J Therm Anal Calorim (2016) 124:767–774
DOI 10.1007/s10973-015-5191-y

Stabilization effects of POSS nanoparticles on gamma-irradiated polyurethane

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Received: 24 June 2015 / Accepted: 29 November 2015 / Published online: 14 December 2015

Abstract The characterization of radiation stability of polyurethane nanocomposites by chemiluminescence and optical spectroscopies (FTIR and UV–VIS) is presented. Samples consisting of polyurethane and various percentages of polyhedral oligomeric silsesquioxane (POSS), namely 0, 2, 4, 6, 8 and 10 mass% loading, were aged by $\gamma(^{137}Cs)$-irradiation. The polyurethane composites with 2 and 4 mass% POSS have presented slower rate of degradation in comparison with unmodified polymer. The consequences of the increase POSS loading are analyzed starting from the structural configuration of POSS which allows the scavenging of free radicals formed in polymer phase. The received moderate doses (10 and 20 kGy) like a sterilization procedure at a dose rate of 0.4 kGy h^{-1} brought significant changes in the thermal behavior of our hybrid composites, splitting the formulations into two groups: one group is characterized by the increasing thermal stability, while the second group presents an advancing oxidative degradation.

Keywords Polyurethane · POSS · Irradiation degradation · FTIR · Chemiluminescence

Introduction

On the last period considerable attention has been paid to the synthesis [1–5] and characterization [6–10] of polyurethanes because of the multitude of synthesis routes and the expending operation ranges. The application areas of polyurethanes (flexible or rigid foams, coatings, sealants, adhesives or thermoplastic items—in particular automotive, aircraft and biomedical products) for the manufacture of long-term products have been continuously enlarged due to their satisfactory stability and stress resistance [11–19]. Polyurethanes are characterized by –NHCO–O– units, which generate various decomposition products previously reported [20]. The mechanism of their formation follows a three stage process (Fig. 1). The scission of macromolecules is caused not only by the energetic depositing, but also by the attack of free radicals on the methylene group in the neighborhood of urethane moieties [21]. Spectral investigations on the photodegradation of poly(ether urethanes) [22] confirm the presented approach of the degradation progress in polyurethanes. The long-term service of medical wear subjected to several degrading factors requires the improvement in the stability of polyurethanes. The modification of polyurethane matrix with polyhedral oligomeric silsesquioxane (POSS) offers numerous utile alternatives for the enlargement of various application areas such as scaffolds, catheters, blood vessels and drug delivery membranes [23].

The general formula of POSS, $[R(SiO)_{3/2}]_n$, is associated with a large molecule size (about 25 Å on axis direction) in comparison with average dimension of polyurethane hard domain [24]. The structural configuration of POSS allows to be penetrated by free radicals acting as efficient scavenging cage. A detailed study on the physical and electrical characteristics of PU/POSS nanocomposites was already

Electronic supplementary material The online version of this article (doi:10.1007/s10973-015-5191-y) contains supplementary material, which is available to authorized users.

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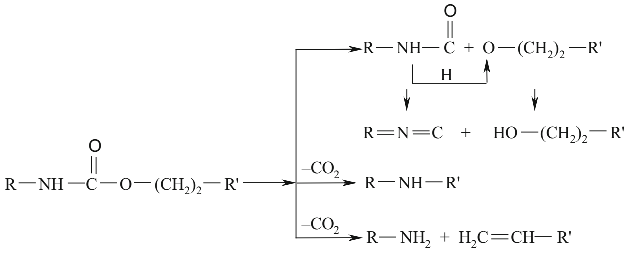

Fig. 1 Mechanism of thermal degradation for polyurethanes

published [25] emphasizing the modifications induced by POSS nanophase by the interaction with basic polyurethane.

Several other polymer materials modified with POSS were qualified for various applications, because this nanofiller ameliorates their functional features. Different types of polymers modified with POSS were studied: high density polyethylene [26], polypropylene [27, 28], polystyrene [29], polyethylene terephthalate [30], polycarbonate [31] and many others. The similar effect in the increasing the usage temperature, stability to oxidation, mechanical properties of host material is based on the sorption activity of nanofiller [32].

The radiation effects on POSS composites were scarcely investigated. Choi et al. [33] managed the grafting of POSS particles on polypropylene by γ-exposure and the decomposition temperature decreased with about 10 %, while de-elasticity of composed samples increased sharply. Gorna and Gogolewski [34] have demonstrated that radiation treatment applied to polyurethane/POSS hybrid composites generates materials properly used for cardiovascular implants, artificial skin, pericardial patched and scaffolds for repair of articular cartilage because of their adequate compliance, fatigue resistance and sufficient tear and burst strengths. In the circumstances of firing or ignition, when the oxidative degradation of polyurethanes is accelerated by the reaching local high temperatures, an efficient stability can be obtained by the modification of basic material with nanoclay [35, 36]. For the delaying of degradation induced by light stressing activity, the addition of antioxidant is also a proper solution [37].

The thermal and radiation stabilization of polymers can be easy obtained by the presence of antioxidant additives [38, 39] by scavenging effect. The resistance of polyurethanes to the oxidation by ignition can be efficiently improved by the addition of flame retardants like ammonium polyphosphate [40] and these types of intumescent polyurethane foam systems may be used where potential fire events would be imminent.

This paper presents the radiation stability of polyurethane/polyhedral oligomeric silsesquioxane hybrid composites starting from previous studies on radiochemistry of polyurethanes [41] and thermal stability of these nanosystems [42]. Complementary determinations by optical spectroscopies and chemiluminescence prove the stabilization potential of POSS during accelerated degradation promoted by high-energy radiation.

Materials and methods

The basic polyurethane matrix was prepared starting from 4,4′-methylenebis(phenylisocyanate) and poly(tetramethyleneglycol) as is has been previously reported [43]. Nanocomposites were obtained by the substitution of chain extender with 1,2-propanediol-heptaisobutyl-POSS. The loading polyhedral oligomeric silsesquioxanate of each sample is listed in Table 1.

The radiochemical aging was performed in an irradiation machinery (Gammator M-38) provided with ^{137}Cs source by exposure in air at room temperature. The dose rate was 0.4 kGy h^{-1}. Because the γ-irradiated metals provide energetic electrons (δ-electrons) as the result of interaction of incidental radiation with material sheet, during γ-irradiation our composite samples were covered with aluminum thin foil for more efficient energetic transfer. In this manner the energy received by polymer samples is maximized; otherwise, the samples would absorb only a small part of dissipated energy from electromagnetic rays. The total doses are placed on the medium dose range up to 100 kGy, but the most relevant effect of stabilization was observed at 10 and 20 kGy). The measurements were carried out immediately after the end of irradiation. For avoiding the errors brought about by sample preparation, the irradiation procedure by accumulation was applied.

Chemiluminescence (CL) determinations were carried out with LUMIPOL 3 (Slovakia) equipment. The measurement temperatures for isothermal regime were carefully selected ensuring convenient degradation rate. The applied chemiluminescence procedure for isothermal measurements was previously reported [44]; the non-isothermal experiments were carried out according with the method described by Rychlý et al. [45]. This equipment

Table 1 POSS loadings of hybrid polyurethane composites

Sample	POSS content/mass%
P1	0
P2	2
P3	4
P4	6
P5	8
P6	10

maintains constant temperature with an error of ±0.2 °C for the accomplishment of isothermal measurements, while the rate of heating for nonisothermal assays was established as optimal value of 2 °C min^{-1}. The activation energies, *E*a, were calculated by Arrhenius method at three temperatures around central values. The first set of *E*a was evaluated in the range of 98, 100 and 102 °C, while the second and the third sets used the oxidation rates measurements were done at 138, 140 and 142 °C. Although the temperatures are closed to each other, the rates were enough different to allow the accurate calculation of activation energies for oxidation of polyurethane samples (supplementary documents).

Optical spectroscopies (FT-IR and UV–VIS) were performed on JASCO 4200 and JASCO V570 spectrophotometers, respectively. For FT-IR investigation, the vibration band between 3350 and 3650 cm^{-1}, which corresponds to bond hydroxyls, while UV–VIS records were performed on the spectral region from 400 to 300 nm, which is ascribed to a $n - \pi^*$ transition in ketone structures. The successive records for increasing dose were done on the same point of each sample avoiding the involvement of any thickness deviation.

Results and discussion

The polyurethane-based POSS nanocomposites are pendant on the relative proportion of components. The evidence on microphase morphology in POSS phase [24] brings about the problem of interaction degree between sample constituents, which determines the cage effect on small molecule products generated during degradation. The main advantage of the filler presence consists of the control on diffusion process, either for molecular oxygen that penetrates material or for the scavenging of the intermediates of degradation. It must be taken into account the energetic effect of phenyl rings that act as energy-depositing structural unit where excitation is retained for a long time [46]. Apart from the structural stability conferred by geometrical configuration, the phenyl content is an additional factor that increases the radiation stability of POSS.

Optical spectroscopy

Even though composite films were thick enough for transmission measurement, UV–VIS and FT-IR records have revealed modifications in the accumulation of degradation products occurred during radiolysis because two degradation agents (high-energy radiation and oxygen) induce combined effects.

Figure 2 illustrates the increase in the hydroxyl content due to the simultaneous actions of γ-radiation (scission of bonds) and diffused oxygen (oxidation reactions involving free radicals) according with the mechanism of oxidative degradation. The evolution of the ratios of transmission at each dose divided by initial transmission value for aged PU/POSS samples which were subjected to the hard action of γ-rays is shown in Fig. 3. This bonded-hydroxyl group accumulation which seems to follow quasi-linear dependency on irradiation dose depicts the formation of this type of function directly from peroxyl intermediates. The increase in the absorbance values of neat polyurethane at 320 nm (Fig. 4) proves the accumulation of carbonyl-containing degradation products, which determines the variation of absorbances in this spectral region for polyurethane/POSS hybrids (Fig. 5). The continuous augmentation of relative absorbance figures as destructive energy is transferred on polymer samples is the consequence of the

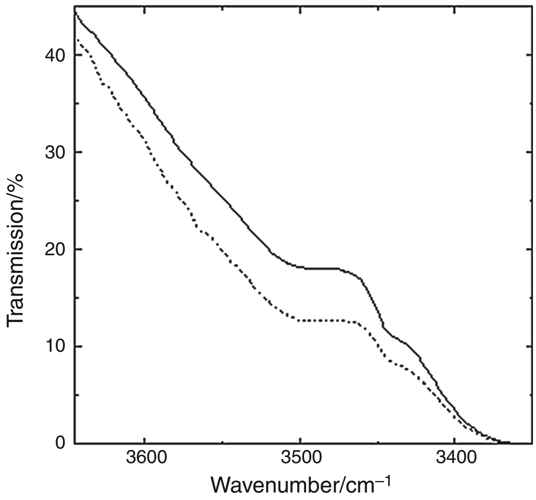

Fig. 2 3350–3650 cm^{-1} band for pristine polyurethane. *Solid* 0 kGy, *dash* 100 kGy

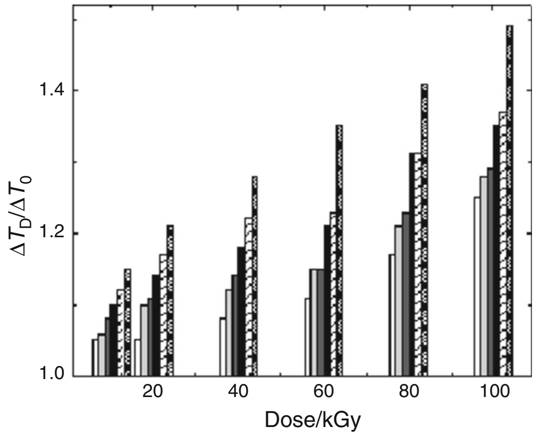

Fig. 3 Transmission ratios (T_D/T_0) for PU/POSS composites recorded at 3460 cm^{-1}. *White* neat PU, *light gray* PU + 2 %, POSS, *dark gray* PU + 4 %, POSS, *black* PU + 6 %, POSS, *sparse* PU + 8 %, POSS, *dense* PU + 10 %, POSS

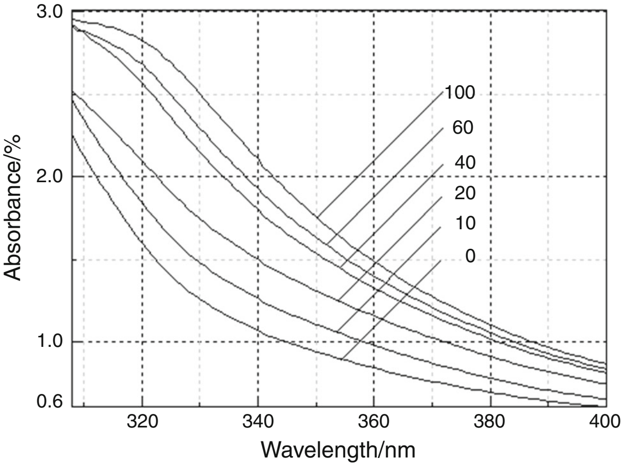

Fig. 4 400–300 nm region in the UV–VIS spectra of neat polyurethane. *Inner figures* are related to received doses expressed in kGy

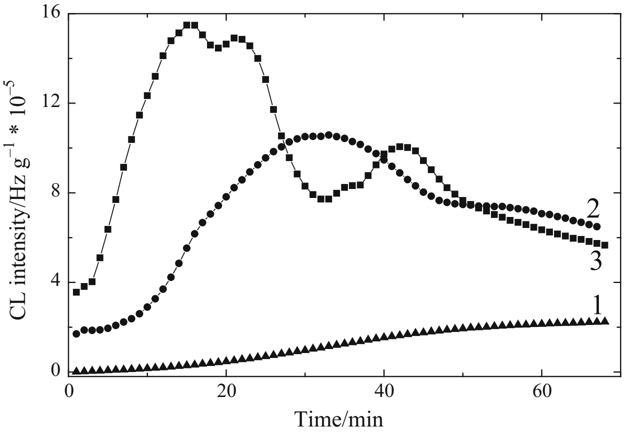

Fig. 6 Nonirradiated chemiluminescence curves recorded on neat polyurethane samples. *1* 100 °C, *2* 140 °C, *3* 180 °C

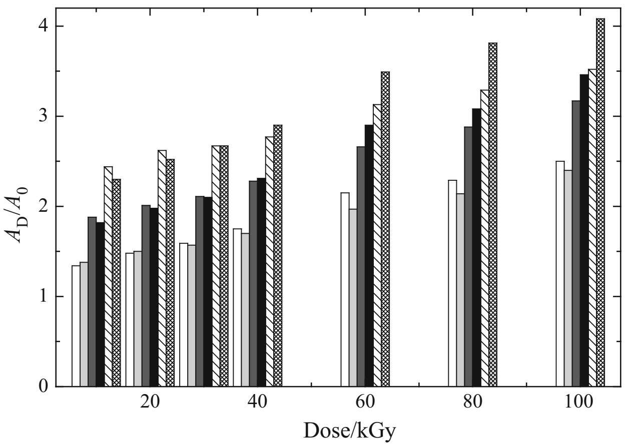

Fig. 5 Absorption ratios (A_D/A_0) for PU/POSS composites recorded at 320 nm. The meaning of coloring is the same as in Fig. 3

scission occurred in polyurethane molecules. The differences in the oxidation level indicate the contribution of dispersed POSS nanoparticles to the propagation of oxidation during irradiation.

According to ESR study, the formation of primary radical >$\dot{C}$(NCO) initiates the addition of molecular oxygen to form peroxyl moieties [9]. Their amounts depends on the irradiation dose because of the increased scission number at increasing dose and on the POSS loading because it acts as the adsorbent of intermediates.

Chemiluminescence

The thermal degradation of neat polyurethane advances differently, if the applied temperature is increasing (Fig. 6). At medium temperature (100 °C), oxidation takes place smoothly that does not present a well-defined oxidation induction time, because the oxidation process progresses at low rate. At higher temperature (140 °C) one large peak appears which describe the scissions of polyurethane segments. According with the mechanism presented in Fig. 1 and with the photodegradation mechanism of polyurethanes and with the photodegradation mechanism of polyurethanes [47], the radicals can appeared either by the breaking of urethane units or by the scission of vicinal methylene groups. At 140 °C, when the energetic transfer is more intensive, the second peak appears demonstrating the formation of double bonds by releasing carbon dioxide. By enhancing degradation temperature, the main peak becomes more conspicuous and shifted toward shorter appearance times.

The scission rate that characterizes the organic component is modified by the presence of POSS nanoparticles. At 100 °C the filler nanoparticles act as scavengers for degradation initiators (Fig. 7a). The continuous descendant CL intensity is the proof for the subtraction of oxidizing intermediates, which are prevented to react with oxygen being locked inside POSS geometry. The increase in temperature at 120 °C, the differences between the developments of oxidation in the six PU/POSS composites appears (Fig. 7b). The samples containing 2 and 4 mass% POSS present higher thermal stability relative to the neat polyurethane. The other three POSS loadings induce faster oxidation than pristine material. It can be supposed that an equilibrium adsorption/desorption of radicals is turned onto the expelling the covalent inclusions. If the samples with low POSS content are slightly oxidized over 120 min, the samples incorporating higher amounts of POSS present an accelerated degradation on the first 40 min followed by a pseudo-steady-state progress of oxidation. The sample with 10 % POSS has a similar behavior as neat PU so that it may be suppose that on the surface of filler nanoparticles the uptake and release rates are similar.

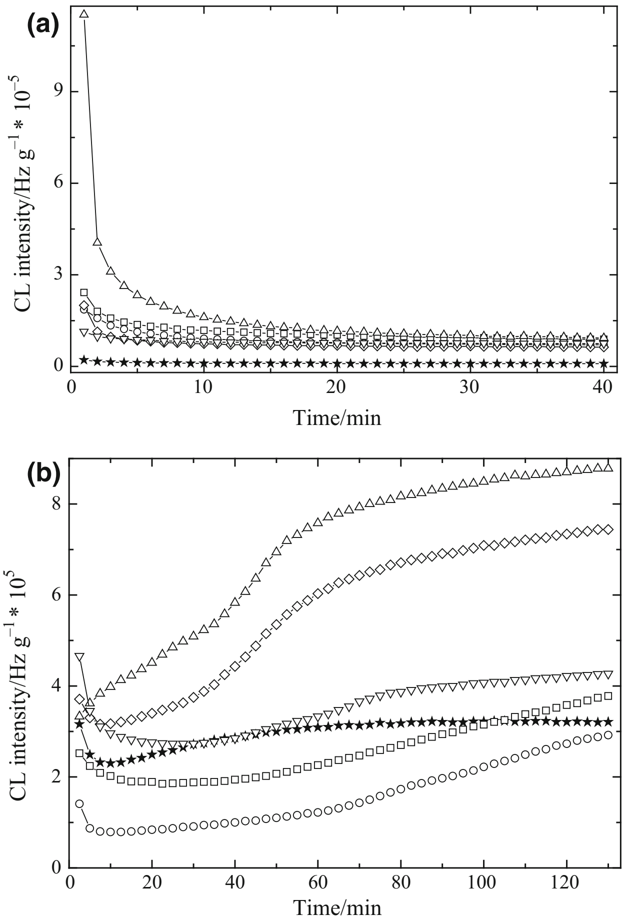

Fig. 7 Isothermal CL spectra of PU/POSS hybrid compounds recorded at **a** 100 °C and **b** 120 °C. POSS loading: *star* 0 %, *circle* 2 %, *square* 4 %, *triangle* 6 %, *diamond* 8 %, *inverted triangle* 10 %

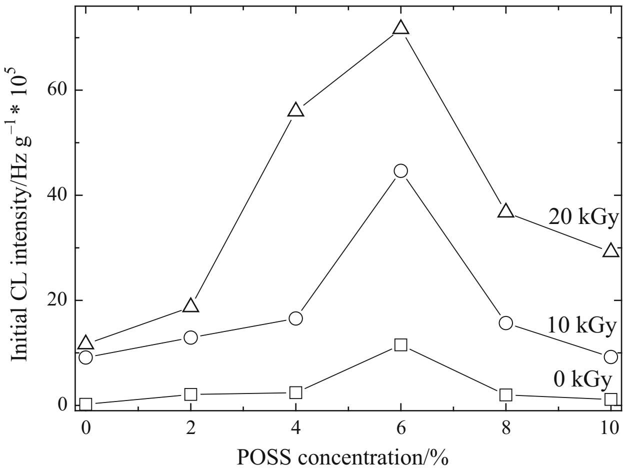

Fig. 8 Correlation between initial CL intensity and concentration of POSS nanoparticles. 100 °C. *1* 0 kGy, *2* 10 kGy, *3* 20 kGy

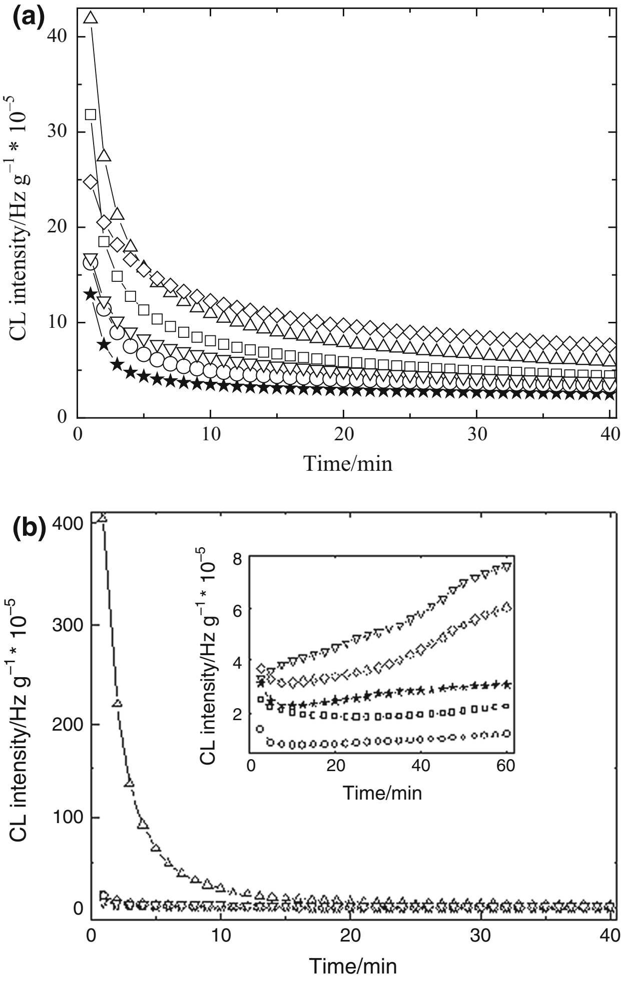

Fig. 9 Isothermal CL spectra measured at 100 °C on hybrid samples irradiated at **a** 10 kGy and **b** 20 kGy. The meaning of signs is the same as in Fig. 7

The contribution of nanocomponent to the stability of PU/POSS hybrids is illustrated by the variation of CL intensity emitted on the first minute of isothermal investigation. This value, which depicts the initial concentration of radicals, increase from neat polyurethane to the sample containing 6 mass% POSS, followed by the significant diminution (Fig. 8). Even different irradiation doses (0, 10 and 20 kGy) are applied, the degradation level is intensified, and the shape of variation curves remains the same. In all the cases, the most instable system is the POSS nanocomposite in which the filler concentration is 6 mass%.

The accelerated degradation in organic substrate from PU/POSS nanocomposites during γ-irradiation proceeds with different rates depending on filler content (Fig. 9). If at 10 kGy the decrease in the CL intensities happens similarly starting from corresponding to initial higher emissions (Fig. 8), a constant degradation rate is attained after 10 min from the start of heating. The increase in dose at 20 kGy modifies the behavior of sample containing 6 mass% POSS. It is considerably degraded during γ-exposure, when it receives a large amount of energy

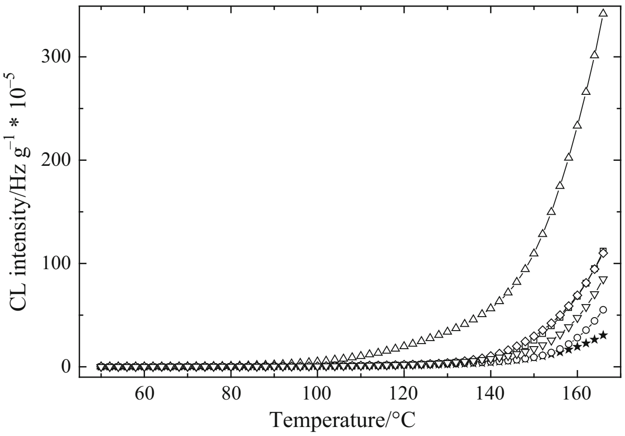

Fig. 10 Nonisothermal CL spectra of PU/POSS samples. The meaning of signs is the same as in Fig. 7a

Table 2 Transmission values for PU/POSS composites recorded at 3460 cm^{-1}

Dose/kGy	Type of composite					
	P1	P2	P3	P4	P5	P6
0	16.81	12.15	17.20	14.43	12.41	5.60
10	16.82	10.37	14.66	10.84	8.77	3.60
20	16.85	12.29	17.10	12.35	10.64	4.62
50	16.99	20.82	22.98	17.63	16.44	9.43
100	12.87	19.48	19.57	14.26	17.47	6.40

Table 3 Activation energies required by the oxidation of polyurethane/POSS hybrid composites

Sample	Correlation coefficient	Slop. 10^{-3}	*Ea*/kJ mol^{-1}
From oxidation rates at milestone temperature of 100 °C			
P1	0.99996	7.3	49.38
P2	0.99196	5.93	59.31
P3	0.99967	7.14	61.64
P4	0.99963	10.89	90.54
P5	0.96591	8.74	72.66
P6	0.99844	8.30	68.90
From oxidation rates at milestone temperature of 140 °C			
P1	0.99993	10.46	76.96
P2	0.99985	8.25	88.60
P3	0.99952	15	124.71
P4	0.99950	−17.45	145.08
P5	0.99999	−12.5	103.92
P6	0.99973	−9.16	76.16
From final oxidation periods (100 min) at milestone temperature of 140 °C			
P1	0.99992	14.16318	117.75
P2	0.99999	21.10024	175.42
P3	1	15.78951	131.27
P4	0.99997	14.5455	120.93
P5	1	11.96148	99.48
P6	0.99994	10.13452	84.26

becoming quite susceptible to oxidation. The order of stability established for unirradiated studied systems is maintained. The oxidative degradation is initiated in polyurethane and POSS nanofiller can modified the rate of process by modification of reacting entities as the result of surface interaction. The evolution of oxidation state in PU/POSS samples is also related on the modification in the length of polyurethane molecules according with the proposed mechanism and previously reported data [37].

The same sequence of thermal stability is obtained by nonisothermal chemiluminescence determinations. The oxidation starts in polyurethane/POSS composites at the temperature around 130 °C, except in sample with 6 % filler, where oxidative degradation begins before attaining 100 °C (Fig. 10). The CL emission intensities at elevated temperatures are moderate, which suggests the relative thermal stability at these temperatures.

The accelerated degradation by γ-irradiation of polyurethane/POSS hybrids is the result of the influence of inorganic particles of hard and soft blocks of elastomer. The influence of filler content is revealed by the restriction of oxidation at low POSS content and the acceleration of degradation for the concentration exceeding 6 mass%. Actually, the chemiluminescence measurements can characterize the interaction of the two components in order to evaluate the influence of filler concentration on the material stability (Table 2).

The scavenging action of POSS structure is well understood by the activation energy figures which vary in the direct connection with the free interstitial volume and the allowed amount of intermediates temporary captured in the octahedral configuration (Table 3). According with the oxidative degradation mechanism, the nanoparticles of POSS retain free organic radicals in a certain proportion, which attains saturation at about 4 %. The exceeding POSS loading diminishes the thermal stability of studied hybrid systems because the accumulation of hosted entities does not allow the undefined amount. The increase in the degradation temperature involves higher concentrations of absorbing entities determining a competition for space occupation and, indeed, higher activation energies (Table 3). When the oxidation is on the terminal step, the degradation products are highly accumulated and the hindering each other controls the oxidation level. The POSS nanoparticles play the role of absorbent, which acts slower and slower when the amount of intermediates exceeds a certain quantitative limit.

Conclusions

The PU/POSS nanocomposites with different compositions present selective stabilities in respect with filler loading. Although the thermal stability differentiates studied systems, the slow oxidation rates in low POSS content formulations is obtained in comparison with pristine polymer. The sequence of stability levels obtained by either isothermal or nonisothermal chemiluminescence places nest polyurethane between improved materials (PU modified with 2 and 4 mass% POSS) and less stable composites containing 6, 8 and 10 mass% POSS. Even though γ-irradiation modifies the molecular length of elastomer, the behavior of irradiated these nanocomposites reflects the contribution of filler to the initiation and progress of oxidative degradation in polymer component. The relevant stability of low POSS content in irradiated materials recommends them for the preparation of various high-performance items, which are subjected to accelerated degradation.

Due to the absorbent feature of POSS nanoparticles, these systems can be preferentially applied in the medical areas, manufacture of scaffolds, carriers of drugs, covering layers for injuries and many other purposes, including pharmaceutics. The assessment of oxidation strength by the application of γ-irradiation for accelerated degradation allows the correct qualification of products. The present results recommend the extension of utilization purposes as absorbent of radioactive contamination in the radiation chemistry laboratories or nuclear power plants (outer “clean” areas).

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