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## **Extruded phosphorescence based oxygen sensors for large-scale packaging applications**

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**Key words:** Optical sensors; phosphorescence based oxygen sensors; sensing materials; non-destructive measurement of oxygen; smart packaging;

## **Abstract**

Extruded phosphorescent O<sub>2</sub>-sensitive composite materials comprising cross-linked polystyrene-divinylbenzene (PS-DVB) microspheres impregnated with Pt-benzoporphyrin dye and dispersed in low-density polyethylene (LDPE) or polylactic acid (PLA) carrier polymer are described. The sensors produced by hot melt extrusion method are specifically tailored to large-scale packaging applications and non-destructive measurement of residual O<sub>2</sub> in packaged food products. A panel of LDPE and PLA based sensor materials in the form of extruded pellets and thin film structures were produced and their structural features and O<sub>2</sub> sensing characteristics assessed with the view of packaging applications. The extruded LDPE film sensors were also integrated in packaging materials by heat lamination, to produce 'smart' packaging materials which also protect the sensor from direct contact with food. Analytical performance of extruded sensors was demonstrated by incorporating them in modified atmosphere packaged meat and cheese samples and monitoring residual O<sub>2</sub> levels in these packs non-destructively with a handheld Optech® reader over product shelf life. The extruded O<sub>2</sub> sensors show superiority over the sensors previously used or usable in packaged food products. This technology advances scaled manufacturing of optical O<sub>2</sub> sensors, their integration in packaging platforms and cost reduction.

## 1. Introduction

Detection of molecular oxygen ( $O_2$ ) is of high importance in many areas of human practice, including process control, biomedical and life science research, food and environmental applications [1].  $O_2$  sensors based on phosphorescence quenching provide a versatile platform which can perform many analytical tasks related to  $O_2$  detection [2]. The main advantages of such systems are operation with fully detachable, calibration-free, solid-state sensor elements; real-time, reversible response and no  $O_2$  consumption; possibility of non-invasive, contactless measurements in a sealed vessel; robust and accurate phosphorescence lifetime based sensing with a simple standalone detector that can serve many disposable sensors or samples; low cost [3]. Over the last years, such sensor systems underwent major development and have become useful tools in many research labs, industrial settings and applications [1].

One promising area for optical  $O_2$  sensors is packaging applications, particularly food packaging [4, 5]. Most foods are highly perishable,  $O_2$ -sensitive products, therefore they are normally packed under controlled environment, such as vacuum or modified atmosphere packaging (MAP) [6]. This, in turn, requires analytical systems to control in a non-destructive manner the integrity of such packages and correct  $O_2$  levels inside individual packs [4, 5]. Corresponding ‘smart’ packaging systems integrated with sensors are much needed for the food and packaging industry [7], and the global market for such systems is expected to reach \$26.7bn by 2024 [8]. For this to happen, robust, affordable and mass-produced  $O_2$  sensors, and smart packaging systems integrated with such sensors, need to be developed. Their use on a large scale can ensure high quality

and safety of finished packaged products, minimise potential hazards associated with accidental damage, deterioration and spoilage of packaged foods during their preparation, handling, transportation and storage [4].

However, packaging and food applications impose a number of special requirements on O<sub>2</sub> sensing materials and systems, which include: reproducible and calibration-free operation; high safety and stability (also in direct contact with food) of sensors used on a mass scale and disposable basis; sensor compatibility with common materials and processes used in packaging; ease of sensor integration into packages, massive production volumes (millions and billions of sensors per batch) and minimal costs of finished materials [4]. Several companies are now offering O<sub>2</sub> sensor systems which are generally suitable for packaging applications, with instruments costing 1.5 – 10k \$ and sensors - 4 – 30\$ a piece [4]. While the instruments look rather affordable, the price of individual sensors remains prohibitive. To become viable in mass-scale packaging applications, sensor costs need to be reduced by at least ~2 orders. And their working characteristics and fabrication methods need to be fine-tuned to packaging applications.

Current O<sub>2</sub> sensors are fabricated by the two main methods. One method involves dissolving sensor components (dye and carrier polymer) in an organic solvent, then casting or printing this ‘cocktail’ on a substrate and allowing it to dry and produce solid-state photoluminescent coating [9, 10]. However, this multi-step process induces high mechanical stress within the sensor coating due to large volume reduction upon drying. Another method uses a liquid precursor (e.g. of a sol-gel or silicone rubber with dissolved dye), which is cast on a substrate and allowed to polymerise and solidify and produce a thin film coating [1, 9]. Both processes are complex, relatively slow and

difficult to control and standardise as they depend on many factors. This results in significant batch-to-batch variability, limited scalability and a high cost for the sensors thus produced.

From this prospective, tailoring sensor fabrication processes to those used in packaging, particularly hot melt extrusion and lamination of common polymers, is attractive. Several such systems have been described in recent years. Thus, LDPE blended with hydrophilic silica nanoparticles containing adsorbed pH indicator dye thymol blue was extruded into a 40  $\mu\text{m}$  film to produce a sensor for gaseous and dissolved  $\text{CO}_2$  with robust and selective colorimetric response [11]. A similar fluorescence based  $\text{CO}_2$  sensor used HPTS dye coated on hydrophilic fumed silica particles together with an ion-pairing agent tetrabutylammonium hydroxide which were extruded into a low density polyethylene, i.e. LDPE, film [12]. An extruded plastic film colorimetric sensor for ammonia and volatile amines used bromothymol blue indicator adsorbed on hydrophobic silica nanoparticles, Aerosil®, embedded in LDPE [13]. This approach gave rise to a commercial ‘After Opening Freshness’ indicator for packaged food products offered by Insignia Technologies ([www.insigniatechnologies.com](http://www.insigniatechnologies.com)).

So far, one study on extruded  $\text{O}_2$  sensors was conducted, in which a cationic  $[\text{Ru}(\text{dpp})_3]^{2+}$  luminophore was ion-paired to the surface of anionic P25  $\text{TiO}_2$  nanoparticles (size 21 nm, a mixture of anatase and rutile) in an aqueous solution at pH 11, and then embedded in LDPE in the form of a 40 micron film [14]. However, this dye and sensor have non-optimal spectral characteristics for food packaging [4]. Also surface immobilisation on  $\text{TiO}_2$  nanoparticles produces heterogeneous and moderately

bright sensors, and is not applicable to non-ionic dyes such as Pt-porphyrins. So, extruded sensor technologies require further development.

Here, we describe the production of novel, plastic film phosphorescent O<sub>2</sub> sensor materials produced by hot melt extrusion, in which polystyrene-divinylbenzene (PS-DVB) microparticles, impregnated with a near-infrared O<sub>2</sub>-sensitive dye, Pt(II)-tetrabenzoporphyrin (PtBP), are dispersed in extrudable polymers such as LDPE or biodegradable polylactic acid (PLA). Sensor materials in the form of extruded pellets, thin films and laminated multi-layer structures are described. These extruded sensor materials are characterised for their analytical and O<sub>2</sub> sensing performance, and suitability for food and packaging applications.

## **2. Materials and Methods**

### *2.1. Materials*

The powder of 7 µm PS-DVB particles dyed with PtBP (1% w/w) was kindly provided by Luxcel Biosciences (Cork, Ireland). The linear low-density polyethylene, LDPE, (pellets, **Melt Flow Index**, MFI = 20) was from PW Hall (Glasgow), the PLA, type RXP 7502 (powder, MFI = 6) was from Resinex (Belgium). The 80 micron PET film and 40 micron HDPE film were from Goodfellow Corporation (USA). The O<sub>2</sub> and N<sub>2</sub> gases, 99,99% purity were from Irish Oxygen (Cork, Ireland).

### *2.2. Polymer extrusion and lamination*

8 g of the microparticle sensor powder were mixed with 152 g of LDPE pellets (1:20 or 5% w/w ratio) and then extruded and pelletised twice on a Rondol Microlabs Twin Screw extruder, with operating temperatures of 90, 115, 125, 135 and 125 °C for the feed zone, barrier zones 1–3 and die zone, respectively, and a mixture feed hopper rate of 41 rpm. The extruder screw speed was 80 rpm and the pelletizer speed was 0.5 m/min. The PLA pellets with 5% weight pigmentation were extruded similarly, at operating temperatures 110–125–135 °C for the barrier zones 1–3, respectively, and finally 140 °C for the sheet die. The resulting LDPE and PLA based sensor pellets were then re-extruded as pellets to ensure that the sensor powder was dispersed evenly throughout the LDPE and PLA carrier. The pelleted material was then extruded into ca.  $20 \pm 10 \mu\text{m}$  thick LDPE film and  $50 \pm 6 \mu\text{m}$  dark green PLA film, both having width of approximately 110 mm. These extruded sensor materials were stored in a dark place at room temperature.

Surface and sandwich lamination of LDPE film sensors was performed on a LV250HS office laminator (Rexel, UK) operating at a temperature of 150°C. Sensor pieces were placed on a 10x10cm sheet of PA/PE laminate (PE side), covered with HDPE film (optional), then inserted in the silicone-coated carrier and passed through the laminator.

### *2.3.Characterisation of sensor materials*

Thickness of extruded sensor films was measured with a digital thickness gauge (Kaefer Messuhren, Germany). Their phosphorescence excitation and emission spectra were measured on a Cary Eclipse fluorescence spectrometer (Agilent). Phosphorescence intensity and lifetime signals from the sensors were measured with Optech® Platinum



(Mocon, USA) and Firesting® (PyroScience, Germany) readers, which are tuned for PtBP based sensors [4]. Micro-structure of the PLA and LDPE sensor films was analysed on wide-field (LaVision Biotech, Germany) and confocal (Becker&Hickl, Germany) Phosphorescence Lifetime Imaging Microscopy (PLIM) systems, which are described in detail in [15] and in **Supplementary Information**.

O<sub>2</sub> calibrations were produced using standard O<sub>2</sub>/N<sub>2</sub> gas mixtures generated by a precision gas mixer/tonometer (LNI, Switzerland). Gases from the tonometer were purged through a 20 mL plastic vial with O<sub>2</sub> sensor, submerged in a circulating bath which was set at 10, 20 or 30 °C. At each O<sub>2</sub> concentration (0–100 kPa range), after sample equilibration, phosphorescence lifetime signals were recorded with Firesting® fibre-optic reader, mean values were calculated and used to plot O<sub>2</sub> calibrations and analyse the changes induced by the changing conditions (temperature, humidity, contact with food).

#### *2.4. Experiments with packaged foods*

Pieces of cheddar cheese and fresh beef steak obtained from Lidl (Cork, Ireland) were placed in standard MAP trays (EVOH/PE, O<sub>2</sub> permeability 8–12 cm<sup>3</sup> m<sup>-2</sup> day<sup>-1</sup> at STP). Pieces of the O<sub>2</sub> sensors were adhered with a Scotch tape to the inner side of the lidding material consisting of a 20 µm oriented polypropylene (OPP) and a 50 µm co-extruded PE/EVOH/PE (O<sub>2</sub> permeability 3 cm<sup>3</sup> m<sup>-2</sup> day<sup>-1</sup> at STP, Cryovac/WR Grace, Kriens, Switzerland). The laminate film with attached sensors was then used to heat-seal the trays with cheese and meat samples on a VS 100 BS packaging system (Gustav Muller

and Co., Bad Homburg, Germany). MAP was performed under 32% CO<sub>2</sub> and 68% N<sub>2</sub> (i.e. 0% O<sub>2</sub>) for the cheese samples and under 55% O<sub>2</sub> and 45% N<sub>2</sub> for the beef samples. After this the trays with packaged foods and sensors were stored at 4°C in either upright (sensor exposed to headspace gas) or inverted position (sensor in direct contact with meat/meat juice or fatty cheese). The sensors were measured with an Optech<sup>TM</sup> reader periodically, over 32 days for the cheese samples and over seven days for the meat (typical shelf-life for these products). At the end of the study, packs were opened, sensors removed, washed and analysed for any changes in O<sub>2</sub> calibration.

### **3. Results**

#### *3.1. Design and fabrication of extruded O<sub>2</sub> sensing materials*

Extrusion technologies are used on a large scale in packaging, with various polymers including polyethylene (PE), polypropylene (PP), polyamide (PA), polyethylene terephthalate (PET). Normally, a heat-sealable layer such as PE or PP film, which also have moderate gas permeability, is placed at the inner side, while layer(s) with high gas barrier properties (e.g. PA or PET films) - at the outer side or middle layer of the packaging laminate [16]. Biodegradable polymers are gaining popularity in packaging, with PLA being the most commonly used polymer [17]. For these reasons, the heat-sealable LDPE and the biodegradable PLA were selected as matrices for the fabrication of extruded O<sub>2</sub> sensors.

With regards to the O<sub>2</sub>-sensing component, one approach is to directly disperse the indicator dye (PtBP) in the extruded polymer, so as the latter acts as quenching medium

[18]. This however requires complete dissolution, monomerisation of crystalline dye and its uniform distribution in the extruded polymer, leading to prolonged and rigorous mixing of the melted polymer at elevated temperatures, which may cause thermal degradation. Here the range of usable polymers is limited by dye solubility and quenching by O<sub>2</sub>. Another strategy is to disperse a pre-made particulate sensor material in the extruded polymer. This approach overcomes the issues of solubility and aggregation of indicator dye, its non-optimal quenching in extruded carrier polymer, and also facilitates uniform dispersion of the sensor material. It is worth noting that powder sensor ingredients are commonly used in conventional O<sub>2</sub> sensors, fabricated e.g. by dispersing the particles in gas-permeable binders such as silicone rubber or hydrogel [9]. This second approach was deemed more favourable and was selected for making extruded O<sub>2</sub> sensors.

We used ~7 µm cross-linked PS-DVB particles dyed with PtBP (~1% w/w) as the powder sensor ingredient – the 'smart' O<sub>2</sub>-sensitive pigment. PtBP is a bright NIR-emitting phosphorescent dye, which is widely used in O<sub>2</sub> sensors, in conjunction with many common polymers including polystyrene and its analogs [1,9]. Such sensors are well-suited for packaging applications and compatible with several commercial instruments including Mocon, PyroScience and Presens readers [4]. Importantly, both PS-DVB and PtBP do not melt at temperatures up to 200°C, and withstand extrusion temperatures (140 °C for LDPE and 160 °C for PLA) without marked degradation or melting. Using a laboratory extruder, we produced a panel of materials based on the LDPE or PLA carrier polymers blended with PS-DVB-PtBP sensor particles. Initially, sensor pellets were produced (the 'master batch') and then re-extruded into micrometer

thick sensor films. These sensor materials (see photographs in **Fig. 1**) were then analysed with respect to their O<sub>2</sub> sensing performance in food packaging applications.

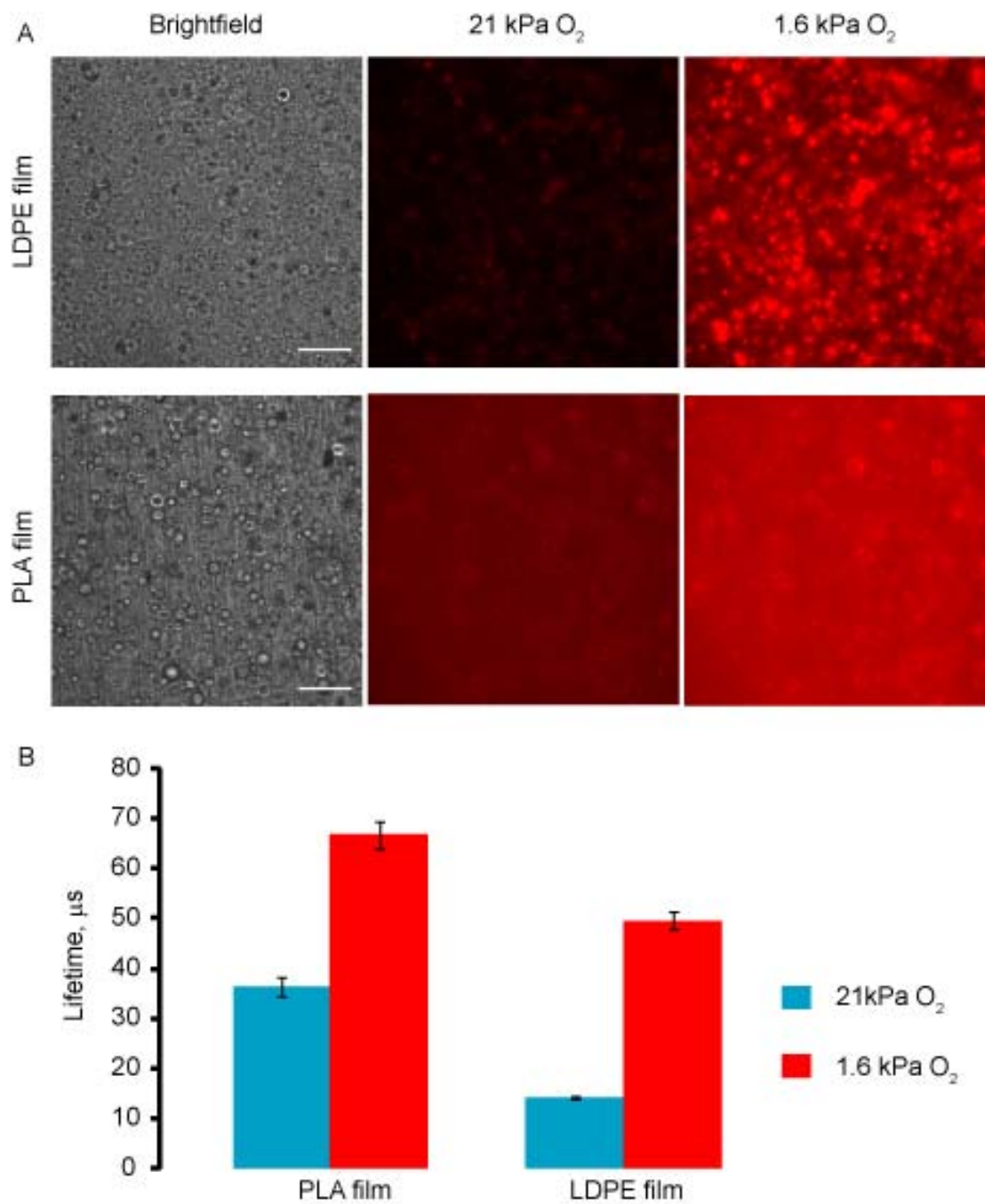


**Fig. 1.** Images of the PS-DVB based sensor powder pigment (1), extruded LDPE sensor pellet masterbatch (2) and final extruded O<sub>2</sub>-sensitive polymer film (3).

### *3.2. Morphological characterisation of the extruded O<sub>2</sub> sensors*

Wide-field transmission and fluorescence microscopy revealed the heterogeneous, micro-particulate structure of LDPE sensor film. This agrees with the anticipated structure of the composite containing two immiscible polymer phases. PS-DVB sensor particles were seen to be distributed rather evenly in LDPE, i.e. without large void areas, giving consistent phosphorescence intensity signals across the film (Fig. 2A). Bright spots correspond to the sensor particles and dark areas – to bulk carrier polymer (LDPE). When changing from 21 kPa to 1.6 kPa O<sub>2</sub>, emission intensity of LDPE sensor film increases markedly and the associated lifetime changed in a reversible manner from 14  $\mu$ s to 49.5  $\mu$ s, respectively, i.e.  $\sim$ 3.5 fold (Fig. 2B). These characteristics are close to those of pure PS-DVB sensor powdered pigment before its blending with LDPE and extrusion (Table 1).

The images of the PLA film showed significantly different patterns, with more homogeneous distribution of the phosphorescence intensity, which poorly correlated with the microparticulated structure of the film (the particles were still clearly visible in transmission mode). Abundant micro-bubbles producing low intensity signals are also clearly seen (Fig. 2A). Importantly, lifetime values for the PLA sensor were significantly higher than for the LDPE, changing from 36  $\mu$ s at 21 kPa to 66  $\mu$ s at 1.6 kPa, i.e. a 1.8-fold change (Fig. 2B). Confocal PLIM with optical Z-sectioning further confirmed the above findings and also revealed the in-depth homogeneity of the extruded sensors (Fig 3A,B). The lifetime values produced by confocal PLIM at 21 kPa O<sub>2</sub> were also similar to those generated by the wide-field PLIM.



**Fig. 2.** Wide-field microscopy of extruded LDPE and PLA based sensor films in dry gas at 23°C. A. Bright field (left panels) and phosphorescence intensity images at 21 kPa and 1.6 kPa of O<sub>2</sub> (middle and right panels), 40x magnification, scale bar - 50 μm. B. Average lifetime values for PLA and LDPE sensor films with standard deviations, calculated from three independent PLIM measurements.

**Table 1.** Phosphorescent signals from extruded sensors, at 23 °C, 21 kPa O<sub>2</sub>.

Sample	Mean Lifetime	Mean Intensity
	Signals, $\mu\text{s}^*$	Signals, RFU
PLA film, 50 micron	$40.14 \pm 0.03$	$4977 \pm 1599$
PLA pellets	$38.44 \pm 0.18$	$9082 \pm 272$
LDPE film, 20 micron	$18.06 \pm 0.27$	$1143 \pm 674$
LDPE pellets	$17.72 \pm 0.09$	$3345 \pm 50$
PS-DVB powder	$17.35 \pm 0.09$	$16737 \pm 468$

\* - average values and S.D. for 10 independent measurements from different areas.

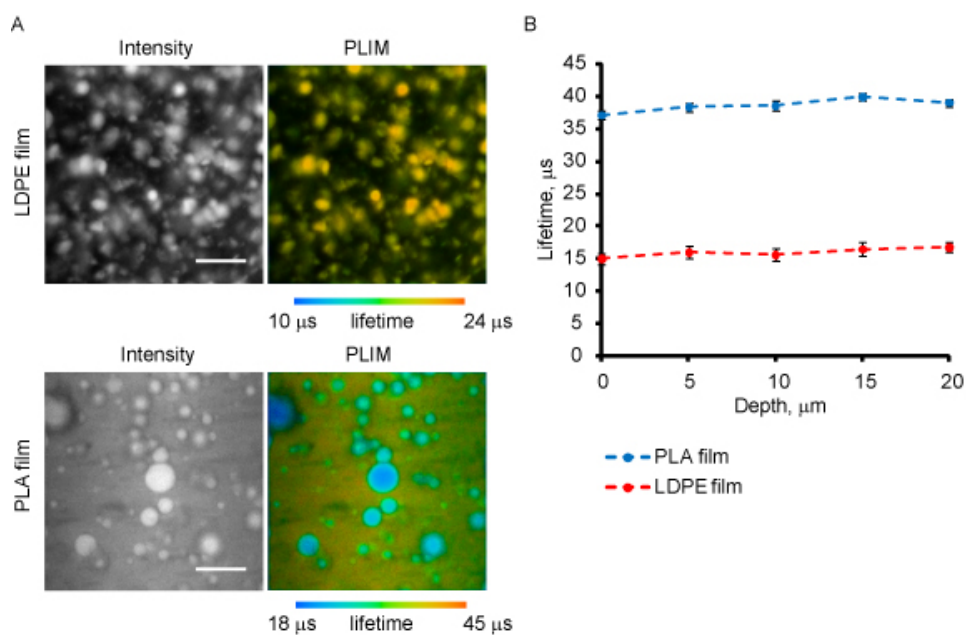


Fig. 3. Confocal microscopy of extruded LDPE and PLA films at 21 kPa O<sub>2</sub>. A. Phosphorescence intensity (left) and lifetime (right) images, 160x magnification, scale bar - 10  $\mu\text{m}$ . B. Average lifetime values for the different optical sections (depth 0 – 20  $\mu\text{m}$ ) of PLA (blue) and LDPE (red) sensor films.

The above results prove that during the extrusion PtBP dye migrated considerably from the PS-DVB phase into bulk PLA, resulting in significantly altered O<sub>2</sub> sensing properties of the extruded sensor. This migration was much less pronounced for LDPE sensors, their lifetime values remained close to those of the PS-DVB powder (Table 1). We explain the different behaviour of the sensor material in PLA and LDPE by: i) much better solubility of PtBP in PLA compared to LDPE; ii) higher extrusion temperature for PLA; iii) dispersion state of the starting material: fine powder for PLA vs large pellets for LDPE.

With respect to general O<sub>2</sub> sensing applications including packaging, high micro-structural heterogeneity and light scattering properties of extruded LDPE and PLA blended with sensor particles are beneficial. Such materials produce brighter phosphorescence intensity signals and are easier to measure with sensor readers which normally interrogate with millimetre-size sensor areas [4]. Indeed, extruded sensor materials measured with an Optech® reader under ambient conditions produced mean lifetime values consistent with microscopy (see Table 1, Fig. 2,3). As expected, the variability of lifetime signals was low, despite the significant variability of intensity signals.

### *3.3. O<sub>2</sub> sensing performance of the extruded sensor materials*

From the sheets of the extruded sensor films individual sensors (~10x10 mm pieces) were cut out and analysed for their sensing performance. Calibration curves were generated using standard gas mixtures (range 0 – 100 kPa of O<sub>2</sub> balanced with N<sub>2</sub>), dry or humidified by bubbling through water, at three temperatures 10, 20 and 30°C. Again,



the two film sensors produced rather different lifetime calibrations (Fig. 4A), with the LDPE showing lower lifetime values and higher sensitivity to O<sub>2</sub> than the PLA. This is consistent with the higher gas permeability of LDPE (and PS-DVB), compared with that of PLA (PLA:  $1.94 \times 10^{-18} \text{ m}^3 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ ; LDPE:  $22 \times 10^{-18} \text{ m}^3 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ )[19].

The activation energy associated with permeability for small molecule gases (such as CO<sub>2</sub>; O<sub>2</sub> and N<sub>2</sub>) diffusion in polymers is typically 50 kJ mol<sup>-1</sup> [20]. Stern-Volmer plots for the two sensor types are close to linear, though small curvature can be seen (Fig. 4B). For the thicker and less O<sub>2</sub>-permeable PLA film, response time to changes in O<sub>2</sub> from zero to 21 kPa was ~5 min (Fig. 4C), which is acceptable for packaging applications. Sensor temperature dependence is flat and close to linear (Fig. 4D), which makes T-compensation of optical readings rather straightforward [21].

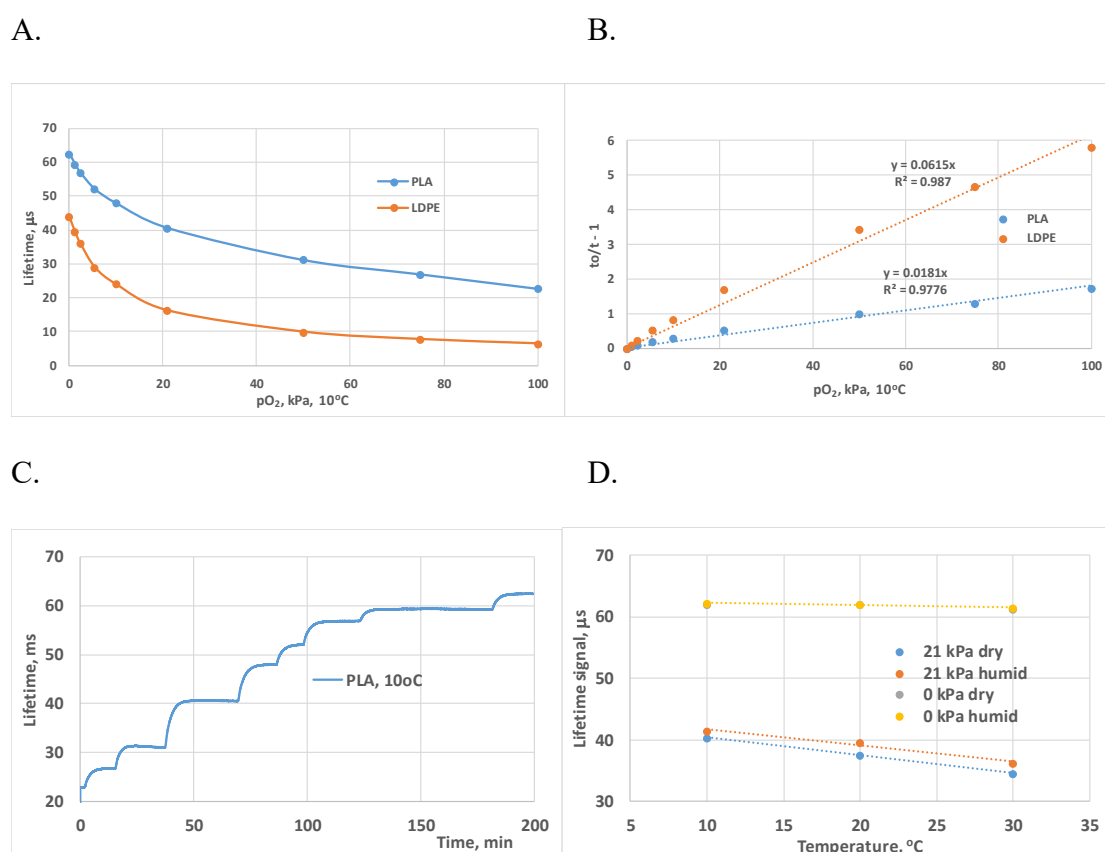


Fig. 4. O<sub>2</sub> sensing characteristics of extruded LDPE and PLA sensor films. Lifetime (A) and Stern-Volmer (B) calibrations, in dry gas at 10°C; C - response of the PLA sensor to changes in pO<sub>2</sub> from 100

to 0 kPa (same points as in the calibration graphs); D – effects of temperature and humidity on the PLA sensor lifetime signals.

### *3.4. Integration of sensors in packaging materials*

Incorporation of O<sub>2</sub> sensors in packaging materials and final packaged products remains challenging, and is still performed manually using customised sensor inserts [22], adhesive stickers or patches [23]. This is not suitable for large-volume applications and raises concerns about potential hazard, safety and regulatory approval for such sensors, especially if they come in direct contact with the food or consumer [4]. From this prospective, heat sealing and lamination of discrete O<sub>2</sub> sensors onto, or inside, the packaging materials is attractive. Therefore, extruded materials can help to automate sensors incorporation in packs and shield them from direct physical contact with food while retaining diffusional contact with sample O<sub>2</sub>. We investigated these options with the new sensors.

Performance-wise, both types of extruded thermoplastic sensor materials look suitable for general O<sub>2</sub> sensing and packaging applications. We selected LDPE sensors, as LDPE is commonly used for heat-sealing, has lower melting temperature and sensor film thickness (to avoid bulges). The PLA sensor films are also heat-sealable, but require more care to reduce formation of mixed polymer phases during lamination, which may alter sensor characteristics. We applied a conventional office laminator to heat-seal pieces of LDPE sensor film onto or between the common polymeric materials used in flexible packaging. The one and two-layer (produces higher intensity signals) LDPE film sensors were heat-sealed directly to the inner PE layer or the PA/PE film

laminate, or sandwiched between the PA/PE and HDPE films. The resulting laminated sensors were tested for their sensing performance.

Fig. 5A and **Supplementary Table S1** show that heat lamination has little, if any, effect on the sensor unquenched and quenched lifetime values. This is also consistent with the comparison of the particulate sensors, extruded LDPE pellets and films (Table 1). O<sub>2</sub> calibrations of laminated LDPE sensor also look normal (Fig. 5B), covering well the most useful 0 – 21 kPa O<sub>2</sub> range (or 0 – 21 % O<sub>2</sub>). Laminated sensors show no sensitivity to humidity (**Supplementary Table S2** and **Fig. S1**), so they should work equally well in the gas and liquid phase, such as MAP, vacuum or skin packaged foods.

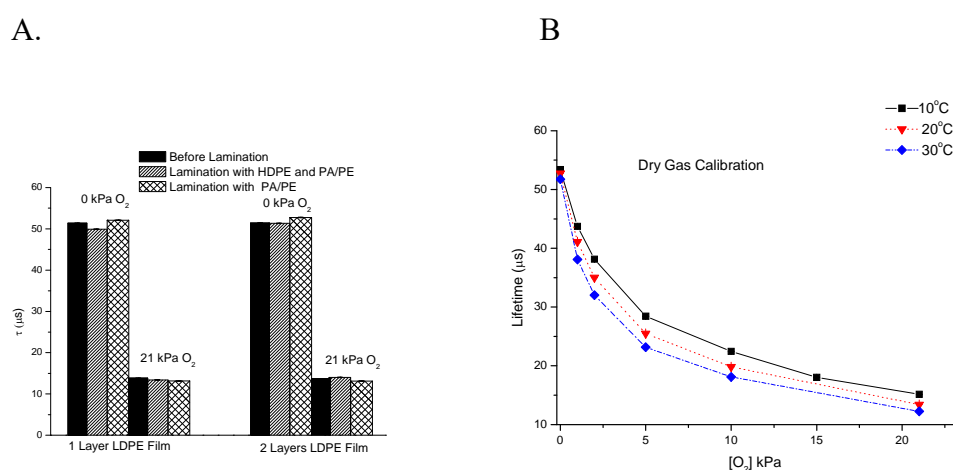


Fig. 5. Effects of heat-lamination on operational performance of LDPE sensors. A. Quenched (21 kPa) and unquenched (0 kPa) lifetimes of the sensor before lamination and after heat-sealing onto PA/PE packaging or between PA/PE and HDPE films. B. O<sub>2</sub> calibrations of the LDPE sensor laminated onto PA/PE film, at different temperatures.

On the other hand, sensor response time increased significantly: from <5 min before lamination to ~10 min after surface lamination on PA/PE and to ~35 min after ‘sandwich’ lamination between the HDPE and PA/PE films. This was expected, due to

the increased sensor thickness and diffusion barrier for O<sub>2</sub> molecules. Nevertheless, such response times are acceptable for packaging applications, which do not require fast-responding sensors, and can be optimised by reducing the film and sensor thickness.

### *3.5. Sensor use in food packs*

To demonstrate their usability and operational performance in real-life applications, extruded LDPE sensors were incorporated in standard MAP food packages. Samples of two different product types – cheddar cheese packaged under low O<sub>2</sub> levels and raw beef meat packaged under high O<sub>2</sub> levels - were prepared on a laboratory packager (see 2.4), and then monitored with an Optech® reader over their shelf life period (32 days and 7 days at 4°C, respectively). Half of the packs were held in upright configuration, so that the sensors were exposed to the headspace (i.e. in fluidic but not direct contact with food), while the other half was inverted, so that the sensors were directly exposed to the fatty cheese or juicy meat. Optech® sensor stickers (Mocon), were also incorporated in the same packs and used as a reference to trace the actual O<sub>2</sub> levels in the headspace of food packs (extensively validated in this application [23]).

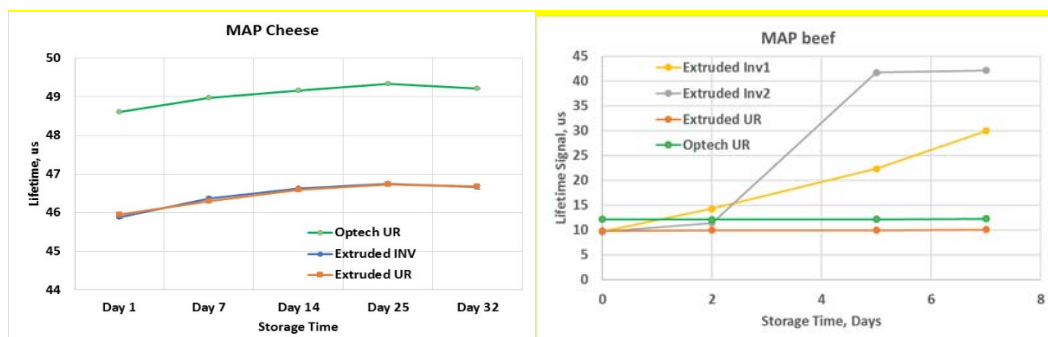
Fig. 6A shows that for the MAP cheese, lifetime signals from the extruded O<sub>2</sub> sensors in upright and inverted packs stayed at high levels and followed exactly the same trend as the Optech sensors (validated for use in direct contact with food [4]). The calibration-free Optech sensor indicated a gradual decrease in headspace level of O<sub>2</sub> in the pack from 0.13% on Day 1 to 0.005 % O<sub>2</sub> on Day 25, and then a small increase to 0.020% O<sub>2</sub> on Day 32 (lifetime readings 48.61µs, 49.33 µs and 49.21 µs, respectively,

measurement accuracy  $\pm 0.02\%$  O<sub>2</sub>). The corresponding lifetimes for the extruded sensors were 45.96  $\mu$ s, 46.73  $\mu$ s and 46.67  $\mu$ s. The difference in lifetime signals between the Optech and extruded sensors is due to the difference in their O<sub>2</sub> calibrations (slightly shifted, similar to Fig. 4A).

For the meat samples, Optech sensor produced low lifetime signals which stayed flat for the whole period, meaning that headspace O<sub>2</sub> concentration stayed high and did not change (Fig. 6B). The extruded sensor in the upright pack (i.e. headspace) showed the same trend, whereas in the inverted pack the two LDPE sensors showed large changes in their lifetime signals over the time. These prominent increases are attributed to growth of aerobic bacteria in the packs, particularly at meat-sensor interface. This process caused gradual depletion of *local* O<sub>2</sub> in this constricted and thin layer of *liquid* (meat juice ‘seals’ the sensor), without affecting much bulk O<sub>2</sub> levels in package headspace. Note that the volume of this sealed *liquid* layer and the amount of O<sub>2</sub> in it are many orders smaller than for the package *gaseous* headspace. The different lifetime and O<sub>2</sub> profiles for the two LDPE sensors in the inverted pack are due to the different microbial load and/or sealing conditions in these sensor areas.

A.

B.



**Fig. 6.** Profiles of sensor lifetime readings in MAP cheese (A) and beef (B) samples, generated over shelf life storage at +4°C: Optech sensors in upright packs (green and blue lines), extruded LDPE sensors in upright (yellow line) and inverted packs (grey and brown lines).

The above results prove that extruded O<sub>2</sub> sensors perform adequately and robustly in food packaging applications, providing useful and relevant information about packaged products and processes occurring in such packs. Measured changes in sensor signal clearly indicate the changes in package conditions or local environment, but not in the sensor itself. Even in unprotected/un-laminated form, sensor analytical performance is unaffected by sample optical properties (meat juice or cheese fat) and by its direct contact with food. After use in food packs such sensors showed no changes in O<sub>2</sub> calibration.

## **Conclusions**

Presented data shows that extruded LDPE and PLA based sensors, both neat and laminated film structures, display stable and predictable sensing characteristics, usable working range of O<sub>2</sub> concentrations, robust and reversible response to O<sub>2</sub>. The sensor dye and PS-DVB particles are effectively embedded in the carrier polymer and shielded from direct contact with food and the consumer. The additional heat sealing process and production of packaging film laminates with built-in sensors make the latter better and safer than the sensor previously used in packaging [4]. Such extruded O<sub>2</sub> sensors and their manufacturing and deposition procedures are compatible with common processes currently used by packaging and food industries, such as extrusion, heat sealing and lamination. The PLA sensor films produced in this study showed high phosphorescent signals, but somewhat lower sensitivity to O<sub>2</sub>, which makes them better suited for products packaged under high O<sub>2</sub> levels up to 100% (e.g. 55% in MAP raw meat). The LDPE sensors have more stable and predictable O<sub>2</sub> sensing characteristics,

they are more common materials for heat-sealing and better suited for packaging at low O<sub>2</sub> conditions (e.g. vacuum packaging or 0 – 21 kPa O<sub>2</sub> range). Compared to existing techniques of O<sub>2</sub> sensor fabrication, extruded sensor technology offers high speed and high volumes of sensor production, low sensor cost and material waste, high stability and reproducibility of individual sensors and batches of sensors, sensor integration in packs capabilities, applicability to various food products, packaging materials and conditions. After their initial fabrication, extruded sensor films and pellets were stored for >3 years at ambient conditions, without any signs of degradation or changes in working characteristics. This initial study opens scope for further development and fine-tuning of extruded O<sub>2</sub> sensors, including optimisation of thickness, brightness, use of other polymers and sensor dyes, up-scaling and production of smart packaging materials for wide practical use.

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