Qualification of Ecological Alkyd Lacquer for Metallic Surface Protection in Nuclear Engineering

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Alkydic resin 715 EZ that is used in nuclear application exhibits proper thermal and radiation resistances. The investigations concerning the radiation and thermal stability performed on γ (^{137}Cs) irradiated samples by nonisothermal chemiluminescence, swelling in water and toluene lead to the confirmation of good long term behaviour, even after low irradiation doses in the case of this material. The dose limit which characterizes the preservation of initial properties is 40 kGy. The synergistic consequences of heat and radiation actions are discussed.

Keywords: alkyd resin, titania, degradation, chemiluminescence

The long term applications of equipment in nuclear power plants require the qualification of raw materials, which are subject to the action of different stressors [1]. This behaviour evaluation involves the answer of tested material subject to the energetic transfers, which may cause the degradation accompanied by the shortening life time [2].

The nuclear applications of surface protector against corrosion involves not only the testing of endurance under the action of ionizing radiation, but also the emphasizing the effects brought about by heat and solvent. The investigation of radiolysis effect leads to the formation of oxidized intermediates, which decrease the material quality and, consequently, the protective efficiency is sharply diminished. The correspondence between the structural modifications induced during degradation and the amplitudes of material answers represent the key of qualification, through which the possibility of equipment conservation for long term usage is demonstrated.

The conjugated action of heat and radiation may lead to high damage effects, which illustrates the material features deteriorating during nuclear events or the overcharged work of equipment [3, 4]. The degradation rate is the main functional characteristic that is considered for the assessment of quality control [5]. The synergistic effects caused by heat and γ-irradiation must be known, because their cumulative consequences reduce sharply the lifetime of material [6]. The purpose of this study is the radiation strength qualification of alkyd resin in respect with real conditions of nuclear incidents.

Experimental part

Material and methods

In this paper the insulating lacquer with electrical applications, alkyd type material – 715 EZ, produced in Romania- as ecological material was investigated. The behaviours under thermal ageing, radiation degradation, swelling in toluene were investigated for the evaluation of material durability. The initial properties of this lacquer are proper for the application in nuclear field: high adherence onto metallic surfaces, good values of electrical and mechanical functional features. The pristine material is an alkyd resin which was modified with phenolic component. It belongs to the materials of class H of electrical insulation, which resists at temperatures up to 180°C.

Sample preparation

Low amounts of 715 EZ lacquer were preloaded in aluminum trays, which were dried in an electrical oven for 4 h at 150°C error in reading temperature ± 2°C. The resin was cured as pellicles on aluminum plates as it happens with the metallic surfaces by immersion for the intimate coverage with anticorrosive protection film under the same thickness conditions.

Irradiation

The exposure of prepared samples was managed in irradiation machinery (source ^{137}Cs) at room temperature. This source provides a dose rate of 0.4 kGy.h^{-1}. All measurements on irradiated samples were done immediately after the end of exposure for avoiding any chemical modifications due to the short-life intermediates.

Sample processing and measurements

For the determination of radiation strength, the temperature selected for thermal ageing was 200°C. This high figure of temperature is justified by the similarity of the present study with accident conditions, when thermal overcharge is achieved. The superposition of thermal and radiation effects is obtained, because during nuclear events

Table 1
THERMAL REGIME FOR MATERIAL AGEING

Ageing temperature (°C)	Duration of thermal treatment (h)
200	24
210	72
220	120

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both types of degradation agents act simultaneously. The thermal treatment was managed in successive steps. The temperature of the first degradation step was selected at 20°C below the working conditions (table 1), according to accepted testing standards [6]. For this kind of investigation, two absorbed γ-doses (50 and 100 kGy) were applied.

Radiolysis effect on insulating lacquer 715 EZ was investigated by nonisothermal chemiluminescence over a large temperature interval (30 – 250°C) on LUMIPOL 3.

For the determination of swelling levels of processed alkyd samples, they were separately placed in water and toluene for 24 h at two different immersion temperatures, 25 and 50°C, in an oven with automatic controlled heating. For drying, samples were gently swept with smooth filter paper. Each sample was weighed before and after immersion and the differences between analogous figures signified the weight loss. The specific weight loss was calculated by abstracting the final weight from initial weight. The temperature index was computed according to international regulation CCI 214/4.

Results and discussions

The degradation of alkyd resin takes place gradually as irradiation dose increases (fig. 1). The neat resin is slowly oxidized on the temperature interval from room temperature to 170 °C. The rise of temperature brings about an acceleration of oxidative degradation, whose rate depends on the irradiation dose. The increase in the maximum intensity at 225 °C is caused by the accumulation of free radicals, which react promptly with diffused molecular oxygen. For the irradiation dose of 100 kGy, when samples received a high energy on a short time a maximum of oxidation around 150 °C was noticed. It means that a branching structure is preferentially broken and the free radicals that are formed react with oxygen and CL emitting intermediates (ketone structures) gave a high intensity at this temperature. As the temperature increases, a sharp enhancement is noticed that illustrates the availability of alkyd resin to form radicals at higher irradiation doses, in contrast with low dose range, where the amount of radicals is significantly small.

A slight shift in chemiluminescence intensity peak around 230°C can be noticed. This behaviour is explained by the molecular scissions during radiolysis, when oxygen-centered radical is formed. This process diminishes the average molecular weight and provides radicals as the initiator in the formation of peroxyl structures. The shoulder appears at 150 °C for the sample exposed at 100 kGy is due to the cleavage of O – O bonds, whose dissociation

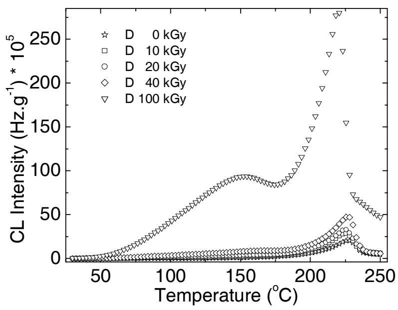

Fig. 1. Modification of CL intensity on temperature for irradiated alkyd resin

energy is 142 kJ/mol, much less than 347 kJ/mol and 360 kJ/mol, the energies required for the dissociation of C – C and C – O bond, respectively [7].

The thermal strength of alkyd resin is depicted by the durability under different heating regimes (table 2). The acceptable values of life time at 170 and 180 °C, even though in the cases of irradiated materials recommend this material as good covering film up to 180°C. Higher temperatures accelerate degradation and the durability of adhesive anticorrosive sheet becomes more and more improper for long term operation conditions. The lost mass which is associated with degradation process (fig. 2) describes the progress in the damaging mass. The irradiation at 50 or 100 kGy causes faster ageing of material because of the structural modification induced by interaction of incidental γ radiation with resin molecules.

The degradation process is always associated with mass loss, when volatile products (low mass fragments from scissions and oxidation) formed during ageing are removed from material matrix. In figure 3, experimental data concerning the variation in sample mass during thermal ageing of nonirradiated and radiation exposed lacquer are presented. It can be noticed that the advanced degradation is accompanied by the generation of low mass products that result from the simultaneous processes of thermal oxidation, in which radiolytic free radicals are involved. The sensitive places that are activated for scission during the heating are the bonds of oxygen, which become higher polarized and easier for breaking, the assessment confirmed by chemiluminescence spectra (fig. 1). This behaviour is the result of the synergistic action of radiation and heat, the former generates active intermediates and the last promotes oxidation by oxygen diffusion.

The endurance evaluation of this lacquer is presented in figure 4. Table 2 lists the durability of processed samples revealing the cumulative effect of radiation and heat. The irradiation, which is a procedure for accelerated

Table 2
CALCULATED DURABILITY OF 715 EZ LECQUER

Ageing temperature (°C)	Durability (h)		
	0 kGy	50 kGy	100 kGy
170	1890	20121	22337
180	4800	8136	8253
190	2639	3010	2603
200	926	827	821
210	500	443	366
220	145	118	106

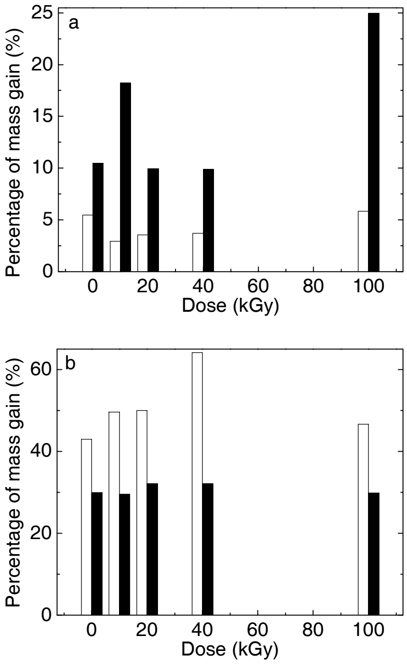

Fig. 2. Swelling of irradiated alkyd resin in water (a) and toluene (b) (white) room temperature, (black) 50 °C

degradation causes very slight modifications in the susceptibility of material for oxidative degradation promoted during high energy irradiation. The increases in temperature and irradiation dose diminish the material strength, but under applied conditions the tested alkyd resin is not damaged. This behaviour is similar to the experimental information earlier found [8]. According to international standard CCI 214/4, this alkyd lacquer shows acceptable resistance required for the applications in nuclear energy areas.

The presence of penetrating molecules generated by various solvents, in our cases water and toluene, modifies the integrity of lacquer films. The environmental temperature at which protective 715 EZ resin sheets exist plays an important role in the accumulation of solvent inside lacquer. The absorption of water by this material presents a smooth increase at room temperature, while the swelling occurred at 50 °C for 24 h presents a maximum at 10 kGy and an evident increase for 100 kGy. The explanation of this shape is the decrease in molecular weight, which accompanies the scission during radiolysis.

A contrary aspect in the swelling evolution of irradiated alkyd resin is presented, when toluene penetrates resin mass. This difference between the two solvents consists of the hydrophilic character of material. The polarity of water molecules has a determined role, when material received sufficient energy to be converted into polar products, alcohols, ketone, acids.

The convenient behaviour of this resin at the action of water allows the films to be used for a long time without the contact of metallic surface with water vapours. The low dose irradiation does not convert this ecological material in a degraded product, so that the protection capacity of films becomes effective for long term operation of equipment.

Conclusions

The ecological lacquer in resistant to weak degradation is promoted by γ-irradiation at 50 and 100 kGy. The capacity of this material for the preservation of initial structure acts up to 40 kGy, when low amount of peroxide intermediates are formed. The endurance information on the thermal resistance of lacquer 715 EZ proves the possibility of usage in nuclear fields. The chemiluminescence investigation reveals the proper resistance at moderate and relative high temperatures, up to 180°C for samples irradiated at medium exposure doses (not exceeding 50 kGy).

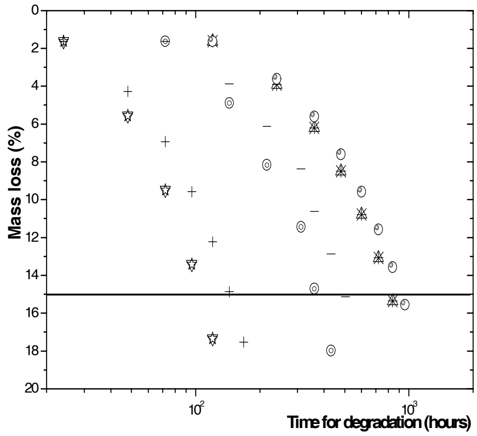

Fig. 3. Representation of degrading alkyd resin (*) unirradiated sample; (▷) dose: 50 kGy; (◁) dose: 100 kGy.

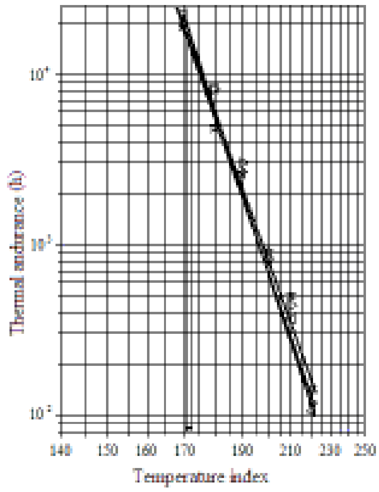

Fig. 4. Mass loss of processed alkyd resin (Δ) dose 0 kGy, 220 °C; (o) dose 0 kGy, 210 °C; (△) dose 0 kGy, 200 °C (*) dose 50 kGy, 220 °C; (o) dose 50 kGy, 210 °C; (✧) dose 50 kGy, 200 °, (+) dose 100 kGy, 220 °C; (-) dose 100 kGy, 210 °C; (●) dose 100 kGy, 200 °C

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