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Novel photocatalyst-based colourimetric indicator for oxygen

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ABSTRACT

The preparation and characterisation of a novel, UV-activated solvent-based, colourimetric indicator for O_2 is described, comprising a redox dye (methylene blue, MB), semiconductor photocatalyst (TiO_2), and a sacrificial electron donor (SED), all dispersed/dissolved in a polymer medium (sulfonated polystyrene, SPS). Upon exposure, the indicator is readily photobleached as the MB is converted into its oxygen-sensitive, leuco form, LMB. Unlike its water-based counterpart, the recovery of the original colour is very slow (ca. 5 days cf. 6 min), probably due to the largely hydrophobic nature of the polymer encapsulation medium. The kinetics of film photobleaching appear to fit very well, in terms of: irradiance, [TiO_2] and [MB], to the usual Langmuir-Hinshelwood type equation associated with a photocatalytic process. The glycerol appears not only to function as a SED, but also a plasticizer and medium for dye dissolution. The kinetics of colour recovery of the photobleached film appear directly dependent upon the ambient level of O_2 but shows a more complex dependence upon the relative humidity, RH. The photobleached film does not recover any of its colour over a 24 h period if the RH < 20% at 21 °C but does recover at an increasing rate with increasing RH above 20%. The dye appears to form a very stable, water-insoluble ion-pair moiety with the SPS, so much so that the dye cannot be leached out by immersing the indicator in water. Potential uses of this UV light activated indicator are discussed briefly.

1. Introduction

Oxygen is an essential element for all living organisms; it also plays an important role in many chemical industrial processes, especially where a fine control of oxygen concentration, or the absence of oxygen, is required. Detection of oxygen is therefore important in many technologies, although many of the preferred methods (such as: gas chromatography (GC), mass spectrometry (MS) and electrochemical techniques) require rather expensive equipment and trained operators. Optical oxygen indicators [1], on the other hand, are fast-responding, inexpensive and easy to use. As a result, significant research has been conducted in their development, especially with regards to their use in modified atmosphere packaging (MAP). MAP is a common food-packaging technique in which the oxygen inside the package is either removed, or replaced by an inert gas, such as N_2 or CO_2, to help maintain the freshness of food for longer [2,3]. Research into optical O_2 indicators in MAP has been dominated by luminescence-based indicators, and although several commercial products have emerged [4,5], all are presently still too expensive, both in terms of the indicators and the associated supporting analytical equipment, for routine incorporation in MAPed packages. As a consequence, they remain a useful R&D food-packaging tool. As an alternative, an easy to read, inexpensive, colour-based O_2 indicator would appear a potential ideal quality control device in MAP, as it would provide the necessary assurance that the integrity of the package remained uncompromised during the journey from package to consumer. Some commercial colourimetric oxygen indicators are already on the market, for example Ageless Eye^{TM}, but their retail costs are currently too high (typically 1 Euro ea for Ageless Eye^{TM}) to realistically provide 100% QA for MAP. None of the oxygen colour-based indicators reported to date are irreversible in response and printable as inks [6,7], both of which are additional, desirable features of a quality control optical O_2 indicator for MAP.

Recently this group reported [8] a novel, *water-based* colourimetric O_2 indicator that is UV light activated and comprises: a redox dye, methylene blue (MB), a sacrificial electron donor (SED), glycerol, and a nanoparticulate semiconducting photocatalyst (SC), TiO_2. Unfortunately, because of its water-based nature, this indicator is not suitable for direct printing on most polymer packaging material, which is largely hydrophobic. This paper describes a solvent-based, O_2 indicator which is sufficiently water-proof to allow direct contact with water, without loss of dye, and suitably hydrophobic to allow direct printing on polymer materials commonly used in food packaging such as polypropylene.

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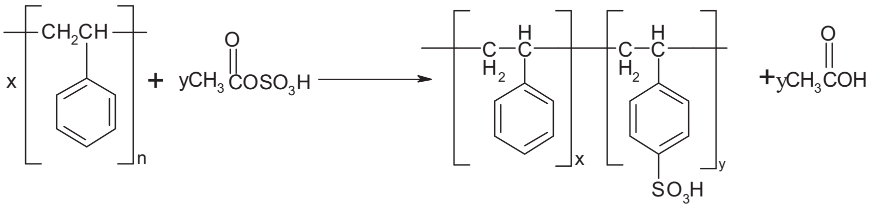

Fig. 1. The reaction scheme of the sulfonation of polystyrene.

2. Experimental

Unless stated otherwise all chemicals were obtained from Aldrich Chemicals and the water used to make up solutions was double-distilled and de-ionised.

2.1. Sulfonation of polystyrene

Previous work by others [9–11] have shown that hydrophobic polystyrene (PS), can be rendered increasingly soluble in polar solvents, by increasing the degree of sulfonation (see Fig. 1). Thus, in this work an acetone-soluble sample of 10% sulfonated PS was prepared according to an establish literature method [12,13], in which 52 g of polystyrene (average molecular weight 250,000, supplied by Acros Organics) were placed in a 3-necked, round-bottomed flask and dissolved in 245 mL of dichloromethane (DCM) through vigorous stirring.

In a separate experiment, a sulfonating agent, acetyl sulfate, was prepared by adding 9.5 mL of acetic anhydride to 50 mL of DCM and the resulting solution then placed under an inert atmosphere of argon and cooled to 0 °C. 3.5 mL of 95% sulfuric acid were added to the DCM/acetic anhydride solution dropwise and then 35 mL of this sulfonation reagent mixture were added to the original polystyrene solution, and the mixture refluxed for 4 h. 50 mL of ethanol were added to the solution after the reflux and the mixture then poured slowly into 1.75 L of boiling water. As the solution was added, the sulfonated polystyrene precipitates rapidly as a white solid. After filtering in air, the precipitate was washed with water several times and dried in an oven at 40 °C overnight. Typically the synthesis, as outlined above, yields ca. 50 g of 10% sulfonated PS (SPS) from 52 g of polystyrene (89% isolated yield).

2.2. Ink preparation

0.25 g of the SPS were weighed into a sample vial and dissolved in 2 g of acetone. To this solution were then added 0.25 g glycerol and, for a standard ink, 0.1 g nanorutile TiO_2 (titanium (IV) oxide, rutile nanopowder, <100 nm particle size, 99.5% trace metals basis). The photocatalyst was dispersed throughout the ink, typically by stirring for 15 min, followed by 30 min sonication. Once complete, 2.5 mg of methylene blue was added and the ink, placed in a stoppered bottle, was stirred for 3 h to ensure all the methylene blue had dissolved. The composition of this typical, acetone-based, oxygen indicating MB/SPS/TiO_2/glycerol film can be summarised as follows: 1/100/40/100 pphr where pphr = parts per hundred resin (where the resin is the SPS). The resulting blue ink is very stable and can be used for at least 6 months without showing any signs of deterioration.

2.3. Ink film preparation

A doctor-blade technique was used to cast the MB/SPS/TiO_2/glycerol ink onto a plastic film, typically polypropylene (Goodfellow, 75 μm) using a K-bar no. 4 to produce an ink film which was ca. 4–5 μm thick when dry. The resulting blue, dry ink film on the plastic substrate showed good adherence and was stable for more than 6 months under ambient, dark conditions.

2.4. Methods

All UV/vis spectra and absorbance data were recorded using a Varian Cary 50 Bio UV–visible spectrophotometer. Unless otherwise stated, films were monitored in a static system under ambient conditions (21 °C, 58% RH). However, when gas was blown over the system, the gases were blended using a Cole Parmer gas-blender, and a constant flow rate of 100 mL/min was maintained.

3. Results and discussion

3.1. Photo-activation step (step 1)

The MB/SPS/TiO_2/glycerol type of colourimetric oxygen indicator relies on UV activation to initiate the detection process by generating electron–hole pairs in the semiconductor photocatalyst (TiO_2 in this case). The sacrificial electron donor (SED = glycerol in this work) then reacts rapidly and irreversibly with the photogenerated holes, leaving the photogenerated electrons to reduce the redox dye, D_{ox} (=methylene blue) to its differently coloured, usually bleached, reduced form, D_{red} (=leuco-methylene blue). Upon reacting with the photogenerated holes, glycerol is itself oxidised; oxidation products could include [14]: glyceraldehyde, 1,3-dihydroxyacetone, formic acid and carbon dioxide. The leuco-methylene blue is O_2-sensitive, so that after UV activation (*i.e.* step 1) the UV activated ink film will remain in its bleached, reduced form in the absence of oxygen, but will have its original colour restored upon exposure to air (via step 2). These processes are summarised in Fig. 2.

Thus a typical MB/SPS/TiO_2/glycerol film is first activated, *i.e.* photobleached, by exposing it to ultraviolet light, which takes less then 60 s when using a 2 × 8 W UVA lamp (irradiance 4.5 mW cm^{-2}). The change in the UV/vis absorption spectrum of the film as a function of irradiation time was monitored by UV/vis spectrophotometry and Fig. 3(a) shows the results of this work. Interestingly, the UV/vis spectrum of the original, unbleached film resembles that of the monomer of MB, with a maximum absorbance

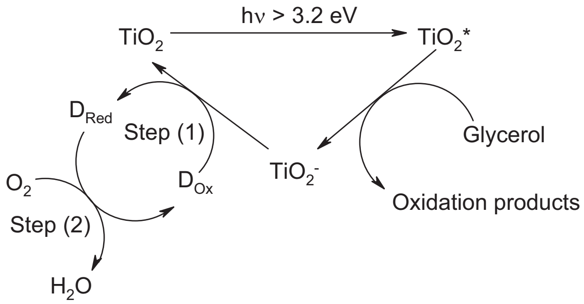

Fig. 2. Mechanism of UV light driven reduction of methylene blue (photoactivation step (1)) and its subsequent re-oxidation by ambient air (if present) (dark step (2)).

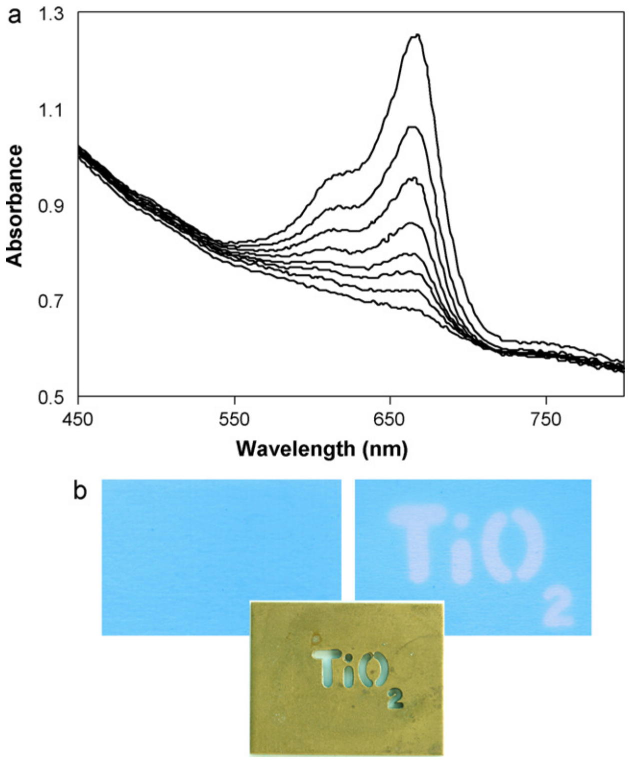

Fig. 3. (a) Plot of UV/vis spectra of a typical MB/SPS/TiO_2/glycerol oxygen-indicating film before and during the UVA light activation (60 s of UVA/4.5 mW cm^{-2}) step (step (1), Fig. 2). The irradiation times are (from top to bottom): 0, 2, 4, 6, 8, 10, 15 and 60 s respectively. (b) Photographs of this film before (left) and after (right) the pulse of UVA light shone through the brass 'TiO_2' mask (middle).

at 665 nm [15], whereas, in contrast, water-based inks generate films in which the MB appears largely to be in the form of its dimer (λ_{max} = 605 nm) [16,17]. These observations are consistent with the fact that MB shows little sign of aggregate formation in non-aqueous solvents [18]. The photographs in Fig. 3(b) show a typical film before and after UVA light activation through a brass 'TiO_2' mask. In the absence of UV light, the photobleached areas regained their original blue colouration within 5 days upon exposure to air. *Note*: this very slow recovery is in striking contrast to that exhibited by its water-based counterpart (where the dark recovery step is complete within 6 min). It is not clear why LMB reacts so slowly with O_2 in a hydrophobic polymeric film; although, such a delay is useful as the indicator could then be used to indicate how long a package has been open, *i.e.* as a 'consume-within' indicator. Such an indicator has some potential in the food packaging industry, as greater attention is given to finding ways to minimise food wastage. A particular problem with regard to the latter is the throwing away of food in opened packages that is still good to eat because of not necessarily warranted concerns regarding freshness. A consume-within indicator would go some way to alleviate these concerns [1] and reduce consumer food waste.

The time needed to fully photobleach a typical MB/SPS/TiO_2/glycerol film was <1 min, which is ca. 3 times faster than that for a similar, water-based indicator, most likely due to the latter's much reduced kinetics for step 2 in Fig. 2; *i.e.* a much reduced rate of response towards O_2.

The initial rate of photobleaching for a typical film was studied as a function of the incident light irradiance and Fig. 4 shows the absorbance at λ_{max} of MB (665 nm) vs. irradiation time profiles for different UVA light irradiances. For most photocatalytic systems, at low irradiances, the initial rate is found to be proportional to the irradiance, I (indicating that electron–hole recombination is not significant) and, at high irradiancies, proportional to $I^{1/2}$ (indicating that recombination is the predominant fate of photogenerated electron–hole pairs) [19]. Often [20], at intermediate irradiances, the initial rate is found to be proportional to I^{Θ}, where $0.5 < \Theta < 1$, and the results of this work is an example of such a case, with $\Theta = 0.57$, as indicated by the insert plot of the data in Fig. 4. For a modest irradiance ($I = 6.5$ mW cm^{-2}) the quantum efficiency of the photobleaching process was calculated to be 2.9%, based on an initial rate of photobleaching at 665 nm of 4.8 absorbance units (au)/min, an assumed molar absorptivity for MB of 84,300 M^{-1} cm^{-1} [21] and a film thickness of ca. 5.0 μm.

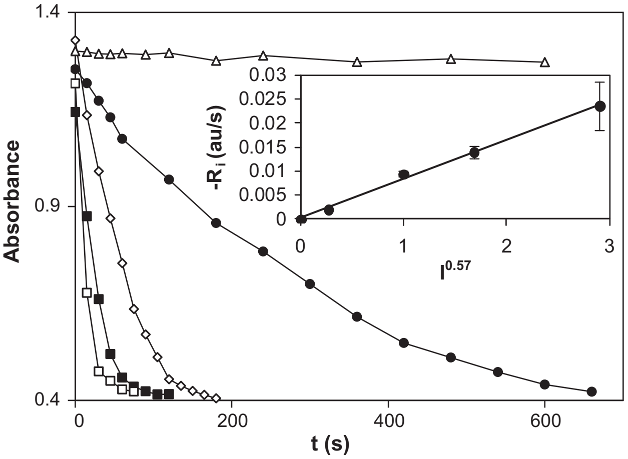

Fig. 4. Absorbance vs. time profiles for a typical O_2 indicator film photobleaching as a function of different UVA irradiances. The irradiances used were: 0 (△), 0.1 (●), 1.0 (◊), 2.5 (■) and 6.5 (□) mW cm^{-2}. The insert shows the initial rate (absorbance units (au)/s) dependence on the irradiance, along with associated error bars.

A study was carried out on the effect of semiconductor photocatalyst concentration in the MB/SPS/TiO_2/glycerol indicator on the rate of film photobleaching, using a series of inks prepared with the following different TiO_2 contents: 0, 4, 7, 10, 20 and 40 pphr. The results of this work are illustrated in Fig. 5 and revealed the initial photobleaching rate to be directly proportional to the amount of TiO_2, which is quite typical of many photocatalytic systems [22]. Further addition of TiO_2 above 40 pphr caused a marked increase in scattering, preventing accurate absorbance measurements.

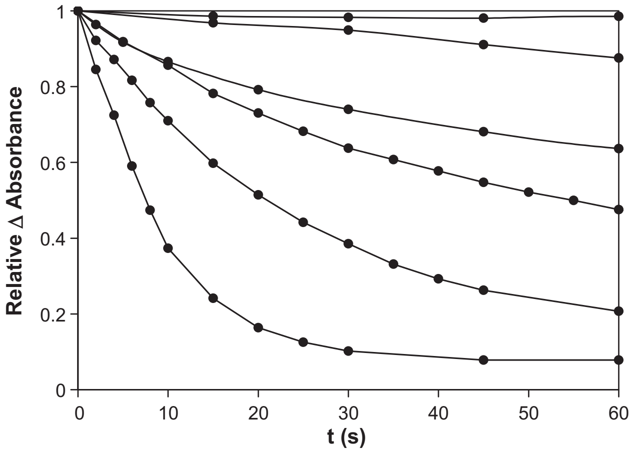

Fig. 5. Relative change in absorbance, ΔAbs, vs. time of UVA photobleaching of a MB/SPS/TiO_2/glycerol film as a function of TiO_2 concentration in the film. The data lines refer to 0, 4, 7, 10, 20 and 40 pphr (top to bottom) of TiO_2 used in the O_2 indicator formulation. The relative Δ Absorbance was calculated via: relΔAbs = $(\mathrm{Abs}_{\lambda_{max}} - \mathrm{Abs}_{\lambda_{800\,nm}})_t/(\mathrm{Abs}_{\lambda_{max}} - \mathrm{Abs}_{\lambda_{800\,nm}})_{t=0}$.

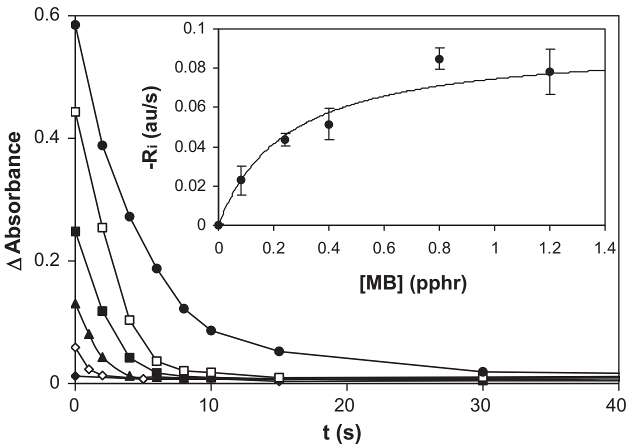

Fig. 6. Plot of ΔAbs vs. the time of irradiation for a typical O_2 indicator film containing different pphr of MB. The covering range: 0 (♦), 0.08 (◊), 0.24 (▲), 0.4 (■), 0.8 (□) and 1.2 (●) pphr of MB. The insert diagram is a subsequent plot of the data in the form of initial rate, r_i vs. [MB], along with associated error bars.

The effect of the variation of the concentration of the sacrificial electron donor, glycerol, used in the MB/SPS/TiO_2/glycerol was also investigated. From the results of this work it was apparent (from the film's initial absorbance, ΔAbs, at λ_{max}(MB) = 665 nm) that the function of glycerol was not just as a source of electrons but also as an aid to dye dissolution. Thus, $\Delta Abs_{t=0}$ decreased with decreasing [glycerol] even though the amount of dye used to formulate the ink was the same each time. Indeed, if no glycerol was used, the film was barely blue and no dye-photobleaching (*i.e.* step 1 in Fig. 2) could be observed! At the high glycerol level (100 pphr) used in this work for a typical MB/SPS/TiO_2/glycerol indicator, most of the MB appeared to be dissolved, since further additions of glycerol had no effect on the initial absorbance of the film.

Finally, the effect of MB concentration used in the film formulation on the kinetics of the photobleaching step was also studied and results of this work are illustrated in Fig. 6. The insert shows that the kinetics are described by a simplified Langmuir-Hinshelwood type equation which is common [23] in semiconductor photocatalysis:

$$r(\mathrm{MB}) = k\frac{K[\mathrm{MB}]}{1 + K[\mathrm{MB}]} \qquad (1)$$

where r(MB) is the rate of photobleaching and k and K are apparent constants.

The shape of the plot illustrated in Fig. 6 is typical of semiconductor photocatalytic reactions carried out in solution and implies Langmuir-Hinshelwood type kinetics also apply in the polymer ink films under study here. An analysis of the data illustrated in the insert diagram in Fig. 6 revealed values of 0.09 absorbance units (au)/s and 4.02 pphr^{-1} for k and K, respectively, for the line of best fit to the data according to Eq. (1).

3.2. *Dark recovery step (step 2)*

As noted earlier, what is most striking about the MB/SPS/TiO_2/glycerol colourimetric O_2 indicator reported here, is the very slow (ca. 5 days) dark recovery step (step 2 in Fig. 2), which, in contrast, takes only 6 min in a water-based version of the ink, as illustrated by the recovery data for the two different films in Fig. 7. In order to gain a better understanding of the cause of this slow recovery step (step (2)), two 10^{-5} M methylene blue solutions were prepared using, respectively, water and acetonitrile as a solvent. Both solutions were purged with nitrogen for 10 min and zinc amalgam (0.5 g into 100 mL of the MB solution) added to reduce the MB to LMB. After the solutions were bleached and the amalgam was filtered off, the recoveries, due to reaction (2), of the original colours of these two solutions were monitored in a spectrophotometer in an open, well-stirred, UV/vis spectrophotometer cell. The rate of recovery in water was found to be 15 times faster than that for acetonitrile. This slower recovery in acetonitrile is even more remarkable given that the molar solubility of oxygen is ca. 9 times higher in acetonitrile than in water [24]! The key reaction associated with this dark, colour recovery, reaction is as follows:

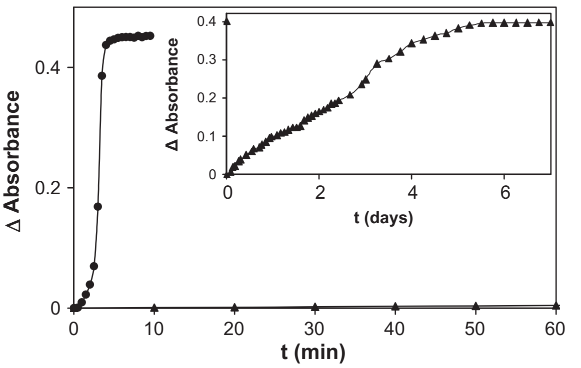

Fig. 7. A comparison of the recovery (step (2), Fig. 2) kinetics exhibited by two different MB-based oxygen indicators, namely, an aqueous-based P25 indicator (●) and the novel acetone-based nanorutile indicator; which recovers in ca. 5 days (▲) as shown in the insert plot.

$$2\mathrm{LMB} + \mathrm{O_2} \rightarrow 2\mathrm{MB^+} + 2\mathrm{OH^-} \qquad (2)$$

Thus, the neutral leuco-methylene blue is oxidised by oxygen to form the original cationic, oxidised form of the dye, MB^+ and OH^-, both of which are charged species. The results of the above work in films and solutions indicates that the kinetics of reaction (2) are much slower in a less hydrophilic medium (such as that of an ink film or in acetonitrile), rather than in an aqueous solution or a water-based ink film, presumably because the reaction products are much less stable, and so more difficult to form, in such a hydrophobic environment. It is not surprising that charge separation is inhibited in a solvent with such a low dielectric constant.

This slow recovery feature opens up new potential uses for this indicator, such as the 'consume-within' indicator, mentioned earlier. It also enhances their potential utilisation in MAP, since there would be less need for maintaining an O_2 free atmosphere during the UV-activation step.

The kinetics of the dark, recovery step (2) appear insensitive to variations in [glycerol] and [TiO_2] as expected given the nature of reaction (2). However, unlike water-based O_2 inks, the recovery of the original blue colour was found to be significantly dependent upon the relative humidity in the ambient gas phase, as illustrated by the results in Fig. 8. As well as acting as the SED in the film, and helping solubilise the dye, it is believed that glycerol acts as a plasticizer by improving gas-diffusion within the film. Thus, the observed increase in dark step recovery time with decreasing RH is possibly due, in part at least, to the improved plasticizing action of the glycerol due to the latter's hygroscopic nature and tendency to become less viscous, and so, more permeable, with increasing RH. However, the increased level of water in the film, due to an increase in RH, could also contribute to the improved kinetics of reaction (2), by stabilising the ionic products. Interestingly, further work showed that the film exhibited no or little recovery at RH < 20% (over 24 h) at 21 °C and this feature opens up the possibility of using the solvent-based indicator as an indirect detector of water vapour for RH values >20% (at 21 °C).

Additional work showed that the rate of the dark film recovery step (step (2), in Fig. 2) is proportional to the $\%O_2$ in the ambient gas phase. Thus, in a series of experiments, nitrogen and oxygen

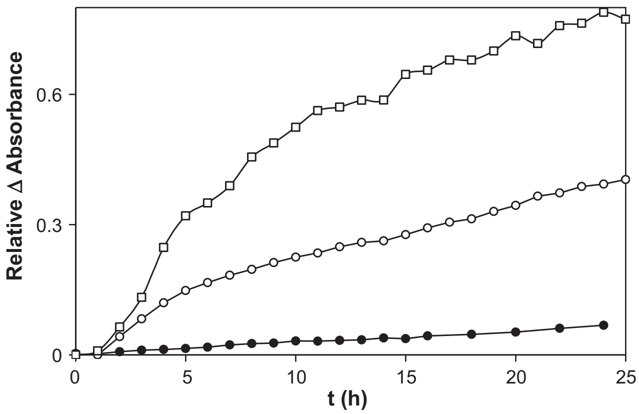

Fig. 8. Plot of the relative absorbance of a typical, photobleached indicator vs. time of recovery, in air at 21 °C, as a function of relative humidity (RH). In this work the humidity was maintained at: 18%, 57% and 96% RH, respectively (bottom to top).

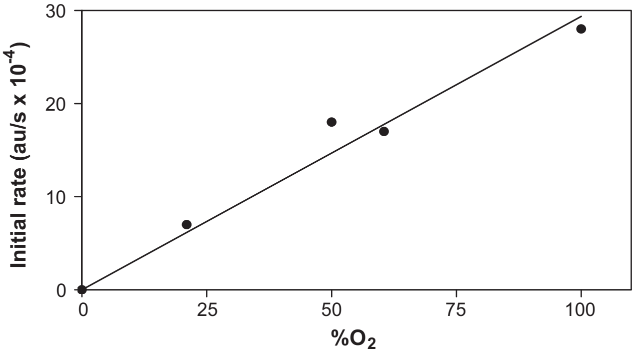

Fig. 9. Plot of initial rate of recovery of a typical photobleached film vs. concentration of oxygen in 100% RH blends of oxygen and nitrogen gas. Associated errors were found to be <2%.

gas were blended to produce O_2/N_2 mixtures of defined %O_2, and then, saturated with water vapour. These were then flowed over a typical, photobleached O_2 indicator and their recoveries monitored spectrophotometrically. A plot of the initial rate of recovery against oxygen concentration revealed a linear dependence as indicated by the results in Fig. 9 and suggested by reaction (2).

A final, significant advantage of the solvent-based O_2 indicator is its striking stability in water. For example, when a *solvent-based* and an *aqueous-based* oxygen indicating film were immersed in water, the dye in the *aqueous-based* indicator was leached out very rapidly (<1 min), whereas the ion-paired MB in the MB/SPS/TiO_2/glycerol film remained contained in the film indefinitely. The water-proof nature of the *solvent-based* oxygen indicator was further tested under water. In this experiment, the film was first bleached and then put in a cell filled with water, purged with a N_2/O_2 mixture with a defined oxygen content, and the recovery monitored with UV/vis spectrophotometer. When this was repeated using different O_2/N_2 mixtures (0%, 21% and 100% O_2) it was found that the recovery in water was about 5 times faster than in 100% RH (at 21 °C) ($t_{1/2} = 1.5$ h compared to ca. 8 h at 21% O_2) and dependent directly upon the dissolved oxygen concentration. Thus, a final further potential application of this solvent-based O_2 indicator is in the measurement of dissolved levels of oxygen in water.

4. Conclusion

A novel, solvent-based, water-proof oxygen indicator that coats on hydrophobic polymers, such as polypropylene, was prepared and characterised. The coloured indicator is readily photobleached but has a slow (5 days) recovery. The kinetics of the latter process are independent of [glycerol] and [TiO_2], but dependent upon RH above a value ca. of 20% at 21 °C; the photobleached film does not recover any of its original colour below this value over a 24 h period. The very slow recovery process makes it possible to use the indicator as a ‘consume-within’ or humidity threshold indicator.

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