

Gamma Radiation Effects on the Stability of Epoxy Resin Modified with Titania Nanoparticles

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This paper presents the radiation stability of epoxy resin modified with different amounts of titania (1, 5 and 10 %). The isothermal chemiluminescence investigation performed at 150°C has pointed out the high radiation stability of investigated systems. The sharp decrease in the early stage of oxidation emphasizes the benefit brought by the filler. Even though the initial chemiluminescence intensity enhances with filler content, the oxidation level after 20 min does not essentially differ. The application of high irradiation doses up to 1000 kGy does not affect the thermal stability of composites.

Keywords: radiation stability, epoxy resin, chemiluminescence intensity, filler

The use of nanostructured plastic materials has substantially increased over the last decade for various industrial, medical and environmental applications. In the same time, the manufacture of nanocomposites must satisfy the market requirements related to the improved properties during long term service [1-3].

An avalanche of physical and chemical phenomena stimulated by the action of ionizing radiation and often self-sustained, leads to the failure of materials, which limits the life of different products [4-15]. Nanocomposites belong to a product class, whose level of interactions is determined by the nanodimensions of spread filler. The dependence of physical and chemical properties on the average size of particles characterizes the depth of modifications occurred in polymer during the energy transfer from the outside of material [16-18].

The addition of nanoparticle filler induced usually an improvement in the properties of base polymers [19, 20]. The forces that act in these materials may differently affect the macroscopic behaviour of nanocomposites. An important role in this feature is played by filler concentration, which can be reported to the interphase area. This means that irradiated polymers offer several possibilities for attending foreseen parameters that delimit implementation range. The presence of nanoscale inorganic fillers improves mechanical, thermal and gas barrier characteristics [21-24]. The depreciation of material quality is mostly related to the polarity of functions that are presented in/on molecular backbone. The availability of material for the migration of intermediates or final products through the polymer bulk represents a main factor which controls the progress and the profundity of changes.

The stability of processed material requires detailed knowledge on the scission process in polymer matrix and the reactivity (or availability) of nanoparticles of filler for the scavenging or coupling of radicals which are involved in the radiation degradation macromolecules.

A large number of studies on the preparation and characterization of polymer/nanoparticles matrix were reported [21-25] due to their excellent functional properties. Several promising formulations of polymer hybrids were proposed for satisfying various requirements for a large number of applications. However, the problem

of thermal stability of polymer composites is of a great interest being directly related to the material durability. The topic of thermal degradation has received a special attention due to the strong influence of the service conditions on the behaviour of composites. The characterization of material depreciation by heat and high energy radiation provides useful information for storage, processing and long-term use, namely the life of products.

The application of epoxy resins for surface protection represents a large direction on which this class of polymers is used.

The degradation is an important process through which material loses its functional features. The investigation of structural modifications induced in this material provides the trends of ageing through which product is damaged. The nanocomposite systems consisting of epoxy resin and titania can be applied on metallic surfaces for the inhibition of deterioration under specific conditions, such as environmental corrosion or they may be used in the manufacture of hard items, which present high mechanical strength. The degradation of deposited layer of nanostructured epoxy resin takes place with low rate and this behaviour delays the replacement of components and prolongs the life time of equipment in which they are used. These systems can be attractive for the production of electrical insulations or piezo-composites.

This paper presents the oxidation resistance of epoxy resin nanostructured with TiO₂, which may be used in electrical engineering for covering wires and for insulating of rigid plates on which electronic circuits are placed.

Experimental part

Materials and methods

Basic polymer material was obtained by curing of liquid epoxy resin, D. E. R.™ 353 (Dow, USA), which is a C₁₂-C₁₄ aliphatic glycidyl ether modified bisphenol A/F based epoxy resin in the presence of hardener Epilox H 10-30, a modified cycloaliphatic polyamine epoxide adduct (LEUNA-Harze GmbH, Germany). The filler added in this curing systems was titania (ultrafine rutile – crystalline form, 17 nm) UV-TITAN L181 type (Kemira Pigments Oy, Finland). The selected concentrations of titanium dioxide were 1, 5 and 10 % (w/w). The neat sample was also investigated.

The preparation of samples started with the mixing of appropriate filler amounts with liquid epoxy resin; then,

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hardener was added and sheets and films were cast after 30 min. The complete curing was accomplished after one week. This operation was carried out under controlled conditions (temperature: 23°C; humidity 50%).

Isothermal chemiluminescence (CL) measurements at 150°C were carried out in LUMIPOL 3 (SAS, Slovakia). Specimens of about 4 mg were placed in aluminium tray for chemiluminescence investigation. The applied procedure for this kind of investigation was previously reported [26].

FTIR spectra were recorded on a JASCO 4200A spectrophotometer at 50 scans and 4 cm⁻¹ resolution. The region of 1762 – 1609 cm⁻¹ was found to be characteristic for spectral modification under γ -radiation exposure.

Electrical measurements were performed by a laboratory equipment megohmmeter METREL under the tension of 1000 V. The presented values mean the average of ten measurements on different points placed inside a square of 1 cm².

Irradiation was performed in air at room temperature in GAMMATOR M-38-2 installation (USA), provided with ¹³⁷Cs source. Dose rate was 0.4 kGy/h.

Results and discussions

The degradation of studied epoxy resin systems starts after samples receive medium irradiation doses. The modifications in IR spectra appear later, when exposure dose exceeds 50 kGy because of the radiation resistance of base material. The changes in IR spectra on the region of 1730 – 1600 cm⁻¹ were noticed, where unsaturation appears. Figure 1 presents the variation in absorbance for neat and TiO₂ (1 %)-modified epoxy resin. It can be noticed that initial unsaturation is diminished, these absorption bands being replaced by the bands of oxidation products.

The thermal resistance of unirradiated samples containing TiO₂ determines a slight modification in the IR spectra. The deep difference between pristine and modified epoxy resin may be revealed by chemiluminescence determinations. The initial values of I_{CL} demonstrate the increasing content of oxygen adsorbed on titania nanoparticles (fig. 2). The initial decrease in the CL emission of TiO₂ modified epoxy resin illustrates the fast consumption of oxygen that is incorporated in material during sample preparation (fig. 2). On the other side, the ascending values of chemiluminescence intensity (I_{CL})

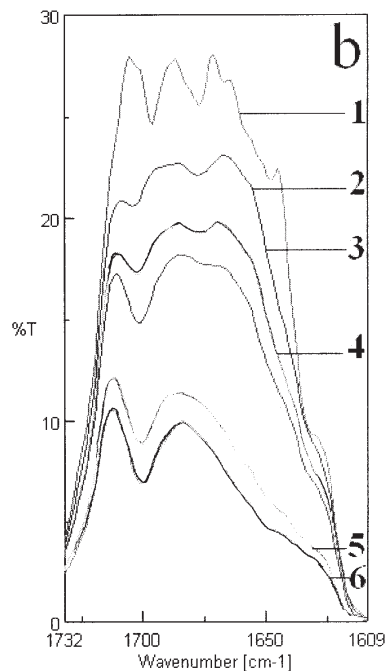
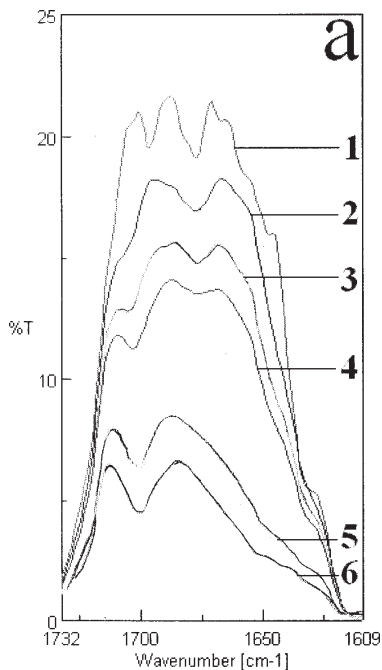


Fig. 1. Modifications in FTIR spectra occurred in neat resin (a) and (b) 1 % TiO₂-resin exposed to different doses. (1) 0 kGy; (2) 25 kGy; (3) 50 kGy; (4) 75 kGy (5) 150 kGy; (6) 250 kGy.

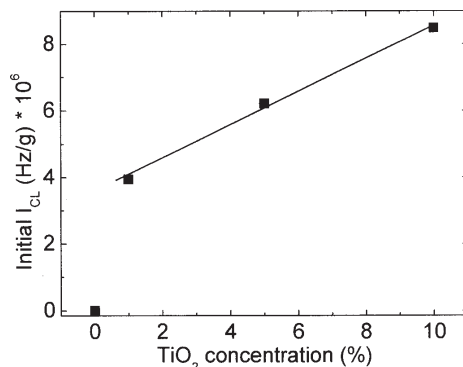


Fig. 2. Initial chemiluminescence intensities recorded for different filler concentrations in unirradiated epoxy resin

denote a continuous oxidation as the result of oxygen diffusion (fig. 3), which allows oxygen to penetrate polymer matrix while oxygen content is partially consumed. However, the sharp decrease over short time elapsed from the start of heating does not represent a disadvantage; it depicts the attaining of an equilibrium state after which the material completes oxidation.

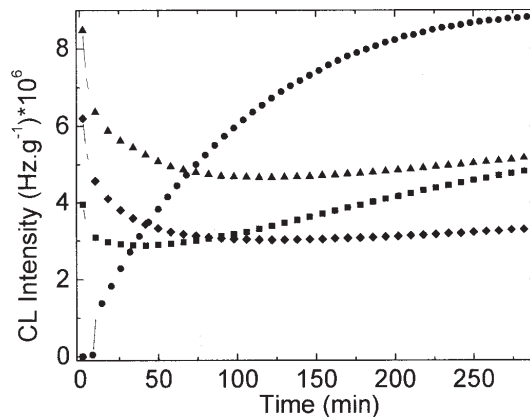


Fig. 3. Chemiluminescence curves recorded for epoxy resin (ER) with different formulations. (●) pristine material; (■) ER + TiO₂ 1 %; (◆) ER + TiO₂ 5 %; (▲) ER + TiO₂ 10 %

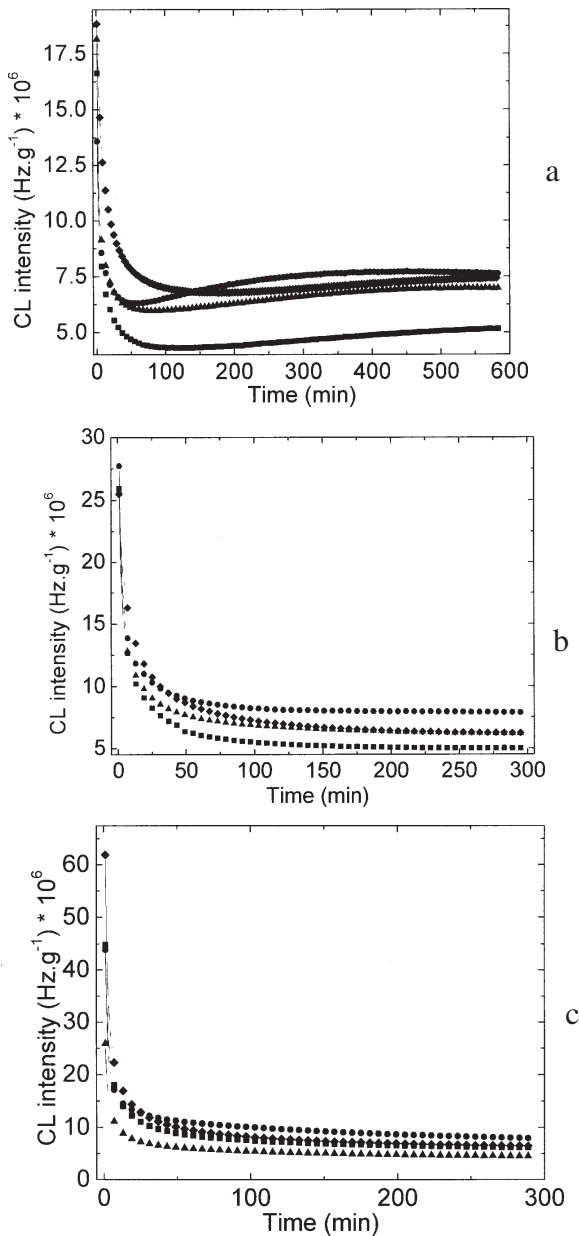


Fig. 4. Chemiluminescence curves drawn for irradiated samples irradiated at various doses.
(a) 20 kGy; (b) 50 kGy; (c) 1000 kGy.
(●) pristine material; (■) ER + TiO₂ 1 %; (◆) ER + TiO₂ 5 %; (▲) ER + TiO₂ 10 %.

The thermal oxidation of irradiated epoxy resin progresses somewhat similar at different exposure doses. The sharp decrease in the chemiluminescence emission over the first 15 – 20 min from start characterizes the decay of free radicals formed during radiolysis. The ascendant slop of curves emphasizes the slow oxidation rate on the propagation stage of oxidative degradation. The most important feature for 20 kGy irradiated samples is the higher level of oxidation for neat resin (fig. 4a). The increase in the absorbed dose up to 1000 kGy determines the slight rising of long term chemiluminescence intensities (figs. 4b and 4c). The advanced oxidation states of irradiated samples at higher doses do not essentially differ, because the progress in the oxidation process does not appear to be promoted due to the low reactivity of intermediates.

Several aspects of trends in oxidation must be revealed:

- in spite of the scission caused by irradiation (fig. 5), the stability of radiation processed material is modified due to the radiation effects induced in epoxy resin;

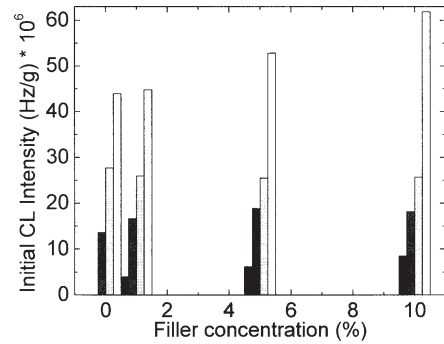


Fig. 5. Initial CL emission of irradiated epoxy resin/nano-TiO₂ systems. (black) neat material; (dark grey) ER/TiO₂ 1 %; (light grey) ER/TiO₂ 5 %; (white) ER/TiO₂ 10 %.

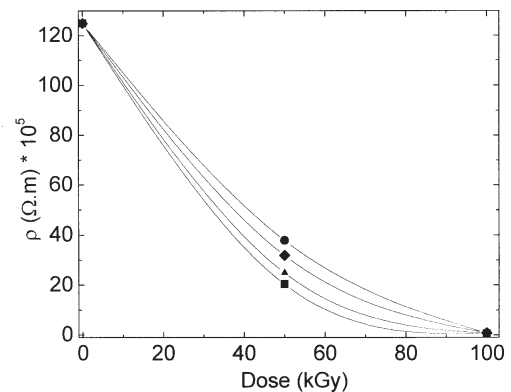


Fig. 6. Decrease in the resistivity values for irradiated epoxy resin/TiO₂ samples. (■) neat material; (▲) 1 % TiO₂; (◆) 5 % TiO₂; (●) 10 % TiO₂.

- extreme low oxidation rates occurs, even if sample is pristine one or titania is added in different concentrations;
- higher doses erases differences between the levels of maximum CL intensities on advanced oxidation;
- the presence of filled diminishes the degree of oxidation, probably by the adsorption of intermediates on the surface of nanoparticles;
- the thermal stability of irradiated epoxy resins is high due to the proper molecular structure which allows energy dispersion.

Electrical measurements confirm the slow rate of radiation degradation. Figure 6 shows the decrease in the electrical resistivity evaluated on a large dose range (up to 100 kGy). The values calculated for the irradiation dose of 10 kGy are similar to those obtained on unmodified samples.

The sequence of curves demonstrates the influence of nanofiller on the electrical properties of basis polymer. The nanoparticles encapsulated in epoxy resin interact with macromolecules modifying the conductivity level of samples. However, the difference between the manner of decreasing resistivity are small, which emphasizes the minor effect of concentration of the variation of this property in spite of higher concentration of polarizable oxygen atoms.

Conclusions

Polymeric nanocomposites materials can be properly characterized by chemiluminescence. This method can provide information on stability for a large variety of ageing conditions.

The thermal resistance of epoxy resin modified with nanoparticles of titania is significant, due to the action of

filler concerning the adsorption of degradation intermediates. The application of these studied formulations can be done in good conditions, because the exposure doses exceeding 20 kGy do not promote significant degradation. The application of high irradiation doses up to 1000 kGy does not affect the thermal stability of composites. The slight increase in the chemiluminescence intensity measured after 300 min of heating demonstrates the stability of polymer matrix promoted by filler (TiO₂). The differences between the chemiluminescence intensities exposed by epoxy samples with different content of filler becomes smaller and smaller as the irradiation dose increases. It emphasizes the beneficial contribution of filler to the stability of polymer base material.

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