Oxidative Degradation of Polyether Polyol - Silica Hybrids Prepared by Sol - Gel Process

MONIKA SANDOR[1], CRISTINA LAVINIA NISTOR[2]*, CRISTIAN PETCU[2], VIOLETA PURCAR[2], MIRCEA VULUGA[2], SABINA NITU[2], BOGDAN TRICA[2], DAN DONESCU[2]

[1] Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Str., 400028, Cluj Napoca, Romania
[2] National Research&Development Institute for Chemistry and Petrochemistry – ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania
[3] Romanian Academy, C. D. Nenițescu Organic Chemistry Centre, 202B Splaiul Independenței, 060023, Bucharest, Romania

The paper presents the preparation and properties of new silica hybrid materials, synthesized in the presence of two commercially available polyether polyols (PETOL-36-3 BR or PETOL-48-3 MB), as such or functionalized with (3-isocyanatopropyl)triethoxysilane (NCOTEOS). The two polyether polyols are actually branched polyether triols, produced from glycerine-propoxylated-ethoxylated and having primary (PETOL-36-3 BR) and respectively secondary (PETOL-48-3 MB) hydroxyl end-groups. The functionalization of the two triols with NCOTEOS was made in the lab, in order to improve the coupling efficiency of the polymeric component to the silica network, produced in situ by the sol-gel reactions of triethoxymethylsilane (MeTES) and triethoxyvinylsilane (VTES). The polyol/NCOTEOS molar ratio was 1/1. Thus, the attachment of the ethoxysilane functions to the end of one of the polyol's branch was achieved through urethane bonds, formed after the reaction of the hydroxyl end group of the polyol with the isocyanatopropyl- function of NCOTEOS. Evaluation of the coupling degree of the polyols to the silica network and of the rheological behavior during synthesis, as well as the ^{13}C NMR spectra indicated that the functionalization of the polyols with NCOTEOS occurred. The oxidation onset temperature (OOT) of hybrid materials was investigated for evaluating the hybrids stability towards the oxidative degradation. The intensity of chemiluminescence (CL) emission of the obtained materials was measured after exposing to ionizing radiation (radiation dose 0.5 kGy/h). It was found that the oxidation onset temperatures for the reference samples decreased faster with the increase of the irradiating dose for samples based on the un-modified polyols, comparing with samples based on the polyols functionalized with NCOTEOS. Therefore, by the functionalization of the polyols with NCOTEOS an improved quality of the final hybrid materials was observed.

Keywords: sol-gel method, hybrid systems, polyether polyols, chemiluminescence

Organic-inorganic (O-I) hybrid materials prepared by the sol-gel process have become a unique class of high-performance materials in industrial and academic research because of the integration of the properties of both organic polymers (i.e., flexibility, low density, toughness, and formability) and ceramics (i.e., excellent mechanical and optical properties such as surface hardness, modulus, strength, and transparency and a high refractive index) [1-5]. The sol-gel process makes possible a relatively easy incorporation of a pure inorganic phase into an organic matrix. Thus, nanocomposites with a high degree of mixing can be prepared.

A considerable number of literature reports show that block copolymers play a role of templates in the sol-gel processes and exhibits a good compatibility with the inorganic networks [6–12]. One type of O-I network is produced from O-I precursors containing both organic and inorganic functionalities, e.g., organofunctional trialkoxy-silanes. Their polymerization leads to the formation of O-I block copolymers. [13-18].

Including organic polymers in an inorganic silica framework makes the final material more flexible and less susceptible to cracking during the drying stage. This approach was used for synthesis of new organic-inorganic materials, based on polyether chains, covalently linked to silica framework by urea bridges, referred as ureasilicates or ureasils [19].

Applications of radiochemical investigations on nanostructured polymer materials cover a large area of interest because of the diversity of useful information on material stability [20, 21] and on various modifications that can be induced in this sort of products [22-26] for enlarging performance spectra. Polymer degradation generally results from a chemical or physical attack by environmental agents that involves some chemical mechanism. For example, polymers may be sensitive to photo-degradation by solar radiation. In this case, photochemical reactions involving ultraviolet (UV) light photons and oxygen result in scission of the polymeric chain. Another important degradation process is thermal oxidation, which may be caused by high temperatures during polymer synthesis, processing and use [27].

The degradation of some polymer structures, previously studied by chemiluminescence [28] has demonstrated that this process occurs via peroxyl intermediates. Two parameters, specific for the early stage of oxidation, can be used for the delimitation of this conservative period: oxidation induction time (OIT) and onset oxidation temperature (OOT). These two kinetic characteristics depict properly the thermal strength of polymers (i.e., polyurethanes) on the first term of oxidation, when insignificant modification of polymer matrix may be noticed. The molecular structure plays an important role in the defining of degradation progress [29]. Chemiluminescence's method can ensure the necessary sensitivity and accuracy of forecasting durability of hybrid materials.

In this work, we investigated the functionalization process of two commercially available polyether polyols, PETOL 36-3BR (here noted PEO) and PETOL 48-3MB (here

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* email: lc_nistor@yahoo.coma

noted PPO) with (3-isocyanatopropyl)triethoxysilane (NCOTEOS) and the degradation of the resulted materials by chemiluminescence's method. Polyether polyols (as such or functionalized with NCOTEOS) were used in the sol-gel process, beside two other silica precursors: triethoxymethylsilane (MeTES) and triethoxyvinylsilane (VTES). By functionalization with NCOTEOS, the polyether chains were able to covalently link to silica framework by urethane bridges. All samples were irradiated using a Cs^{137} source, with 0.5 kGy/h dose and the onset oxidation temperature (OOT) of hybrid systems was evaluated.

Experimental part

Materials

The sol-gel precursors: triethoxymethylsilane (MeTES, Merck/Suchardt), triethoxyvinylsilane (VTES, Merck/Suchardt) were used as main silica sources. Tetraisopropylorthotitanate (TIP, Fluka) was used as cross-linking agent. Benzoinedimethylacetal (FIN, ICPAO) was used as photoinitiator for the UV-initiated radical polymerization of VTES. (3-isocyanatopropyl)triethoxysilane (NCOTEOS) (Fluka) was used to introduce sol-gel reactive ethoxy functions in the terminal positions of the polyether polyols molecules.

Two commercially available polyether polyols, PETOL-36-3 BR (PEO) and PETOL-48-3 MB (PPO) (Oltchim, Romania) were used as polymeric components. The differences between the two types of polyether polyols consist of terminal hydroxyl group and of different molecular structure. 1,4-diazo bicyclo[2.2.2]octane (DABCO) (Fluka), the catalyst of the functionalization reaction of polyols with NCOTEOS, was used as received. They were added to the reaction as received or end-capped with ethoxy groups (after reacting with NCOTEOS).

PETOL 36-3 BR (PEO) is a tri-functional polyether polyol, initiated by glycerol, having alternating units of propylene oxide (PO, 85%) and ethylene oxide (EO, 15%), distributed as microblocks, and an average molecular mass of 5000 g/mol. It is a polyether polyol with high reactivity toward isocyanates and possesses terminal groups of primary hydroxyl (*EO terminal microblocks*).

PETOL-48-3 MB (PPO) is also a polyether triol, containing structural blocks of EO and PO, but with *terminal PO microblocks*. As a consequence, it has mainly terminal groups of secondary hydroxyl (less reactive toward isocyanates than the primary hydroxyls).

Techniques

NMR measurements were performed on a Varian Gemini 300BB instrument, at room temperature (25 °C) in $CDCl_3$. The number of scans was 10.000 transients/min.

Rheological measurements were carried out during the hybrid synthesis, with a Brookfield DV-II+ instrument (Brookfield Engineering Labs Product. Inc.), equipped with a THERMOSEL thermostatic system. Evaluation of rheological behavior was performed at two temperatures: 23 and 60°C. The volume of sample used for measurements was 8 cm^3 and geometric characteristics of rheometer were as follows: - for container: diameter ($\varnothing_c$) = 19.05 mm; height (h_c) = 64.77 mm; - for the rotating cone-shaped body (SC-21): diameter ($\varnothing_{cr}$) = 16.76 mm; effective length (L_{cr}) = 35.15 mm. Measurements were performed at two speeds: N_{20} = 20 rpm and N_{50} = 50 rpm, resulting the following shear rates: $\dot{\gamma}_{20} = 18.6\ s^{-1}$ and $\dot{\gamma}_{50} = 46.5\ s^{-1}$ respectively ($\dot{\gamma}[s^{-1}] = 0.93*N[rpm]$).

The *coupling degree* of polyols to the silica network was evaluated by extraction in isopropyl alcohol, based on the assumption that only the polyol molecules that are not covalently bonded to the silica frame are soluble in this solvent, while the reacted molecules remains attached. The cross-linked species were gravimetrically evaluated on the samples dried at room temperature, after the removal of the solvent and of the extracted polyols.

The *oxidative degradation of* samples prepared in the presence of polyether polyols were analyzed by LUMIPOL 3 chemiluminograph (SAS, Slovakia). Samples were irradiated using a Cs^{137} source, with 0.5 kGy/h doses. The chemiluminescence investigations were performed immediately after the end of irradiation, because of the presumable presence of short life intermediates formed during radiolysis.

Synthesis

a) Preparation of functionalized polyether polyols

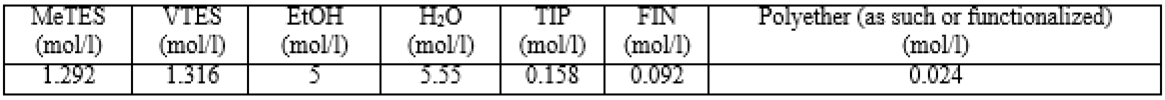
Functionalized polyether polyols were obtained in a similar way to that we previously reported [5, 30]. The purpose of polyether polyols functionalization with (3-isocyanatopropyl)triethoxysilane (NCOTEOS) was to connect the triethoxy silane groups from NCOTEOS to the polyetheric chains. Urethane bonds are formed by reaction between the hydroxyl (–OH) functions from polyols and isocyanate (–N=C=O) functions from the NCOTEOS. End-capping of the polyols with ethoxy groups will contribute to the formation of covalent bonds between the block copolymers and the silica frame generated through the sol-gel reactions of MeTES and VTES.

b) Synthesis of the hybrid materials

Polyether polyol - silica hybrids were prepared by the sol-gel method as we previously described in ref. [5]. Thus, in all preparations, MeTES and VTES were pre-hydrolyzed for 1 h in an acid water solution, in the presence of ethanol, under continuous stirring, at room temperature. Beside this sol-gel precursors, was added the polyether as such or functionalized with NCOTEOS. It was demonstrated before that the vinyl-terminated alkoxyde (VTES) has a very high reactivity and its organic group can be more easily integrated in a growing inorganic network [31]. The molar ratio between the precursors (MeTES/VTES) was 1:1 (Table 1). The final mixtures (table 2) were placed into open plastic vials and dried overnight, at room temperature (25°C). After drying, the plastic vials were passed under a UV lamp (from Vilber Lourmat; λ = 365 nm, irradiation time = 15 min) in order to accomplish the UV-initiated radical polymerization of the double bonds from VTES. One part of the resulted materials was crashed into a mortar and then the powder was irradiated with 0.5 kGy/h dose in order to observe the oxidative degradation by chemiluminescence's method.

Table 1

THE COMPOSITIONS FOR PREPARING THE POLYETHER POLYOL - SILICA HYBRID MATERIALS



MeTES (mol/l)	VTES (mol/l)	EtOH (mol/l)	H_2O (mol/l)	TIP (mol/l)	FIN (mol/l)	Polyether (as such or functionalized) (mol/l)
1.292	1.316	5	5.55	0.158	0.092	0.024

Table 2
SILICA HYBRID SYSTEMS BASED ON POLYETHER-POLYOLS

Sample no.	Hybrid type	Polyol
1	M+PEO	un-functionalized
2		functionalized with NCOTEOS
3	M+PPO	un-functionalized
4		functionalized with NCOTEOS

Note: The base formulation - comprising the sol-gel precursors (MeTES and VTES), water, ethanol, cross-linking agent (TIP) and the photo-initiator (FIN)) - was noted with M, for all the hybrid samples, in order to simplify the figures legends.

Results and discussions

The degree of covalent coupling of the modified polyols to the silica network

As expected, for samples functionalized with NCOTEOS, the values of the degree of covalent coupling are much higher than for the references (samples with un-modified polyols). This is due to the presence of the ethoxysilane groups, introduced at the end of the polyol chains, which allowed a better coupling of the polyol molecules to the silica frame (fig. 1). Also, the hybrids belonging to the PPO series, exhibits much lower values of the degree of covalent coupling than those obtained for the PEO series. As explained above, the main differentiation between the two polyols is the type of hydroxyl end-groups (primary and respectively secondary –OH). Thus, the much higher reactivity of the primary hydroxyls of PEO towards isocyanate functions (–N=C=O) allowed a much better connection through urethane bonds of NCOTEOS to the polyol molecule and, as a consequence, a more efficient coupling of the functionalized block copolymer to the hybrid network (~89 %).

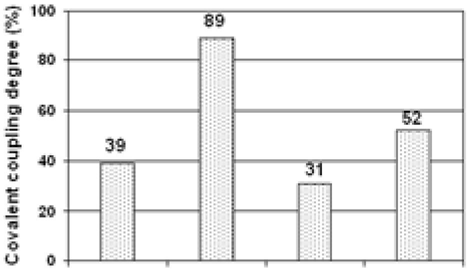


Fig. 1. The degree of covalent coupling of the polyols to the silica frame for samples 1-4 (as in table 2)

^{13}C NMR spectra of the polyol-silica hybrids

The results of the coupling degree experiments were also confirmed by NMR analyses. Thus, the spectra show that the PEO polyol, which has terminal primary hydroxyl groups and, as a consequence, a high reactivity, is almost completely functionalized with NCOTEOS (sample **(2)**). After functionalization with NCOTEOS, in the NMR spectrum of the PEO polyol appears the signal corresponding to -CH_3 (from ethoxy group connected to Si) at 58.3 ppm (fig. 2).

For the polyol PPO, which contain both -OH primary and secondary groups, can be noticed the presence of -CH group from terminal units. It is also possible to assign -CH_2 group of terminal units (~ 68.4 ppm). Depending on the primary and secondary groups, the methyl groups were assigned to the terminal units as follows: 18 ppm for –OH primary group and 18.6 ppm for –OH secondary group (sample **(3)**).

The integral of corresponding signal is in good agreement with the proposed structure. It can be concluded that the -OH groups are present in a molar ratio of 8% comparing with the total number of propylene oxid units contained in the polyether, the CH-OH/CH_2 molar ratio being 1.

By functionalization of PPO with NCOTEOS (sample **(4)**), CH-OH/CH_2 ratio decrease to ~ 0.76 and it is observed the signal corresponding to CH_2 unit from triethoxy silane (whose integral is proportional to the difference caused by the absence of CH-OH). Calculating the variation of concentration of these groups, a coupling degree of only ~13% was observed. The

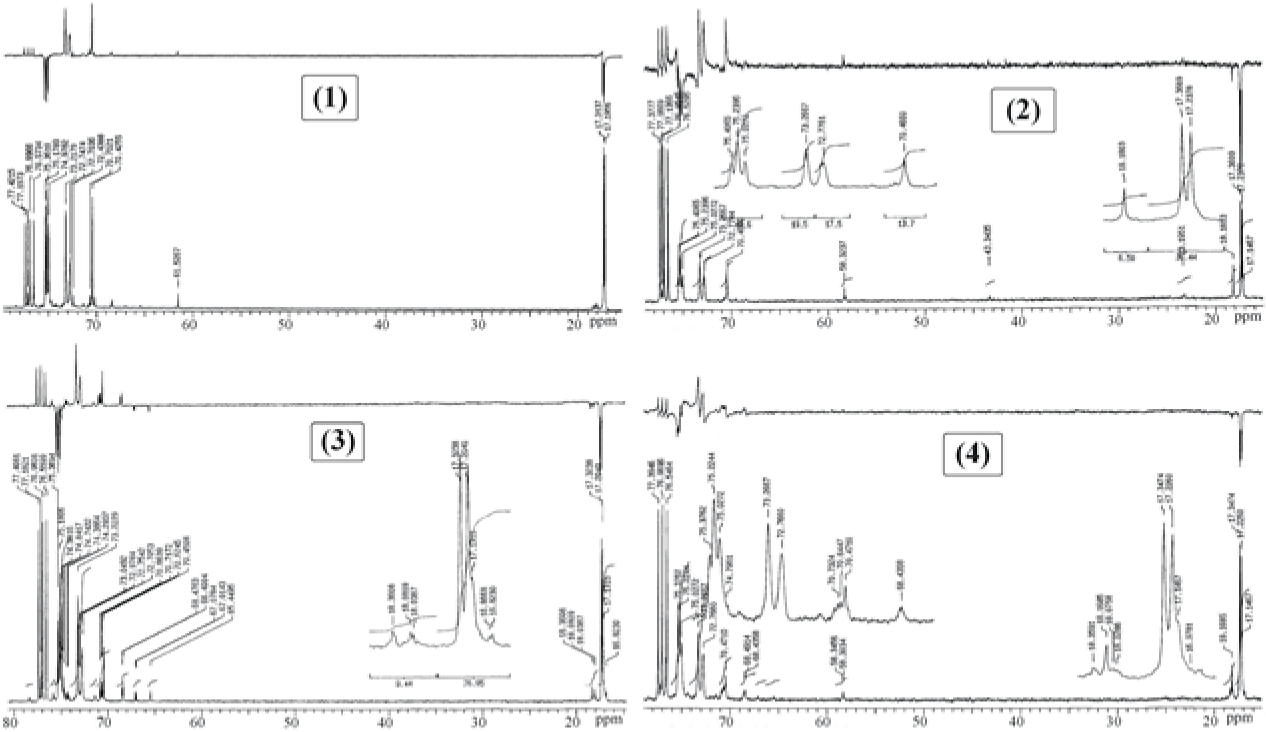


Fig. 2. ^{13}C-NMRspectra of the resulted polyol-silica hybrids (samples 1-4, as in table 2)

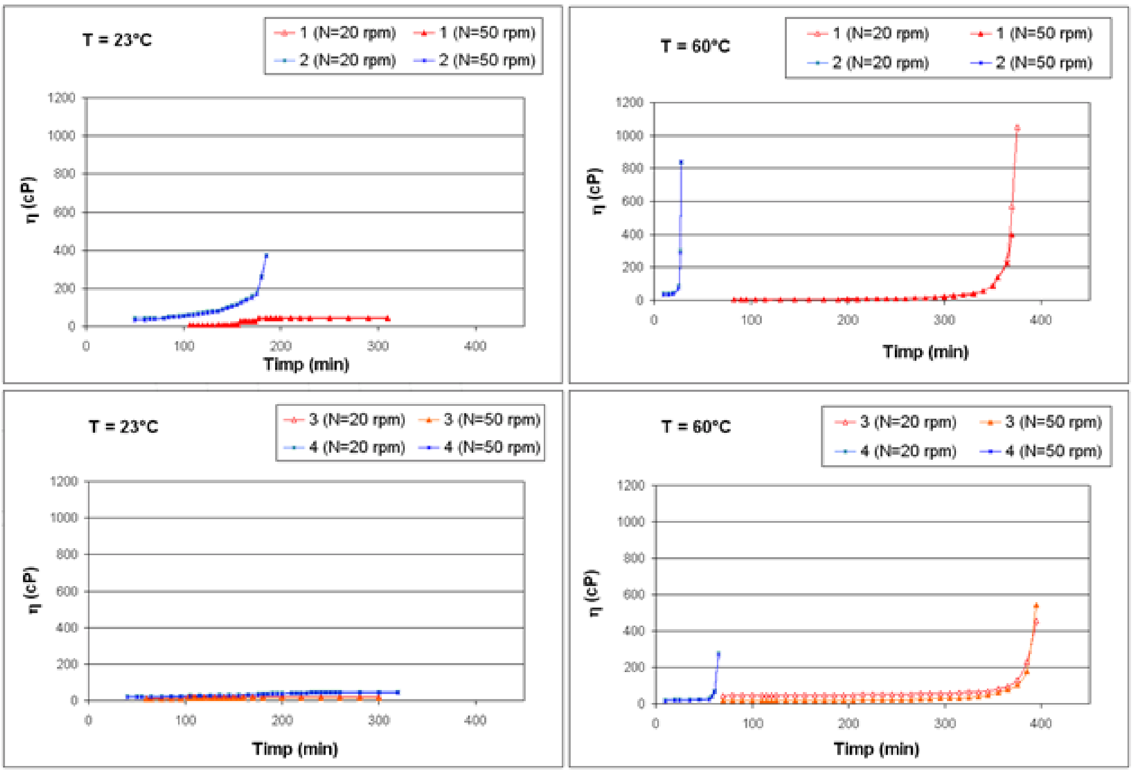


Fig.3. Evolution in time of the viscosity of the synthesized hybrid systems (samples 1-4, as in table 2)

structure is confirmed by the presence in the methyl region of signal at 18.16 ppm, corresponding to the -CH_3 group from the ethoxy silane.

Rheological measurements

Evaluation of the rheological behaviour was performed during the synthesis of the hybrid systems specified in Table 2. The sol-gel systems were prepared at two different temperatures: 23 and 60 °C and subjected to two different shear rates (fig. 3).Observing the time assigned to the beginning of gelation (sol-gel reaction) for the various systems studied, a much shorter reaction time was revealed for the PEO series. It was confirmed once again the much higher reactivity in the sol-gel reactions of the PEO polyol and especially of the PEO polyol functionalized with NCOTEOS. When the sol-gel process was performed at a higher temperature (T = 60 °C), the viscosity evolution experienced a period of inertia, then a sharply increase. Especially for the most reactive polymeric component (PEO functionalized with NCOTEOS, sample **(2)**), the cross-linking reaction occurs within a few minutes after the addition of the sol-gel cross-linking agent (TIP).However, when the sol-gel reactions were carried out at the room temperature (T = 23°C), the increase of viscosity was generally slow. But even at this low temperature, the gelation time of the sol-gel system derived from PEO functionalized with NCOTEOS (sample **(2)**), is much shorter than that of the system based on PPO functionalized with NCOTEOS (sample **(4)**). Moreover, it can be concluded that a higher reaction temperature (50-60 °C) and the functionalization of the polyol with NCOTEOS is necessary to achieve a better attachment of the polymeric component to the hybrid network.

However, in all the studied systems, a further increase of the solution temperature would cause a faster evaporation of the solvent and, therefore the resulted materials would exhibits a less ordered structure [18]. The results confirm that the self-assembly of alkyl siloxane oligomers depends heavily on temperature. During film formation, self-assembly of the alkyl siloxane species is induced by the solvent evaporation and, finally, the film is solidified by cross-linking.

Evaluation of oxidative degradation

The major effects of the polymers' irradiation are oxidation and reticulation; these take place in a ratio which depends on the irradiation dose. Polymer oxidation prevails at the smaller doses and its reticulation at the higher doses.

In this paper, we present the onset oxidation temperatures (OOT) of the hybrid systems based on polyether polyols, recorded by the chemiluminescence method (Figure 4a). The values obtained for onset oxidation temperature (OOT), are good indicators for the level of compound stability. It means that these temperatures represent the threshold, where oxidation effectively starts, depicting the peculiar resistance to thermal degradation [32].

Analyzing figure 4b, it can be observed that OOT decreases with the increasing of the irradiation dose. This phenomenon can be explained by the fact that, during irradiation of the samples, hydroxyl radicals are formed and can react with organic compounds, leading to degradation of the film. For sample based on the un-modified PEO, the onset oxidation temperature was observed at ~130°C and decreases gradually, when sample was irradiated with different doses, reaching ~ 81°C. This OOT can provide a quick means for evaluating the degradation of polymers. In case of sample with PEO functionalized with NCOTEOS, the OOT was recorded at ~126°C and decreases slower compared with the unmodified polyol.

Samples from PPO series present less reactive groups compared with the samples containing PEO. As we mentioned before, PPO has secondary terminal –OH groups, less reactive then the primary terminal –OH group from PEO. Thus, for sample with PEO, the OOT begin at ~ 130°C, while for sample with PPO the OOT begin at 116°C. It is obvious that the samples with PEO are more stable to degradation than the samples with PPO.

A higher dose submitted in material will lead to a more pronounced instability. The decrease of the oxidation temperature was assigned to material's degradation. An interaction of electrons with silica matrix causes the progressive scission of Si-O-Si bonds in the chain of the material and leads to the formation of chain radicals [33]. Degradation,

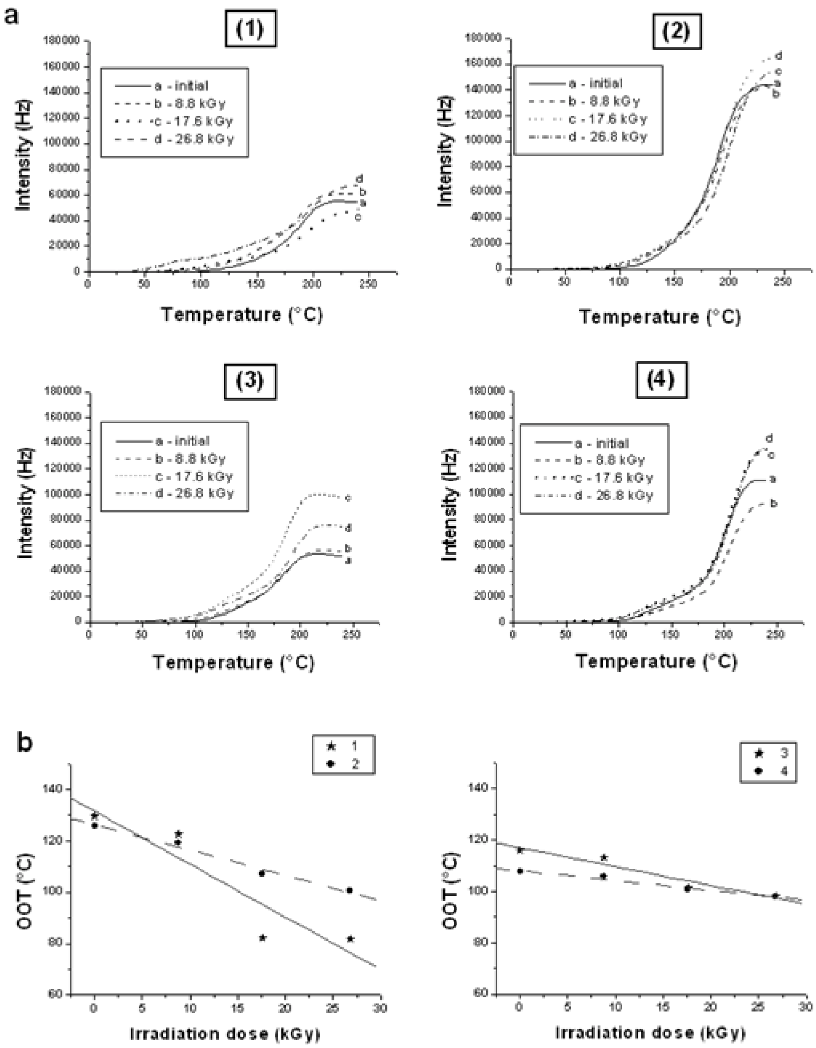


Fig. 4. Increase of chemiluminescence intensity versus temperature (a) and decrease of OOT as function of irradiation dose (b), for samples 1-4 as in table 2

in the case of polymers, is mostly associated with chemical bond scission, cross-linking and oxidation of both the main chains and side groups [34]. The produced chemical intermediate can further react and constitute new chemical structures. The bond scission, cross-linking or weakened bond formation are possible depending on the conditions of excitation.

The addition of the coupling agent (NCOTEOS) seems to cause a lower degradation of the functionalized sample after irradiation. These results also confirm that the functionalization reaction occurred successfully.

Conclusions

Preparation of hybrid silica materials based on two series of polyether polyols and the evaluation of their oxidative degradation are reported. Due to the lower reactivity of their secondary -OH groups, the degree of attachment to the silica network determined for polyols belonging to PPO series is much lower compared to the corresponding polyols belonging to PEO series (by about 12%). The lower reactivity of PPO when compared with PEO (which has -OH primary terminal groups) was also evidenced by ^{13}C-NMR. Thus, it was observed that in case of PETOL-48-3 MB, the degree of functionalization with NCOTEOS was only 20%, while PETOL-36-3 BR was completely functionalized. Evaluation of the rheological behavior revealed that the sol-gel reaction time is affected by many parameters: the polyol's structure, its functional -OH groups and reaction temperature. Observing the time at the beginning of gelation for the various systems studied, a shorter gelation time was shown for the polyols derived from PEO, comparing with polyols derived from PPO. Also, the increase of the viscosity was faster for the polyols functionalized with NCOTEOS, comparing with the systems obtained in the presence of the un-modified polyols.

The chemiluminescence's method was selected to evaluate the oxidative degradation of the synthesized materials. Analysis of the obtained data indicated that the oxidation start temperature (OOT) decreased with increasing the irradiating dose, for all samples. This can be explained by the fact that, during irradiation, the samples generate hydroxyl radicals that can react with organic compounds leading to degradation of the hybrid. Moreover, it was observed that the samples containing PEO are more stable to degradation (~ 130°C) than the samples with PPO (116°C). This happened because PEO has a better reactivity in the sol-gel process and therefore is more efficiently connected to the inorganic silica network. Correlating the data obtained for the reference samples with those obtained for the functionalized samples, it was also observed that the decrease of the onset oxidation temperature with the increase of the irradiating dose is slower for the functionalized samples. This is a further proof that the functionalization of the polyols with NCOTEOS occurred and can improve the quality of the final hybrid material.

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