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## CHEMILUMINESCENCE FROM PRE-OXIDIZED ECOFLEX POLYMERS

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### Abstract

The chemiluminescence of UV irradiated aromatic-aliphatic polyester Ecoflex was examined in nitrogen and oxygen atmospheres during non-isothermal temperature runs in the interval from 40°C to 250°C. With prolongation of the UV irradiation period, the character of hydroperoxides in the Ecoflex changed, and the less stable hydroperoxides predominated. The half times of hydroperoxide decomposition, estimated from chemiluminescence measurements at 58°, were comparable with the mineralization times of the above polymers in composting biodegradation experiments, which may indicate the supporting role of UV light to the final conversion of the polyesters to carbon dioxide in their biodegradation.

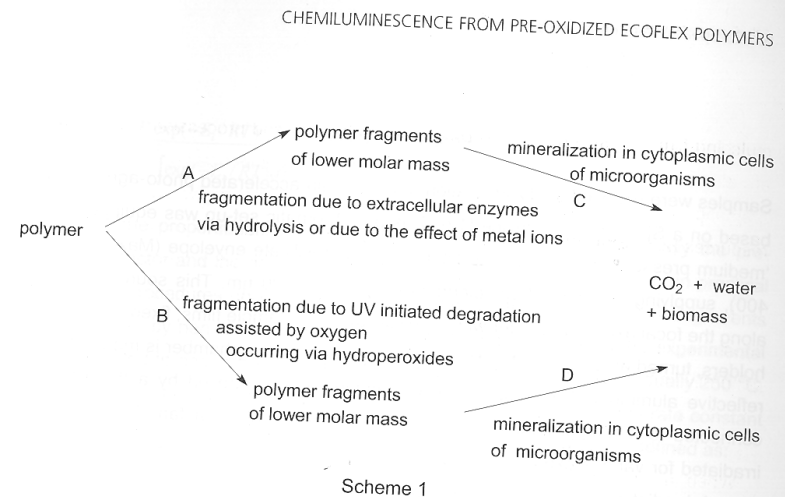
### Introduction

The UV irradiation of environmentally degradable polymers which are used as films in traditional packaging applications and increasingly recently as mulching films [1] in agriculture represents a laboratory means of assessing their applicability. Mulching films are applied directly to the surface of soil, where they retain moisture and increase surface temperature. The proper use of the mulching films can also lead to reductions in non-effective herbicide and pesticide applications. Useful materials for packaging and

mulching films, those exhibiting satisfactory mechanical and processing properties that are also available for a reasonable price, include among others, aliphatic and aliphatic-aromatic co-polyesters, either synthetic or fully or partially derived from renewable resources [2,3]. Examples of such commercially available materials are Ecoflex (BASF), PBAT (e.g. EnPol Ire) and PLA. Ecoflex comprises the subjects of this study. Polylactic acid (PLA) that can be obtained from renewable resources has relatively poor physico-chemical and processing properties [4] and improvements should be sought out. A generally known principle is that, in copolyesters, favorable processing and mechanical properties can be positively influenced by the content of the aromatic component, while an aliphatic component can support the biodegradability of the material [5,6].

When applied to the surface of soil, these materials are heavily influenced by environmental factors, of which the effect of solar radiation is probably essential. A relatively rapid change in the investigated material in an outdoor field experiment, and also in a corresponding laboratory experiment, where the material was exposed to long-wave ultraviolet radiation, has been observed [7,8,9]. At a molecular level, the deterioration of mechanical properties correlated with the crosslinking of polymer chains and the formation of a gel fraction [9,10].

In this paper, the effect of UV irradiation on aromatic-aliphatic copolyester Ecoflex is studied from the changes in the corresponding chemiluminescence patterns under both nitrogen and oxygen atmospheres. The changes in fully controlled laboratory experiments were evaluated from the aspect of accumulation of hydroperoxides (non-isothermal chemiluminescence in nitrogen), while the residual degradability of the above samples was assessed by chemiluminescence measurements in oxygen. As previously indicated [9], photochemical reactions may lead ultimately to crosslinking of the material initiated on the aromatic ring. This was particularly reported for Ecoflex, while polylactic acid underwent degradation only [10]. The search of possible links between photodegradation and biodegradation is justified by the Scheme 1, involving the fragmentation of polymer chains by the action of extracellular enzymes and chain cleavage initiated by UV radiation occurring in parallel.



The two parallel processes should have competitive kinetics under weathering conditions and a sufficiently sensitive method may enable differentiation of the potential effect of UV irradiation on the final mineralization of polymer.

The chemiluminescence of polymer films during temperature runs in oxygen was recorded, compared with the biodegradation data from the controlled laboratory composting experiments [10], and the potential links then discussed.

## Experimental section

### Materials

Ecoflex, PBX 7020, BASF, Germany, melting point 110-120°C, melt flow index 2.7-4.9 g/10 min. at the load of 2.16 kg and 190°C;

Polymer was compression molded to 100 µm thick films. The content of aromatic and aliphatic moieties in Ecoflex was as follows [11]: 75.8 mol % of aliphatic and 24.2 mol % of aromatic components.

The investigated samples contained no additives or fillers that might affect the rate and/or mechanisms of photochemical and degradation processes.

### Photodegradation

Samples were exposed to UV irradiation at 60°C in an accelerated photo-ageing device based on a SEPAP 14-24 device [12]. This polychromatic set-up was equipped with a 'medium pressure' mercury source filtered by a borosilicate envelope (Mazda type MA 400), supplying radiation of wavelengths longer than 300 nm. This source is located along the focal axis of a cylinder with an elliptical base. Sample films, fixed on aluminum holders, turned around the other focal axis. The inside of the chamber is made of highly reflective aluminum. The temperature of samples was controlled by a thermocouple connected to a temperature regulating device, which controls a fan. The films were irradiated for various exposure times from 0-100 hours. It was assessed that one hour of such irradiation is equivalent to one day of outdoor exposure of the polymer in a mild climatic zone during summer months [13].

### Chemiluminescence

Chemiluminescence measurements were performed in a Lumipol 3 photon-counting instrument manufactured at the Polymer Institute of the Slovak Academy of Sciences. The cut film sample (from 5 to 7 mg) was placed on an aluminum pan of diameter 9 mm in the sample compartment. The gas flow (oxygen or nitrogen) through the sample cell was 3.0 L h<sup>-1</sup>. The temperature in the sample compartment of the apparatus increased linearly with time from 40 °C up to 250 °C, at the rate of 5 °C min<sup>-1</sup>. The signal of the photocathode was recorded at a 10-second data collection interval.

### Evaluation of nonisothermal chemiluminescence measurements

The kinetic model used for the deconvolution of nonisothermal chemiluminescence runs takes into account the papers by Ekenstam [15] and Emsley [16] for the degradation of cellulose. It is described elsewhere [17]. We remind here only the resulting equation used for the case of three independent processes composing the experimental pattern of chemiluminescence intensity vs. temperature.

$$I = \sum_{i=1}^3 \frac{P_i \exp(-E_i / RT)}{\left[1 + \frac{A_i}{\beta i_0} \int_{T_{min}}^T \exp(-E_i / RT) dT\right]^2} \quad \text{Eq.1}$$

Here,  $P_i$  is the proportionality constant, whereas  $A_i$  and  $E_i$  are respectively the pre-exponential factor and the activation energy of component  $i$  of the reaction. In practical computation procedures, the corresponding parameters for any of the initiating events are determined by non-linear regression analysis, taking into account the experimental runs normalized to one at the maximum temperature of the experiment, usually 250 °C. Eventually, from non-isothermal run it is possible to calculate the average rate constant  $k_{av}$  for 3 components of initiation ( $i = 3$ ), leading to light emission which is defined as:

$$k_{av} = \frac{P_1}{P_1 + P_2 + P_3} k_1 + \frac{P_2}{P_1 + P_2 + P_3} k_2 + \frac{P_3}{P_1 + P_2 + P_3} k_3 \quad \text{Eq.2}$$

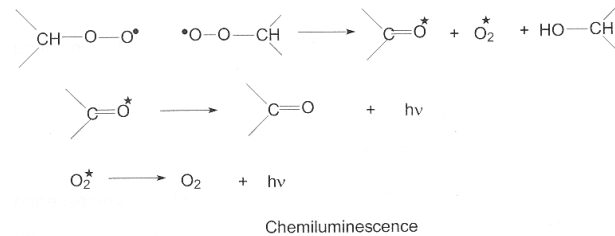
where  $k_1$ ,  $k_2$  and  $k_3$  are rate constants at a given temperature of the respective initiating process. They have the dimension of the first order reaction (s<sup>-1</sup>).

### Results and Discussion

Pre-oxidized samples of the examined polymers gave in nitrogen chemiluminescence records that indicated on the formation of more or less stable peroxides (Fig. 1). Three regions may be discerned on non-isothermal chemiluminescence runs, namely (I) corresponding to the low temperatures where the structural defects are annealed, the second (II) corresponding to the decomposition of hydroperoxides which remain trapped in the polymer after UV initiated peroxidation, and finally region (III), which is brought about by the direct scission of bonds in the polymer accompanied by the recombination of polymer alkyl radicals, also providing light emission. The contribution of the traces of oxygen in nitrogen to this region cannot be excluded, as well. It is quite possible that the respective zones are mutually linked, the lower temperature region, where initial initiation starts, affects the higher temperature zone, and so on.

Kinetic parameters corresponding to the respective regions determined according to Eq. 8 are summarized in Table 1. The half-lives at 58 °C determined for region II, which can be compared with the course of mineralization in compost [10] indicate that peroxidation might quite well contribute to the biodegradation of a sample. The mechanism of the process might well consist of formation of terminal carboxylic groups, not only due to enzymatic hydrolysis, but also due to the peroxidation processes.

The sensitivity of Ecoflex towards oxidation examined by chemiluminescence may be seen in Fig. 2. The intensities of the chemiluminescence signals in oxygen are much more intense than for nitrogen. This is due to the enhanced presence of peroxy radicals in the oxidation process, which in self-disproportionation provide enough exothermicity as well as the proper emitter (triplet carbonyl groups and singlet oxygen, Scheme 2) [21-25].



Scheme 2

Fig. 3 shows the comparison of chemiluminescence runs within the 0.0 – 0.1 fragment of maximum intensity with the biodegradation results from the laboratory composting experiment. It may be of interest the UV degraded samples of Ecoflex gave chemiluminescence records that are shifted towards lower temperatures, with respect to less degraded samples. It seems that there is a coincidence with biodegradation experiment results. This shift was the most significant for the Ecoflex sample UV degraded for 100 hours. This is reflected also in the average rate constants of the

subsequent oxidative degradation extrapolated to 58 °C and 150 °C, which, in the case of Ecoflex, increased progressively, and the 100-hour UV pre-oxidized sample was more than 20 times higher at 58 °C and 10 times higher at 150 °C, in comparison with the initial non-irradiated sample (Table 3). This indicates that UV irradiation creates opportunities for easier subsequent degradation, which might have an impact on easier biodegradation.

### Conclusions

1. The rate constants of the decomposition of hydroperoxides trapped in UV irradiated Ecoflex and estimated from non-isothermal chemiluminescence measurements in nitrogen, were found to be approximately identical to literature obtained data on polypropylene hydroperoxide decomposition.
2. The average rate constant of the oxidative degradation of Ecoflex increased almost 20 times after the polymer was UV irradiated for 100 hours. This may support the role of UV degradation in the subsequent biodegradation process that may be expected for materials exposed to the external environment, for example, on the surface of soil when used as mulching films.

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**Tables**

Table 1. Kinetic parameters from the regions I, II and III of chemiluminescence measurements in nitrogen, calculated according to Eq.8 and the corresponding half-lives for region II approximated to 58°C.

Region	I			II			III			$\tau_{1/2}$	
	Time, hours	$P_1$ , count/g	$A_1$ , $s^{-1}$	$E_1$ , kJ/mol	$P_2$ , count/g	$A_2$ , $s^{-1}$	$E_2$ , kJ/mol	$P_3$ , count/g	$A_3$ , $s^{-1}$		$E_3$ , kJ/mol
Ecoflex	0	9.4e4	1.6e4	53.1	3.7e4	5.3e15	167.9	5.3e6	1.7e20	228.2	>1000
	10	2.1e5	1.1e5	59.6	1.4e6	1.1e8	94.1	1.5e6	6.1e12	153.7	96.5
	25	3.3e5	1.0e7	59.7	1.8e6	5.2e10	113.3	1.8e6	3.4e10	130.2	127.2
	100	1.9e5	1.6e5	59.7	1.2e6	3.3e11	115.9	1.2e6	2.0e9	115.9	53.6

Table 2. The rate constants of the first order determined from peak II of Table 1 (aged samples measured in nitrogen) compared with the rate constants of polypropylene hydroperoxide decomposition from the literature.

Sample	Aged, h	$k_{100}$ , $s^{-1}$	$k_{135}$ , $s^{-1}$	Reference
Ecoflex	10	9.0e-6	1.2e-4	[18], [19], [20]
		2.4e-6→8.7e-5	4.7e-5→1.8e-3	

Table 3. The average rate constants of oxidative degradation of Ecoflex calculated from the fit of the respective chemiluminescence runs according to Equations 1 and 2 for 58 °C and 150 °C.

Polymer	$k_{av}(58\text{ }^\circ\text{C})$ , $s^{-1}$	$k_{av}(150\text{ }^\circ\text{C})$ , $s^{-1}$
Ecoflex, 0 hours	3.3 10 <sup>-10</sup>	3.4 10 <sup>-6</sup>
Ecoflex, 10 hours	1.7 10 <sup>-8</sup>	1.4 10 <sup>-5</sup>
Ecoflex, 25 hours	2.5 10 <sup>-8</sup>	2.9 10 <sup>-5</sup>
Ecoflex, 100 hours	5.7 10 <sup>-8</sup>	3.1 10 <sup>-5</sup>

**Figures**

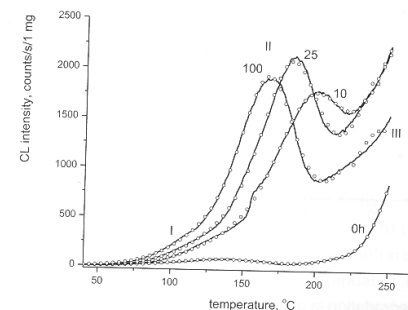


Fig. 1. Non-isothermal records of chemiluminescence intensity in nitrogen for the preoxidized samples of Ecoflex. The rate of heating was 5 °C min<sup>-1</sup>. The numbers denote the time of pre-oxidation in hours in SEPAP. Points denote the theoretical fit by Equation 1.

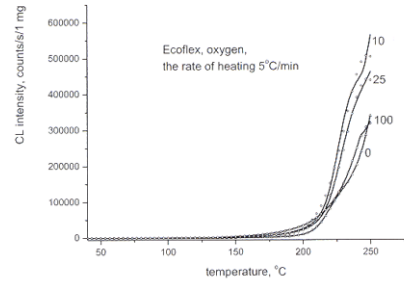


Fig. 2. Chemiluminescence intensity – temperature runs of Ecoflex in oxygen, the rate of heating  $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . The figures denote the duration of UV irradiation in hours. The points denote the theoretical fit by Eq. 1.

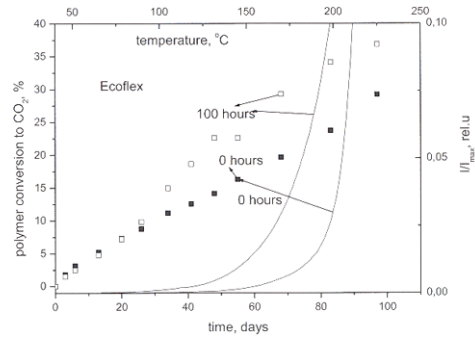


Fig. 3. The comparison of biodegradation in compost [10] at  $58\text{ }^{\circ}\text{C}$  of UV oxidized Ecoflex, with non-isothermal chemiluminescence runs in oxygen (lines) expressed in relative coordinates till the 0.1 of relative value (the upper and left axis). The chemiluminescence was measured at the rate of heating of  $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .