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Journal of Photochemistry and Photobiology A: Chemistry 177 (2006) 328–331
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Short communication

Demonstration of a novel, flexible, photocatalytic oxygen-scavenging polymer film

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Received 1 May 2005; received in revised form 27 May 2005; accepted 1 June 2005
Available online 11 July 2005

Abstract

The preparation of a novel, flexible, photocatalytic, oxygen-scavenging polymer film is described. The film incorporates nanocrystalline titania particles in an ethyl cellulose polymer film, with or without an added sacrificial electron donor of triethanolamine. When coated on the inside of a glass vessel its UV-driven light-scavenging action is demonstrated by platinum octaethyl porphyrin coated glass beads sealed inside, since their luminescence increases with increasing UV-irradiation time. When used as a flexible film, work with an oxygen electrode shows that the film is able to scavenge oxygen at an average rate of 0.017 cm^3 O_2 h^{-1} cm^{-2} over a 24 h period, which compares favourably to other, well-established oxygen-scavenger systems. The potential of using such as system for oxygen scavenging in packaging is discussed briefly.

Keywords: Polymer; Photocatalysis; Oxygen-scavenging; Titania

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1. Introduction

Oxygen is responsible for the deterioration of many materials either directly or indirectly [1,2]. Examples of direct oxidation reactions include the corrosion of metals [2], tainting of beer and the browning of fruit [1,2]. Examples of indirect oxidation processes include the spoilage of food by microorganisms that thrive only under an aerobic atmosphere [1]. In order to limit such undesirable processes, oxygen is often excluded, e.g. by applying a layer of paint onto a metal or flushing a food package with an inert gas, such as carbon dioxide or nitrogen [1–3]. In some cases, e.g. delicate beers, valuable foods, pharmaceuticals or museum pieces, an oxygen scavenger is also incorporated into the package to maintain the oxygen at a very low level, typically <0.1%. Such oxygen scavengers are usually sold in the form of sachets or labels and comprise a mild reducing agent, such as ascorbic acid or finely divided iron or iron(II) oxide [1].

In recent years, there has been a growing interest in the development and application of oxygen scavenging polymers, usually based on ones that simply react with oxygen over time, and several commercial products have been launched successfully. For example, the Oxbar^{TM} and Bind-Ox^{TM}, oxygen-scavenging polymer systems based on the oxidation of an aromatic nylon, MXD6, catalysed by a cobalt salt, are used currently in the manufacture of many plastic beer bottles [1,4]. The identification of new, alternative routes to oxygen scavenging by polymers is of great current interest, and in this communication, we report on a flexible, polymer oxygen-scavenging film that has the novel feature of functioning via a photocatalytic process.

2. Experimental

A typical photocatalytic polymer film casting solution was prepared by adding 1 g of titania (Degussa P25) and 0.1 g of triethanolamine (TEOA) to 10 g of a 20% (w/v)

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doi:10.1016/j.jphotochem.2005.06.001

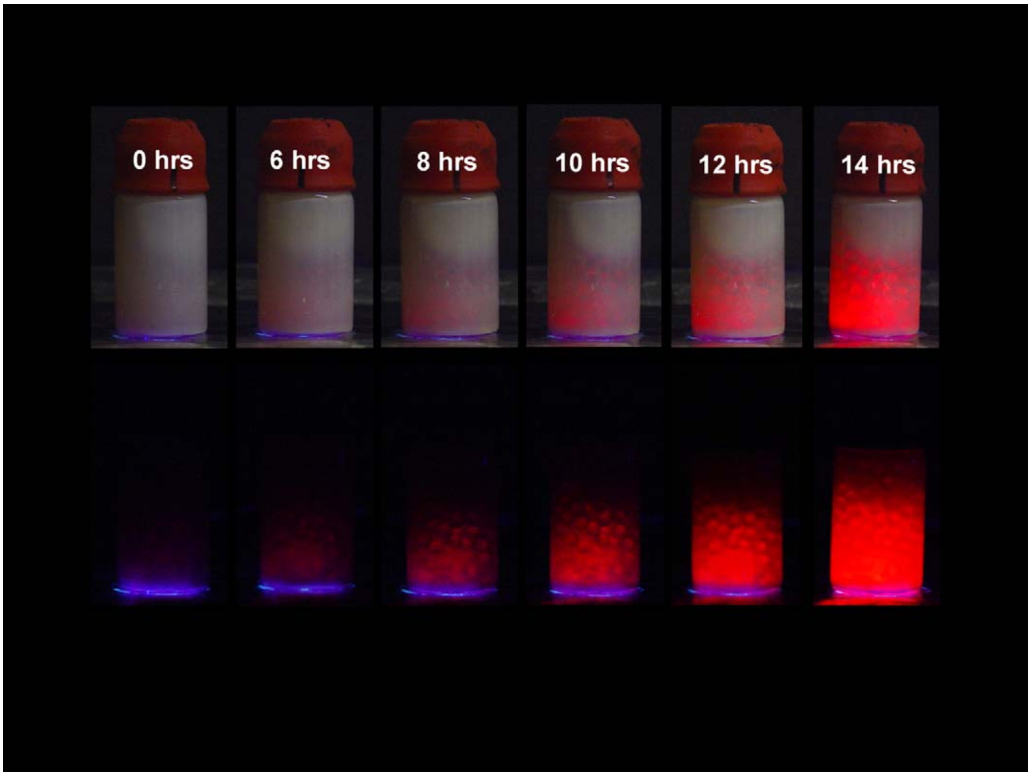

Fig. 1. Sequence of pictures of a TiO_2/TEOA/EC film in a sealed glass bottle, in an initial O_2 atmosphere, taken at different times during its irradiation with UVA light. In order to observe the luminescence of the Pt-OEP coated glass beads inside, for each photograph the bottle was brightly illuminated from below by a UVA light. The top photographs were recorded using some room light to highlight the TiO_2/TEOA/EC coating.

solution of ethyl cellulose (EC) dissolved in a 4:1 (v/v) toluene:ethanol mixture. This pre-polymer film solution was used to coat surfaces and create flexible films. Thus, in one experiment a 10 cm^3 glass sample bottle was coated on the inside with a thin (typically 7 μm) TiO_2/TEOA/EC polymer film, by placing 1 g of the pre-polymer film solution inside the bottle, and then rotating it, whilst in a horizontal position, until fully coated. The film was then dried at 70 °C for 30 min (Fig. 1). In other work, thin (ca. 2 μm), flexible films were created by spin coating a few drops of the pre-polymer film solution onto a 25 mm × 25 mm square glass substrate, from which the films could be easily peeled off (see Fig. 2).

3. Results and discussion

In order to demonstrate the light-driven, oxygen-scavenging action of this film, 3 mm diameter glass beads were coated with an oxygen-sensitive lumophore, platinum(II) octaethyl porphyrin (Pt-OEP), encapsulated in a thin layer of cellulose acetate butyrate (CAB) [5]. These beads were used to fill the polymer-coated glass bottle, which was then flushed with pure oxygen and sealed with a rubber cap; the available gas phase in the bead-filled bottle was 3.7 cm^3. This system was then irradiated from the side with UVA light ($I = 6.5\ mW\ cm^{-2}$) and the change in the luminescence, due to the glass beads inside, monitored photographically as illustrated by the results in Fig. 1. From these results, it appears that with increasing irradiation time the luminescence of the glass beads increases until reaching a maximum at ca. 14 h, corresponding to less than 1% oxygen. The average rate of oxygen scavenging by the film over a 14 h period was calculated as $0.018\ cm^3\ O_2\ h^{-1}\ cm^{-2}$. Under otherwise identical conditions, in the absence of the TiO_2/TEOA/EC film, the weak luminescence of the coated glass beads decreases slightly upon irradiation for 14 h with UVA light, probably due to some photodegradation of the Pt-OEP.

Pt-OEP in CAB is a recognised oxygen sensitive material, with a red luminescence that decreases in intensity as the level of ambient oxygen increases [5]. Thus, the results in Fig. 1 indicate that upon UV irradiation of the polymer-coated vial, the level of oxygen inside decreases, eventually reaching some low value (ca. 1%) after ca. 14 h, at which point the luminescence due to the beads is at its brightest and similar to that observed for the bottle, when flushed with nitrogen, i.e. oxygen free.

The oxygen-scavenging action of the TiO_2/TEOA/EC polymer film can be readily interpreted in terms of semiconductor photocatalysis [6–8], since titania is a recognised semiconductor photocatalyst capable of mediating the destruction of many organic compounds via an oxidative min-

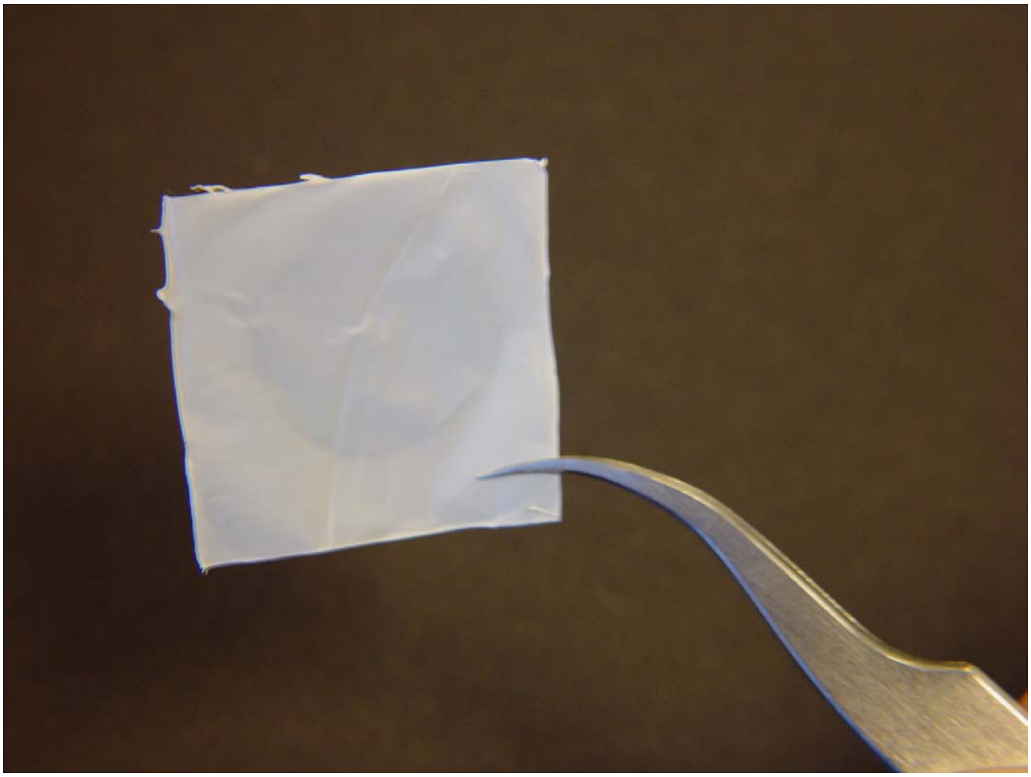

Fig. 2. Typical TiO_2/EC/TEOA flexible polymer film produced by spin coating the pre-polymer film solution.

eralisation process, i.e.

$$\text{organic} + O_2 \xrightarrow[TiO_2]{h\nu \geq 3.2\,eV} CO_2 + H_2O + \text{numeral acids} \qquad (1)$$

Titania is also a large band gap semiconductor and so requires UVA light to drive reaction (1). Thus, UV irradiation of the TiO_2/EC/TEOA polymer film in the sealed bottle will result in the photomineralisation of the EC polymer and/or the added mild reducing agent, TEOA, and the concomitant removal of oxygen. As a consequence, the ambient level of oxygen inside the bottle will decrease with increasing irradiation time, as indicated by the observed change in luminesce intensity of the Pt-OEP coated beads illustrated in Fig. 1. Experiments conducted using just TiO_2/EC films show that photoreaction (1) is slower (ca. 2.5 times) if the TEOA is absent from the polymer film formulation, indicating that the polymer, EC, is more difficult to photooxidise, via reaction (1), than the recognised mild-reducing agent, TEOA [9].

As noted earlier, flexible films of the TiO_2/TEOA/EC polymer can be easily created by spin coating the pre-polymer film solution, and a typical example is illustrated in Fig. 2. In one set of experiments, a typical TiO_2/EC/TEOA film was incorporated into a sealed layered system with the TiO_2/TEOA/EC film on a glass substrate on the top and an oxygen electrode [10] on the bottom, and the two separated by a sandwiched 0.3 cm^3 air gap. Upon irradiation of the film with UVA light, the oxygen level in the sandwiched gas phase, as monitored by the oxygen electrode, decreases to ca. zero within a few minutes. At this point, the covering TiO_2/TEOA/EC film was lifted off, allowing the oxygen in the air gap to be replenished, and then replaced and the procedure repeated. The %O_2 versus time profile, recorded by the oxygen electrode for 15 consecutive irradiation and oxygen replenishing cycles of the sandwich system, is illustrated in Fig. 3 and shows that the film does not appear to lose its oxygen-scavenging capacity with repeated and prolonged UVA exposure. Calculations based on this data show that the film is able to scavenge oxygen at an average rate of ca. 0.017 $cm^3\ O_2\ h^{-1}\ cm^{-2}$ over a 24 h period. Thus, a 200 cm^2 sized plastic film would be capable of scavenging 80 cm^2 of oxygen in 24 h and this compares well with both iron based and polymer based scavengers which are typically able to take up 100 and 0.2 cm^3 of oxygen, respectively, in 24 h [1]. The formal quantum efficiency of this process was estimated as 0.012 molecules of oxygen per photon of incident UVA light. Studies using FTIR spectroscopy shows that prolonged irradiation of the TiO_2/EC/TEOA films leads eventually to the complete mineralisation of the polymer and TEOA, leaving just the TiO_2 behind.

Other work using FT-IR spectroscopy provided no evidence of any major intermediates in a typical TiO_2/TEOA/EC film or the gas phase above it. This lack of major intermediates is not unusual in semiconductor photocatalysis and is often attributed to a much greater reactivity of the intermediates in reaction (1) than the starting material. Further work is required to identify what trace intermediates are generated

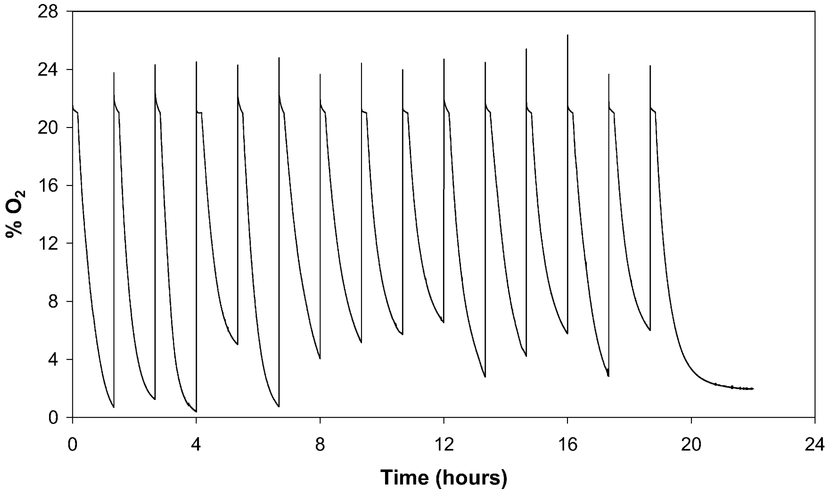

Fig. 3. Observed variation in the %O_2 in a sealed TiO_2/TEOA/EC film/air/O_2 electrode sandwich cell upon repeated cycles of UVA irradiation of the film followed by admission of fresh air to the system (marked by a spikes in the signal) and then resealing.

in such oxygen-scavenging films, in case any are hazardous and capable of contaminating the package. Because of contamination and tainting concerns, in practice it is likely that such oxygen-scavenging films would form part of a laminate film, in which it was sandwiched between two polymers layers, the lower one of which, i.e. the one in direct contact with the package interior was gas-permeable, such as polypropylene, and capable of preventing any intermediates entering the package interior. Such laminate structures are not unusual in plastic food packaging and most polymeric materials that are used in this way, such as polypropylene and poly(ethylene terephthalate) are transparent to UVA.

The latter concept is an essential feature of most current commercial oxygen-scavenging polymer systems; indeed, in general all current oxygen-scavenging systems have to be isolated from the contents of the package to ensure no product contamination.

4. Conclusions

TiO_2/EC polymer films, with or without a mild reducing agent such as TEOA, are able to scavenge oxygen upon UVA irradiation. These films can be completely photomineralised upon prolonged illumination. The oxygen-scavenging rates exhibited by these films compare favourably to those associated with more traditional oxygen scavengers. The major drawback of these new, generic polymer film oxygen scavengers is the requirement of light to drive the scavenging process forward. This may prove a particular problem when titania is used as the semiconductor photocatalyst, since it requires UVA light. However, there is a significant level in sunlight (typically $>1\,\mathrm{mW\,cm^{-2}}$) and most very well-lit food cabinets use white fluorescent tubes that emit some UVA light (typically $<0.1\,\mathrm{mW\,cm^{-2}}$). Although the UVA levels in food cabinets are clearly not sufficient to promote the rapid scavenging of oxygen by the TiO_2/EC/TEOA films reported above, recent work on N- and C-doped titania indicates that these materials can readily drive reaction (1) using UV and visible light [11]. However, these materials are not as yet readily available and are still the subject of some controversy. Thus, as an alternative, more well-established and readily available visible-light absorbing semiconductors, such as WO_3 and CdS, could be used instead of TiO_2 to create a range of visible-light driven oxygen-scavenging films. The results reported here demonstrate the efficacy of a novel, generic, light-driven oxygen-scavenger film, which functions via a photocatalytic process, and opens up new possibilities in the important area of oxygen scavenging in packaging and coatings.

References

[1] A.L. Brody, E.R. Strupinsky, L.R. Kline, Active Packaging for Food Applications, Technomic Publishing Co., Lancaster, USA, 2001.
[2] D.T. Sawyer, Oxygen Chemistry, Oxford University Press, New York, USA, 1991.
[3] M. Smolander, E. Hurme, R. Ahvenainen, Trends Food Sci. Technol. 8 (1997) 101.
[4] I. Bucklow, P. Butler, Mater. World 8 (2000) 14.
[5] A. Mills, A. Lepre, Anal. Chem. 69 (1997) 4653.
[6] A. Mills, S. Le Hunte, J. Photochem. Photobiol. A: Chem. 108 (1997) 1.
[7] N.S. Allen, H. Katami, Polymer Degrad. Stab. 52 (1996) 311.
[8] T.J. Kemp, R.A. McIntyre, Prog. React. Kinet. Mech. 26 (2000) 337.
[9] S. Horikoshi, N. Watanabe, M. Mukae, H. Hidaka, N. Serpone, New J. Chem. 25 (2001) 999.
[10] M.L. Hitchman, Measurement of Dissolved Oxygen, J. Wiley, Geneva, 1978.
[11] R. Ashai, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.