Stability evaluation of polyurethane coatings by gamma irradiation

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Polyurethane coating materials were subjected to the action of gamma radiation for the assessment of stability under hard conditions of operation. Two sorts of urethane systems cured at room temperature were tested by chemiluminescence method. The rates of oxidation were evaluated for characterization of long term service. The irradiation performed in dry and wet environments revealed the contribution of water to the modification of chemical strength of polyurethane strength.
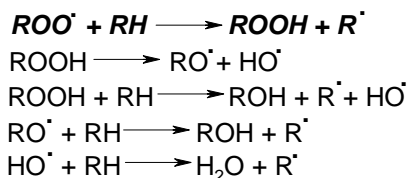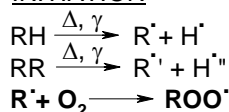
The systematic research on the utilization of polyurethane coating materials is still a subject of interest either for manufacturers or for consumers [1-5]. The stability of coatings applied for surface protection against oxidation and corrosion is a problem of quality control, which can be assessed by accelerated testing under the action of ionizing radiation.

The mechanism through which these materials are radiolytically degraded is based on the formation of free radicals by splitting of macromolecular chains (Fig. 1).

INITIATION

$$RH \xrightarrow{\Delta, \gamma} R^\bullet + H^\bullet$$
$$RR \xrightarrow{\Delta, \gamma} R^{\bullet'} + H^{\bullet''}$$
$$R^\bullet + O_2 \longrightarrow ROO^\bullet$$

$$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet$$
$$ROOH \longrightarrow RO^\bullet + HO^\bullet$$
$$ROOH + RH \longrightarrow ROH + R^\bullet + HO^\bullet$$
$$RO^\bullet + RH \longrightarrow ROH + R^\bullet$$
$$HO^\bullet + RH \longrightarrow H_2O + R^\bullet$$

TERMINATION

$$RO^\bullet + R^\bullet \longrightarrow ROR$$
$$R^\bullet + R^{\bullet'} \longrightarrow RR'$$
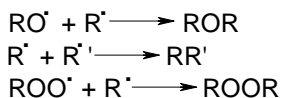$$ROO^\bullet + R^\bullet \longrightarrow ROOR$$

Fig. 1. Mechanism of polymer radiooxidation.

Several papers have dealt with the qualification of polyurethane coatings, which cover surfaces subjected to degradation by environmental factors [6, 7]. The material ageing by photo-degradation occurred in polyurethanes through which hydroperoxides are active intermediates was detailed treated by Rånby and Rabek [8]. They also have emphasized the acceleration role of oxygen and water during accelerated depreciation of polyurethanes when they are exposed under weathering conditions.

The interaction of degradable polymer coatings with metallic support is an important factor, which determines the rate of oxidation [9]. In these cases any trace of metallic impurities that accidentally is present in polyurethane will accelerate degradation and the chemical strength of coating is significantly diminished.

The present results that depict the resistance of polyurethane layers deposited on various service surfaces in electronics, aircraft industry, manufacture of reagents, nuclear equipments subjected to friction. The determination of oxidation rate under the action of high energy radiation allows the highlighting restriction conditions for long-term usage of this kind of coatings. The applied limiting conditions describe the level of operation for oxygen and humidity attack on polymer sheets.

1. Experimental

Polyurethane systems, PU S 6100® and PU S 6200® (Synthopol Chemie, Germany) were used for sample preparation together with hardener – Tolonate HDB (Rhodia, France). These two types of coating systems have different binders: Synthalat A 045 (Synthopol Chemie, Germany) and Worleecry (Synthopol Chemie, Germany), respectively. The mixing ratios of base urethane and hardener were 3:1, 4:1 and 5:1. The material hardening was carried out at room temperature. Average weight of samples was 0.025 g. The polymer blends were poured into round aluminum trays which were sample supports. This metal was selected for this study because it does not induced oxidation at the interface between polymer and itself.

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 either in air or in water at room temperature.

Isothermal chemiluminescence testing was carried out in air at 165 °C or 190 °C for PU S 6100 and PU S 6200, respectively, in an oxyluminograph OL-94 instrument. Details on this equipment and on measurement procedure have been previously presented [10, 11].

3. Results and discussion

The accelerated degradation as a convincing testing procedure for material qualification is based of the oxidation promoted by external energetic source, like photo or ionizing radiation emitter. The availability of material to ageing can be characterized by oxidation rate, which is the functional parameter that depicts the chemical strength of polymer.

The progress in the material modification depends on the intensity and the duration of stressor, whose energy is

consumed for the generation of radicals. Polyurethanes having benzene rings in molecular structure would reveal relative stability regarding fast energy transfer because of the energy depositing on this aromatic units.

The results published on the photodegradation of polyurethanes [12, 13] have pointed out the oxidation mechanism in which the reaction of secondary peroxyl radicals occurs in the sense of Russel's scheme [14]:

$$\frac{R_1}{R_2}C\frac{H}{OO^{\cdot}} \longrightarrow O_2^* + \frac{R_1}{R_2}C\frac{H}{OH} + \frac{R_1}{R_2}C=O^*$$
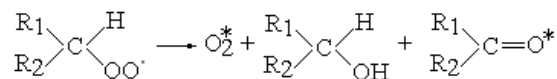
where the asterisks denote the excited singlet state of oxygen and excited triplet state of carbonyl groups in the polymer chain, respectively.

In Fig. 1 chemiluminescence curves describing the advance in the oxidative degradation of the first sort of polyurethane coating are presented.
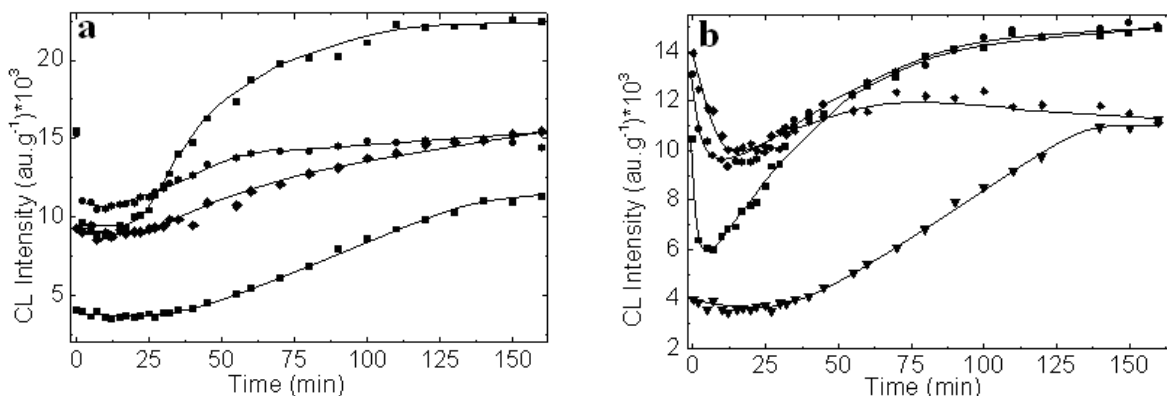

Fig. 1. Chemiluminescence curves recorded for PU S 6100 system irradiated din air (a) and water (b) at various doses.
(▼) 0 kGy; (■) 9.6 kGy; (●) 28.8 kGy, (◆) 67.2 kGy.

The analysis of these two groups of chemiluminescence curves reveals that the radiation treatment of polyurethane paints leads to an increase reactivity in respect to oxygen. The increase in absorbed dose values produces higher concentrations of radicals which are subjected to two simultaneous processes: the first reactions concern their decay by oxidation promoted by diffused molecular oxygen and the second type of reactions is related to the recombination that creates intermolecular bridges. The sequence of curves which were recorded for different irradiation doses demonstrates the crosslinking contribution in cured materials by decreasing of oxidation level. The environment which feeds oxygen for degradation influences the shape of CL dependencies on degradation time. If air is not modified during material radiolysis, water generates reactive entities whose activities are overlapped on the molecular scission

promoted by γ-radiation. Water radiolysis brings about several intermediates [15]:

$$H_2O \longrightarrow e_{aq}^-, HO^{\cdot}, H^{\cdot}, H^+, H_2O_2, H_2$$

that attack outer layer of substrate. In this respect, the active water radiolysis products initiate a reaction chain in which radical state is propagated into the inner material layers.

The formulation of material is a factor which determines the rate of oxidation. The presence of different binders in the compositions of tested materials induces different oxidation rates. The amplitude of oxidation in PU S 6200 system is much pronounced than in PU S 6100 system (Figs. 1 and 2).

The effect of blending ration between based resin and hardener is presented in Table, where variation in oxidation rate characterizes the thermal strength of

protective polyurethane coating. The reactivity of different sites on macromolecules is unlike depending on the intramolecular interactions. The weakest position (a) is placed on the ring because of the delocalization of π electrons [16 – 18].
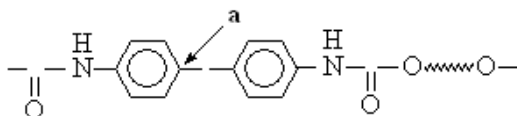
Spectral investigation [19] and chemiluminescence study [4] pointed out that the radical mechanism based on the scission of C-C bonds and the formation of peroxyl structures must be taken into consideration applicable on the propagation step of oxidation (Fig. 3).

The degradation promoted by water proceeds as complex process in which scission brought about the exposure to ionizing radiation is followed by further simultaneous reactions of radicals with molecular oxygen and radiolysis products [3].
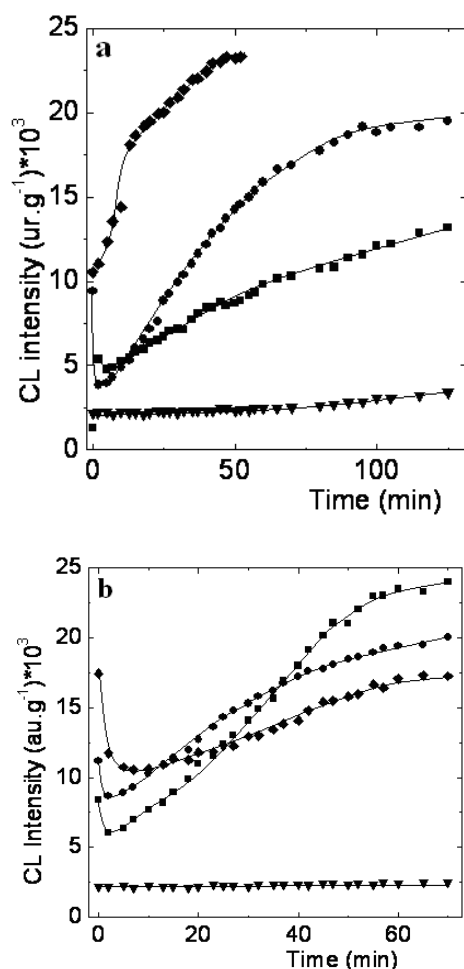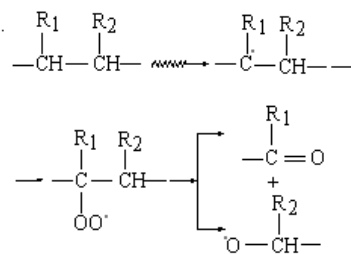

Fig. 3. Mechanism of oxidation applied to polyurethanes.

Similar results were obtained by the degradation of polyurethane systems under weathering conditions [20, 21].
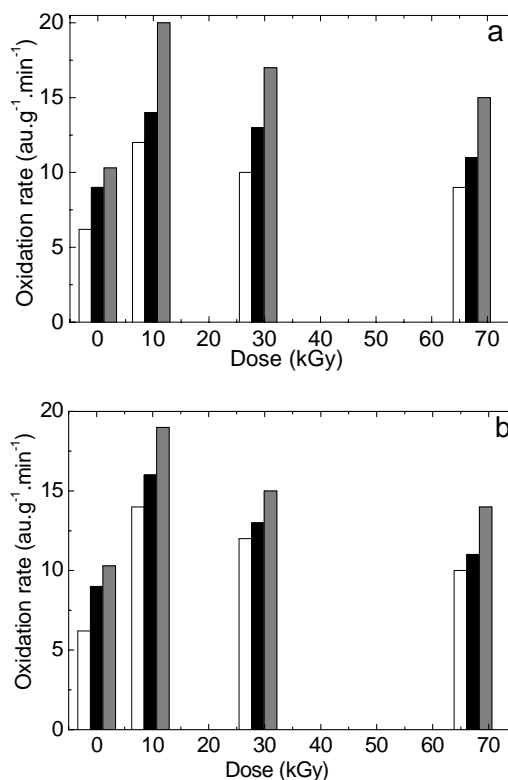

Fig. 3. Modifications in oxidation rate on propagation stages for irradiated polyurethane (PU S 6100) formulation Blending ration of base material:hardener: (white) 3:1; (black) 4:1; (grey) 5:1. (a) environment: air; (b) environment: water.

The accelerated degradation of studied polyurethanes emphasizes the involvement of each component of formulation, which directs the stability of material in connection with their peculiar behavior.

The improvement of thermal and radiation stability would be achieved by the addition of radical scavengers like antioxidants. The efficient stabilizers may be hindered phenols or amines, which have mobile proton on which site can be joint macroradicals generated during radiolysis.

Fig. 2. Chemiluminescence curves recorded for PU S 6200 system irradiated din air (a) and water (b) at various doses. (▼) 0 kGy; (■) 9.6 kGy; (●) 28.8 kGy, (◆) 67.2 kGy.

The durability of this class of materials is in direct connection with the intensity of energy transfer on which the quantity of generate radicals depends on.
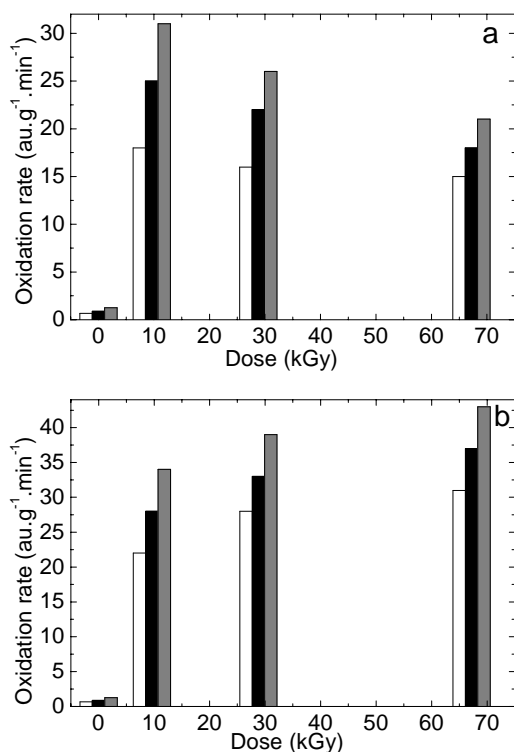

Fig. 4. Modifications in oxidation rate on propagation stages for irradiated polyurethane (PU S 6200) formulation Blending ration of base material:hardener: (white) 3:1; (black) 4:1; (grey) 5:1. (a) environment: air; (b) environment: water.

3. Conclusions

The γ-irradiation of polyurethane coatings allows pointing out that two competitive processes, degradation and crosslinking, taking place as the result of energy transfer from incident radiation. The increase in the thermal stability of γ-exposed polyurethane samples in air is more prominent than the radiochemical treatment occurs in water. The effect of composition, namely the initial ratio between based polymer and hardener consists of the modification in the oxidation rates, which is the consequence of relative component stability.

The differences in radiochemical strength are caused by the scissions of C-C bonds followed by the formation of peroxyl structures. These units provide further degradation by disproportionation.

The connection between material stability and the stability of components has to be established for the individual contribution of components to the overall long term stability of polyurethane coatings.

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

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