



Article Kinetic Analysis on the Stabilization Effects of Substituted POSS Powders Embedded in γ-Radiolyzed Polypropylene

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Abstract: The present paper proposes a reliable alternative for the increasing stability of polypropylene (PP) by modified polyhedral oligomeric silsesquioxanes (POSS). The chemiluminescence measurements and FTIR records point complementarily out the determinant influence of substituents on the progress of oxidation during the accelerated degradation caused by γ -irradiation. The main kinetic approach of oxidation acting in radiation-induced aging recommends some of the studied structures of modified POSS as appropriate compounds for improving stability of polypropylene at low additive concentration. The analysis of the present results is based on the implication of substituted POSS, whose contribution to the limitation of oxidation is conditioned by the influence of substituents. The delay of the oxidative degradation in studied γ -irradiated polypropylene is the consequence of the interaction between molecular PP fragments and the silanol moieties generated during radiolysis, which are the most vulnerable points of POSS structure.

Keywords: POSS; polypropylene; degradation; irradiation; chemiluminescence

1. Introduction

The vulnerability of raw polypropylene against an accelerated oxidative degradation [1] is illustrated by the prominent tendency onto oxidation, which can be ameliorated by the addition of proper compounds involved in the diminution of degradation rate, especially on the early stages of structural damage. For overcoming this disadvantage, a proper alternative that is commonly adopted consists of the addition of antioxidant inhibitors [2,3], crosslinking [4,5], and several inorganic fillers [6,7]. The hybrid compounds containing various types of fillers are versatile solutions by which polypropylene as the main component of material formulation shows improved resistance in respect with pristine polymer [8–10]. The broadness of modifications in the material behavior is tightly related by the filler (POSS) loading [11] because the interaction between the host polymer and filler reaches high intensity in the absence of any screening factor, such as volume hindering [11]. In the cases of solid particles, the interfacial traps formally assimilated as potential gaps are essential elements for the limitation of the propagation rate in oxidative degradation. The scavenging free radicals hinders the further reactions of intermediates, delaying the formation of oxygenated final products [3]. Many works were dedicated to the modification of oxidation progress by the trapping reactive intermediates on the particle surface by their inactivation [12]. Similar effect was reported in the inner part of hydrogels [13], which allow the diminution of their oxidation by the catching molecular fragments. Nevertheless, a real alternative way of protection against oxidation is the addition of modified POSS that maintains the unchanged structure for a longer time in respect with the nature of substituents bonded on the corners of POSS configuration [14]. Consequently, the evolution of



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). intermediates decay is intrinsically controlled by the chemistry of added protection agent, as it was demonstrated by the γ -irradiated ethylene-propylene-diene terpolymer [14].

An efficient stabilization effect of polyhedral oligomeric silsesquioxanes was investigated in the absence of high energy exposure [15–17]. The substituents existing in the POSS structure exert a distinctive influence on the stability of POSS three-dimensional configuration. The selection of substituents is imposed not only by the behavior of polymer [18], but also by their electronic effect induced in the POSS network [14,19–22].

The applications of hybrid compounds need a detailed analysis on the contribution of components, which enhance the material durability by their ameliorating oxidation rates. It is well recognized that polypropylene is easy oxidized by high energy irradiation because of the high content of tertiary carbon atoms, which determines a greater value of radiochemical yield of scission (G(S) = 0.24) in respect with the radiochemical yield of crosslinking (G(X) = 0.16) [23]. The conversion of polypropylene into a resistant polymer can be achieved by the addition of other polymer, like EPDM [24], of a compatibilizer agent [25,26] or of an inorganic filler [5,27]. The stabilization mechanism is a classical sequence of stages where the PP fragments are hindered to be oxidized [3]. The POSS molecules, whose cage activity caused by the break of silanyl structural component, can promote the improvement in the material stability by the formation of free space inside the cubic frame available for the penetration of certain scission fragments [13,14,28]. The interfacial interactions between the POSS particle surface and the neighbor molecular fragments allows their capture, protecting them against the reaction with diffused oxygen available in the material bulk.

The functionalization of POSS structure offers a good chance to find appropriate compounds for attaining better material properties. The polymer that incorporates this kind of fillers may gain some improved characteristics related to the influence of substituents [14,20,22]. The traps distributed on the POSS particle surface mitigate the oxidation of degradation intermediates that extends the material stability in the correlation with the restricted mobility of free radicals. This kind of inorganic filler show a restrictive energetic barrier [22,29], which restrains the progress of oxidative degradation, even in the accelerated degradation initiated by γ -irradiation [11,14].

The previously reported results on the thermal analysis of polystyrene based hybrids containing modified POSS with mono phenyl-polyhedral oligomeric silsesquioxane [30] suggested that PP, a commercial polymer with several wide ranges of applications, including medical items sterilized by γ -exposure, may be taken into consideration. By a detailed introspection on the improvement degree in less resistant polymers like polypropylene, the contribution of this type of fillers may show an appropriate version of the manufacture of high-performance materials. The filled polymer has better heat resistance and lower degradation rate because of the electronic influence of the modifier on the scission strength of POSS-base structure.

The creation of stabilization reinforcement by the presence of substituted POSS develops a new trend in the production of high resistant materials subjected to an accelerated degradation by the intense energetic transfer happened during the accidental exceeding of technological procedures. An excellent effect brought about by structured POSS emphasizes the extension of service ranges by their functional characteristics determined by the contribution to the scavenging free radicals and, subsequently, on the delaying material aging [31].

This paper presents the evaluation of stabilization effect offered by several structurally modified POSS particles embedded in polypropylene. Two complementary characterization procedures, infra-red spectroscopy and chemiluminescence, provided detailed information on the involvement of fillers in the restricted progress of oxidation in polypropylene. The presented results may be considered as the start pointes for the manufacture of long-life products, whose applications can be found in medicine (sterile wear), commodities, food packaging materials, automotive, flexible coatings, electrical insulation polymer blends, green and many others.

2. Materials and Methods

Polypropylene was produced by Borealis AG as EE050AE grade. The synthesis and characterization of the seven structured POSS powders were reported elsewhere [32]. The blended samples loaded with 2 wt% of POSS powders were obtained by the vigorous grinding of both components (PP and POSS powders) in a ceramic mortar, where some drops of chloroform wetted materials for their intimate mixing. The structures of POSS powders are illustrated in Figure 1.



Figure 1. The structures of POSS powders modified by the substitution of outer phenyl unit.

The γ -exposure was accomplished in an irradiator provided with a ⁶⁰Co source (Ob Servo Sanguis, Hungary) at room temperature. The dose rate was 0.6 kGy h⁻¹ during the sample γ -processing by rotating of support can in the irradiation room. The selected doses were 0, 25, 50 and 100 kGy.

Thin films (100 μ m) were obtained by pressing at 150 °C for 5 min. FTIR spectra were recorded on JASCO 4200 A (Japan) by 50 scans per each film. The spectral resolution was 4 cm⁻¹. These spectra were used for the calculation of carbonyl and hydroxyl indices by dividing the transmission values at 1715 and 3380 cm⁻¹ by the reference one (1456 cm⁻¹) [33].

The isothermal and nonisothermal chemiluminescence measurements were carried out by LUMIPOL 3 spectrometer (Slovak Academy of Sciences, Bratislava) based on the proportionality between the amount of peroxyl radicals formed during oxidation and the chemiluminescence emission recorded by CL photomultiplier [34]. The mechanistic details on the formation of the excited carbonyls as precursors of CL emission units were previously presented [35]. The nonisothermal measurements were done at four different heating rates (3.7, 5.0, 10.0 and 15.0 °C min⁻¹), while the isothermal determinations were performed at 150 °C. The onset oxidation temperatures depicting the start of oxidation were obtained from nonisothermal measurements.

3. Results and Discussion

The fragmentation of polypropylene molecules creates free radicals [36], which react with diffused oxygen and form the stable oxygenated products. The rates and the amounts of their accumulation qualify the material resistance, a relevant criterium for the evaluation of stability under various conditions of operation. The evaluation of oxidation levels reached by the γ -processed PP/POSS hybrid samples is conclusive by the investigations either on the formation of hydroperoxides using chemiluminescence, or on the accumulation of stable oxidation products by means of FTIR spectroscopy. The studied composites degraded by radiation damaging were susceptible to a competition between the oxidation provided by present fillers. The substitution effects are conditioned by this simultaneity because the electronic interactions between siloxane units and the substituents from the benzene ring make possible the polarization of bonds [14].

3.1. Chemiluminescence Assay

3.1.1. Isothermal Chemiluminescence

The progress in the delayed degradation of polypropylene component of studied hybrids can be ascribed to the damage of O-Si-O moieties and the creation of splits through which the polymer fragments can penetrate inside the POSS free volume. In Figure 2, the differences between the thermal behavior of PP/modified POSS hybrids can be noticed based on the substituent effects.



Figure 2. Isothermal CL spectra recorded on PP loaded with various substituted POSS powders. Temperature: $150 \degree$ C. (a) nonirradiated samples; (b) hybrids exposed to 50 kGy.

Some essential features must be discussed. The pristine polypropylene divides the curve family into two groups that acts contradictorily on the polymer matrix. While the upper curves denote an oxidative action of fillers, the lower curves describe the proper stabilization activity. In all the cases, the nonsubstituted benzene ring does not show any protection trend that indicates the necessity of structural modifications for the delocalization of π electrons in the benzene configuration. The difluorbenzene does not allow the penetration of molecular fragments in the free hole of the POSS network. The same compound exhibits a proper protection action characterized by a slower oxidation rate over the whole duration. A similar behavior is shown by the compound, where phenyl units present chlorine atom in the p-position.

The most important attribute of γ -irradiated PP/modified POSS hybrids is the efficacious contribution of filler on the slowing down the propagation of oxidation. Except the structure P 3, all compounds inhibit the conversion of free radicals into different oxygen-containing stabile products. The oxidation rates are correlated with the duration of degradation. It can be noticed that the lower the oxidation rate, the longer the time attaining the end of ageing. The remarkable efficiency induced by P 5, the compound where two methyls in the o-position. The substituted POSS structures that present high dipole moments (P4, P6 and P7) [14] act effectively on the protection of PP against its quality depreciation by oxidation. The comparison of induced effects of the same compounds in EPDM [14], it may be notified that the content of tertiary carbon atoms in the degrading material influences the values of oxidation induction times. While in EPDM, the alternation of ethylene and propylene moieties from the molecular sequence determines extended earlier periods of stability, followed by faster oxidation rate, in PP, the reverse situations are revealed. It means that the oxidation starts preferentially on the propylene segment. For the majority of studied hybrids, the evident improvement of thermal behavior by the interference of added filler in the reduction of polymer stability by oxidation is explained by the polarization of jointing bond of phenyl substituent in the POSS configuration. Consequently, the bonds O-Si would be weakened, making them easily broken, and

the penetration of radicals into the free space of POSS becomes possible. This consideration is firmly based on the behavior of PP samples containing powder P1, the POSS structure that has not any substituent.

The modification of degradation rate is correlated to the nature of filler and the irradiation dose. As it can be pointed out from Figures 2 and 3, the phenyl units having monosubstituents (P3: p-metoxy) and disubstituents (P5: o-dimethyl and P6: p-difluor) display higher rates of oxidation in respect with the control (pristine polypropylene) specimen. These substituents have an +I induction effect that determines the rearrangement of electron density.



Figure 3. Histograms of oxidation rates for studied hybrids for different γ -exposure doses. (**a**) nonirradiated samples; (**b**) irradiation doses: 50 and 100 kGy.

As can be remarked from the results obtained by isothermal chemiluminescence, our irradiated polypropylene is efficiently stabilized by the studied POSS powders, whose protection activities recommended them as antirad agents. Definitely, the presence of p-metoxy substituent turns the behavior of filler on the oxidation feature. On the opposite side there is the effect of the two dimetyls. This structure offers the lowest oxidation rate for all irradiation doses, even at 100 kGy, which is a very high dose processing for PP. At this dose, there are other three modified POSS structures, P4, P6 and P7, that emphasizes that the presence of halogen atoms induces an improved thermal resistance for γ -irradiated polypropylene. If the radiation sterilization would be applied on studied PP/modified-POSS hybrids, only P3 sample would be incompatible with this fast damage of microbial contamination. During the exposure of POSS loaded polypropylene at the γ -dose of 50 kGy, the probability of the trapping radicals is increased with dose, because the filler is also affected by γ -incidental rays (see comments at Section 3.1.2).

The radiation treatment of polypropylene mitigates usually by the addition of crosslinker, for example—triallylisocyanurate [37] or acetylene [5], as well as proper filler, like glass fiber [38]. Similarly with other polymers, namely PLA [39], POSS powders acts predominantly as an efficient trap for the degradation fragments. The modified POSS, where the electronic effects are present, are also suitable for the extension of thermal and radiation stability of polypropylene. This catching activity is correlated with the polarization of joining bonds that unit substituted phenyls on the POSS frame. The interaction between the pendant group from polymer backbone and the POSS hybrid component was previously analyzed [40], when the uniting bridges are weakened under stress conditions. Therefore, the protection activities of present studied compounds are naturally determined by the contribution of substituents on the electronic distribution surrounding the spot of radical connection.

This screen effect is also related to the stability of filler, which made differences between the propagation rates of degradation (Figure 3), which orders the stability of

hybrids for their selection purposes according to the foreseen durability and the mixing compatibility in several polymer blends.

3.1.2. Nonisothermal Chemiluminescence

The nonisothermal determinations, when the temperature characterizing the start of degradation (onset oxidation temperature, OOT, Figure 4) can be obtained, allows the evaluation of amplitude of stabilization effect brought about by the modified POSS fillers loaded in polypropylene.



Figure 4. OOT values for the start of oxidation in PP/modified-POSS hybrids.

The evolution of oxidation of nonirradiated PP/modified-POSS hybrid samples is presented in Figure 5. The shape of CL spectra indicates that the increase in the CL photoemission is tightly correlated on the diffusion of oxygen which feeds the propagation of this process.

The presence of stabilizing POSS places the nonisothermal CL spectra under the curve recorded on the pristine polypropylene, especially for the investigations performed at lower heating rates. Nevertheless, the there is a visible difference between the evolution of oxidation state. The presence of shoulder in the temperature region of 200–220 °C would be ascribed to the availability of rearrangement of radicals having lower kinetic energies of movement. It disappears gradually, defining a determinative contribution of environmental conditions on the polypropylene-based products. The supply of oxygen into the polymer matrix influences the oxidation state at the temperatures exceeding 150 °C. From Figure 5, it can be observed that a smooth increase in the amounts of oxidized fraction is recorded at the faster heating $(15.0 \,^{\circ}C \,^{mn-1})$. The acceleration degrees are not strictly respected for all of the heating rates, but the initiation of degradation is somewhat unlike still the moderate temperature, namely 140 °C, when the accumulation of oxidation initiators, peroxyl radicals, reaches a critical threshold.



Figure 5. The progress of oxidation in the nonirradiated PP/modified-POSS samples at different heating rates: (a) $3.7 \degree \text{C} \min^{-1}$; (b) $5.0 \degree \text{C} \min^{-1}$; (c) $10.0 \degree \text{C} \min^{-1}$; (d) $15.0 \degree \text{C} \min^{-1}$.

The Figure 6 illustrate the answers of modified POSS powders to the heating in the degradation room of a chemiluminescence device. The CL curve representing the pristine material divides the family spectra into two groups in respect with the contribution of filler on the progress of oxidation in unirradiated polymer.



Figure 6. The nonisothermal CL spectra recorded on modified POSS powders. (**a**) neat materials; heating rate: $10.0 \degree \text{C min}^{-1}$; (**b**) materials irradiate at 50 kGy, $15.0 \degree \text{C min}^{-1}$.

An opposite effect can be noticed in the irradiated samples (a medium dose of 50 kGy), where this substitution offers the highest stability over the whole temperature range of investigations. In fact, these configurations can be directly obtained as the consequence of γ -irradiation [41], so that the propagation of oxidation is sustained by the nature of intermediates.

The lower positions are occupied by the more stable hybrids, while the upper region is populated by the less stable compositions. A distinguished behavior is shown by the sample having methoxy units in the structure of POSS. It is rapidly degraded at temperatures exceeding 170 °C. In this case, the decay of oxidation intermediates easy converts them into stable oxygen-containing products, according to the degradation mechanism of polyolefins [41] integrating the structure through the instable configurations on the transformation routes to the final oxidized units.

The stability of intermediates is described by the maximum CL emission measured at 110 °C. These peaks may serve as the indicators for the material stability because they are tightly related by the evolution of oxidation, while the hydroperoxides are stabilized as the oxygen-containing products. The majority of hydroperoxides (Figure 6b, detail) are quite instable in comparison with the neat material, because the filler provides supplementary amounts of intermediates that are involved in the material degradation.

The degradation profiles of materials are influenced not only by the structure of the filler, but also by the heating rate, when the diffusion of molecular oxygen feeds the oxidation process (Figure 7). The oxidation of more exposed material starts earlier than the less irradiation samples due to the higher concentrations of hydroperoxides, the greater heating rates allows the quick oxidation on the spot, because the amount of diffused oxygen is significantly higher according to the Fick's laws [42].



Figure 7. Nonisothermal CL spectra recorded on PP/modified POSS powder. (a) γ -dose: 25 kGy; heating rate: 10.0 °C min⁻¹; (b) γ -dose: 50 kGy; heating rate: 15.0 °C min⁻¹.

The contribution of studied fillers is different from one structure to the other (Figure 8). The amounts of component units provided by the scission of POSS structure feed differently the degradation chains, when the movement of conveyed fragments is mainly restricted by the electronic distribution influenced by the substituents.



Figure 8. The nonisothermal CL spectra of powder and PP hybrid modified with the same filler in the unirradiated states. Heating rate; $10 \degree C \min^{-1}$. (**a**) P3; (**b**) P1; (**c**) P 2. (1) hybrid; (2) powder.

The thermal resistance of polypropylene hybrids would be depicted by the interaction between the basic polymer matrix and the fillers, which are simultaneously degraded. However, the modification occurred in the filler stability will define the evolution of oxidation in PP, as the spectral measurements indicate.

The behavior of filler brings an essential contribution to the evolution of oxidation in the polymer phase. Figure 9 illustrates the differences that exist between the oxidative degradation of PP/POSS hybrids initiated by the filler. There are many differences that define the progress in the PP matrices. Some POSS powders (P3, P5 and P7) present an evident early degradation at about 110 °C that initiates a premature oxidation of PP (Figure 2). For the other POSS structures, the onset oxidation temperatures are somewhat different, so that they influence the oxidation induction times of the basic polymer (Figure 2). The POSS configuration containing chlorine substituent causes a fast oxidation of polypropylene hybrid irradiated at 50 kGy (Figure 2). In means that the simultaneous degradation of components by structural scissions has an ageing effect on polypropylene. Therefore, the weaker positions represented by substituted carbon atoms in polypropylene [43] or structural configuration of cellulose [44] change the degradation profiles relative to the availability to oxidation.



Figure 9. The nonisothermal CL spectra of studied POSS powders exposed to two irradiated doses. Heating rate; $10 \degree \text{C} \min^{-1}$. (a) P 1; (b) P 2; (c) P 3; (d) P 4; (e) P 5; (f) P 6; (g) P 7. (1) D 0 kGy; (2) 50 kGy.

3.2. FTIR Assay

The progress of oxidation is well described by the evolution of two main vibration bands in the FTIR spectra: the carbonyl band placed at 1715 cm⁻¹ and hydroxyl band situated at 3350 cm⁻¹. The values of transmission, converted into carbonyl and hydroxyl indices, state the stability order. The comparative analysis of the two families of bands (Figure 10) provides the cumulative evolution of the main final products, as well as the conversion from the hydroxyl functions into carbonyl ones.



Figure 10. The distribution of FTIR spectra of PP hybrid modified with the same filler in irradiated at 100 kGy. (**a**) hydroxyl band; (**b**) carbonyl band.

The accumulation of the main degradation products of polypropylene is properly analyzed by the changes occurred in the structured laminated composites [39]. The carbonyl and hydroxyl indices (Figure 11) are modified in respect with the contribution of electronic effect of substituents, whose contributions are evidenced by the level of transmission characteristic for each powder filler. The complex mechanism of degradation [40] that involves the conversion of hydroperoxides into carbonyl moieties and the generation of carbonyl functions is the result of dissection of molecular oxygen on the weaker positions (tertiary and quaternary carbon atoms) of PP chains providing a complicate picture on degradation. Nevertheless, the most important features of the evolution of carbonyl and hydroxyl indices are correlated with the oxidation rates, as it can be noted from the chemiluminescence isothermal spectra (Figure 2).



Figure 11. The evolution of hydroxyl (**a**) and carbonyl (**b**) indices during the degradation of PP/modified POSS hybrids exposed to gamma radiation.

For the selection of optimal stability, the POSS configuration, including two methyls seems to be the proper filler, which protects more satisfactorily polypropylene against accelerated oxidation caused by the exposure to gamma irradiation. The limitation of the propagation rate may be considered a good feature of the majority of tested POSS structures, this assessment being based on the temporal behavior of PP hybrids in respect to pristine polymer (Figure 11).

4. Conclusions

This paper characterizes the stabilization effects of various POSS structures that play the role of radical scavengers. The inclusion of these fillers in the formulations of polypropylene offers a possibility to delay oxidation, even in the cases of gamma irradiation, a proper procedure of sterilization. The electronic interaction between various substituents and the O–Si–O structure, that allows the penetration of radicals into the inner free space of POSS. This protective barrier prevents oxidation even where the concentration of free radicals is high enough, for example in γ -irradiated polymers. The chemiluminescence measurements describing the evolution of degradation indicate the differences between the levels of stabilization due to the chemistry of the inorganic phase. The association of polymeric fragments with the spatial configuration of polyhedral oligomeric silsesquioxanes is possible over a large range of irradiation doses or at high temperature, for example 150 °C. Consequently, the durability of PP/POSS hybrids is improved due to the involvement of substituents that redistribute bonding electrons in the attached structure.

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