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Qualification of epoxy resin by radiochemical ageing

E. CRĂCIUN[a], I. JITARU[a], T. ZAHARESCU[b,*], S. JIPA[c]
[a]"Polytechnica" University of Bucharest, 313 Splaiul Independenței, Bucharest, Romania
[b]INCDIE ICPE CA, 313 Splaiul Unirii P. O. Box 149, Bucharest 030138, Romania
[c]"Valachia" University of Targoviste, 18-22 Unirii Av., Targoviste 130082, Romania

Epoxy resin samples modified with oxide nanofillers were subjected to the action of gamma radiation for the assessment of stability under hard conditions of operation. The presence of titania (anatase) and silica influences the thermal stability of basis The rates of oxidation evaluated by chemiluminescence characterize the long term service of aged material The difference in the filler effect on the progress of oxidation can be explained on the scavenging behavior of oxides.

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The assessment of material quality is a priority requirement for long term operation of materials. The evaluation of developing oxidation, which occurs due to the reactions between molecular fragments and diffused molecular oxygen, always leads to an advanced degradation of material. The involvement of additives and fillers may turn the stability onto other ranges in connection with their chemical properties and the interaction between basis materials and the other components.

Nanocomposites which are characterize by an enormous interface surface. Several formulations based on nanoparticles of titania [for example 1-6] and silica [for example 7-12] were prepared and characterized. These compounds are studied because they offer a proper alternative for improved materials with peculiar electrical, thermal, mechanical properties. The homogenous dispersion of nanofiller into polymer matrix ensures the isotropic behavior and confers to material certain stability under energetic attack of stressors and the capability for long-term constancy of properties.

The practical reasons directed onto the improving the resistance of protective sheets to degradation, the optimization of composite formulations and the achievement of convenient stability are the goal of this study.

This paper presents the stability levels attained by epoxy resin modified with nanoparticles filler of titania (anatase) and silica when it is subjected to accelerated ageing. The difference between two oxides reveals the unlike chemical potential, which may explain the rates of oxidation occurred in γ-irradiated samples.

1. Experimental

Basic polymer material was obtained by curing of liquid epoxy resin, D. E. R.™ 353 (Dow, USA), which is a C_{12}-C_{14} aliphatic glycidyl ether modified bisphenol A/F based epoxy resin in the presence of hardener Epilox H 10-30, a modified cycloaliphstic polyamine epoxide adduct (LEUNA_Harze GmbH, Germany). The fillers added in this curing systems were titania (anatase) Tioxide A-HR type (Huntsman, England) and silicon dioxide provided by Degussa Germany as AEROSIL 200. The nanoparticles of silica are covered by siloxane having hydrophilic groups on their surface. The selected concentrations of titanium dioxide were 1, 5 and 10 % (w/w), while the concentrations of silica in this resin was 1, 5 and 7 % (w/w). The neat sample was also investigated.

The dry testing sheets from where aliquots were obtained were manually spread on stainless steel plate at 200 μm thickness.

The exposures to γ-radiation were performed in an irradiator GAMMATOR M-38-2 (USA) provided with ^{137}Cs source. Dose rate was 0.4 kGy.h^{-1}. γ-Irradiations were accomplished in air at room temperature.

Isothermal chemiluminescence testing was carried out in air at 150 °C using Chemiluminograph LUMIPOL 3 (Slovakia) Details on this equipment and on measurement procedure have been previously presented [13]. The measurement temperature was selected after material testing at two temperatures for the illustrative description of the progress in thermal oxidation.

FTIR spectra (the region around 1700 cm^{-1}) were recorded on JASCO 4200A spectrophotometer at 50 scans and 4 cm^{-1}.

2. Results and discussion

The degradation of epoxy resin takes place by the oxidation and the decay of double bonds that exist in the raw material.

In Figs 2a, b and c the modifications in infra red spectra are illustrated. This spectral region characterizes the unsaturation on the spectra of epoxy resins [14]. The spectra prove that the low amount of double bonds is consumed over low dose range, when the generation of oxygenated products occurs. There is not difference between the records obtained on neat and SiO_2-modified resin, because this oxide is not polar oxide and it can not tightly scavenge oxygen-containing intermediates formed during radiolysis of polymer.

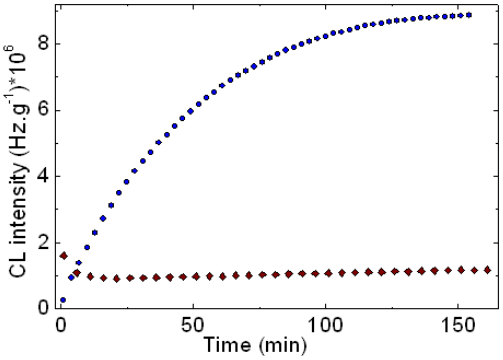

Fig. 1. Chemiluminescence curves recorded on neat resin at (●) 100 ^{0}C and (◆) 150 ^{0}C.

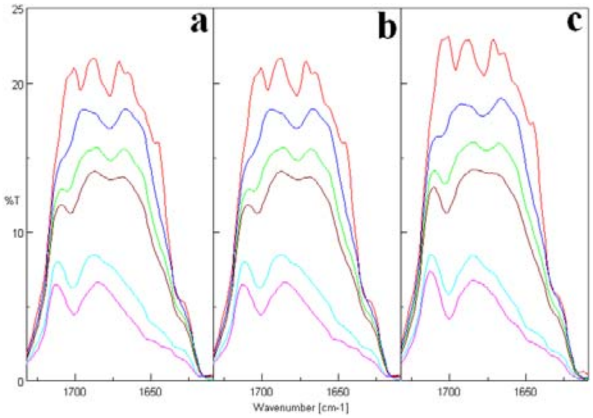

Fig. 2. FTIR records for epoxy resin samples at different γ-irradiation doses. (a) pristine material; (b) epoxy resin modified with nano SiO$_2$; (c) epoxy resin modified with nano TiO$_2$. (--) 0 kGy; (--) 10 kGy; (--) 20 kGy; (--) 30 kGy; (--) 100 kGy; (--) 150 kGy.

The contribution of nanoparticles filler to the oxidation of epoxy resin substrate consists in the diminishing of oxidation rates. The sharp difference between the four epoxy resin/TiO$_2$ composites is revealed for unirradiated state (Fig. 3a). The increase in the CL emission intensity demonstrates the continuous progress of oxidation, which occurs in polymer phase. The inhibition of oxidation appears after the first 25 minutes, when the CL intensity revealed by TiO$_2$-modified epoxy resin exceeds the similar values of pristine resin. However, the initial emission decreases quickly on 10 minutes illustrating the consumption of primary unsaturation decay catalyzed by titanium dioxide nanoparticles.

The γ-irradiation of TiO$_2$-modified epoxy resin samples causes a modification in the oxidation behavior of basis resin. The similar manner in the advancing oxidation depicted by the decrease in the CL intensity recorded on the first stage of radiochemical oxidation (20 minutes) proves that polymer matrix easily looses the reactive positions. The concentration of titania nanoparticles does not act efficiently for hindering oxidative degradation on the same period of degradation. When oxidation occurs, the filler nanoparticles play the role of radical scavenger, which blocks the autocatalytic oxidation process.

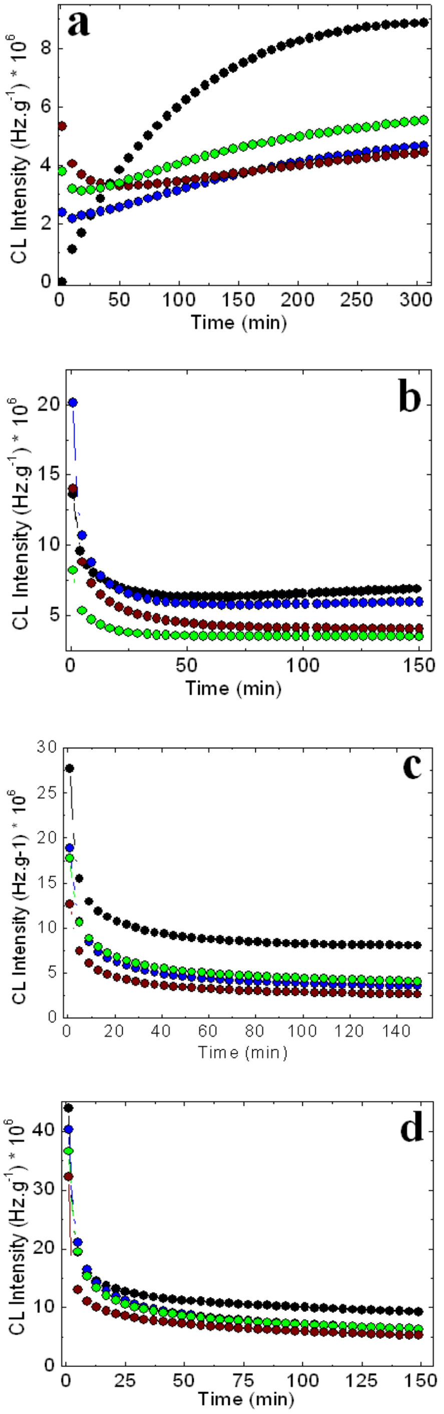

Fig. 3. Chemiluminescence curves drown for TiO$_2$-modified epoxy resin at various irradiation doses. (a) 0 kGy; (b) 20 kGy; (c) 50 kGy; (d) 100 kGy. (●) neat; (●) 1 % filler; (●) 5 % filler; (●) 10 % filler.

The position of curves describing the oxidation progress in TiO_2-modified epoxy resin below the curve followed by the degradation of neat material highlights the beneficial effect brought about by the presence nanofiller.

The proportion of filler in polymer matrix determines the relative positions related by the efficiency of oxide filler particles for adsorption of intermediates breaking the oxidation chain in which molecular resin fragments and peroxyl radicals are involved.

In contrast with TiO_2-modified epoxy resin, the presence of silica in various proportions does not change the development manner in the oxidation of polymer substrate (Fig. 4). It must be remarked the lower oxidation rate exhibited by the sample containing 1 % SiO_2 on the whole degradation time, but the close values of this rate for the other concentrations of this filler on the start of radiochemical oxidation is confirmed.

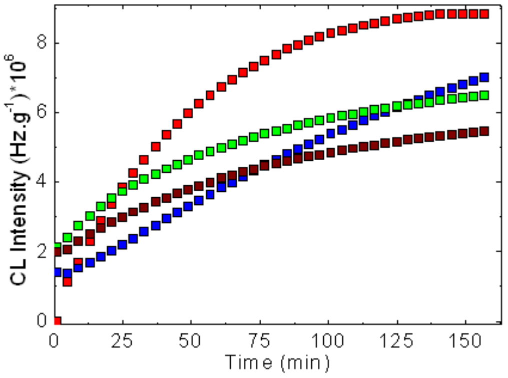

Fig. 4. Chemiluminescence curves obtained for unirradiated SiO_2-modified epoxy resin samples (🟥) neat polymer; (🟦) 1 % filler; (🟩) 5 % filler; (🟪) 7 % filler.

The inert filler (silica) has not ability to the decrease of oxidation rate, but it suppresses the continuous increase of chemiluminescence emission (Fig. 5). It means that filler nanoparticles can remote radicals from polymer by the inactivation on their surface. The difference between the radiation effect induced in SiO_2-modified epoxy resin consists of the level of initial amounts of radicals that are first oxidized.

In Figs. 6a and 6b initial values of CL emission in irradiated nanocomposites based on epoxy resin are illustrated. The changes in this parameter depict the resistance formulation during radiolysis. The increase in absorbed dose causes higher concentration of radicals which react with oxygen starting degradation process. However, the increase in the filler concentrations brought about certain stability because of the capacity to absorption of radicals on their large particle areas.

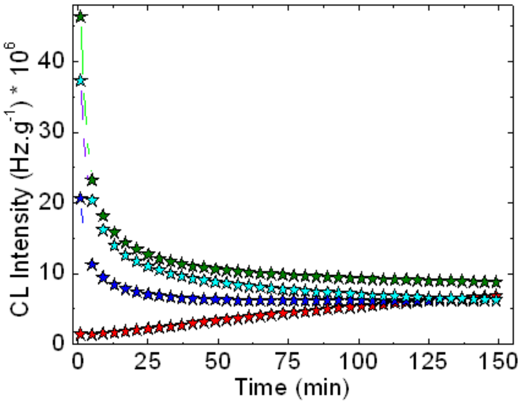

Fig. 5. Chemiluminescence curves obtained for irradiated SiO_2-modified epoxy resin samples. Dose: 50 kGy (🟥) neat polymer; (🟦) 1 % filler; (🟩) 5 % filler; (🟪) 7 % filler.

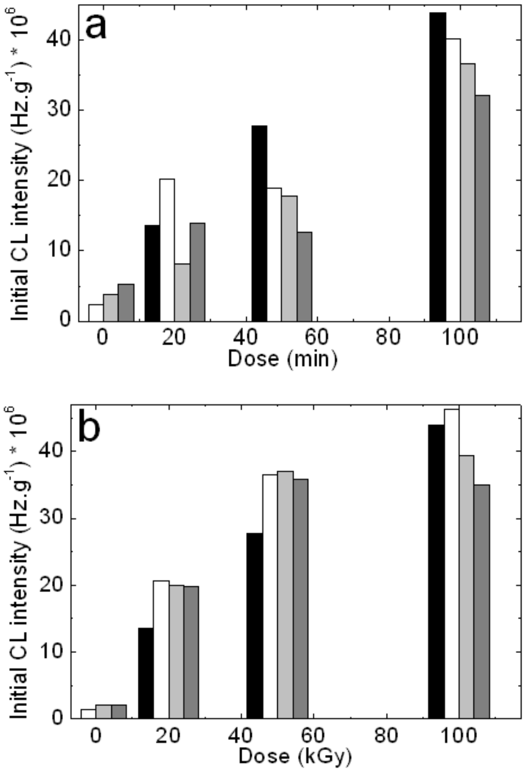

Fig. 6. Initial values of CL intensity for studied modified epoxy resin. (a) (black) neat resin; (white) 1 % TiO_2; (light grey) 5 % TiO_2; (dark grey) 10 % TiO_2. (b) (black) neat resin; (white) 1 % SiO_2; (light grey) 5 % SiO_2; (dark grey) 7 % SiO_2.

3. Conclusions

γ-Irradiation of nanostructured epoxy resin in the presence of titania (anatase) and silica reveals the possibility of thermal stabilization by increasing the filler concentration.

The differences in radiochemical strength of these composites consists of the behavior of filler that is capable to tight scavenge (TiO_2) or not (SiO_2) free radicals for avoiding their reaction with oxygen.

The connection between material stability and the stability of formulations is established for each composition depicting the overall long term stability of epoxy resin substrate.

Chemiluminescence is a proper investigation method because its high sensitivity allows the evaluation of existing differences between similar formulations of nanocomposites.

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*Corresponding author: traian_zaharescu@yahoo.com