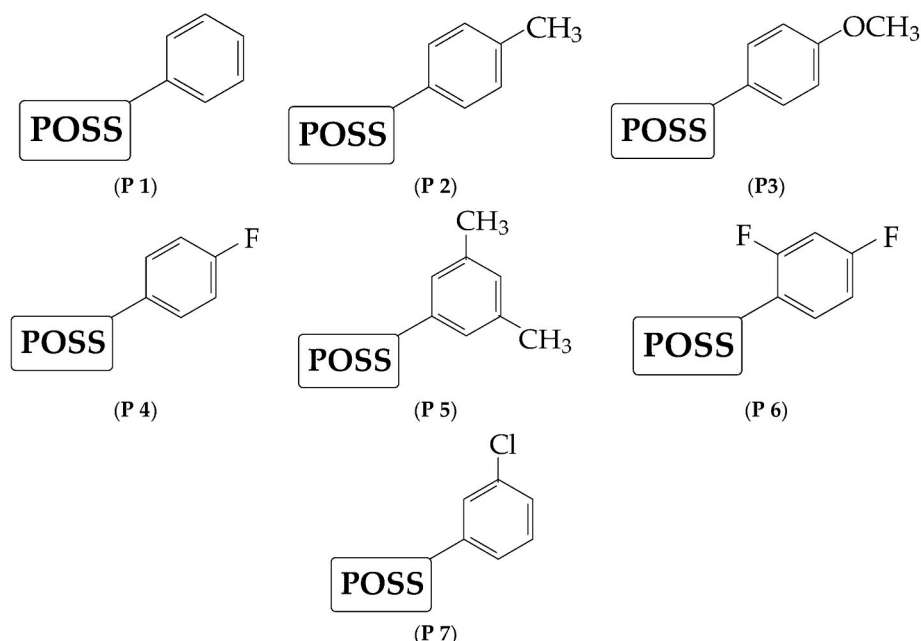


Fig. 3. The structures of substituents that modify POSS molecules.

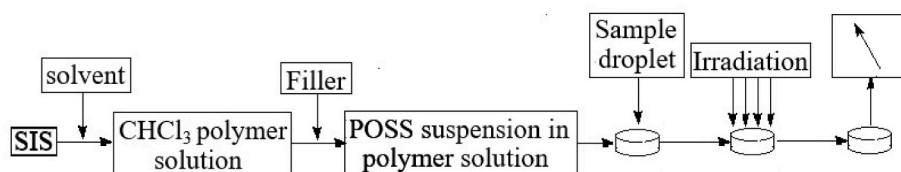


Fig. 4. The preparation chain for the SIS/POSS samples.

This study is a challenge proof for the efficient stabilization by an inorganic structure whose own integrity allows the extension of the durability for polymer materials, which are subjected to a long period and progressive ageing without the synthesis of antioxidants. The elimination of organic antioxidants by their replacement with an inorganic compound gains two main benefits: a long-term scavenging of radicals into the lattice of POSS and the simultaneous improvement of product lifetime and functional properties.

2. Experimental details

The investigated polymer, linear styrene-isoprene-styrene triblock copolymer, was provided by KAPRON CHEMICALS (USA) as D1165 PT, which presents linear macromolecules with a content of 30 wt% styrene. All the modified POSS structures, samples P1–P7, were prepared at the University of Catania by Corner Capping Reaction of isobutyltrisilanol with the suitable aryltrimethoxysilane, and the synthesis procedure for P2 sample is reported as an example, since the same procedure was used for all the used POSSs. 3.95 g of isobutyltrisilanol (5.0 mmol) was dissolved in 50 ml of ethanol, afterwards 1.10 g of *p*-tolyltrimethoxysilane (5.2 mmol) and 2.0 ml of tetramethylammonium hydroxide were added under stirring. The clear solution was stirred at room temperature for 24 h, by obtaining a solid sample that was then filtered and washed with two portions of anhydrous ethanol (10 ml). Thus, the obtained white solid was dried under reduced pressure and crystallized from an acetonitrile-tetrahydrofuran mixture. A scheme for the POSS synthesis is reported in Fig. 2. Yield, ^1H NMR spectroscopy, and elemental analysis of the synthesized POSSs are reported elsewhere (Blanco et al., 2012, 2014).

The samples were obtained by the addition of each filler powder in

the chloroform polymer solution, followed by the solvent removal from the aluminum round pans, the rigid support for the thin films. The concentration of POSS compounds is 1 wt%.

The structures of the added powders as stabilization fillers are presented in Fig. 3, while the preparation chain of the investigated samples is illustrated in Fig. 4.

The accelerated degradation by γ -exposure was carried out in an irradiation machine provided with ^{60}Co source (Ob Servo Sanguis, Hungary). The radiation processing was conducted at two doses at room temperature at a dose rate of 0.5 kGy h^{-1} . The degradation dose of 50 kGy was chosen for the illustration of the deterioration of materials, because this value may be considered as a boundary limit between the sterilization processing and the industrial conditions. The usual exposure of 25 kGy is a specific treatment for the lowest condition of the manufacturing praxis being the lower technological limit, as well as for the radiation sterilization. The CL measurements were done immediately after the stopping of irradiation, because any modification caused by a more or less long keeping of the samples would be avoided.

The stability measurements were accomplished by chemiluminescence (CL) spectroscopy using the high-performance unit, LUMIPOL 3, provided by the Institute of Polymers, Slovak Academy, Bratislava (Slovakia). The isothermal chemiluminescence spectra were recorded at three of four temperatures (120 °C, 130 °C, 140 °C and 150 °C). The oxidation induction times (OIT) obtained from these measurements were used for the calculation of the activation energies characterizing the material thermal resistances by means of the Arrhenius procedure using the program ORIGIN 15. The nonisothermal CL measurements were accomplished at the convenient value of heating rate (10 °C min^{-1}), which allows the comparison of onset oxidation temperatures (OOT), when the oxidation process effectively starts.

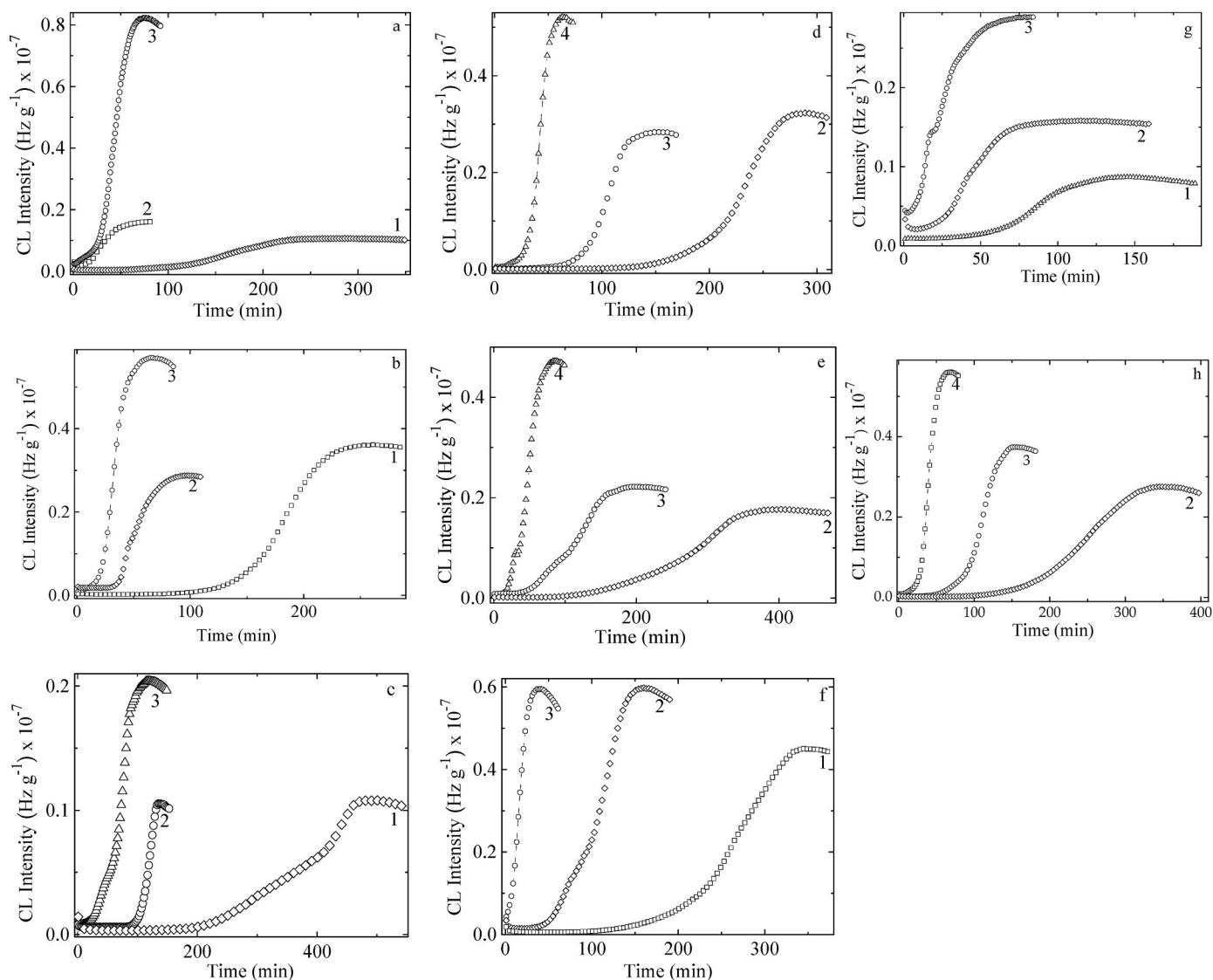


Fig. 5. Isothermal CL spectra recorded for unirradiated SIS hybrids.

(a) neat polymer (P 0); (b) SIS/P 1; (c) SIS/P 2; (d) SIS/P 3; (e) SIS/P 4; (f) SIS/P 5; (g) SIS/P 6; (h) SIS/P 7. (1) 120 °C; (2) 130 °C; (3) 140 °C; (4) 150 °C.

3. Results and discussion

The interactions between the filler represented by the POSS structures with various substituents and the hosting polymer materials lead to a variation of emitted chemiluminescence photons. It is deeply influenced by the activation of some superficial spots with respect to the subtraction of oxidizing radicals. Accordingly, the large surface of POSS particles diminishes the rate of propagation on the degradation chain, so that the extent of interaction range is a main factor that controls the development of oxidation (González-Orive et al., 2018). The polymer composites are the symbolic materials, where the mitigation of ageing is sustained by the optimization of interface interconditioning (Bhiogade et al., 2020). The performances of the composite polymer systems are understood due to the capacity of the inorganic phase to be linked or protected as a result of the interaction of components (Bouregba et al., 2024).

3.1. Isothermal chemiluminescence

The recording of CL emission photons allows the explanation of structural and compositional modifications that happened in the

investigated samples (Rychlý et al., 2020). The accurate CL determinations reveal the differences that exist between the stability of investigated SIS hybrids, starting from the determination of the degradation durations. The selected temperatures, the values of oxidation induction times, the kinetic parameters characterizing the early stability, and the degree of inclinations depicting the various rates of progress of ageing are the main factors that characterize the evolution of the degradation of the investigated systems (Fig. 5).

The first sight analysis of this set of curves allows the primary examination of the protection effects, which places the compounds P 2 and P 7 as the most efficient fillers added in the unirradiated material. The surface of the particle plays the role of the active factor of scavenging, which allows the retention of degradation initiators and the control of degradation progress by the diffusion of free radicals in the free space of the inner tetrahedral structure. The interpretation of these present results is suitably based on the electronic interaction between the POSS lattice and substituted phenyls. The theoretical approach is difficult to be presented, because the electronic densities on the benzene rings are different in correlation with induced polarity and the number of substituents. We consider that the two sequences presented in the section of Conclusions may be stated as informal guides for further investigation

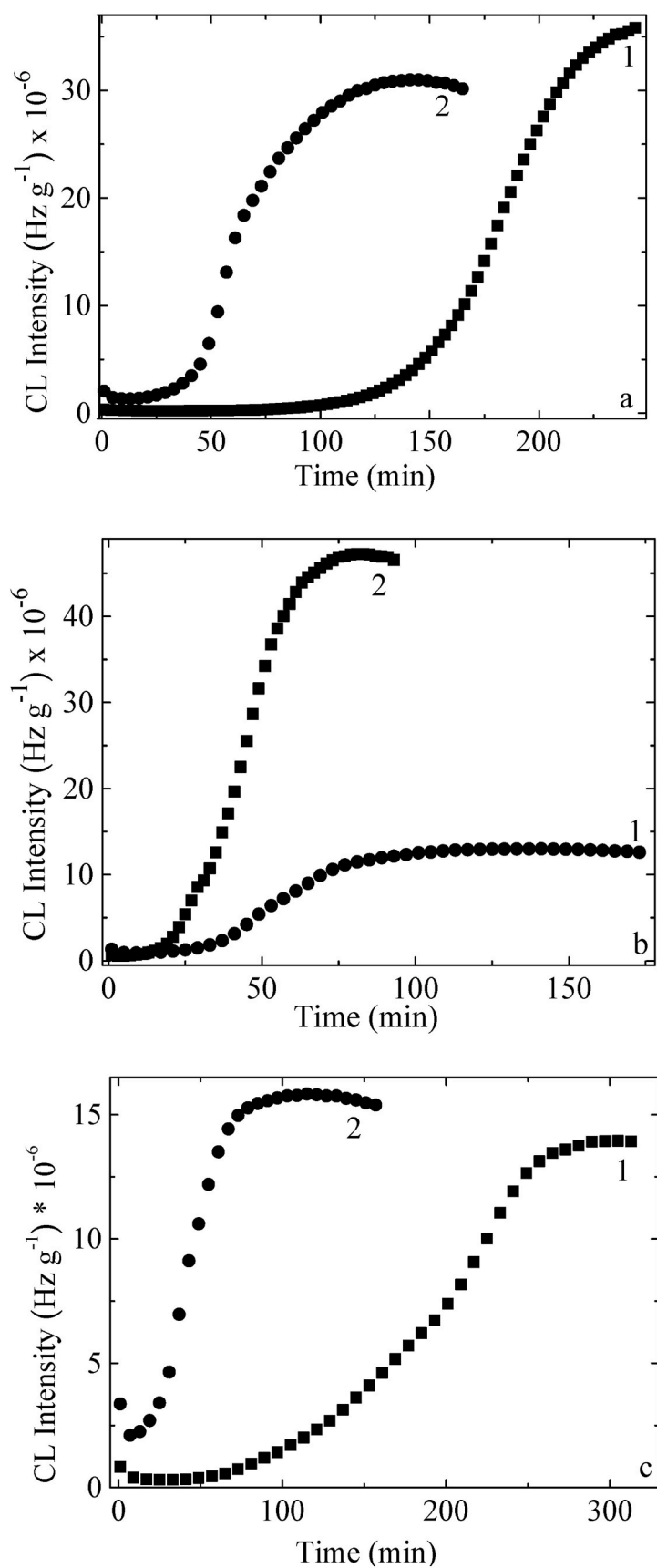


Fig. 6. Comparative presentation of the isothermal CL spectra of some SIS/POSS hybrids under different degrees of γ -irradiation recorded at 130 °C. (a) SIS/P 1; (b) SIS/P 4; (c) SIS/P 6. (1) 0 kGy; (2) 50 kGy.

Table 1

Activation energies calculated for the oxidation of SIS/modified POSS hybrids for to irradiation levels.

Sample	OIT (min)			Relationship	Correlation factor	E _a (kJ mol ⁻¹)
0 kGy						
	130 °C	140 °C	150 °C			
P 0	75	31	12	Y = 33.3 + 15.6 X	0.99941	129.7
P 1	131	46	20	Y = 33.0 + 16.9 X	0.99985	140.7
P 2	200	51	22	Y = 37.4 + 18.8 X	0.99249	165.4
P 3	192	65	30	Y = 30.0 + 15.8X	0.99663	132.1
P 4	185	65	28	Y = 30.7 + 16.1X	0.99884	133.8
P 5	162	52	25	Y = 30.6 + 16.0X	0.99393	133.0
P 6	140	50	21	Y = 31.1 + 16.1X	0.99938	133.8
P 7	165	78	28	Y = 31.6 + 16.5X	0.99893	137.2
25 kGy						
	120 °C	130 °C	140 °C			
P 0	44	18	10	Y = 22.8 + 12.0X	0.99456	99.8
P 1	135	42	18	Y = 32.7 + 16.4X	0.99702	136.4
P 2	90	42	18	Y = 40.2 + 13.0X	0.99987	108.1
P 3	212	93	36	Y = 27.1 + 14.4X	0.99849	119.7
P 4	70	31	14	Y = 24.9 + 13.1X	0.99997	108.9
P 5	108	37	20	Y = 26.7 + 13.7X	0.99014	113.9
P 6	56	20	8	Y = 32.1 + 15.8X	0.99981	131.4
P 7	28	12	6	Y = 24.4 + 12.5X	0.99906	103.9

would be foreseen somewhere.

The pristine polymers (Fig. 5 a) present a large difference in the evolution of oxidation at 120 °C, on one hand, and the progress of degradation at 130 °C and 140 °C, on the other hand. This unexpected behavior suggests the existence of a stability threshold between 120 °C and 130 °C that suggests that the addition of a suitable protector like POSS, whose particle surface is involved in ameliorating the material durability, is a pertinent solution for the extensive durability of products.

The stability features may be emphasized by the comparison between the progress of oxidation in unirradiated materials and the exposed patterns at 50 kGy (Fig. 6). The high-energy exposure like γ -irradiation, is a suitable treatment through which the efficient stabilization activities are emphasized by any appropriate inorganic additive. The induced radiolysis affects essentially only the polymeric phase. The present fillers would be damaged either by the scission of –O–Si–O– to siloxyl moieties on the POSS skeleton or by the radiolysis of the substituents.

From Fig. 6, it may be noticed that the oxidation strength of the studied hybrids must take into account the specific effect of the hybrid on the polymer substrate, whose structure is intimately affected by the energetic interaction between the incidental rays and its molecular component. Based on the calculated oxidation induction times (OIT), in Table 1 the values of activation energies involved in the oxidation process are presented. The analysis of activation energy values offers the real image of electronic interaction between the basic spatial structures of polyhedral POSS and the substituents that correlate the electron clouds with their electrical affinities. The substitution effect is extended,

and the contributions of the electronic structures on the attraction of radical intermediates may be addressed to the qualification of protection activities. Accordingly, the damaged states achieved after γ -irradiation impose a lower temperature range for the accurate determination of kinetic behavior. The discussion on the calculated values of activation energies may point out that the influence of substituents on the benzene nuclei determines these E_a figures. Basically, they become the result of electronic interaction, which is correlated with the electrophilic effects. The inductive effect promoted by halogen atoms polarizes the σ -bond electrons onto these atoms, decreasing the electronic density on benzene nuclei. On the other side, the resonance donation of alkoxyl substituents makes possible the conjugation of bonding electrons with the π electrons belonging to the ring. Both interactions induce in the POSS lattice a corresponding electrical field, which would attract or reject the neighbor of the free radicals. The penetration of POSS configuration by the polymer molecular fragments created during degradation is controlled by the induced electronic effect, which adjusts the amounts of scavenged radicals. The localization of scavenging centers on the surface of particles is related to the availability of –O–Si–O– structures to break the bond O–Si, as well as the creation of an electronic deficit that is filled with the unpaired electron of a free radical.

3.2. Nonisothermal chemiluminescence

The nonisothermal CL spectra allow the determination of the temperatures when the 7degradation starts (Fig. 7). The influence of the filler substituent and the irradiation degree on the thermal degradation of SIS/modified POSS hybrids makes differences between various filler contributions on the strengths of composite materials. While the neat polymer is the less resistant material without irradiation, as it usually happens when it operates in the regular activities, the irradiated pristine SIS shows certain stability because of a slight crosslinking achieved due to the former unsaturation of the soft segment (isoprene units).

The interaction between the two components (polymer and filler) is modeled by the electrical interaction between the lattice defects appeared by the scission of Si–O bonds and the radiolysis oxidation products (Rizwan and Chandan, 2022), predicting the improvement of product stability. The increase in the CL emission is tightly related to the accumulation of degradation products, which is accelerated by the diminution of this attraction at higher temperatures (Yang et al., 2022).

The preservation of structural configurations attained in polymer composites is sustained by the interaction between the inorganic filler and the polymer phase (Kodal et al., 2018; Zhou et al., 2022; Guadagno et al., 2023). In the cases of the accelerated energy transfer, like photolysis and radiolysis, the damage of the lattice cells occurred by the scission of Si–O bonds creates a favorable condition for the penetration of molecular fragments from polymer backbones (cage effects) (Cheng et al., 2024). The observed modifications in the values of kinetic parameters (onset oxidation temperature for nonisothermal CL measurements and oxidation induction time for isothermal CL determinations) characterizing the progress of oxidation are strong background proofs for the stabilization effects of POSS, which are the consequences of the contribution of inorganic phase on the abstraction of free radicals from the polymer phase subjected to accelerated degradation by γ -irradiation. This effect was also found in other materials (Zaharescu and Mateescu, 2022), whose oxidation process is mitigated by the content of silsesquioxane structures.

The addition of POSS nanopowders is an efficient way for the improvement of material durability (Peng and Han, 2023; Peng et al., 2024; Ullah et al., 2024; Wang et al., 2024) involving advanced superficial interaction, because the investigated compound can promote in a large extend the deceleration of the ageing of polymer products by its availability to withdraw the reactive intermediates as the result of the breaking oxidation chain on the outer threshold of particles. The high performances achieved by the POSS/polymer composites demonstrate the profound involvement of POSS structures in the deactivation of the

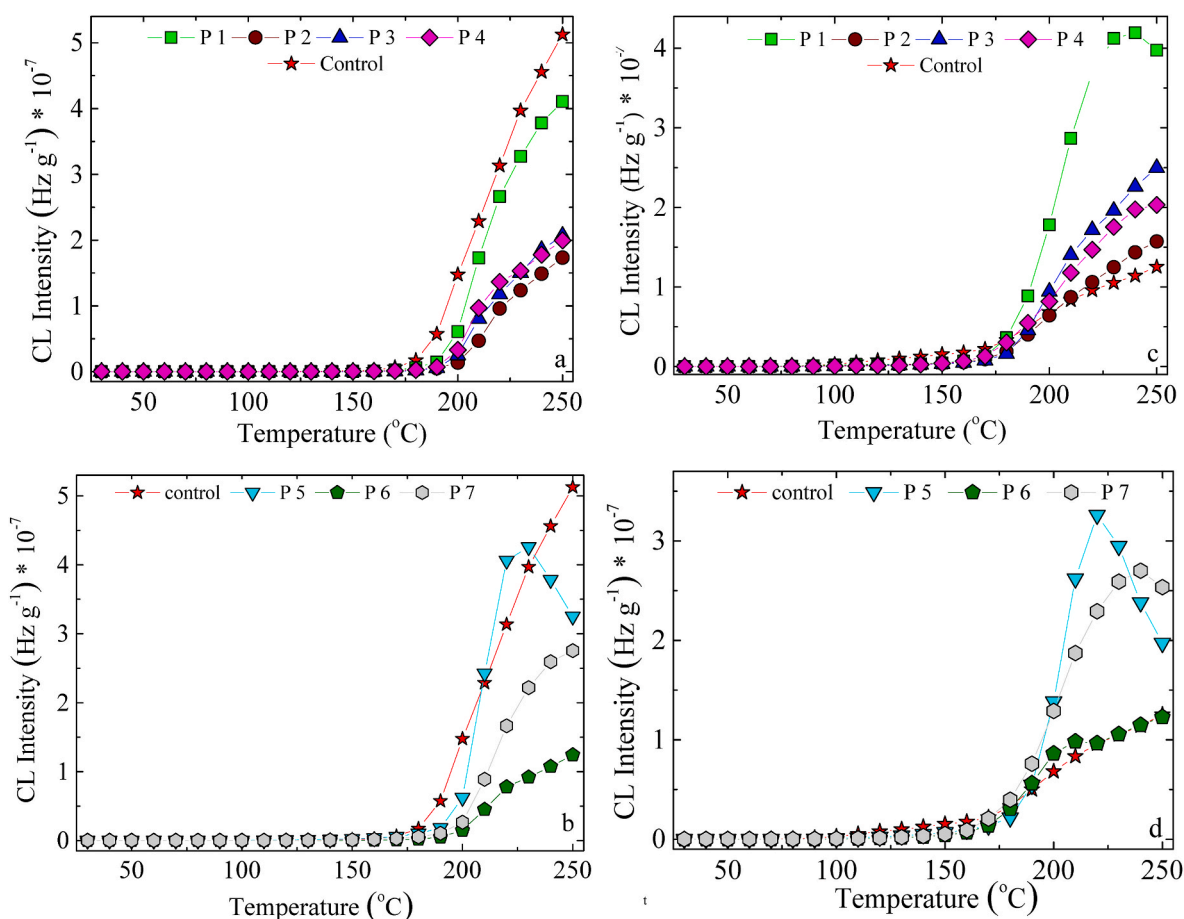


Fig. 7. The nonisothermal CL spectra recorded on SIS/modified POSS hybrids (a, b) unirradiated samples; (c, d) samples after their exposure to 50 kGy of γ -radiation. Heating rate: 10 °C min⁻¹.

oxidation of free radicals, especially occurring during the accelerated ageing induced by high-energy exposures (Choi et al., 2012, 2013). The functionalization of POSS configuration and the addition of these new structures into the polyethylene composites bring about similar effects as are obtained in the present study (Perrin et al., 2013; Frone et al., 2013). The radiation processing of POSS composites is susceptible to the crosslinking process (Xing et al., 2018) due to the mitigation of oxidation by the retention of radicals on the superficial cages. The superior stabilities of biopolymers like poly (lactic acid) modified by POSS are attained (Ullah et al., 2022), and the utilization of substituted fillers enlarges the stability class. The radiation treatment of POSS/polymer nanocomposites becomes an interesting procedure if it is appropriately applied for the control of filler jointing on the polymer backbones (Chmielewski, 2023).

4. Conclusions

The monitoring of induced effects by the presence of inorganic structure in the formulation of polymer composites is selectively and accurately accomplished by chemiluminescence, a very sensitive experimental procedure.

The stabilization activities of several modified polyhedral oligomeric silsesquioxane added in styrene-isoprene-styrene triblock copolymer are investigated by the CL records, where the interaction between filler and polymer is developed by means of some basic kinetic parameters: oxidation induction time, onset oxidation temperature, and activation energy. This study proves that the substituents (CH₃, OCH₃, Cl, F) on the benzene ring may influence the mitigation degree of oxidation. The

kinetic parameters, like oxidation induction time, serving as the input values for the calculation of activation energies, are the characteristics that illustrate the localization of scavenging spots on the surface of POSS particles. These values that characterize the stabilization efficiency order the substituents in the following sequences based on the isothermal measurements:

Unirradiated polymer composite: free < 4-methoxyphenyl < 3,5-dimethylphenyl < 4-fluorophenyl ~ 2,4-difluorophenyl < 3-chlorophenyl < phenyl < 4-methylphenyl.

25 kGy γ -irradiated polymer composite: free < 3-chlorophenyl < 4-methylphenyl < 4-fluorophenyl < 3,5-dimethylphenyl < 2,4-difluorophenyl < phenyl < 4-methoxyphenyl.

The nonisothermal measurements demonstrate that the nonirradiated composites are more stable than the polymer reference, while the γ -processing at 50 kGy affects especially the inorganic phase, which decreases the contribution of POSS to the mitigation of oxidative degradation. The comparison of results indicates the availability of these structured POSS for the protection of polymers subjected to the radiation sterilization, but the role of protectors is missed at increased doses. The presented series is determined by the electrical interaction of substituents with the energetic gaps placed on the surfaces of POSS particles, where the electron deficit scavenges free radicals. This study proves that a certain substituent induces its own consequence on the polymer span due to the influence of the substituent on the electron distribution in the filler and the mitigation of oxidation by the interaction on the surface of inorganic particles.

It is difficult to compare the present results with the other ones, because the mechanisms of interaction are totally different. In fact, the

results indicate a proper stabilization activity of POSS structures, which qualifies them as the pertinent fillers for the long-term operation of polymer composites containing this class of protective compounds. The testing of these composite systems by γ -irradiation is a very good proof for the delay of oxidation under the accelerated conditions of degradation.

CRediT authorship contribution statement

Traian Zaharescu: Writing – original draft, Visualization, Validation, Investigation, Conceptualization. **Ignazio Blanco:** Writing – review & editing, Methodology, Conceptualization. **Ademar B. Lugao:** Writing – original draft, Validation, Supervision. **Radu Mirea:** Formal analysis, Data curation.

Declaration of competing interest

In behalf of the author team, I strongly affirm that any financial and personal relationships with other people or organizations that could inappropriately influence (bias) their work. Accordingly, no any author hides any information related on this dependency or on any personal pressure or the launching patent proposal.

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Data availability

Data will be made available on request.

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