

LUMINESCENCE TECHNIQUE FOR CHARACTERISATION OF OXIDATIVE DEGRADATION OF SOLID POLYMERS IN AMBIENT TEMPERATURE

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Abstract. The simple and sensitive method to detect the oxidative degradation of solid polymers in ambient temperature has been described. This method employs UV-B light excitation of polymer chromophores to electronically excited states, followed by characteristic fluorescence. Luminescence from three types of thermoplastic polymers: polyamide 12 (PA12), poly(ethylene terephthalate) (PET), and poly(butylene terephthalate) (PBT), before and after ageing has been measured. Different light conditions, values of pH, and hydrogen peroxide concentrations were used during ageing of polymers. The Fourier Transform Infrared spectroscopy (FTIR-ATR) and thermogravimetry (TG-DSC) were used in the research to compare the luminescent technique with the analytical methods.

1. INTRODUCTION

The oxidative degradation of thermoplastic polymers and its prevention are very important processes from both the scientific and the industrial point of view [1-4]. Oxidation of polymers in air occurs under mild conditions and may result in modification, chain degradation or crosslinking. This process changes the physical and mechanical properties and is a radical chain reaction which propagates in the presence of molecular oxygen [5,6]. Small amounts of hydroperoxides, carbonyl groups or aromatic compounds contained in polymers are responsible for the initiation, i.e., for the first step of the degradation process. A particular problem in the study of polymer degradation is the detection and estimation

of peroxides which are very important intermediates. The relaxation of electronically excited triplet carbonyl groups formed in a bimolecular termination of two alkyl-peroxy radicals and singlet oxygen (¹O₂) is probably responsible for the light emission and may be measured using luminescent techniques. This process requires at least one of the reacting radicals to be secondary. Products of the termination reaction are compounds containing carbonyl group and singlet oxygen [7,8].

A simple and sensitive method to detect the oxidative degradation of solid polymers in ambient temperature is described in this paper. This method employs UV-B light excitation of polymer chromophores to electronically excited states, followed by characteristic light emission.

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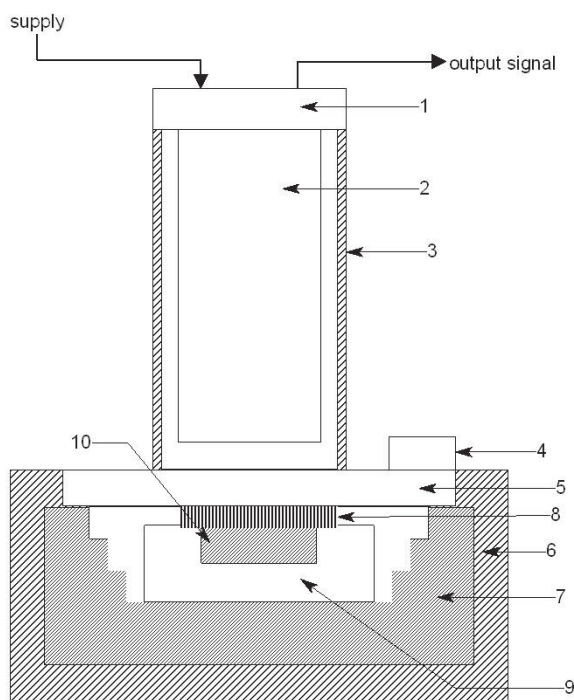


Fig. 1. The scheme of the solid state polymer luminescence photometer. 1 – pre-amplifier suite, 2 – photomultiplier tube, 3 – photomultiplier tube chamber, 4 – samples chamber blockade, 5 – shutter, 6 – samples chamber box, 7 – samples chamber, 8 – filter, 9 – aluminium cuvette, 10 – sample.

2. EXPERIMENTAL

Materials and preparation

Polymer samples in a form of granules were obtained from Polymer Institute, Szczecin University of Technology, Poland (PA12), Boryszew S.A, division 'Elana', Toruń, Poland (PET), and 'JELCHEM-POLIMERY Sp.z.o.o.', Jelenia Góra, Poland (PBT). Polymers were used as obtained. Degradation of polymers was carried out at room temperature in water at different pH, in the presence of air, sunlight or its absence, and using different concentrations of H_2O_2 . Citrate and boraxate buffers were used during the polymer ageing.

Method of research

Luminescence was induced by irradiation of polymers with UV Famed-1 170W (type L6/58) mer-

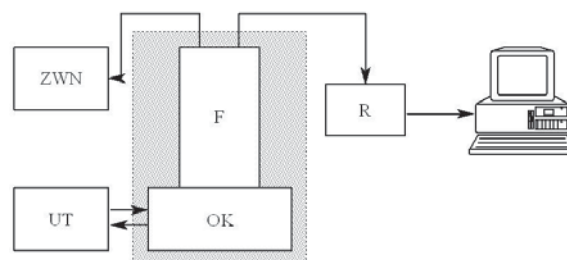


Fig. 2. Block diagram of polymer luminescence measurements system. F- photomultiplier light-tight box, OK – samples chamber box, ZWN – high voltage supply unit, UT – thermostated system, R – recorder.

cury lamp with a Wood's filter. The optimum time found for the UV irradiation was 30 min. The light emission was detected for 6 seconds after the end of irradiation. The basic instrumentation used for luminescence measurements consists of a specially designed chamber containing aluminium cuvette with 50 mm diameter and 12 mm depth placed in light-tight box (Fig. 1). Luminescence decay curves were recorded with a set specially designed and constructed in Institute of Physics, Szczecin University of Technology (Fig. 2). An irradiated polymer sample (10) (Fig. 1) emitted luminescence. After the shutter (5) was opened, the emitted luminescence directly fell on the photomultiplier cathode (2). A photomultiplier tube type M12FQC51 (Germany) with S-20 cathode, sensitive from 180 nm to 800 nm and with a maximum sensitivity at 450 nm was used to detect the emitted luminescence. Photomultiplier (F) (Fig. 2) was supplied by a stabilized 1000 V current with a high-voltage power supply ZWN-42, (POLON ZelMech, Zielona Góra, Poland) (ZWN). The photomultiplier current was recorded with K-200 recorder (Karl Zeiss Jena, Germany), with a 0,5 nA maximum electric current sensitivity. For data acquisition and handling, photomultiplier was interfaced with a personal computer. The computer provides the opportunity for simultaneously calculation of the light sum, i.e., area (ΣI) under the kinetic curve, $I=f(t)$, within any chosen time interval ($\Sigma I = \int_0^t I(t) dt$, where $I(t)$ – luminescence intensity, t_0 – measurement time starting after UV irradiation has stopped, t – measurement time ending). Light sums were recorded during 600 s. Changes in IR

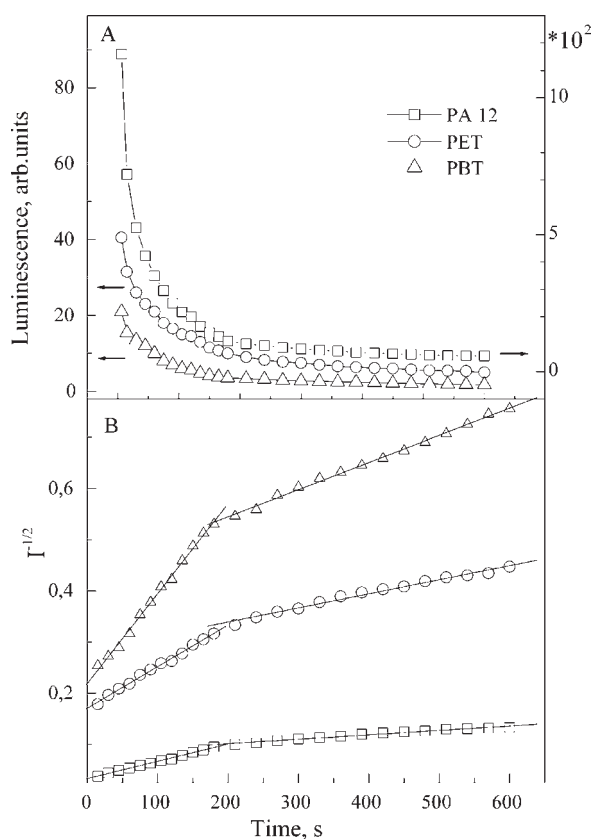


Fig. 3. Typical curves of the decay of luminescence $I=f(t)$ after UV-B irradiation of nonageing polymers PA12 (right axis), PET and PBT (left axis), part A. Part B – Analysis of the decay curves $I^{-1/2}=f(t)$ shown in part A.

spectra of the polymers caused by the degradation process were detected by reflection method ATR with a Thermo Nicolet spectrophotometer NEXUS FTIR and GOLDEN gate countershaft in the range 4000–400 cm^{-1} . Spectra were obtained at 4 cm^{-1} resolution and 34 scans number. Calculations and transformations were performed by a PC using OMNIC package. For calorimetric studies, a SETARAM (France) thermogravimeter TG-DSC 95-15 was employed. The experiments were carried out on 5.0 ± 0.3 mg samples in argon atmosphere with $17 \text{ cm}^3 \text{ min}^{-1}$ flow rate, and heating rate $10 \text{ }^\circ\text{C min}^{-1}$ in the temperature range 20–700 $^\circ\text{C}$. The data are reported as the relative changes of the signals $\Delta X = [(X - X_0) / X_0] \cdot 100\%$, where X – signal measured after a polymer degradation, X_0 – signal measured before the polymer degradation. The average related error in

the determinations of light sums did not exceed 5 percent.

3. RESULTS AND DISCUSSION

The PA12, PET, and PBT tested for oxidative degradation were previously subjected to oxidation by the visible light, water solutions of different pH in the absence and presence of two concentrations of H_2O_2 . Typical light intensity vs time curves for the examined polymers are shown in Fig. 3, part A. These data show that luminescence decays very rapidly down to close-to-zero values. The luminescence decay could not be fitted by simple kinetics, but it can be fitted by two consecutive second order reactions $I_j(t) = (A_j + k_j t)^{-2}$, where $j=1$ for $t < 180$ s, and $j=2$ for $t > 180$ s (Fig. 3, part B). Values for the rate constants for the light decay were an order of 10^{-4} s^{-1} ; they depended on the type of a polymer and on degradation conditions. The ageing process changed the rate constants of the light decay only a few times as compared with those measured for nondegraded polymers.

Since luminescence was stimulated by UV-B radiation at ambient temperature, it can be associated with a reactive fraction of the peroxides initially present in a polymer or formed during the oxidative degradation process which had been decomposed up. There exists general agreement that the luminescence emitters are an excited carbonyl group and singlet oxygen [9]; however, reactions of their production are still a matter of discussion [10]. In the reference literature on this subject, the following three basic ways of emitters generation are reported to explain luminescence in solid polymers: (i) bimolecular recombination of alkyl peroxy radicals, (ii) decomposition of hydroperoxides, (iii) the charge recombination of photoejected electrons. It is also obvious that hydroperoxides, ROOH, can decompose by unimolecular or bimolecular process with generation of electronically excited carbonyl containing compounds and $^1\text{O}_2$ [11]. Additional experiments by measuring the light emission through a series of cut-off filters (in spite of the low quantum yield of luminescence) allowed us to determine the emission spectra. The spectra revealed two major bands in the range 400–650 nm with maxima at about 460 ± 10 nm and 500 ± 10 nm (data not shown). The emission bands may originate mainly from carbonyl groups excited to the triplet state directly or in consecutive reactions. The emission from $^1\text{O}_2$ dimers in the singlet states $^1\Delta_g$ and $^1\Sigma_g^+$ may also participate in the band of 500 nm [12].

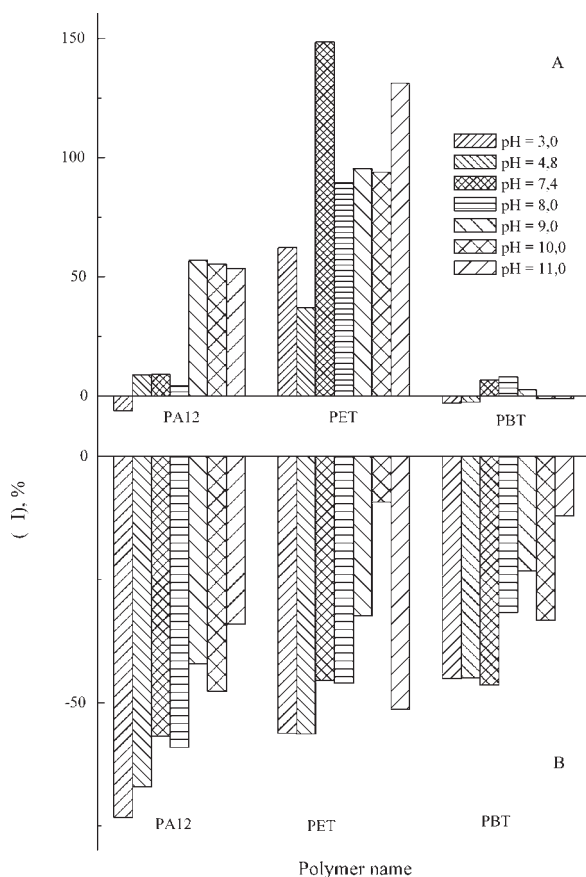


Fig. 4. Relative changes of the light sums after ageing PA12, PET, and PBT in different pH water environment conditions. A – in darkness, B – in light.

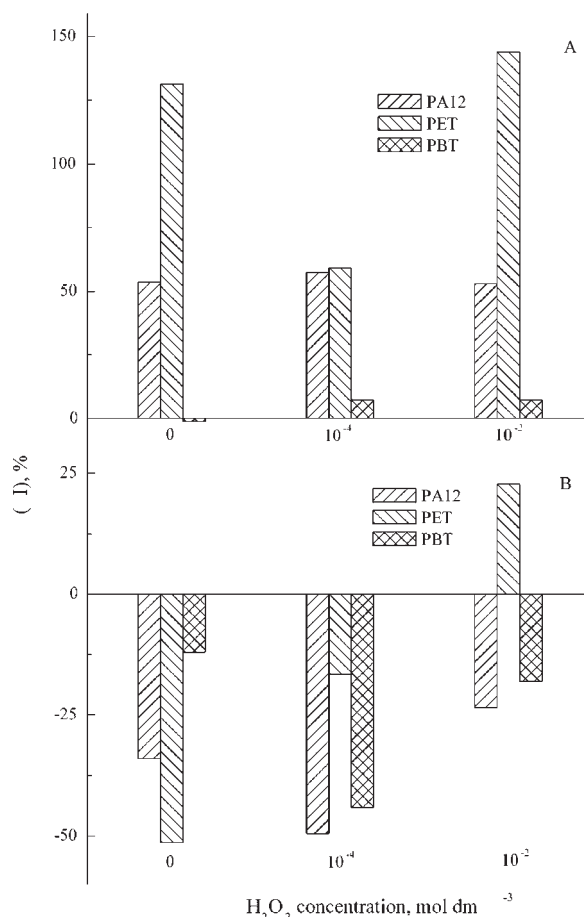


Fig. 5. Relative changes of the light sums after ageing PA12, PET, and PBT in pH 11,0 water environment with different H_2O_2 concentration. A – in darkness, B – in light.

In order to estimate usefulness of the luminescent technique to study the oxidative degradation of polymers, luminescence signals were measured before and after the polymer degradation at different pH and in presence and absence of H_2O_2 . All measurements were carried out in the presence and absence of daily light (Figs. 4 and 5). As can be seen from Fig. 3, the light emission strongly depends on pH of solutions in which polymers were aged as well as on the presence of daily light as measured by the relative changes of the light sums ($\Delta S = [(\Sigma I - \Sigma I_0) / \Sigma I_0] \cdot 100\%$). The highest changes in ΔS were observed for PET degraded at pH 7,4 in darkness (about 150%). Fig. 4 shows the relative changes in the light sum with the presence of H_2O_2 in the ageing solution at pH 11,0. Also, ΔS values in this case strongly depended on the oxidant pres-

ence, reaching the maximum value about 140% for PET.

In order to demonstrate the applicability of the luminescent technique, samples of the polymers were examined before and after the oxidative degradation process using FTIR-ATR spectroscopy and thermogravimetry at almost the same conditions. Fig. 6 presents the representative data of the relative changes in absorbance of carbonyl compounds caused by ageing at pH 11,0 in the presence of daily light and H_2O_2 or their absence. These results show that the maximal changes in the carbonyl content caused by degradation reached 30%. Much less relative changes were noticed by calorimetric

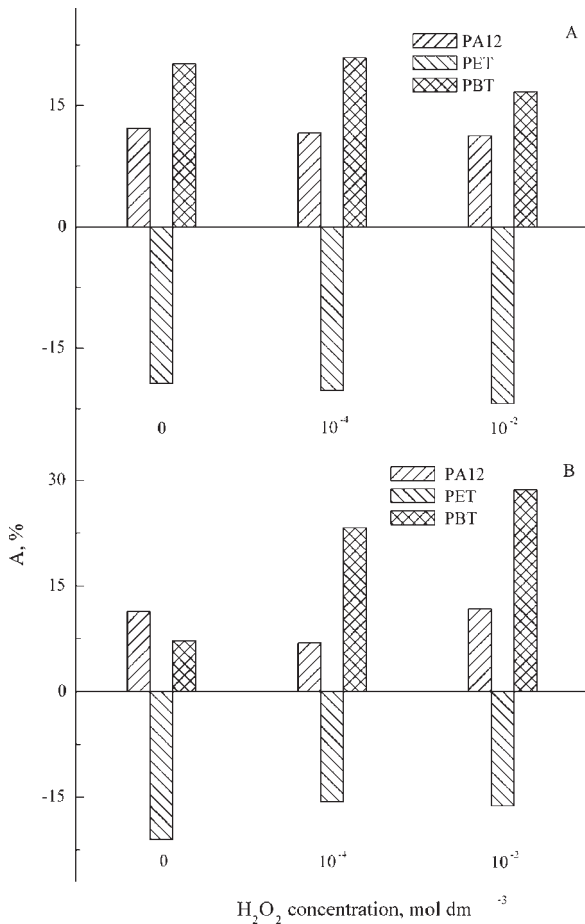


Fig. 6. Relative changes of IR absorbance in C=O regions after ageing PA12, PET, and PBT in pH 11,0 water environment with different H₂O₂ concentration. A – in darkness, B – in light.

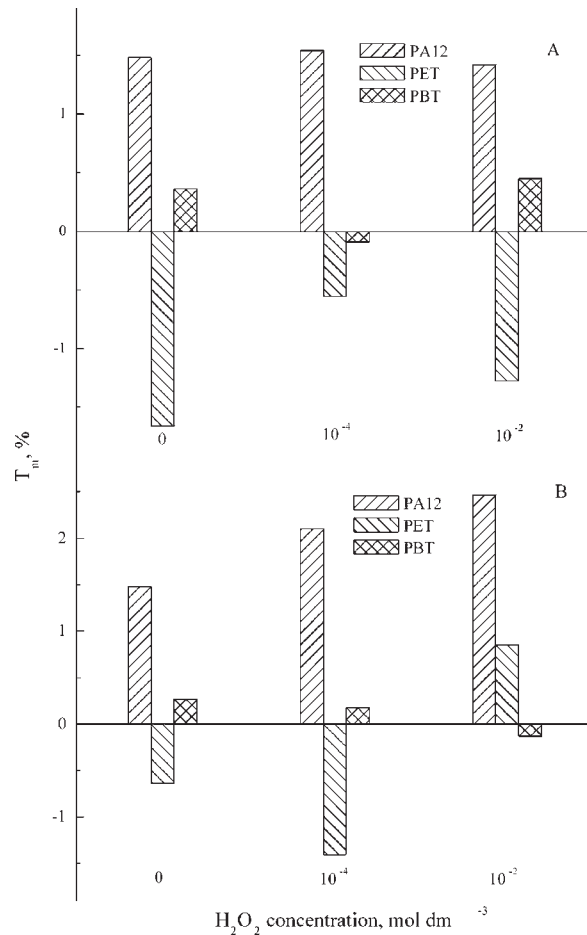


Fig. 7. Relative changes of melting temperature after ageing PA12, PET, and PBT in pH 11,0 water environment with different H₂O₂ concentration. A – in darkness, B – in light.

technique. Maximum relative changes caused by oxidative degradation of the polymers occurred in melting temperature, and do not exceed 3%. Fig. 7 shows these representative data after ageing the polymers in water solution at pH 11,0 in the presence and absence of antioxidant and daily light.

It can be seen from a comparison of the luminescence signals of the examined polymers that the degradation rate can be measured with greater sensitivity and at short times by luminescence, independently on the oxidative degradation conditions, with the extent of oxidation measured by carbonyl group absorbance from IR or the thermogravimetry parameters.

4. CONCLUSIONS

The luminescence is a simple and convenient technique to study the polymer degradation at ambient temperature. It is believed that a carbonyl group and singlet oxygen are responsible for the luminescence polymers. The proposed method is simple, rapid, convenient, economical, and nondestructive; it requires no tedious sample preparation. The method can be used to analyse polymers in powder, granules, sheets, fibres, and chips. It can provide unique information which can not be obtained by other methods and may be used in many areas of basic and applied research. While luminescent method

is very sensitive, to achieve its full potential in obtaining useful kinetic, mechanistic, and structural information about the degradation process, the method must be coupled with other spectroscopic and analytical methods.

The disadvantage of the luminescent technique is that it gives no information on those polymers which are nonluminescent. Further studies will be carried out in order to optimize the experimental conditions and improve the method specificity for the hydroperoxides analysis.

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