



Phosphorescent oxygen sensors produced from polyolefin fibres by solvent-crazing method



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ABSTRACT

Development of phosphorescent oxygen sensing materials based on commercially available semicrystalline polymer fibres (polyolefins, PP and PE) is described. The Pt-benzoporphyrin dye was incorporated into the nanoporous network of polyolefin fibres formed upon tensile drawing in the presence of physically active liquid environment via the mechanism of solvent crazing. Optimised fibre sensors showed optimal sensitivity to O₂, stable calibration in the range of 0–21 kPa O₂, reversible operation, linear temperature dependence and no significant cross-sensitivity towards humidity. The high surface area to volume ratio of the solvent-crazed polymer fibres enabled relatively bright phosphorescence intensity signals and fast response. Widefield and confocal microscopy combined with lifetime imaging were used to investigate the fine structure, dye distribution and heterogeneity of quenching by O₂ in the solvent-crazed dye-containing polymer fibres.

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1. Introduction

Sensors for molecular oxygen (O₂) based on the quenching of photoluminescent dyes and materials have received increasing attention due to their potential applications in food and pharmaceutical packaging [1–5], biological research [6–8], industrial process control, environmental monitoring and other areas [1]. Solid-state sensors are constructed by incorporating an O₂-sensitive phosphorescent dye into a suitable polymeric matrix, and the response towards O₂ is detected through measurement of the intensity or lifetime signals which are quenched by O₂ [1]. Unlike oxygen electrodes [9], they lack oxygen consumption, are able to monitor O₂ levels in a non-invasive, contact-less manner, and provide accurate quantification of O₂ in gas and liquid phases, fast and reversible response and excellent sensitivity in the low O₂ range [1,2].

Polymeric matrices, such as polystyrene (PS), polysulfone (Psu), silicones, ormosils exhibiting moderate to high O₂ permeability, high chemical and mechanical stability, are widely used to prepare oxygen sensors [1]. Sensor fabrication methods include casting of thin films on a suitable substrate using a cocktail of a dye and a polymer in an organic solvent [10], polymerization and curing of

precursors (e.g., sol–gel, Ormosil) [11,12], covalent coupling of a dye to the polymer [13], incorporation of the dye into micro or nanoparticles, etc. [6,14]. The sensitivity and response dynamics of a sensor are dictated by the O₂ permeability, diffusion rate of O₂ through the polymer matrix, the lifetime of the dye and quenching efficiency.

Polyethylene (PE) and polypropylene (PP) based materials are widely used in packaging and as heat sealable layers [15]. These polymers exhibit moderate O₂ permeability, good chemical and mechanical stability, but their application in O₂ sensing has been limited by poor 'processability' and compatibility with established sensor fabrication technologies and dyes. Recently, solvent (or environmental) crazing of polymers has been suggested for the preparation of O₂ sensors from polymeric substrates, mainly films [16]. This method proved to be universal and allows production of O₂-sensitive materials from various semi-crystalline or glassy polymers. In solvent-crazing, a polymer substrate is subjected to tensile drawing in a physically active solvent at room temperature to a certain tensile strain. Two main modes of solvent crazing are known: the classical one for amorphous glassy polymers and delocalized solvent crazing for semicrystalline polymers [17]. During this procedure, porosity in semicrystalline polymers increases via interlamellar separation and fibrillation, forming a continuous nanoporous network with dimensions of pores and fibrils of ~10 nm [18]. If a phosphorescent O₂-sensitive dye (or other cargo) is dissolved in the crazing-assisting solvent, it gets physically

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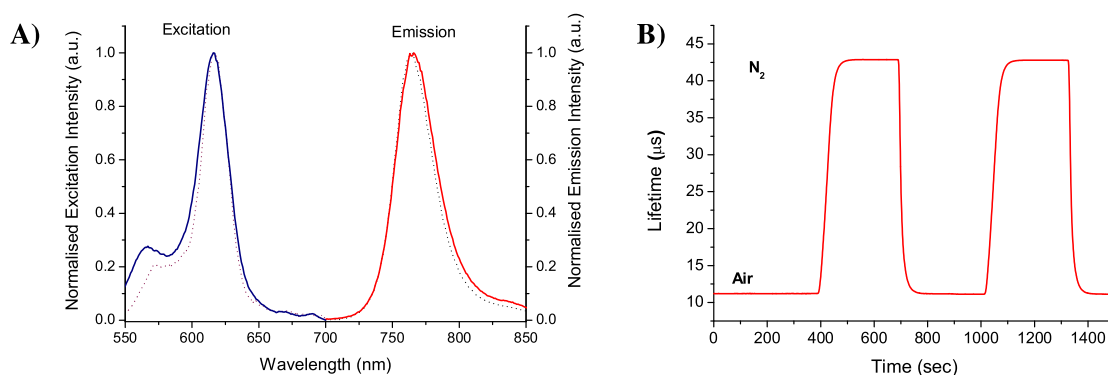


Fig. 1. (A) Excitation and emission spectra of PtBP in solvent-crazed SF3 fibre (solid line) and toluene (dotted line), $\lambda_{ex} = 615$ nm under N_2 atmosphere, (B) reversible response of SF3 at 20 °C.

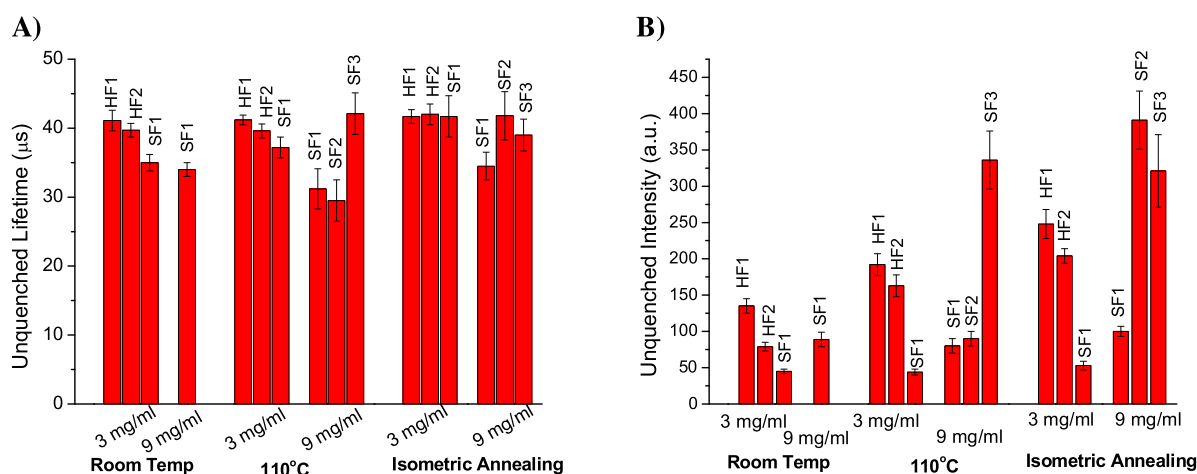


Fig. 2. The effect of post-crazing treatments on the unquenched (a) lifetimes and (b) intensities of various fibers dye concentrations of 3 mg/ml, and 9 mg/ml.

entrapped in the nanopores forming a phosphorescent O_2 -sensitive material. This method was also adapted for the fabrication of discrete O_2 sensor spots from HDPE [19] and PPS films [20,21], coined as “spot or local” crazing. So far, most work on solvent-crazing was performed on commercial polymer films.

In recent years, micro- and nano-sized fibres have been explored with the view of production of sensors for various analytes [22–28]. Such materials display a number of special features (e.g. high sensitivity, fast response, high surface area to volume ratio, porosity, easy access to analytes), which also make them attractive for O_2 sensing applications. Nanofibres produced from polymers with moderate to high O_2 permeability including PS [27,29], biocompatible polymers such as polycaprolactone (PCL) [30] have been fabricated by solution-electrospinning method by applying an electric voltage to droplets of a homogeneous solution of the corresponding polymer in a suitable organic solvent [31,32]. The solution electrospinning method has also been applied to produce core-shell nanofibres using a poly(ether sulfone) (PES) or a polysulfone (PSU) core and polycaprolactone (PCL) shell [26], PDMS (core) and PCL (shell) [28]. The electrospun nanofibres possess very thin diameters (~several hundred nanometers) and display ultrafast response to oxygen, which is advantageous for their applications in biological field (such as monitoring cellular metabolism, tissue engineering, cancer cell research etc) [26,28]. However, large-scale production of nanofibres through this method requires use of large quantity of organic solvent, which can increase the production cost as well as can result in environmental pollution. Despite the wide range of application of solution based electrospinning method for a variety of polymers, use of this method for fabrication of

polyolefin nanofibres at ambient temperature is relatively limited due to low solubility of polyolefins in common organic solvents and their high electrical resistivity [33,34]. Commonly, electrospun polyolefin nanofibres are produced from polymer melt [35,36]. However compared to solution based method, melt electrospinning technique requires additional heating setup and addition of additives and conductive materials to reduce the viscosity of polymer melt and increase the electrical conductance [35,37–39].

In this context, solvent crazing of polyolefin fibre polymers offers a convenient alternative for preparation of nanocomposite O_2 -sensitive materials, involving relatively simpler set-up, less processing steps, lower production cost and compatible with large-scale production. Solvent crazing of fibre substrates was previously studied [40] for PET fibres (a typical glassy polymer) which showed that structural behavior of fibres upon solvent crazing appears to be appreciably different from that of films. Deformation of glassy polymers proceeds via classical crazing and is characterized by the formation of alternating crazes with their specific fibrillar-porous structure that can be loaded with dye, and the dye-free regions of dense bulk polymer. This structure of alternating dyed and undyed regions seems to be less advantageous for sensors as it produces non-uniform dye distribution in the polymer. Moreover, PET by itself is not a good material for O_2 sensors [8]. In contrast, semicrystalline polyolefins prove to be effective matrices for O_2 sensors. Deformation of semicrystalline polymers proceeds via delocalized crazing which, in contrast to classical crazing, provides uniform development of nanopores and porosity via interlamellar separation, thus ensuring uniform distribution of the dye within fibre [18]. To the best of our knowledge, no studies on solvent

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