

Polymer films doped with colorants as oxygen sensitive materials

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The aim of this work was to make a polymeric material exhibiting oxygen quenching photoluminescence (PL) and to characterize its sensitivity to oxygen pressure variation. The following main results were obtained: - polystyrene thin films exhibited intense fluorescence emission at ca. 400 nm upon irradiation with UV light (313 nm), that is oxygen sensitive. - we found, using some xanthene dyes that, by doping with adequate substances, a luminescence emission in the visible region can be obtained and this emission is oxygen sensitive. - the emission spectra of the film has been very similar, upon experimental conditions, to that from an oxygen sensor (pressure sensitive paint) used as a reference; - film samples, and reference, exhibited linear correlation of luminescence signal and O₂ partial pressure; the sensitivity as it has been evaluated from the slope of the straight line [$I_{PL} = f(p_{O_2})$] is depending on the nature and concentration of the dye. The results are important to prepare new oxygen sensors for various technical appliances, because the resulting materials are very cheap and easy to be prepared.

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1. Introduction

Evaluation of oxygen concentration in various liquid environments is of prime interest for several appliances, such as quality inspection of vacuum or modified atmosphere food packaging, or medical tests concerning oxygen content in blood. On the other hand, there are some appliances concerning the aerodynamics (determination of pressure distribution measurements in wind tunnels and turbomachines), in which is of great interest to know the distribution of the air pressure on various surfaces.

Among various methods applied to evaluate the above mentioned characteristics, that based on oxygen quenching of the photo-luminescence from a suitable material seems to be simple and versatile. Therefore it has been developed during last years [1 -4].

In the case of solutions or packaging, classic methods of evaluation of oxygen concentration are based on chemical analysis, usually based on chromatographic methods. The main disadvantage of these methods consists in their intrusive and destructive character. Thus, in the case of the analysis of the integrity of the vacuum or modified atmosphere packaging, the gas sample is taken off by a micro- syringe, that leads to their irreversibly destruction. As a result, the quality control of the modified atmosphere packed food products cannot be total, leading to some risks for consumer health. Such a procedure is also inconvenient from economical point of view because the samples which passed the quality inspection are either

lost or should be re-packed and included in next fabrication lot and re-submitted to quality inspection [2]. Chemical assessment of oxygen concentration completely excludes the inspection of packaging integrity by the customer or by the consumer.

The evaluation of the pressure on various aerodynamic conditions is usually performed by piezoelectric sensors and radio-telemetry. The disadvantages are similar to those above mentioned, namely the sensor covered area is less than 5% of the analysed one, and the aerodynamic profile is more or less altered by sensors [5].

Evaluation of oxygen pressure or content by luminescence quenching caused by oxygen molecules is a relatively new method, even the phenomenon is well known from several decades ago. Thus, the principle of such a method, called *optical detection of oxygen*, is very simple consisting in oxygen quenching of fluorescence or phosphorescence that occurs when a suitable luminophor is irradiated with light radiation able to excite its luminescence. Then, oxygen pressure or concentration can be evaluated on the basis of calibration curves [2].

Several materials adequate for optical detection of oxygen were proposed during last years for various technical and clinical applications [6]. Thus, so called pressure sensitive paints were developed for evaluation of oxygen pressure in aerodynamic applications [5]. Optical oxygen sensors for blood analysis or for food packaging inspection were also recently reported.

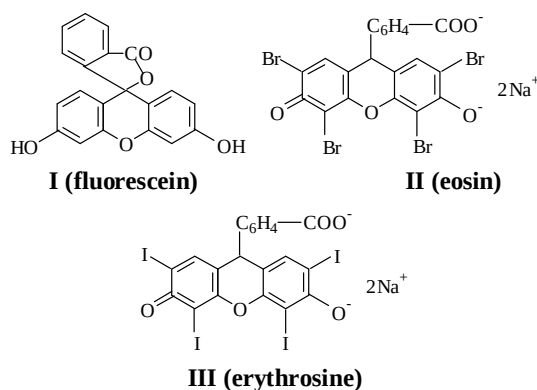
Basically, an oxygen sensor for optical detection of oxygen consists in a luminophor exhibiting oxygen quenched photo-luminescence, which is incorporated in a suitable organic matrix. Ruthenium [7] and Palladium [3] complexes are largely reported as luminophors in these sensors. The most important property of the organic matrix seems to be its oxygen permeability, which controls the access of oxygen molecules to the luminophor [8].

The aim of this work was to investigate another way to evaluate the oxygen pressure by optical method, trying to avoid the use of metal complex. Thus, the photoluminescence quenching by oxygen of some polymer materials prepared in this work has been characterised.

2. Experimental

Polystyrene used in this work has been Styron 634 (Dow Plastics), for general purposes. Solutions of 2.5 g polystyrene in 100 cm³ solvent were prepared by mixing the polymer with pure chloroform (p.a. grade) at room temperature. Under these conditions, the polymer has been completely dissolved and no gel fraction has been observed therefore, no filtration of the resulted solution was performed.

The structures and denomination of the xanthene dyes used in this work are shown bellow. All these substances were p.a. grade (Merck) and were used as solutions of 0.25% in concentration in ethyl alcohol.



Then, 5 cm³ of polystyrene solution and 0.325 cm³ of dye solution were put together and stirred in a porcelain cell (15 ml in capacity). Then, the resulted mixture has been painted on an aluminium plate (10 mm × 10 mm × 1 mm) that was previously polished and clean (by 24 hours acetone immersion). After solvent evaporation, a thin layer (50 ± 5 μm) of polystyrene doped with xanthene dye (C = 0.8%) resulted and has been used as oxygen sensor in this work. Several samples of doped polystyrene were prepared in each case, and only those fulfilling the thickness condition were kept to be used in the experiments. The structure of the resulted sensor is shown in Fig. 1.

A pressure sensitive paint (PSP) based on a metal complex has been also used in this study. This material has been kindly provided by a foreign company.

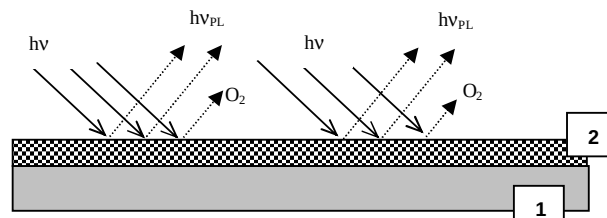


Fig. 1. The structure of the oxygen sensor based on xanthene dye doped polystyrene.

In order to characterize the behaviour of the studied materials, was used an installation that is schematically shown in Fig. 2. The film sample has been placed in a cell (see Fig. 3) that allowed both irradiating the sample with suitable light to occur excitation of polystyrene fluorescence and measuring photoluminescence (PL) signal. The excitation and photoluminescence signals passed the same window, but this did not considered a problem, because the spectrometer used as detector was able to discriminate between the signals. On the other hand, the pressure inside the cell can be controlled in the range 0.02 atm to 1.0 atm.

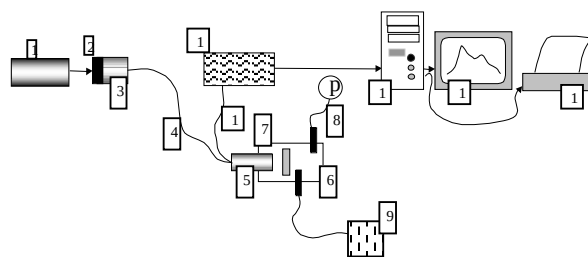


Fig. 2. Bloc scheme of the installation used for measuring of the photoluminescence emission at various pressure values: 1 - light source; 2 - filter; 3 - optical coupling; 4 - optic cable for excitation light; 5 - light detector of the spectrometer; 6 - measuring cell; 7 - sample; 8 - manometer; 9 - vacuum pump; 10 - optic cable PL signal; 11 - spectrometer; 12 - computer; 13 - display; 14 - printer.

An AvaSpec 256 optic fibre spectrometer (Avantes) has been used to record PL signal from the studied samples.

The light has been provided by a halogen source has been HL 2000. No filter has been used to separate some components of the emitted light.

AvaSoft full has been used to data acquisition and processing.

The measurements were made following the procedure presented bellow: the lamp is started to reach its normal working regime, without coupling to the optic cable; the sample is put on its support, then the cell is hermetically closed by means of the screws (10, see Fig. 3). The pressure in the cell is initially raised to 1 atm., by opening the tap (14, see Fig. 3) to allow the air access. Then, the tap is closed and the signal of the sample is detected and recorded by the spectrometer coupled to the

computer. The spectra of the detected signal can be displayed in the range 200 - 1100 nm, but usually the visible region has been explored, due to the emission spectra are located there.

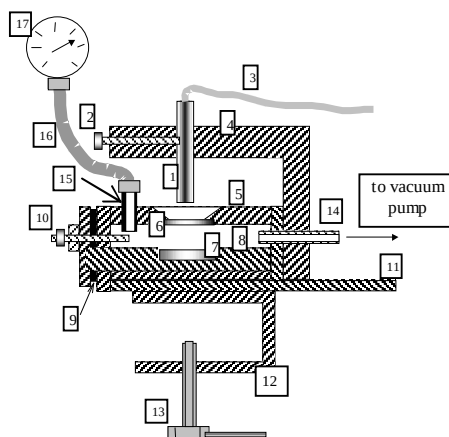


Fig. 3. Detail of the installation used for measuring PL - the cell with controlled pressure: 1 - light detector of the spectrometer; 2 - screw for fixing the detector; optic cable; 4 - support of the detector; 5 - circular opening; 6 - window; 7 - sample (polystyrene film); 8 - sample mobile support; 9 - rubber seal; 10 - screw for fixing the sample support; 12 - cell support; 12, 13 - fixing system parts; 14 - gas outlet to vacuum pump and tap (three ways); 15 - connection to the manometer; 16 - vacuum tube; manometer (0 - 1 atm.).

3. Results

The emission spectrum from polystyrene submitted to UV excitation ($\lambda = 313$ nm) is shown in Fig. 4. The emission maxim is at ca. 390 nm and it can be clearly observed that the intensity of the signal increased when the partial pressure of oxygen decreased.

Photoluminescence spectra at various pressure of air in the case of fluorescein doped polystyrene are shown in Fig. 5. The intensity of the signal increased as decreasing the air pressure, i.e. the partial pressure of oxygen (see Table 1).

Similar results were obtained with other studied dyes as it is shown in Tables 2 and 3.

The effect of the concentration of the xanthene compound has been studied in the case of eosin and erythrosine. In both cases, were prepared films containing 2.4% dye. The results are summarised in Tables 4 and 5 and in Fig. 6.

A comparison between the above oxygen sensitive materials and an oxygen sensor, namely a pressure sensitive paint (PSP) based on a metal complex has been also performed under the experimental conditions. The PL spectra and results obtained with this material are shown in Fig. 7 and Table 6, respectively.

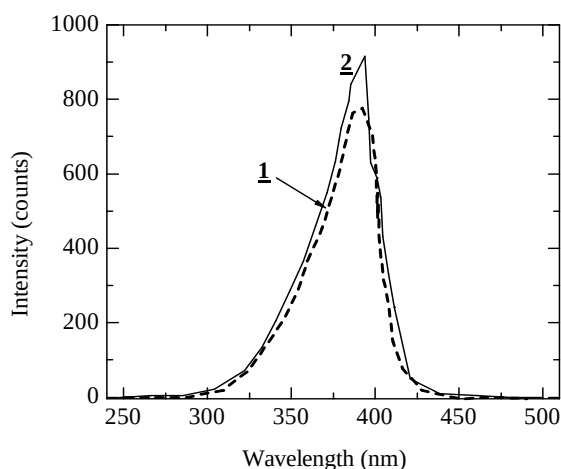


Fig. 4. Emission spectrum from the polystyrene: 1 - normal atmospheric pressure; 0.8 pressure of air (excitation with UV light, 313 nm).

Table 1. PL signal from fluorescein doped polystyrene ($C = 0.8\%$) at various air pressure.

P (atm)	max. at 630 nm (counts)	shoulder at 590 cm^{-1} (counts)
1.0	2278.8	2208.3
0.56	2355.6	2214.7
0.2	2477.6	2241.5
0.02	2604.0	2363.4

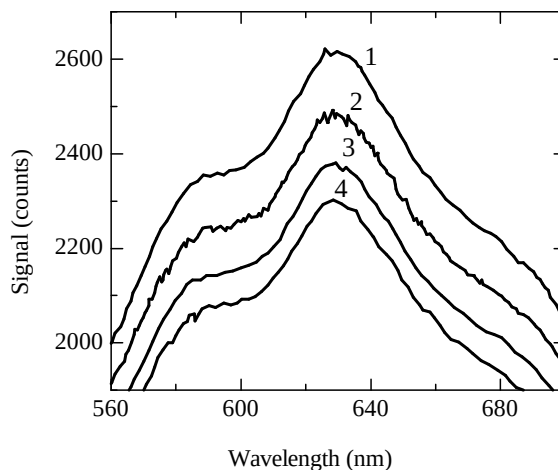


Fig. 5. Luminescence spectra from fluorescein doped polystyrene ($C = 0.8\%$) at various air pressure values: 1 - 0.02 atm; 2 - 0.2 atm; 3 - 0.56 atm; 4 - 1 atm.

Table 2. PL signal from eosin doped polystyrene ($C = 0.8\%$) at various air pressure.

P (atm.)	max. at 630 nm (counts)	shoulder at 695 nm (counts)
1.0	794.5	630.7
0.6	817.1	645.1
0.4	832.1	656.7
0.14	848.2	671.2
0.02	839.6	670.0

Table 3. PL signal from erythrosine doped polystyrene ($C = 0.8\%$) at various air pressure.

P (atm)	max. at 625 nm (counts)	shoulder at 580 nm (counts)	shoulder at 680 nm (counts)
1.0	897.7	822.2	825.1
0.55	986.5	818.6	821.4
0.2	999.2	810.4	806.3
0.02	1005.2	793.7	739.0

Table 4. PL signal from eosin doped polystyrene ($C = 2.4\%$) at various air pressure.

P (atm)	max. at 630 nm (counts)	shoulder at 680 nm (counts)
1.0	1231.2	1091.0
0.6	1270.8	1140.9
0.4	1286.2	1157.4
0.02	1344.8	1217.8

Table 5. PL signal from erythrosine doped polystyrene ($C = 2.4\%$) at various air pressure.

P (atm)	max. de la 630 nm (counts)	shoulder at 590 nm (counts)	shoulder at 590 cm^{-1} (counts)
1.0	2864.4	2421.3	2483.1
0.56	2939.5	2463.2	2533.0
0.26	3040.5	2494.8	2588.5
0.2	3031.1	2503.5	2597.4
0.02	3015.2	2552.7	2635.7

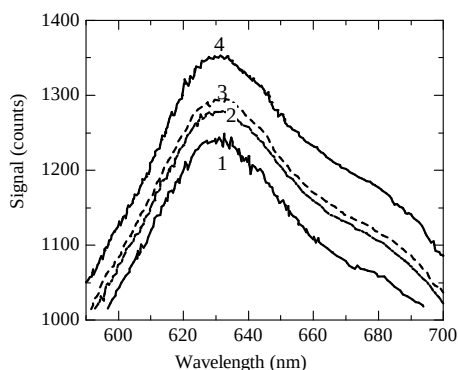


Fig. 6. PL spectra from erythrosine doped polystyrene ($C = 0.8\%$) at various air pressure values: 1 - 1 atm; 2 - 0.6 atm; 3 - 0.4 atm; 4 - 0.02 atm.

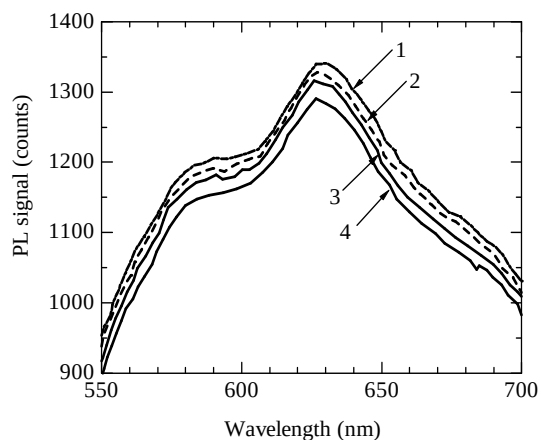


Fig. 7. PL spectra from PSP at various air pressure values: 1 - 0.02 atm; 2 - 0.18 atm; 3 - 0.4 atm; 4 - 1 atm.

Table 6. PL signal from PSP at various air pressure.

P (atm.)	shoulder at 584 nm (counts)	max. de la 630 nm (counts)	shoulder at 684 nm (counts)
1.0	1149.0	1285.0	1046.2
0.54	1167.9	1308.1	1068.9
0.4	1177.7	1321.1	1074.2
0.18	1187.5	1331.1	1090.3
0.02	1202.4	1343.4	1102.2

5. Discussion

All studied xanthene dye polystyrene doped materials exhibited pressure sensitivity under the experimental conditions. It can be assigned to the induced "shifting" of the luminescence of pure polystyrene that exhibited a maximum at ca. 390 nm under UV irradiation (see Fig. 4). This maximum seems to be oxygen sensitive.

All studied materials exhibited a maximum of PL (under irradiation with a halogen lamp) located at ca. 630 nm and several shoulders that seem to be more or less characteristic to the xanthene compound. The maximum at 630 nm as well as the shoulders seem to be oxygen sensitive as suggest the data shown in Tables 1 - 5 and the spectra shown in Figs. 5 and 6. This effect could be explained by the above mentioned "shifting" of luminescence maximum of polystyrene. In fact, we suppose that the luminescence emission of the polymer, that is oxygen sensitive, activates the fluorescence of the xanthene dye. This secondary luminescence is oxygen sensitive even if the emission of the dye could be not directly influenced by oxygen molecules.

If we plot PL signal as a function of the air pressure or of partial pressure of oxygen, a linear relationship between the signal and the pressure is found in all cases as it is shown in Fig. 8. The slope of such a straight line could be related to the sensitivity of the material to oxygen pressure. Thus, the sensitivity should increase as

increasing the slope (in fact its module, all slope values being negative). Taking into account the data in Table 7, the sensitivity of the xanthene dye doped materials ($C = 0.8\%$) decreases in the following order:

$$PS-1a > PS-3c > PS-3b > PS-c > PS-b > PSP$$

So, under the experimental conditions, all polystyrene based materials seem to be more sensitive than the pressure sensitive paint (PSP) based on metal complex, but the linearity of the signal seems to be comparable to that of the PSP only in the case of the less sensitive materials, namely PS-b and PS-3b, namely those containing eosin.

On the other hand, the sensitivity seems to be less influenced than the PL intensity when the concentration of xanthene dye is increased (see data in Table 7). This could be related to less important direct influence of oxygen molecules on the luminescence of xanthene dye, as compared to the influence of concentration on the intensity of the PL induced by polystyrene.

Table 7. Parameters of the linear relationship of PL signal and air pressure in the case of the materials studied in this work.

Material	Material code	Slope	Intercept	Correlation coefficient
PS* + 0.8% fluorescein	PS-a	-284.194	2603.15	0.833
PS + 0.8% eosin	PS-b	-62.68	856.46	0.999
PS + 0.8% erythrosine	PS-c	-108.07	1019.97	0.929
PS + 2.4% eosin	PS-3b	-114.15	1340.90	0.989
PS + 2.4% eosin	PS-3c	-177.49	3045.67	0.950
PSP**	PSP	-57.34	1342.51	0.995

*polystyrene

**pressure sensitive paint

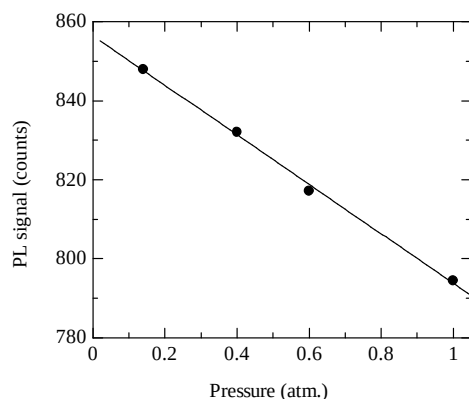


Fig. 8. Linear dependence of PL signal on air pressure in the case of eosin doped polystyrene: $C = 0.8\%$.

6. Conclusions

Polystyrene thin films exhibited intense fluorescence emission at ca. 400 nm upon irradiation with UV light (313 nm), that is oxygen sensitive.

We found, using some xanthene dyes that, by doping with adequate substances, a luminescence emission in the visible region can be obtained and this emission is oxygen sensitive. The emission spectra of the film has been very similar, upon experimental conditions, to that from an oxygen sensor (pressure sensitive paint) used as a reference. Film samples, and reference, exhibited linear correlation of luminescence signal and O_2 partial pressure. The sensitivity as it has been evaluated from the slope of the straight line [$I_{PL} = f(p_{O_2})$] is depending on the nature and concentration of the dye.

The results are important to prepare new oxygen sensors for various technical appliances, because the resulting materials are very cheap and easy to be prepared.

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