Optical sensing of molecular oxygen

Optical sensing of molecular oxygen is gaining approval in many areas, such as biological research, [1] clinical and medical applications, [2] process control in the chemical industry [3] and in food [4] and pharmaceutical [5] packaging, to name just a few. The best sensor should be stable, robust, easy-to-use and not prone to electrical interferences. [6, 7]

Quenched-luminescence oxygen sensing has attracted a great deal of attention and scientific endeavor in recent years. In particular, solid-state sensors holds many advantages over traditional oxygen sensing techniques like Clarke-type electrodes [8] as they fulfil the above requirements and additionally have a reversible response to oxygen and can measure oxygen non-invasively without being put in contact with the sample. [9] Solid-state sensors usually consist of an indicator dye encapsulated within an oxygen permeable polymer matrix. [6, 10] The properties of the encapsulation matrix used, for instance its dye compatibility, oxygen permeability, wettability and mechanical properties, determine the final sensor operating parameters such as sensitivity and response time. [6] The selectivity of the sensor is dependent on the indicating dye used. Compounds such as ruthenium and iridium compounds have been investigated, [11, 12] however oxygen sensors based on platinum [13] and palladium [14, 15] metalloporphyrins has been the main focus of many research groups in the past. [13]

Polymers with high and moderate oxygen permeability have been used as encapsulation matrices, for instance, polystyrene, placticized polyvinylchloride, polydimethylsiloxane and fluorinated polymers. [6] Many sensors require an additional support material due to the thin-film nature of many dye encapsulation matrices. The support material improves the mechanical properties of the sensor and aids handling and optical measurements. [16] These oxygen sensors are usually produced by solution-based techniques by which the polymer is dried from an organic solvent cocktail, [17] or by polymerization or curing of liquid precursors. [18] Other dye incorporation methods include adsorption, [19] covalent binding, [20] solvent crazing, [21] and polymer swelling methods (REF US). However, as previously shown in a study (REF US), some microporous membranes materials can be used as stand-alone sensor materials as they have sufficient thickness and light-scattering properties in addition to good mechanical properties and reasonably fast response times to oxygen in the gas phase.

Although used in many applications (see above), many current sensor materials, fabrication techniques and polymeric matrixes are unsuited to large-scale applications such as packaging. A sensor for packaging should exhibit high robustness and reproducibility between batches, low cost (less than 1c per cm ^{3}) [6] and be easily incorporated into existing packaging processes. Care should be taken when developing such sensors to limit the number of ingredients in order to limit their overall production costs. [22] To be suitable for food and pharmaceutical packaging applications specifically, the sensor should be non-toxic, [23] easily incorporated into the packaging and provide an adequate shelf-life for the required application. [9] The sensors must also be capable of being mass produced in a continuous basis.

Polyolefins such as polypropylene (PP) and polyethylene (PE) are common polymers which represent over half the total polymers produced in the world. [24] Although the mechanical and gas-permeability properties of PP and PE are capable of oxygen sensing, [25] there are obstacles regarding insolubility in common organic solvents and incompatibility with many oxygen sensing dyes. However, some PE and PP-based oxygen sensors have been created by solvent-crazing, [25] hot polymer extrusion [26] and swelling methods (REF US) that show potential for packaging applications.

Of late, non-woven polyolefin materials have been developed for a range of industrial applications including textiles, membranes, filtration systems [27] and charge separators in Li-ion batteries. [28] These materials are cost-effective, have suitable chemical and thermal stability, gas permeability, uniformity and thicknesses between 20-150 microns. [27, 29] In addition, they are micro-porous, light-scattering and have a large surface area. [28-31] These membranes can also be modified to improve wettability by grafting the surface of the polymer with hydrophilic monofibres. [32, 33]

In this study, we evaluated two types of grafted PP as a matrix for fabrication of O_2 sensors. The polymer membranes selected for this study consists of PP monofibres bound together by the wetlaid and spunbond method into flat flexible sheets. They possess a high surface area, good mechanical and chemical resistance and light-scattering properties. In addition the membranes have been grafted with a hydrophilic surface in order to improve wettability which is beneficial for opto-chemical sensing applications. Therefore, a simple spotting method can be used to incorporate the dye into the membrane. The advantage of this is the membrane doesn't need an extra support matrix and the spotting method can be carried out with readily available commercial equipment when it progresses to upscaling. In addition, due to the size of the discrete spots, consumption of solvents and substrate material is kept to a minimum which lowers production cost.

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