

INSIGHT INTO THE OXIDATIVE DEGRADATION OF PHENOLIC RESIN DESTINED FOR THE CORROSION PROTECTION OF METALLIC SURFACES

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Abstract. *The effects on the stability under accelerated degradation of phenolic resin used for the corrosion inhibition of metallic surfaces in aeronautical and nuclear spare parts are evaluated by nonisothermal chemiluminescence (CL) at four different heating rates: 5, 10, 15, and 20 °C min⁻¹. The simulation of the interface interaction between the metallic bodies and protection layers is achieved by the addition of metallic oxides as corrosion promoters: Gd₂O₃, CeO₂, Pr₂O₃, MgO, MnO₂, Cr₂O₃, and In₂O₃. These metallic atoms may be the main alloying elements that are present in the compositions of special application products. The presence of a specific peak in the CL spectra between 160 and 177°C proves the oxidation activity of filler in the connection of electronic interference. The differences between the emission intensities of the studied formulations certify the unlike contributions of alloying components. The heating rate plays also the role of oxidation factor that influences the refreshing surrounding atmosphere. The present results define the thermal technological limits of peculiar operation conditions for any metallic item subjected to a high level of warranty. The initiation of degradation in phenolic resin is done by γ -irradiation when free fragments are provided for the interaction with metallic structures. The development of oxidation is analyzed by the modification of CL emission intensities from room temperature to 250°C. The diminution of this process parameter over 200°C is found an essential factor for the preservation of surface integrity.*

Keywords: *Phenolic resin; oxide filler; accelerated degradation; nonisothermal chemiluminescence.*

1. INTRODUCTION

The preservation of surface integrity for the metallic items operating under hard conditions like nuclear power stations and irradiation devices, aircraft, automotive transportation, underwater parts of ships, and outdoor electrical power stations asks for compulsory protection of their exposed faces against corrosion attack, which may entirely modify the working regime and the operation warranty. The protection of metallic areas, which play essential functions in long-term equipment can be achieved by electroplating with

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a proper other resistant material [1] or by the application of a conservation organic sheet able to be adherent and stable [2].

The deterioration of metallic products by corrosion or superficial oxidation is strongly dependent on the material composition [3], because electronic densities modify differently the local potentials. The correlation between the product composition and the adhesive degree of the protective layer demonstrates the involvement of the atoms belonging to both phases in local interactions on various coupling molecular fragments [4]. The adhesive joining technology must provide suitable background knowledge on which the product manufacturers are based in the selection of covering materials [5]. Because the phenolic resins are the polycondensation products of the reaction of phenol with formaldehyde, they must be subjected to a thermal treatment for curing on the protected surface, which induces a certain decomposition degree [6] (Fig. 1) influencing the further linkage of resin layer on the surface. The radiolysis of this organic substrate takes place according to the scheme presented in Fig. 1, where the oxidation is according to the radical mechanism [7].

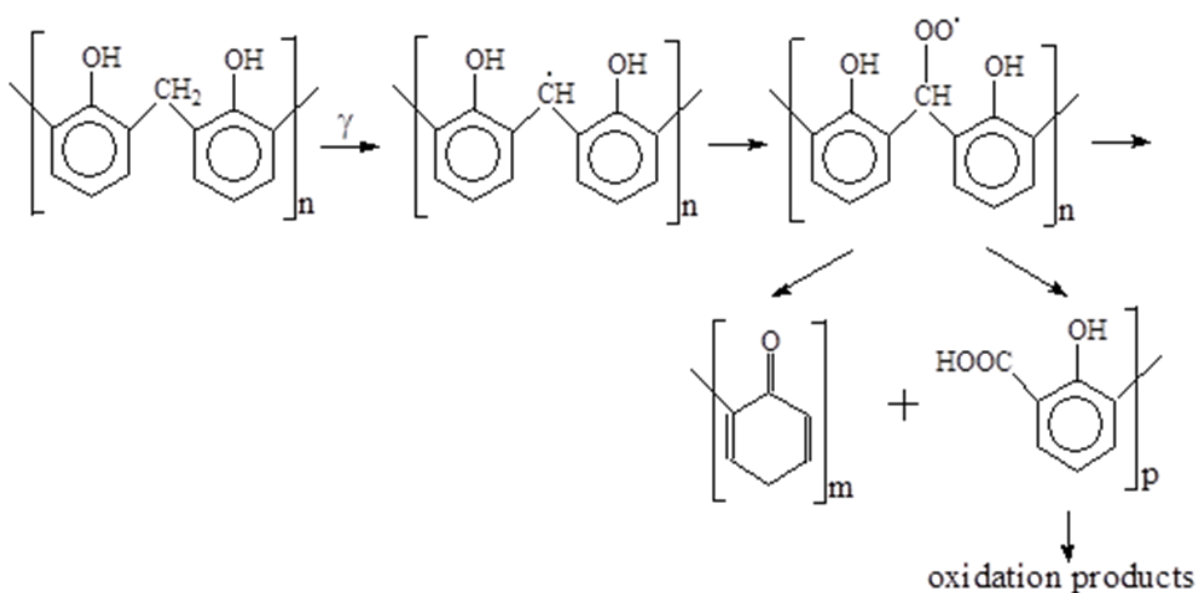


Figure 1. The decomposition of phenolic resin by accelerated oxidation during γ -radiolysis.

The durability qualification of phenolic resin is related to the preservation of adhesive properties conditioned by the structural modifications [8]. The thermal resistance and the radiochemical strength as well, are the intrinsic properties, which determine the operation duration when the oxidation state remains unchanged despite the energetic transfer onto the insulator layer [9]. The conservation of sheet integrity may be achieved by the addition of either an appropriate stable fraction [10] or a nanoparticle powder [11]. Replacing a resin constitutive component [12] is another pertinent solution for the extension of the durability of dried resin.

The addition of the oxide phase in the phenolic resins would follow the effects induced by them into various host polymers, which gain a remarkable resistance with respect to the pristine materials [13]. The stabilization efficiency is promoted by the interaction between the lattice defects existing on the nanoparticle surface and molecular fragments that appeared by the scissions that occur in the organic substrate during its degradation [14].

The characterization of evolution stability in anticorrosion resins is seldom done, because it requires structural knowledge which is severely preserved by the manufacturers. However, there are reported some papers, where the modification of chemical configurations

is tightly correlated with the duration and intensity of degradation for various synthetic resins under thermal and radiation processing [15, 16].

In this paper, the survey on the stabilization effects of several metallic oxides on the phenol-formaldehyde resin are discussed for the explanation of corrosion action on the heavily stressed items in aeronautics, nuclear engineering, the automotive industry, and many other areas where the degradation agents act for longer durations and intensive operation parameters.

2. MATERIALS AND METHODS

2.1. MATERIALS

The pristine resin is provided by Hüttenes-Albertus Chemische Werke GMBH (Hannover, Germany) as Resital B. The oxide fillers (Gd_2O_3 , CeO_2 , Pr_2O_3 , MgO , MnO_2 , Cr_2O_3 , and In_2O_3) were delivered by Sigma Aldrich Chemicals P Ltd. (USA) as pro analysis reagents. The oxide powders were dispersed individually in separated flasks conducting to specific suspensions, whose filler loadings were 1 wt%.

2.2. METHODS

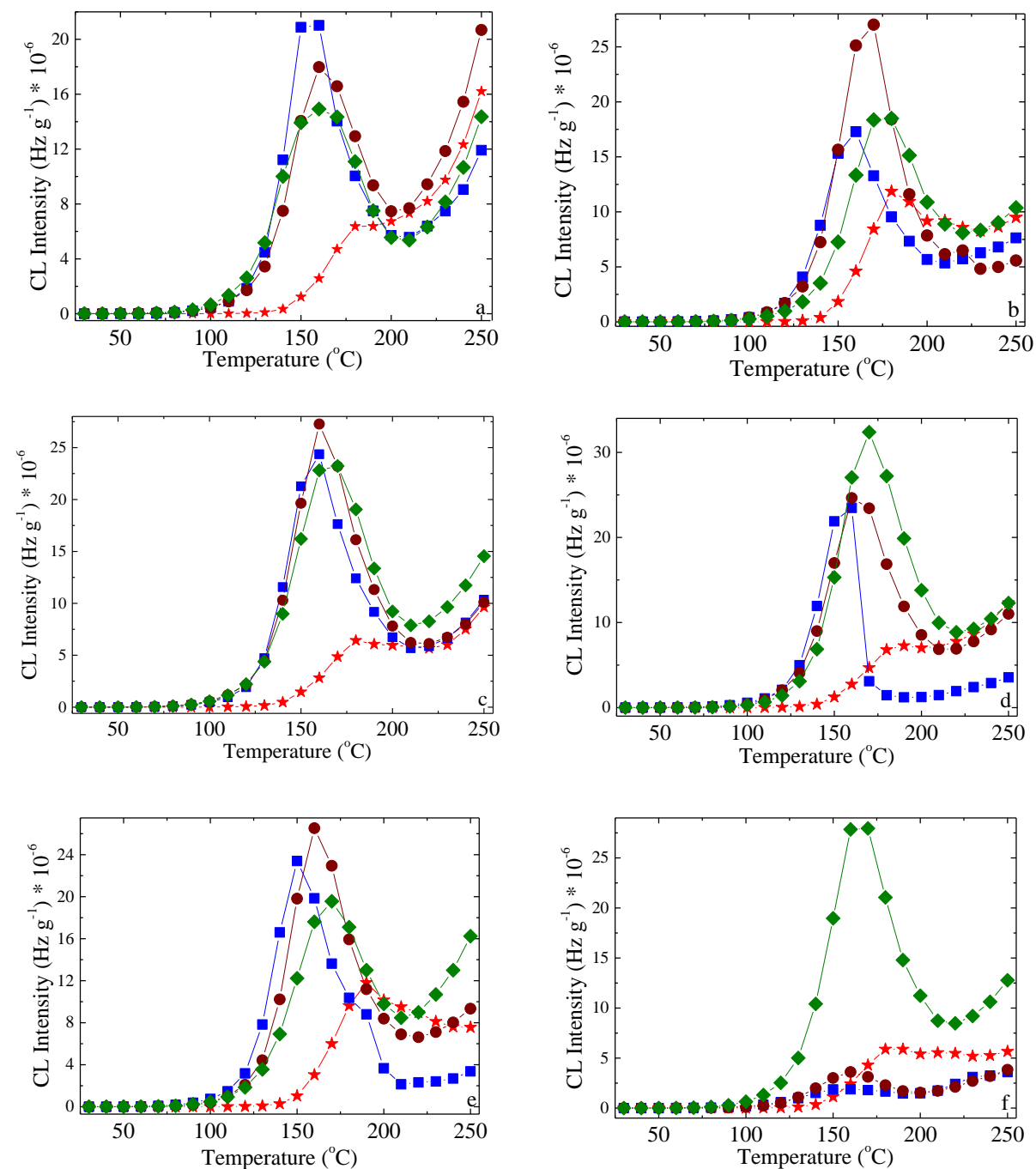
The oxide powders were transferred into individual flasks producing various composites after drying. For the preparation of investigating samples small volumes (100 μ L) were poured on aluminum trays, which support the dry films after the gentle solvent removal at room temperature. The samples destined to the chemiluminescence determinations were weighted after the preparation of final films having 3-5 mg. For the preparation of samples two material characteristics are relevant: specific density: 1.228 g cm^{-3} and viscosity at 20°C : $817 \text{ mPa}\cdot\text{s}$.

The accelerated oxidative degradation was achieved by the γ -irradiation in an exposure machine (Ob Servo Sanguis, Budapest, Hungary) provided with a ^{60}Co source. The dose rate was 0.5 kGy h^{-1} . Four γ -processing doses (0.25, 50, and 100 kGy) were applied for the characterization of thermal and radiation resistances of composite specimens.

The chemiluminescence (CL) measurements were performed using LUMIPOL 3 unit produced by the Institute of Polymers, Slovak Academy of Sciences, Bratislava. The nonisothermal measurements were carried out at four heating rates: 5, 10, 15, and $20^\circ\text{C min}^{-1}$. The temperature range of measurement applied for these CL determinations is placed between room value and 250°C continuously increased. The chemiluminescence intensities are recorded by the automatic counting of emitted photons according to the energetic process (Fig. 2) [17].

The chemiluminescence spectra were recorded as the result of the variation of irradiation dose, the type of filler, and rates of heating. They describe the evolution of oxidation states when the temperature applied in the heating zone increases inducing the degradation of organic substrate. Because the fillers are inorganic compounds, they are never decomposed simultaneously with the polymer component. Accordingly, the contribution of aluminum plates and the emission of the oxide component can be reasonably described.

The noticeable peak that appeared at 160°C is persistent for all investigated compositions because the resin generates hydroperoxides at this temperature like various hydrocarbon polymers [18]. However, the oxidability of the organic phase is shifted onto the superior temperatures for the samples containing Pr₂O₃ and In₂O₃ (Figs. 3g-h). These abnormal answers may be explained either by the experimental errors of measurements or, more possibly, by the slight crosslinking of the substrate due to the self-adsorption of radicals.



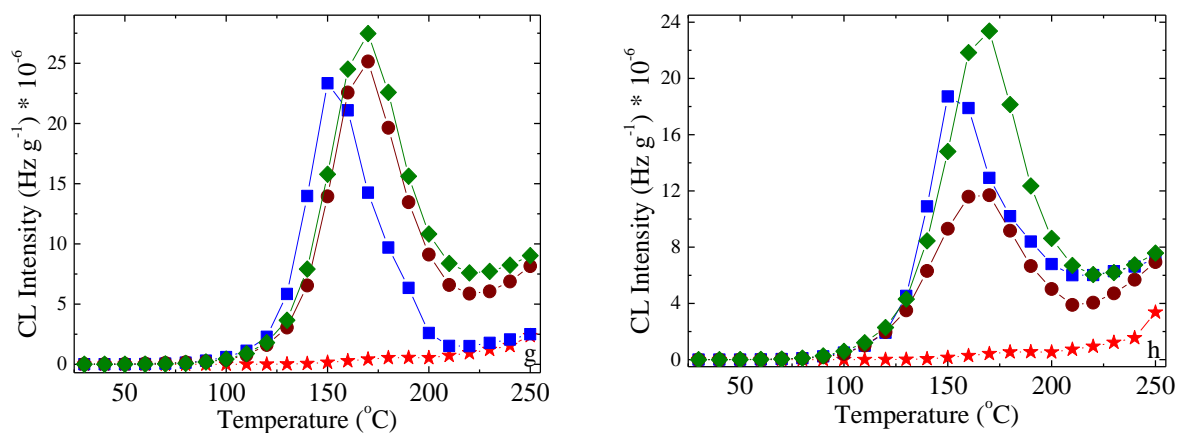


Figure 3. The nonisothermal CL spectra recorded on the phenolic resin in the presence of metallic oxides. (a) control, (b) CeO_2 , (c) Cr_2O_3 , (d) Gd_2O_3 , (e) MgO , (f) MnO_2 , (g) Pr_2O_3 , (h) In_2O_3 . Irradiation doses: (red stars) 0 kGy, (blue squares) 25 kGy, (brown circles) 50 kGy, (green diamonds) 100kGy. Heating rate; $10^\circ\text{C min}^{-1}$.

The oxidation of these samples starts very early when the hydroperoxides begin to be generated (Fig. 4). The proof of involvement of oxides in the starting and development of oxidation are the differences between the emission intensities measured at 160°C (Fig. 4a) and the values of onset oxidation temperatures (Fig. 4b), which vary from one composition to the other.

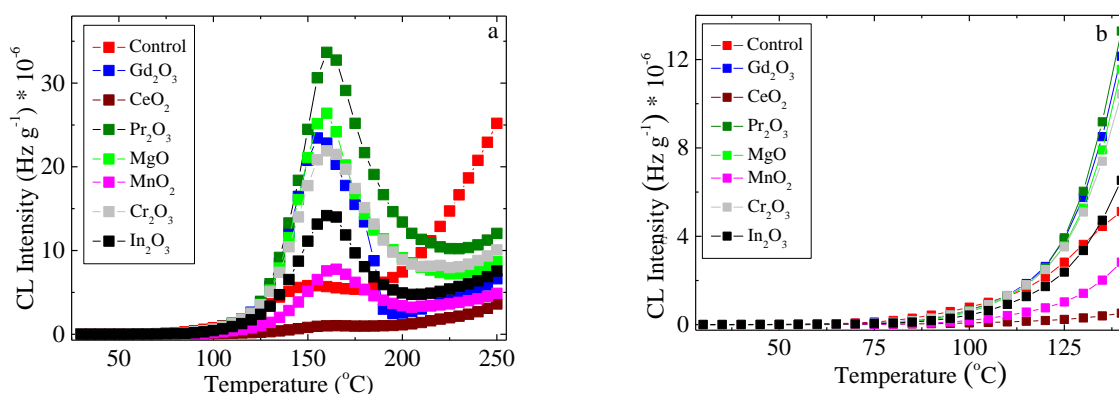


Figure 4. The nonisothermal CL spectra recorded on the phenolic resin/metallic oxide systems. Irradiation dose: 100 kGy. Heating rate: 5°C min^{-1} .

The rate of heating has a defined role in the development of degradation. The differences in the amplitudes of emissions recorded during the CL measurements accomplished at two heating rate probes reveal the influence of the diffusion process involving oxygen. The relative positions of CL curves are not repeatable and the number of photons increases when the heating rate has a higher value. The maximum CL intensities are shifted onto higher temperatures (176°C and 182°C for the experiments done at $15^\circ\text{C min}^{-1}$ and $20^\circ\text{C min}^{-1}$, respectively).

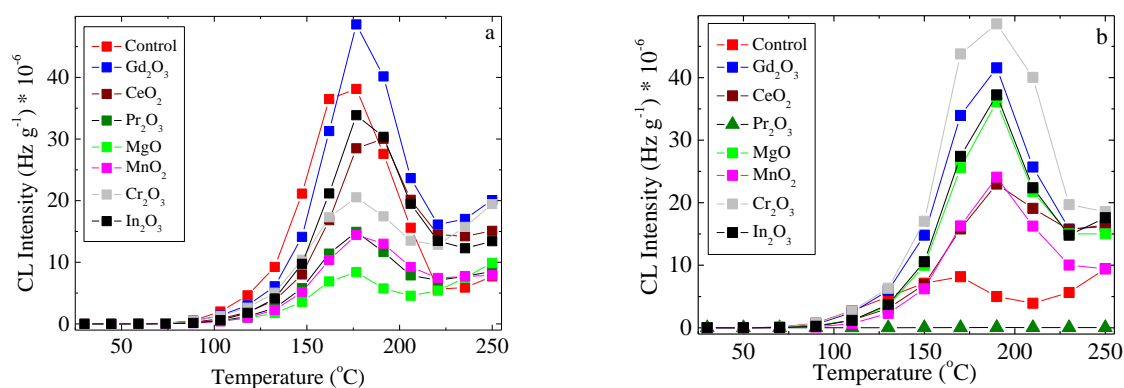


Figure 5. The nonisothermal CL spectra recorded on the phenolic resin/metallic oxide systems. Irradiation dose: 100 kGy. Heating rate: a) 15°C min⁻¹, b) 20°C min⁻¹.

The modification of temperature values characterizing the highest emission intensities of similarly processed probes under different heating rates (Figs. 4a and 5) suggests the consequences of energy transfer onto the inner molecular shells. The organic substrates are slowly degraded, when the oxygen stream sweeps the surface of nanoparticles and where the macromolecules of polymer are bonded.

3.2. DISCUSSION

The oxidative degradation of organic components from a nanocomposite is supported by the diffusion of molecular oxygen. The formation of free radicals available for the feeding of the oxidation chain is simultaneously competed with the stabilization action of filler or the promotion of its pro-oxidant activity [19]. The agglomeration of reacting radicals on the particle surface allows the partial jointing of neighboring units. The progress of oxidation is controlled by the scavenged proportion, which determines the rate of oxidation [20].

The evolution of oxidation states in the phenolic resin/metallic oxide composites (Fig. 3) is controlled by the chemical nature of the filler, which is defined by the electronic density of the metal atoms. Consequently, if the CL degradation curves for nonirradiated/nonaged samples are placed on the bottom side of graphs (curves illustrated by red stars). The increase in the processing dose has different effects. The presence of Gd₂O₃, MnO₂, Pr₂O₃, and In₂O₃ is associated with the increasing of CL intensities for higher irradiation doses that describe an advanced scission degree. Even though they present similar progress in the oxidation states, the increasing manners are unlike. The striking accumulation of emitting entities during oxidation occurs only at the highest applied dose, 100 kGy (Fig. 3f). This sudden jump in intensity values indicates efficient stabilizing activities at low and medium doses, up to 50 kGy. The other pro-oxidant fillers (Figs. 3 d, g, and h) promote a monotone advance in the oxidation level when the accelerated degradation progresses.

The interaction between the filler particles and organic substrate takes other way when the degradative oxidation is accompanied by a slight crosslinking. This competition is suggested by the decrease of CL intensities for the samples receiving 100 kGy (Figs. 3 a, b, c, and e). This behavior is governed by the availability of filler for the subtraction of free radicals from the oxidation chain. The connection between the development of an oxidant state and the assistance of pro-oxidant effects of metallic oxides existing in the studied dried phenolic resin composites reveals the different affinities towards the scavenging of free radicals as well as the capacity of oxides to keep tightly the degradation intermediates feeding the oxidation chains.

The CL measurements achieved on the resin samples in liquid and solid states (Fig. 6) show the significance of particle mobility on the progress of oxidation. The differences in the evolution of oxidation are revealed when the progress in the depths of degradation enlarged the dissimilarity between the two curves. This feature may be ascribed to the differences in the mobility of free radicals and to the accessibility of oxidizing entities on the oxide particle surface. The involvement of the oxide surface is revealed by the values of the onset oxidation temperature, which becomes larger in the liquid samples when the heating rate is higher. The application of a phenolic resin layer on a metallic surface conducts the interaction process by the action of the alloying elements, which creates the condition of oxidation especially at higher temperatures exceeding 150°C [21].

The initiation of oxidation in the phenolic resins containing metallic oxides is fulfilled by superficial adsorption, when the free radicals may be easily converted due to the initial amounts of gaseous oxygen initially existing in the organic phase [22]. However, the catalytic auto-oxidation process is sustained either by the interaction between the filler and resin, or by the propagation of the oxidation chain [23]. The energetic conditions, under which the degradation occurs, influence to a large extent the aging degree of protective sheets. As the present results highlight, the composition of the conserved surface may indicate the degradation of sense and depth.

The long-term stability and integrity of phenolic resin layers are influenced by the interphase interaction, which is conditioned by the concentration of alloying elements. Of course, the evolution of the adhesivity is tightly related to the degree of oxidation as well as to the roughness of the covered surface.

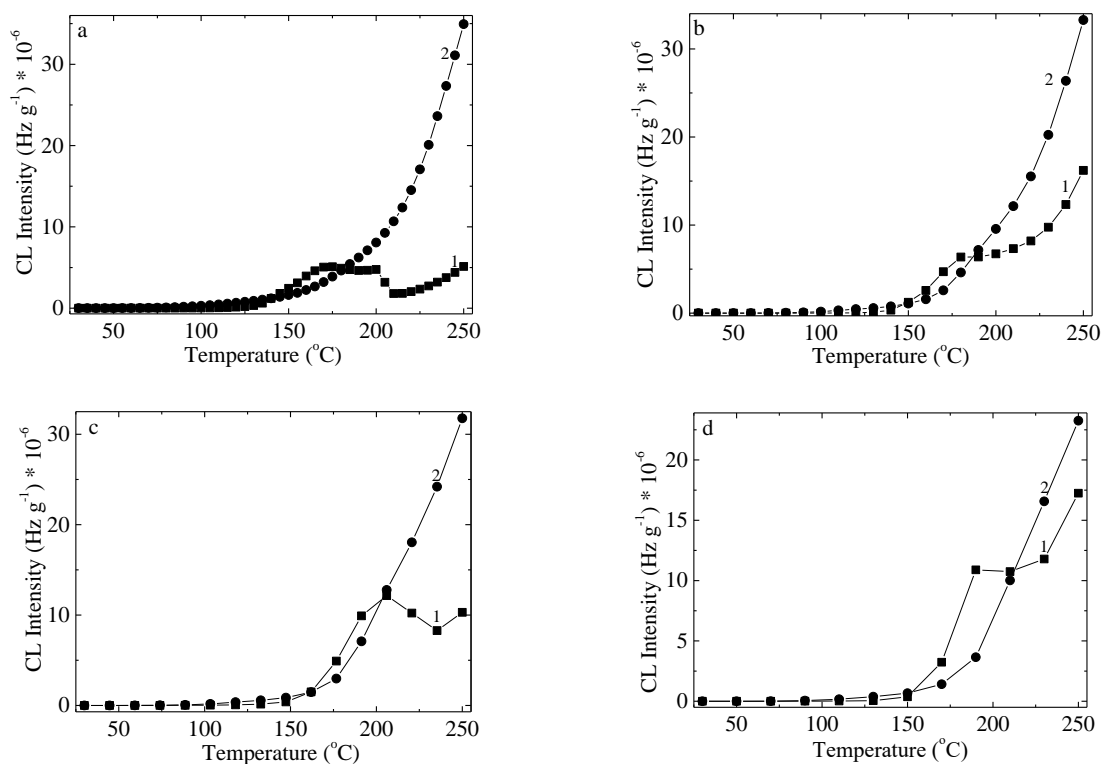


Figure 6. The CL nonisothermal spectra recorded on the phenolic resin samples in liquid (1) and solid (2) states. Irradiation dose: 50 kGy. Heating rate: a) 5°C min⁻¹, b) 10°C min⁻¹, c) 15°C min⁻¹, d) 20°C min⁻¹.

4. CONCLUSIONS

The present paper presents the dependence of oxidation rates in the phenolic resin layers on the composition of metallic surfaces. The nature of alloying elements influences the thermal resistance of organic substrate when an accelerated degradation takes place due to the environmental energetic conditions. The presence of an intense oxidation peak at 159°C in the unaged samples demonstrates the formation of high amounts of hydroperoxides. The variation in heating rate provides a significant shift in the position of this peak due to the difference in the contact times. The progress of the degradation state is strongly influenced by the contribution of electronic distributions in oxide fillers, which contribute to the promotion of oxidation by energetic transfer.

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