Oxygen Diffusion in Polymer Films for Luminescence Barometry Applications

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This chapter reviews recent results on the measurement of oxygen diffusion and oxygen permeability in thin polymer film coatings by luminescence quenching experiments. These coatings have the potential to serve as “pressure-sensitive paints” for luminescence barometry applications. We compare results of steady-state measurements with those of pulsed-laser experiments for polydimethylsiloxane (PDMS), a series of commercial silicone resins, and several poly(thionyl-phosphazene) homopolymers (C\textsubscript{n}PATP) and copolymers. In some systems we compare the quenching properties of two different dyes and conclude that the efficiency of quenching by oxygen of platinum octaethylporphine triplets has twice the efficiency as quenching the excited state of tris(diphenylphenanthroline) ruthenium dichloride. Our major interest is the relationship between the polymer structure and oxygen permeation and diffusion in the polymer. When the polymer is crystalline, as in the case of poly(tetramethylene oxide) (PTHF), these properties evolve as the polymer undergoes slow crystallization. In PATP-PTHF block copolymers, microphase separation introduces another level of complexity, since the dye is likely partitioned into both microphases. The block copolymers have the very attractive feature that they exhibit the high permeability of PATP itself, without the surface tackiness of the homopolymer.

12.1 Introduction

This chapter reviews recent results on the measurement of oxygen diffusion and oxygen permeability in thin polymer film coatings that have the potential to serve as “pressure-sensitive paints” for luminescence barometry applications. In this technology, an object is coated with a thin film containing a fluorescent or phosphorescent dye and placed in a wind tunnel. The object is illuminated with light while exposed to flowing air. The dyes in the film are excited by the illumination, but the dye excited states are quenched by oxygen present in the film. Because the concentration of oxygen in the film is related to the partial oxygen pressure at the surface, the extent of quenching provides a measure of the surface air pressure profile across the object. One monitors the fluorescence of the coating with a digital camera. These intensities must then be converted to air pressure at each point on the surface of the object. The object can be an airplane, or airplane part such as a wing or propeller. It can be a turbine blade, or racing car, or even a building or bridge [1].

Engineering aspects of luminescence barometry have received a great deal of attention over the past ten years. Less attention has been paid to problems of design and selection of optimum materials for the pressure sensitive paint itself. The important issues involve the choice of dyes and polymer matrices. There are a variety of materials issues that need to be considered. The dye must resist
photo-decomposition (photobleaching) during use. The polymer must exhibit abrasion resistance when exposed at high velocities to dust that is always present in large volumes of flowing air. Rapid response to pressure changes is essential. One must also have a sufficient understanding of the fundamental principles that connect the air pressure at the surface of the polymer film to the changes in intensity and decay time for the dyes in the matrix. This topic, the connection between changes in air pressure and changes in quenching parameters, particularly as they are affected by the choice of dye and polymer, is the major focus of this review. We begin by considering how the fundamental parameters that describe oxygen transport in polymers are determined. We then consider the use of luminescence quenching experiments on thin polymer films themselves to determine the permeability and diffusivity of oxygen in the films. Finally, we consider the behavior of a number of polymer films and film-dye combinations examined in our laboratory as candidates for pressure-sensitive paints (PSPs).

12.1.1 Measuring Oxygen Transport

The diffusion of oxygen (and other gases) in polymers is most commonly determined by measuring the rate of gas permeation across a membrane [2]. The parameters of interest are the diffusion coefficient $D_{O_2}$, oxygen solubility in the film $S_{O_2}$, and its permeability $P_{O_2}$. These parameters are related through the expression $P_{O_2} = D_{O_2} \times S_{O_2}$. In a membrane diffusion experiment, one measures the gas flux as a function of time. $D_{O_2}$ is determined from the kinetics of the approach of the flux to its steady-state value, and $P_{O_2}$ is calculated from the steady-state flux. These membrane diffusion experiments require freestanding films, and are most convenient for glassy and semi-crystalline polymers. Viscoelastic polymers that flow cannot be examined directly in this way. One has to introduce cross-links to convert the polymer to an elastic film, and an uncertainty is introduced into the measurement. The cross-links have the potential to perturb both the diffusivity and solubility of a gas in the film.

Because oxygen is such a powerful quencher of fluorescence and phosphorescence, there has long been an interest in using oxygen quenching to determine oxygen transport parameters for polymer films [3–6]. In these experiments, one prepares a polymer film containing a luminescence dye, illuminates the film at a wavelength absorbed by the dye, and monitors the emission intensity or emission decay profile as a function of partial pressure of oxygen. To obtain diffusion coefficients, one has to carry out experiments in which the extent of oxygen penetration into the film or efflux from the film is somehow determined. A useful strategy for analyzing these experiments involves developing a model that couples Fick's Laws of diffusion to describe the oxygen transport with Stern-Volmer kinetics [3–7] to describe the quenching process. Early attempts at formulating a proper model did not take account of the spatial concentration profile created as a consequence of diffusion that satisfies Fick's Laws. Mills and Chang [7] were the first to take this concentration profile properly into account; they analyzed numerically the contribution of oxygen diffusion to oxygen quenching experiments in thin polymer film.