Improved stability of alkyd resin by modification with TiO_2 nanoparticles

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Alkyd resin modified with waterborn phenolic component was loaded with different loadings of titania nanoparticles (2, 5 and 10 wt %). These systems were subjected to accelerated degradation by γ-irradiation, when the formation of radicals occurred. The highest studied concentration of TiO_2 brings about the most efficient stabilization effect. The isothermal and nonisothermal chemiluminescence procedures have proved the improvement in material durability by the adsorption of radicals on the large surface of filler nanoparticles.

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1. Introduction

The long term stability of materials is the main problem of durability, which characterizes the optimization of equipment service. The organic materials are always subjected to oxidative degradation in the tight connection with energetic factors: heat, mechanical charge, irradiation, environmental agents. The composition plays the key role in the preservation of integrity. The selection of appropriate formulation can bring an improved behavior under degradative conditions [1-3]. The coating layers applied to metallic surfaces assures the anticorrosive protection, which delays the deterioration of material quality due to the diffusion of humidity and oxygen from operation environment. The consistancy of coating product determines the prevention of oxidation because the barrier against the penetration of degradation agents reduces the presence in their surface concentration. The protection efficiency depends not only on the thickness of layer, but also on the capacity of material to resist against oxidation.

There was reported previously a review concerning the chemistry of alkyds used in the drying of paintings focusing on the catalytic effect upon autoxidation [4]. The formation of peroxides and oxidation initiators is analyzed starting from radical mechanism. The similarity with the oxidation of polymers suggests the characterization of this type of coating materials in accelerated conditions [5].

The investigation on induced effect of titania on epoxy resins was accomplished, where an improvement in radiation stability was highlighted [6]. The presence of TiO_2 nanoparticles decreases the rate of oxidation due to the interaction between new formed radicals and titanium atoms on the oxide surface, whose free inner electronic orbitals are available for unpaired electron of radicals.

The simulation of degradation in the radiation field is based on the radical mechanism, which starts with the scission of weak bonds. The loading cured materials with nanoparticles that are superficially active may influence the progress of oxidation. The interaction between radicals and inorganic filler promotes notably thermal stability and their particles act as traps [7]. The nanocomposites behave as stable systems, if the nanosize component scavenges the primary radicals. The formation of peroxides is hindered and the advance in the oxidation state is delayed.

Ionizing radiation like γ-rays produces high concentration of radicals along their tracks and they are involved in various reactions: proton abstraction, oxidation, recombination, disproportionation. The main intermediate playing the role of chain initiator are peroxyl radicals, which are decayed by dimolecular processes [8]. The diminution of the initiator concentration either by consumption reaction, or by the absorption on particle surface improves the stability of material. The loaded phase with large specific area reinforces the cured resin and allows achieving a slower oxidation rate. The polarity of bonds in added inorganic oxide would be involved in the scavenging of radicals by the appearance of Van der Waals bonds between metal atom of oxide and oxygen atom belonging to oxidized substrate [9]. The advantage obtained by the modification of resins with titania nanoparticles consists of the expected thermal stability and the extension of material durability.

In our work we demonstrate the stabilization effect by the reinforcement of alkyd resin with titania nanoparticles as basic material processed by γ-irradiation. The efficiency of loading is the result of the embedding of TiO_2 particles, which allows the optimal operation of protected items. Radiation exposure in air simulates the hard condition of stressing depicting the participation of environment to the degradation process. The contribution of titania to the modification of thermal stability is connected directly with its application as inorganic pigment loading. This paper is an extension of earlier report on polymer [10, 11], which has demonstrated the availability of organic materials, for

example polymers, to form hydroperoxides as the start points of oxidative degradation.

2. Experimental

Alkyd resin is EZ 715, which is applied for the protection of coils. It was provided in liquid state by CHIMTITAN (Romania) being modified with phenolic resin component. It is waterborn material. Small amounts of resin were poured in aluminum trays for further hardening and investigation. The amount of dry material was around 50 mg. The concentrations of TiO_2 in alkyd resin were 2, 5 and 10 wt%. The curing was accomplished in an electrical oven at 150 ^oC for 4 h. γ-Irradiation was carried out in an exposure machinery (Gammator M 38, USA) provided with ^{137}Cs source in air at room temperature. The exposure doses were 10, 20, 40 and 100 kGy. The reference unirradiated samples were also analyzed. The appropriate dose rate of 0.4 kGy/h was applied for degradation studies, because the rate of radical formation is comparable with the rate of oxidation. Composite samples covered with aluminum foil destined to the conversion of γ-rays into δ-electrons for a more efficient energetic transfer were continuously rotated for homogenous irradiation.

Chemiluminescence (CL) procedure was performed for the determination of the stability characterization by LUMIPOL 3 (Slovak Academy of Science, Bratislava), because there is the proportionality between the amount of peroxyl radicals and the emission of photons [12]. For proper comparison of results, the specific CL intensities are expressed in Hz g^{-1}. The temperature range for nonisothermal CL measurements covers the values from room temperature up to 250 ^oC. The heating rate was 0.2 ^oC/min. Isothermal CL measurements were performed at 170 ^oC, 180 ^oC and 190 ^oC. The error in temperature measurements was ± 0.2 ^oC.

3. Results and discussion

3.1. Nonisothermal measurements

The oxidation of polymers is an autocatalytic process, which starts with the reactions of free radicals with molecular oxygen. The propagation rate of oxidation depends on the intensity of degradation agent, the duration of action and also on the mobility of intermediates [13]. However, the buildup and decay of hydroperoxides decide the kinetics of oxidative degradation, which may occur according to different schemes [14].

The thermal treatment applied to alkyd resin formulations can induce oxidation, whose rate depends on temperature. The moderate heating may induce bond scission, if the material has not strong bonds.

The nonisothermal chemiluminescence spectra recorded on the nonirradiated alkyd resin loaded with different concentration of TiO_2 (Fig. 1) show very good thermal stability of these materials up to 120 ^oC, which indicates the appropriate thermal resistance of all studied formulations. The increase in temperature initiates the start of oxidation, which rate depends on the sample composition. The presence of low concentration of titania, namely 2 %wt, does not modify significantly the amount of peroxides, which are decomposed totally at around 230 ^oC. The higher the concentration of titania nanoparticles, the lower the chemiluminescence intensity is recorded.

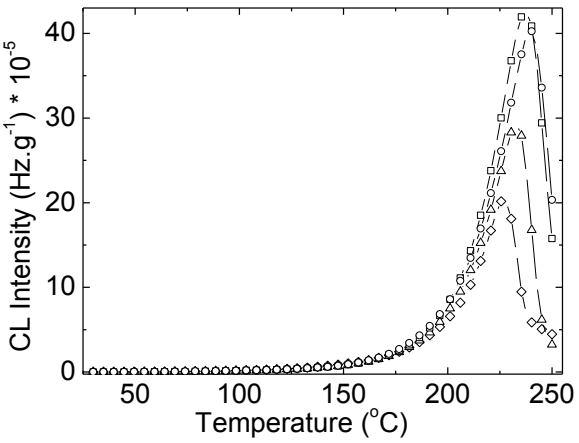

Fig. 1. Nonisothermal CL spectra recorded on nonirradiated alkyd resin loaded with different concentration of TiO_2. (□) pristine; (○) 2 wt%; (Δ) 5 wt%; (◊) 10 wt %

The maximum chemiluminescence intensity is centered at high temperature indicating the resistance of basic resin against oxidation. The irradiated neat samples have different shapes that nonexposed specimen, because the formation of radicals is accelerated by the energy transfer from incidental γ-rays onto organic molecules (Fig. 2). The appearance of high intensity at lower temperature (150 ^oC) assumes the early start of oxidation in the high dose irradiated material. This maximum CL emission is softer in the samples, because the amounts of peroxyl intermediates are not accumulated in enough concentrations for the relevant rate of oxidation.

The comparative analysis of Figs. 1 and 3 points out the contribution of energetic transfer onto resin molecules. If the unirradiated samples present large differences between the development in increasing CL intensities, the irradiation at 20 kGy reveals the similarity in the accumulation rates of peroxides; they are decomposed at 150 ^oC and 230 ^oC. The sequence of the bond sission is determined by the figures of bond energy: C – C of 348 kJ.mol^{-1}, C – O of 358 kJ.mol^{-1} and C – H of 413 kJ.mol^{-1} [15]. The closed values for the first two types of bonds suggest that their scissions create radicals, which are decomposed at the temperatures of two CL intensity maxima.

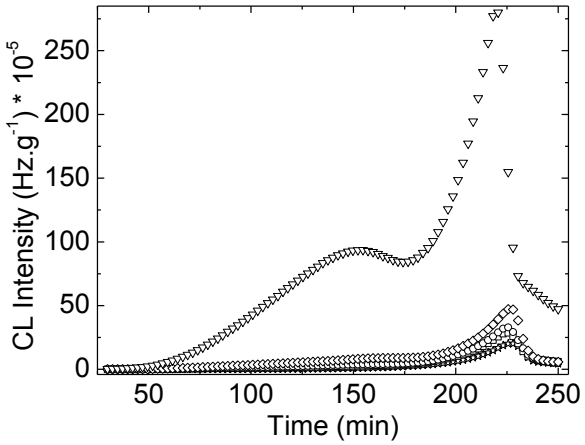

Fig. 2. Nonisothermal CL spectra for neat alkyd resin degraded by γ-irradiation at different doses (★) 0 kGy; (□) 10 kGy; (○) 20 kGy; (◊) 40 kGy;(▽) 100 kGy

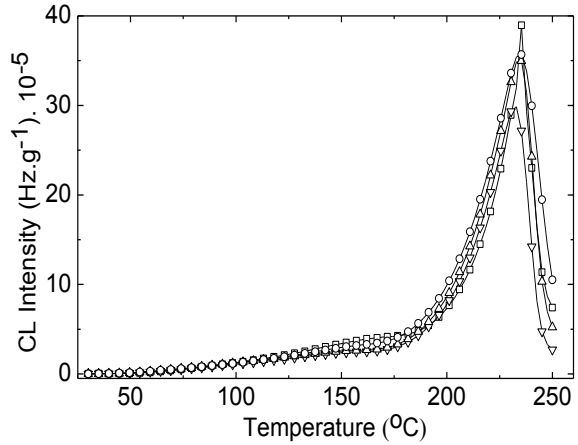

Fig. 3. Modification in nonisothermal CL intensity for alkyd resin loaded with different concentration of TiO_2 after irradiation at 20 kGy. (□) pristine resin; (○) 2 wt%; (Δ) 5 wt%; (▽) 10 wt %

At higher exposure doses the curves describing the progress in sample oxidation exhibit a larger distribution suggesting a significant contribution of filler nanoparticles to the abstraction of peroxyl radicals from the oxidative environment (Fig. 4). The narrowing of intensity maximum in neat samples is related to the higher concentration of peroxyl intermediates, which are dispersed in the bulk of resin.

The thermal stability of alkyd resin modified with titania is influenced by the post-irradiation treatment. The resin itself is post-cured during the application of heat for certain periods. Fig. 5 shows the beneficial contribution of this kind of processing. It allows the long life radicals to decay by recombination, even the resin was subjected to γ-irradiation or not. The life time of protective layer is improved by this practice, because the polymerization of resin is completed and the continuity of protection covering avoids the formation cracks.

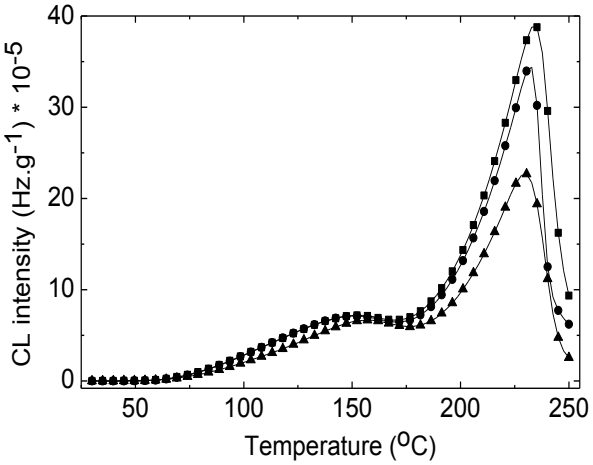

Fig. 4. Nonisothermal CL spectra for different loadings of alkyd resin after irradiation at 100 kGy. Filler concentrations: (■) 2 wt; (●) 5 wt%; (▲) 10 wt%

3.2. Isothermal measurements

The alteration of thermal stability by intense energy transfer accomplished by γ-irradiation leads to the appearance of higher amount of radicals. They are involved in oxidation rather in recombination, because the movement of oxygen molecules is not hindered in comparison with greater size organic radicals. The shapes of isothermal dependencies of chemiluminescence emission on recording time are descending form in the cases of resin/TiO_2 systems. This shape illustrates the consumption of peroxyl intermediates through the reactions which do not generate other further radicals. This behavior is unlike in respect with oxidative degradation of polyolefins, which takes place as radical chain mechanism.

Fig. 6 the evolution of thermal degradation of pristine alkyd resin at three different temperatures is presented. Some differences can be noticed:

- the amount of radicals generated during radiolysis increases with irradiation dose, most of them being oxidized on the early stage of degradation,
- the unirradiated resin presents a slight tendency to oxidation even after 150 minutes at 170 ^{o}C, which proves the slow rate thermal decomposition,
- the samples heated at 200 ^{o}C are quickly oxidized in unirradiated state, because the diffusion of oxygen feeds the reaction with radicals and the intermediates are placed at larger distances from one to another,
- the oxidation time corresponding to the end of process is diminishing as the dose is increased, because the consumption of higher radical concentration occurs more easy,
- the steady state of oxidation is attained faster in irradiated material due to the less confined diffusion of oxygen through the smaller molecules formed during γ-exposure.

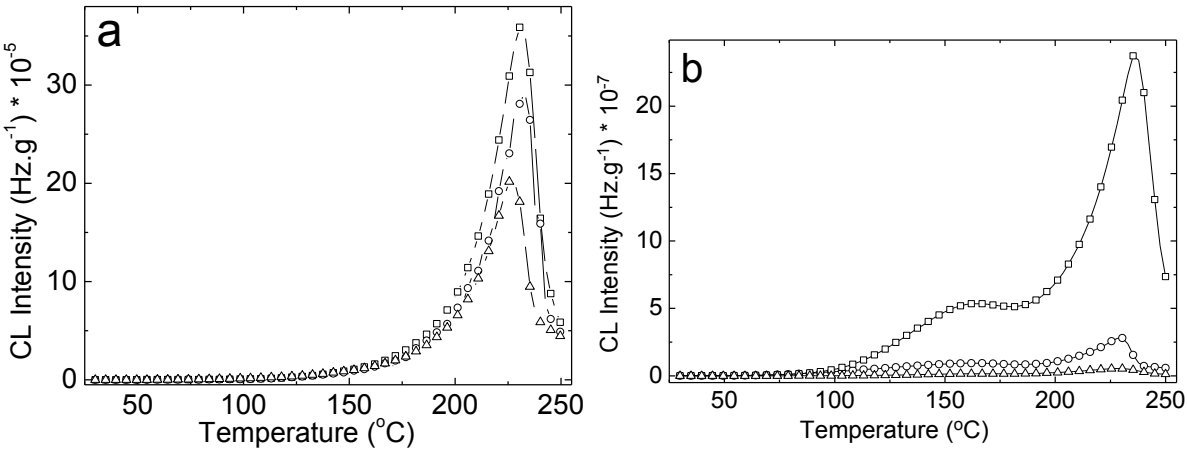

Fig. 5. Nonisothermal CL spectra for different loadings of alkyd resin after irradiation at 100 kGy. Filler concentrations: (■) 2 wt; (●) 5 wt%; (▲) 10 wt%

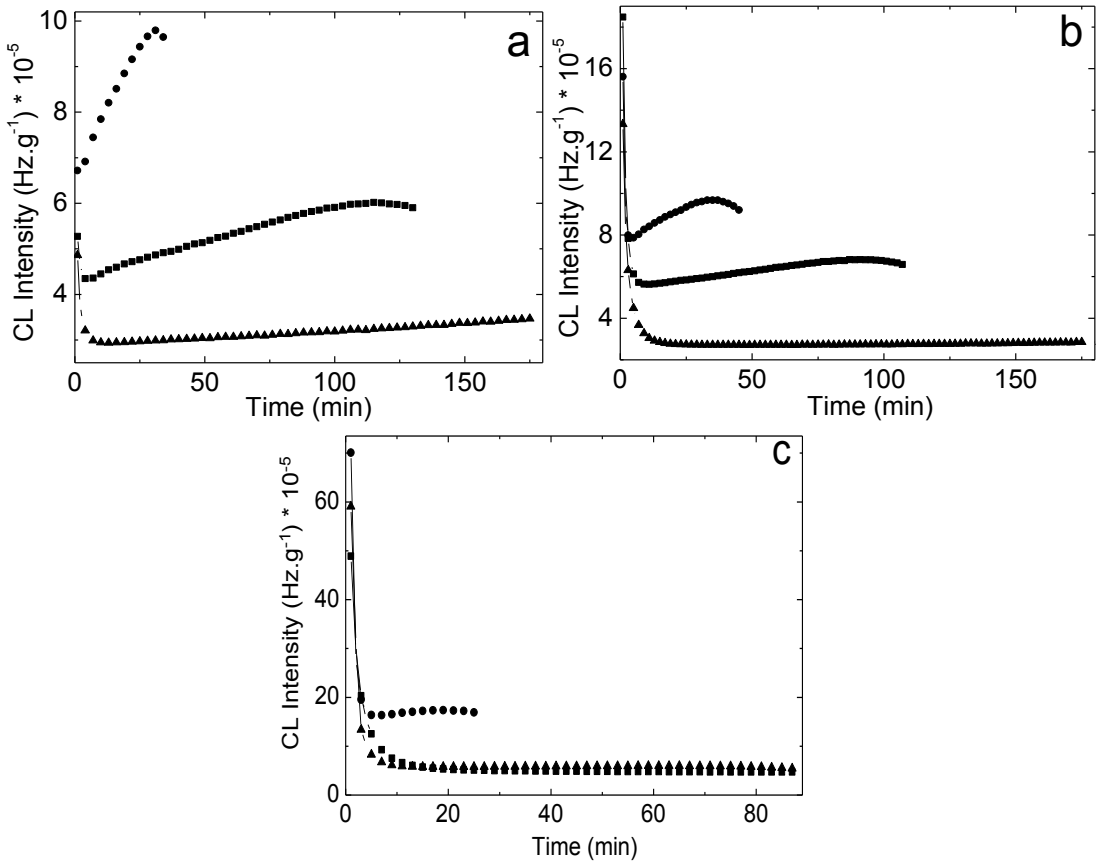

Fig. 6. Isothermal CL curves for pristine alkyd resin. Testing temperature: (▲) 170 °C; (■) 185 °C; (●) 200 °C. (a) 0 kGy; (b) 20 kGy; (c) 100 kGy

The presence of TiO_2 nanoparticles causes an improvement in material stability (Fig 7). The most resistant formulation is the alkyd resin loaded with 10 wt% titania.

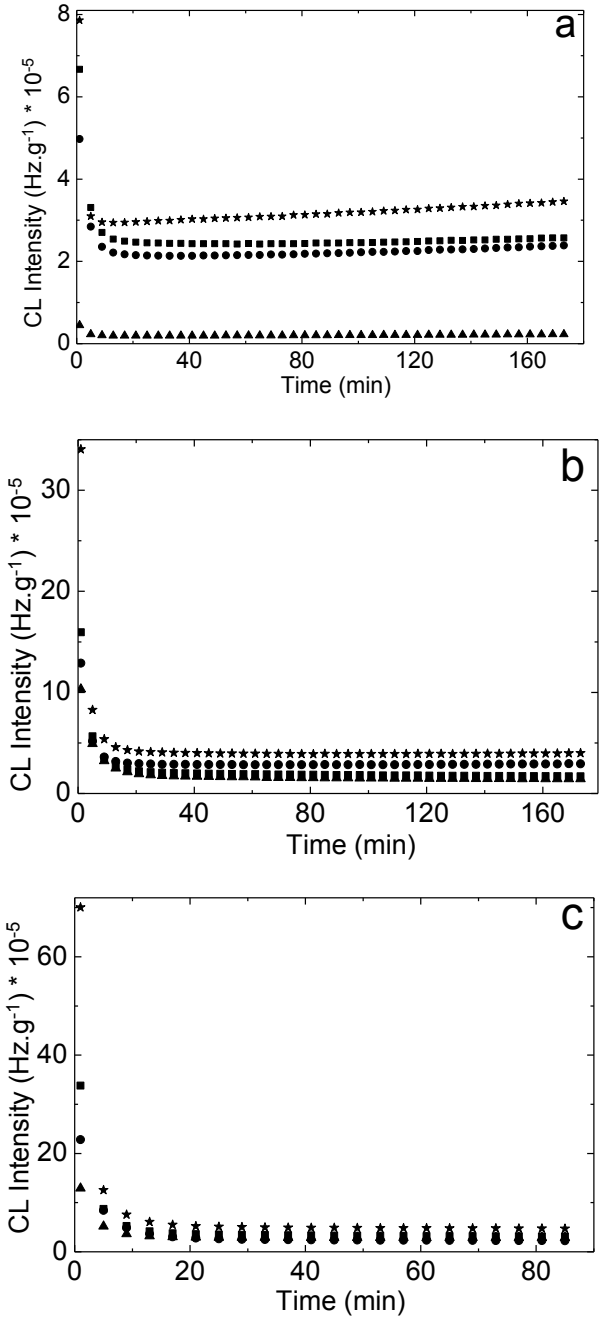

Fig. 7. Isothermal Isothermal CL curves recorded on various alkyd resin formulations at 170 °C. (a) 0 kGy; (b) 40 kGy; (c) 100 kGy (□) pristine; (■) 2 wt; (●) 5 wt%; (▲) 10 wt%.

The action of delaying oxidation would be based on the adsorption of radicals and the diminution of oxidation probability. After about 20 minutes the rates of oxidation occurred in irradiated samples becomes similar for the four concentrations of filler.

4. Conclusions

The studied alkyd resin loaded with titania nanoparticles presents an improved stability after γ-irradiation because of the adsorption on large area of resin/filler interface. The increase in the concentration of oxide induced an enhanced resistance against oxidation. The chemiluminescence investigation proves the presence of two peaks of emission intensity, which can be ascribed to the scission of carbon-carbon and carbon-oxygen bonds. The generation of peroxides starts at high temperatures exceeding 100 °C. It demonstrates the proper thermal stability even these systems are γ-preirradiated. The post-irradiation processing improves the thermal strength of titania-loaded alkyd resin. The application of this treatment brings about an extension of durability.

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