

Chemiluminescence study on the thermal stability of Er³⁺-doped poly(urethane-lactate)

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The thermal resistance of poly(urethane lactate) (PUL) doped with different concentrations of Er³⁺ was investigated by chemiluminescence under isothermal and nonisothermal procedures. The modifications in thermal strength of these formulations are discussed in relation to erbium concentration. For comparison, several other polymers (polyolefins, EVA, polyamide 6, polyacrylates) were selected. Onset oxidation times are compared. The chemiluminescence mechanism for the thermal degradation of PUL doped with Er³⁺ is proposed.

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1. Introduction

The essential characteristics of polymers are related to their thermal resistance in the presence of oxygen. Several papers dealing with this essential and practical aspect have pointed out the significance of this kind of studies [1-4]. Polyurethanes (PUs) are one of the most important engineering polymers because of their technical and scientific applications. They are the basic materials for manufacturing of foams, thermoplastic compounds, which can be processed by injection and extrusion, elastomeric products, sealants, adhesives, protective coatings especially for automotives, fibers [5], blood-contacting devices including vascular prosthesis [6], heart valve [7], electro-optic devices [8], etc. Their long-term usage requires detailed investigations on the effect of thermal degradation. Thermogravimetric analysis on the thermal stability of polyurethane [9,10] reveals the complex aspect of this process. Kinetic results on thermooxidative stability of different PUs can depend on the thermooxidation ageing procedure method and structure of the polymers [11].

The thermal degradation of PUs takes place in two stages: first one, depolycondensation, starts at 250 °C; the second process is attributed to the oxidation of the residual material, which starts from 370 °C. However, before attending the end of structural cleavage, the new intermediates are oxidized and the chemiluminescence signal can be recorded [12].

The degradation of PU structures, poly(ester-urethane) and poly(acryl-urethane) previously studied by chemiluminescence [13] has demonstrated that this process occurs via peroxyl intermediates. Two modes of explanation for the early stage of oxidation can be used for the delimitation of this conservative period: oxidation induction time (OIT) and onset oxidation temperature (OOT). These two kinetic characteristics depict properly the thermal strength of polyurethanes on the first term of oxidation, when insignificant modification of polymer matrix may be noticed. The assay on the effect of hard

operation conditions for polyurethanes was preformed in sea water [14]. The molecular structure plays an important role in the defining of degradation progress. The wearability of polyurethanes, which work in wet environments, depends on the chemical nature of elastomers. Polyurethane coatings are extensively used due to the remarkable resistance to UV light. The photolysis, the accelerated process of degradation, generates a broad hydroxyl absorption band in the IR spectrum, which is accompanied by carbonyl band made up of several overlapped maxima [15]. The FT-IR investigations on the weathering of polyurethane coatings have revealed the large abundance of ketonic structures through the final degradation products [15-17]. The diversity of modified polyurethane structures is now available [18,19] for electronic engineering due to their excellent mechanical properties and water resistance. The degradation mechanism of these organic configurations is based on the molecular splitting, where the molar ratio isocyanate/hydroxyl (NCO/OH) plays an important role in the rate of thermal oxidation [20].

This paper presents the investigation on thermooxidation resistance of PUL doped with Er³⁺ on the medium temperature range by chemiluminescence knowing that the oxidation stability is one of the most severe problems both in processing and in long term application of polymeric materials, chiefly at polymeric biomaterials.

2. Experimental

2.1. Materials

2.1.1. Synthesis of poly(urethane-lactate) and poly(diethylene adipate)diol

Both polyurethane-lactate (PUL) and poly(diethylene adipate)diol (PDEA) was prepared according to [21]. The erbium content in PUL is listed in Table 1 for each studied formulation.

Table 1. Erbium content in PUL studied by isothermal chemiluminescence.

Sample	Erbium concentration ($\mu\text{g}\cdot\text{g}^{-1}$)
Control	0
1	38.25
2	119.48
3	207.84

2.1.2. Synthesis of poly(ethylene adipate)diol (PEA)

Poly(ethylene adipate)diol (PEA) was synthesized by fusion condensation of adipic acid with ethylene glycol (EG) (1:1.2 molar ratio). The reaction of esterification was carried out at temperature of 220 °C, for 4h, accompanied by the continuous moving off the water from the reaction system. After the water elimination was finished, the excess of ethylene glycole was removed by distillation at 220 °C and pressure of 2 mm Hg for 2 h. The synthesized PEA had a number-average molecular weight of 2000, which was determined by gel permeation chromatography (GPC). The prepared PEA is characterized by the hydroxyl number of 56 mg KOH/g polymer, and the acidity index of 0.08 mg KOH/g polymer.

2.1.3. Synthesis of polyurethane models

Two PU models were obtained using 4,4'-methylene diphenyl diisocyanate (MDI) and ethylene glycol (EG) for PU-EG and MDI-diethylene glycol (DEG) for PU-DEG. MDI (purity 99.42%) was reacted separately with ethylene glycol and diethylene glycol in dimethylformamide (DMF) (purity 99.89%). The reactions, under stirring, were carried out at 42 °C, for 8 h under N₂ atmosphere. The reaction products were preserved at the room temperature for 48 h. The crude model PUs were precipitated and washed with distilled water and dried under vacuum.

Elemental analysis was carried out using the Pregl's method. The following results were obtained for polyurethane ethylene glycol, PU-EG, C₁₇H₁₆N₂O₄; calculated C% 65.38, H% 5.16, N% 8.97; found C% 65.26, H% 6.64, N% 8.66, 8.34; for polyurethane diethylene glycol, PU-DEG (C₁₉H₂₀N₂O₅): calculated C% 64.04, H% 5.66, N% 7.86; found C% 64.77, H% 5.59, N% 7.27, 6.98.

Molecular weight was measured by gel-permeation chromatography PL-EMD-950 evaporation mass detector (Polymer Labs., Shropshire, UK). Calibration of the apparatus was performed using monodispersing polystyrene standard samples, with a narrow polydispersity (GmbH, Darmstadt, Germany). Average molecular weight ($\overline{M}_n$): for PU-EG was 56,766 and for PU-DEG was 50,667.

FTIR spectra of the synthesized samples were recorded on an M 80 Specord (Germany) spectrophotometer using KBr pellets. Wave number for PU-EG 3313s, 2948 m, 2892 m, 1705 vs, 1600 s, 1533 vs, 1412 s, 1313 s, 1223 vs, 1130 s, 1064 vs, 1016 s, 939 m, 816 m, 768 m cm⁻¹ and PU-DEG 3319 s, 2954 m, 2913 m, 1709 vs, 1600 s, 1527 vs, 1412 s, 1311 s, 1219 vs, 1063 s, 1016 s, 914 m, 816 m, 766 m cm⁻¹, where: s-strong, m-medium, vs-very strong, w-weak.

2.2. Chemiluminescence measurements

Chemiluminescence (CL) method is based on the triplet state phosphorescence of carbonyl, which is formed during substrate oxidation. Several mechanisms [22, 23] (Fig. 1) were proposed for the explanation of the chemiluminescence emission during polymer oxidation.

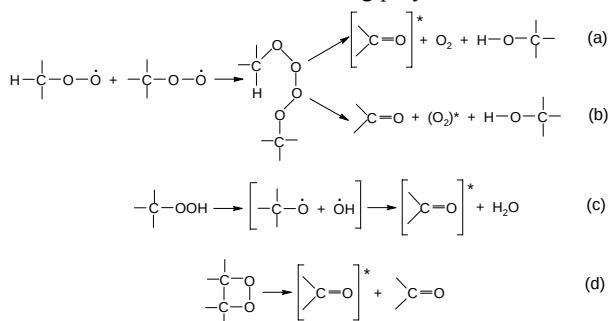


Fig. 1. Exothermal reactions for the formation of ketones in excited state. (a) Russell's mechanism; (b) Stauff's mechanism; (c) Lloyd's mechanism; (d) McCapra mechanism.

For the determination of CL emission dependence on time Oxylumionograph OL 94 has been used [24]. The equipment flow sheet and the typical CL diagram have been presented in an earlier paper [25]. Thin films were punched and identical area specimens were obtained. They were placed in aluminum round trays, which does not influence the degradation process of polymer samples [26]. Isothermal and nonisothermal CL investigation was performed and time dependencies of chemiluminescence intensities were processed for the calculation of kinetic parameters.

3. Results and discussion

3.1. Isothermal measurements

In Fig. 2, the modification of CL emission intensity for investigated Er³⁺ doped polyurethane-lactate samples is presented. Each graph represents the progress in the oxidative degradation of polymer, which shows a peak shifted toward to a longer degradation period, if the matrix is modified with erbium compound in higher concentration.

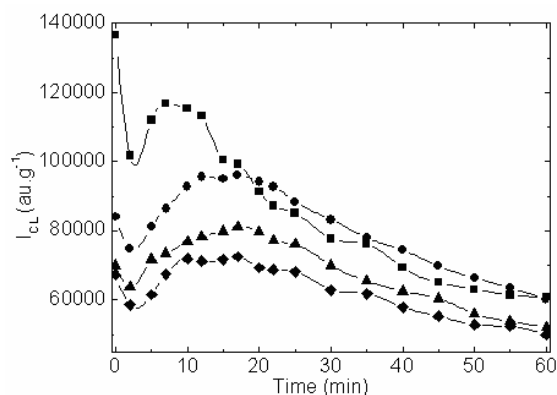


Fig. 2. Isothermal chemiluminescence dependencies of emission intensity on time for several polyurethane samples. (■) reference; (●) PUL with 38.25 µg/g Er³⁺; (▲) PUL with 119.48 µg/g Er³⁺; (◆) PUL with 207.84 µg/g Er³⁺.

The kinetic parameters are listed in Table 2, where it may be noticed the benefit of the presence of erbium. All kinetic characteristics decrease as the erbium content is enhanced, even though the maximum oxidation time (column 4) remains constant. The PUL samples free of erbium present significantly improved CL features (initial CL intensity, maximum emission intensity, the sum of intensity on the first 20 minutes), which explains the lack of additive contribution to the oxidative protection by the structuration of substrate. The values listed in the column of initial emission intensity prove the noticeable availability of compound to thermal oxidation, if the polyurethane substrate does not contain any additive. The kinetic parameters depicting the higher stability in the thermal oxidation of PUL-Er³⁺ systems show the favourable effect of erbium that recommends it as a potential inhibitor of oxidation on the propagation stage.

Table 2. The main kinetic parameters for thermal oxidation of polyurethane-lactate doped with Er³⁺ complex.

Sample	Er ³⁺ content (µg/g)	Initial CL intensity (au/g)	Maximum CL intensity (au/g)	Maximum oxidation time (min)	$\sum_{t=0}^{t=20} I_{CL}$ (au/g)
Control	0	136604	116887	7	987076
1	38.25	84188	96063	17	700041
2	119.48	69924	81136	17	674923
3	207.84	67328	71519	17	611450

In the polyurethane-lactate molecules, it is possible that urethane group ligand would play the selection role in controlling on the energetic absorption properties in the complexes PUL-Er³⁺. It may be assumed that Er³⁺ accepts energy from the -NH-COO- group ligand. The direct consequence would be the diminishing of CL emission intensity, which is demonstrated by the decrease in the value of total intensity (Table 2, column 5).

On the other hand, the modification of the polyurethane-lactate with Er³⁺ led to formation and stabilization of supramolecular structure by increase in the crystallinity level and by improving mechanical and thermal stability [21]. The contribution of Er³⁺ compound could be pointed out by the analysis of nonlinear and continuous decrease in the kinetic parameters of oxidation evaluated for selected additive concentrations (Fig. 3). This falling down in the CL intensities either for initial values, or for the sum on the first 20 minutes demonstrates the involvement of Er³⁺ in the thermal stability of polymer matrix, even at low concentration.

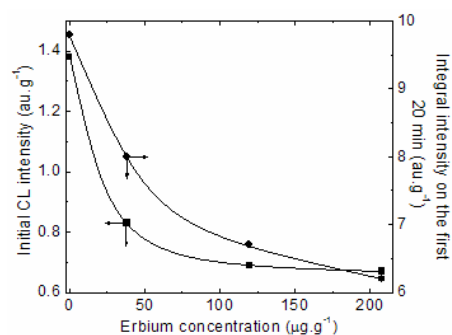


Fig. 3. Modifications in the main chemiluminescence characteristics in the oxidation of PUL samples containing various amounts of erbium complex.

The formulation containing 207.84 µg.g⁻¹ of additive shows about half values for I_0 and $\sum_{t=0}^{t=20} I_{CL}$ in comparison to unmodified polyurethane-lactate. The sharp reduction in the initial CL intensity for the PUL sample containing only 38.25 µg.g⁻¹ confirms the inhibition on the formation of hydroperoxides.

The activation energy values (Table 3) required for oxidation on different degradation stages demonstrate the concern of radical intermediates in the thermal oxidative degradation of polyurethanes. The withdrawing of intermediate content by their reaction with oxygen diminishes the energetic requirements of process.

Table 3. Activation energy involved in the thermal degradation of unmodified polyurethane.

Parameter	Kinetic parameter involved in energy calculation		
	Maximul CL intensity I_{max}	Maximum oxidation time t_{max}	$\sum_{t=0}^{t=20} I_{CL}$
E_a (kJ.mol ⁻¹)	59.36	54.34	50.16
ln A	26.1	11.5	26.1
Correlation factor	0.980	0.986	0.986

These values are in a good agreement with other values previously reported, 46.82 kJ mol⁻¹, by Schard and Russell [27] and Wedlandt [28].

3.2. Nonisothermal measurements

The advance in the oxidation of polyurethane lactate (Fig. 4) occurs dissimilarly in relation with other types of polymers. It shows an intermediate maximum, which may split the temperature range into two regions. They may correspond to different oxidation sites on polyurethane-lactate molecules. Decrease in CL intensity between 175–210 °C can be the result of antioxidant activity provided by amino groups of PUL matrix, which is formed in the oxidation decomposition of PUL [29–31]. Beyond 270 °C the antioxidant contribution of the amine is diminished due to decreases in reactive amino groups during oxidation. The CL intensity grows continuously as temperature increases that demonstrate the fast progress of oxidation.

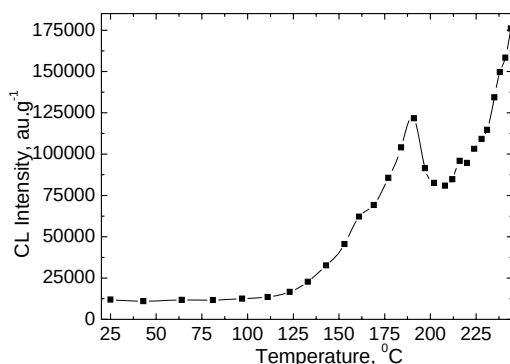


Fig. 4. The dependence of chemiluminescence intensity on temperature for PUL.

The values obtained for onset oxidation time, OOT, (Fig. 5) are good indicators for the level of compound stability. It means that these temperatures represent the threshold, where oxidation effectively starts, depicting the peculiar resistance to thermal degradation.

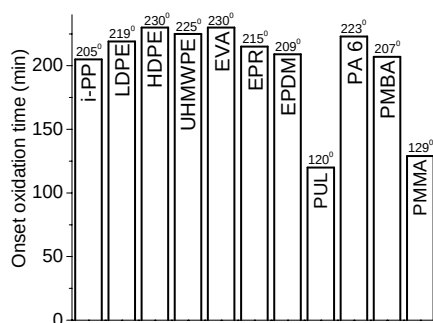


Fig. 5. The values of onset oxidation time for various commercial polymers.

3.3. Thermal decomposition of models

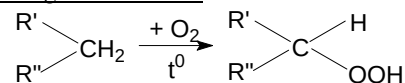
The question of bond splitting in the degradation of polyurethane lactate was solved by the investigation on similar structures. Poly(diethylene adipate)diol, poly(diethylene adipate)diol, poly(urethane ethylene) glycol and poly(urethane diethylene)glycol were subjected to thermal degradation. The main kinetic parameters: half oxidation time and maximum oxidation time, were evaluated at different temperatures. From Arrhenius diagrams, the activation energies and frequency factor were obtained (Table 4).

Table 4. Activation energies and frequency factors for model structures.

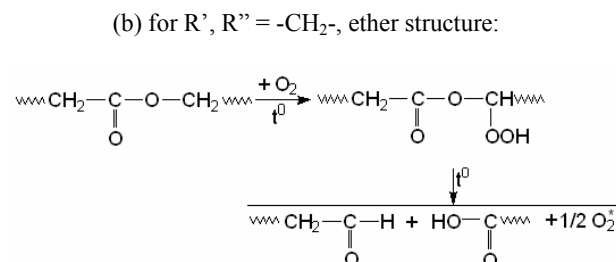
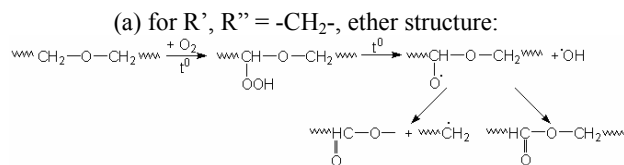
Kinetic parameter considered for evaluation	Activation energy (kJ.mol ⁻¹)	ln A	Correlation factor
Poly(ethylene adipate)diol			
half oxidation time	102.09	22.97	0.997
maximum oxidation time	95.09	19.85	0.999
Poly(diethylene adipate)diol			
half oxidation time	93.14	24.86	0.999
maximum oxidation time	86.88	22.47	0.999
Poly(urethane ethylene)glycol			
half oxidation time	137.33	31.69	0.993
maximum oxidation time	76.72	14.79	0.980
Poly(urethane diethylene)glycol			
half oxidation time	102.59	27.42	0.915
maximum oxidation time	72.92	17.36	0.970

The large differences between the activation energy values for the compounds containing ethylene and diethylene units point out the higher susceptibility of the second configuration on faster oxidation. It means that the ether bond is stronger than the C-C that exists between the two -CH₂- in diethylene fragments. Based on the model structures and on the results obtained for the thermal degradation of PUL, the most probable mechanisms that is applicable for the thermal thermooxidation of PUL involves several elementary reaction such fragmentation, rearrangement and electron transfer (Fig. 6).

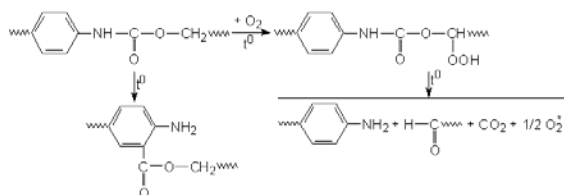
The basic stage of oxidation:



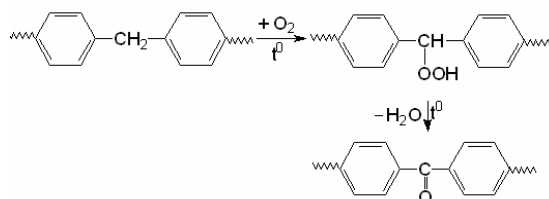
The subsequent reactions depend on the various moieties in the molecules:



(c) for R' = -CH₂-, 4,4' - substituted phenyl, ethylene phenyl urethane structure:



(d) for R', R'' = 4,4' - diphenyl methane structure



(e) for R' = -CH₂-, R'' = 4,4' - substituted phenyl, propylene phenyl urethane structure

Fig. 6. The proposed mechanisms for the thermal oxidation of polyurethanes.

4. Conclusions

The investigation on the thermal stability of PUL-Er³⁺ allows emphasizing some relevant conclusions to the contribution of additive:

- Poly(urethane lactate) presents a intensity maximum at 175 °C, whose value decrease with Er³⁺ concentration,
- Er³⁺ compound improves the stability of polyurethane-lactate matrix on the whole duration of oxidation,
- The activation energy calculated from temporal parameters is in a good agreement with other reported values,
- The ester structure of polyurethane does not

show a tendency to thermal oxidation, in spite of the certain sensitivity of neighbor alkyl moieties to the oxidative degradation,

- The ether unit is very sensitive to the oxygen attack, this molecular fragment being the source for the formation of hydroperoxides, the oxidation precursors of material,
- The thermal oxidation of PUL involving several elementary reaction such fragmentation, rearrangement and electron transfer.

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