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Influence of glycerol on the molecular mobility, oxygen permeability and microstructure of amorphous zein films

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ABSTRACT

The effects of glycerol on molecular mobility, oxygen diffusion and microstructure in amorphous zein matrix were studied using phosphorescence and atomic force microscopy (AFM). Films containing various amounts of glycerol (0, 5, 10, 20 and 30 wt%) were cast from solutions of 0.5% (w/v) zein in 70% ethanol/water (v/v). Erythrosin B (Ery B) phosphorescence was used to monitor the molecular mobility of these matrices over the temperature range from 0 to 100 °C. Analysis of Ery B emission peak frequency and bandwidth and intensity decay provided information about thermally-activated modes of molecular mobility in the matrices. Dipolar relaxation around the triplet state of Ery B was weakened and the extent of relaxation was decreased at low concentration glycerol (≤10%), indicating a role as anti-plasticizer. The rate of non-radiative decay from the Ery B triplet state indicated that glycerol only performed as a plasticizer and increased the local mobility of the zein matrix at and above ~20 wt %, while in films with glycerol at ≤20 wt % the local mobility remained nearly constant or only slightly increased compared with pure zein. Though transitioning from antiplasticizer to plasticizer at higher content, glycerol dramatically suppressed the oxygen permeability of the film in the whole concentration range tested. AFM images indicated that glycerol induced aggregation of zein complexes. These results indicate how the addition of glycerol to zein films could affect the physical properties, structure and thus functional properties in ways that influence their eventual use.

1. Introduction

Environmental concerns about the use of nondegradable plastics for packaging and disposable consumer goods have led to intensified research on the development of biodegradable packaging materials (Zhao, Torley, & Halley, 2008). Edible, biodegradable films and coatings, by acting as barriers to control the transfer of moisture, oxygen, carbon dioxide, lipids, and flavor components, can prevent quality deterioration and increase the shelf-life of food products (Ghanbarzadeh & Oromiehi, 2009; Naushad Emmambux & Stading, 2007). In addition, edible films or coatings may provide mechanical integrity and improve the handling characteristics of the food. They can be effective carriers of many functional ingredients, such as antimicrobial agents to improve safety and stability of foods (Byun, Kim, & Scott, 2010), antioxidants to prevent lipid oxidation (Liang & Ludescher, 2010), and flavorings and pigments to improve quality of foods (Soares & Hotchkiss, 1998).

Zein, the prolamine from maize seeds, has been extensively investigated as a commercial material for edible packaging because of its thermoplastic properties and excellent film-forming behavior (Lawton, 2002; Sanchez-Grarcia, Hilliou & Lagaron, 2010; Subramanian & Sampath, 2007; Tihminlioglu, Atik, & Özen, 2011). Zein is used in the formulation of coatings for nuts, confectioneries, and pharmaceutical tablets. Preparation of zein films generally involves casting alcohol or acetone solutions on inert and flat surfaces. The formed films can be peeled off after the solvent is evaporated (Lai & Padua, 1997). Zein films are brittle and, thus, plasticizers are usually needed to improve their flexibility. Glycerol is one of the most important plasticizers and is widely used in zein films.

The effects of glycerol on the physical properties of polymer matrices have also been extensively studied. Low-molecular weight compounds or diluents, acting as external plasticizers, are an integral part of polymeric systems. They serve to increase the flexibility and workability of the otherwise rigid neat polymers. However, they may serve as mechanical antiplasticizers when present at low concentrations, resulting instead in stiffer polymer –

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diluent blends than the neat polymer. The phenomena that glycerol can act as both a plasticizer and an antiplasticizer are well-known and have received increasing attention from food scientists and technologists in recent years (Chang, Karim & Seow, 2006). It has been reported that glycerol can exert different effects depending on its concentration. Lourdin and colleagues reported that glycerol at a content below 12% could increase the ductility of potato starch film. However, the ductility decreased when the amount of glycerol exceeded 12% (Lourdin, Bizot, & Colonna, 1997). A similar antiplasticizing effect of glycerol was also found in the matrices of trehalose and maltodextrin (Anopchenko, Psurek, VanderHart, & Obrzut, 2006; Roussenova, Murith, Alam & Ubbink, 2010). In most cases, there exists a critical glycerol content that marks the onset of a change in functionality from antiplasticizer to plasticizer. Those conclusions, however, were typically obtained from macroscopic methods like DSC and film stress analysis, while rarely depending upon molecular techniques such as positron annihilation lifetime spectroscopy. In the microscale point of view, data concerning how glycerol can affect the molecular mobility that underlies matrix functionality, as far as we know, are rare.

Gas permeability is an important property of edible biopolymeric film systems. The ease with which mass transfer can occur across a film ultimately determines its value as a gas barrier. Oxygen is responsible for many of the degradative processes that limit the shelf life of foods, and its exclusion or reduction in a food's internal environment is critical. Oxygen permeability (P) can be related to its diffusion coefficient (D) and solubility (S) in a particular material by the equation $P = DS$ (Crank & Park, 1968). Glycerol can affect the oxygen permeability in the zein matrix in two distinct ways: (1) modulate the oxygen diffusion coefficient (D) by changing the matrix mobility as a plasticizer/antiplasticizer, and (2) lower the oxygen solubility (S) in the zein matrix (Liang & Ludescher, 2012).

Phosphorescence probe techniques have been shown to provide detailed information about correlations among local molecular mobility, dynamic heterogeneity, and oxygen permeability in amorphous solid biomaterials (Nack & Ludescher, 2006; Subramanian & Sampath, 2007; Sundaresan & Ludescher, 2008). In this study we have used phosphorescence of Erythrosin B (Ery B), a triplet state molecular probe, to monitor the local molecular properties and mobility of amorphous zein/glycerol films cast from 70% ethanol aqueous solution. Measurements of the Ery B emission energy and excited-state lifetime provide information about how glycerol influences the local molecular mobility of the matrix. Comparison of the phosphorescence lifetime in the presence and absence of air was used to monitor the oxygen permeability. Microstructural changes in the zein film were also determined by atomic force microscopy (AFM). This research provides insight into the molecular mechanism by which glycerol modulates the physical and functional properties of edible polymer barriers, information that can help improve our ability to engineer edible food films with appropriate functionalities.

2. Materials and methods

2.1. Sample preparation

Amorphous zein films were prepared by using our published method with slight modification (Liang & Ludescher, 2011). α-Zein (Biochemical-grade, Wako Pure Chemical Industries, Ltd., Tokyo, Japan) was added to 70% (v/v) ethanol in water solution to reach a final concentration of 0.5% (w/v). Glycerol (99% GC pure; Sigma Chemical, St. Louis, MO) was added to zein solution to obtain the final contents of 0, 5, 10, 20 and 30 percent in dry zein-glycerol films. Ery B (sodium salt, Sigma Chemical, St. Louis, MO) was dissolved in deionized water to prepare 10 mM probe stock solution; aliquots from this solution were added to the zein solution to make sample solutions with probe/zein mole ratio of about 3:20 (assuming a molecular weight 2×10^4 g/mol for zein).

To prepare zein films for luminescence measurements, 15 μl of protein/probe/glycerol solution at room temperature was spread on approximately one third of a quartz slide (30 × 13.5 × 0.6 mm, custom made by NSG Precision Cells, Farmingdale, NY). Before usage, the slides were soaked in Terg-A-Zyme (Alconox, Inc., NY) soap solution for > 24 h to remove surface impurities, washed with deionized water, rinsed with ethanol and dried with acetone. The sample slides were stored at room temperature against the desiccants DrieRite and P_2O_5, in order to maintain 0% RH, for at least one week and protected from light to prevent any photobleaching of Ery B. The desiccants were refreshed as necessary.

For AFM experiments, films were prepared using the same method used to prepare slides for luminescence except that the sample solutions were spread on mica chips (around 0.5 cm × 0.5 cm).

2.2. Phosphorescence measurements and analysis

All measurements were conducted on a Cary Eclipse spectrophotometer (Varian Instruments, Walnut Creek, CA) equipped with a temperature controller and multicell holder. All measurements were made at least in triplicate and the slides were first heated and cooled and then data were collected from 0 to 100 °C in all experiments.

High purity nitrogen (minus O_2) or dry air (plus O_2) was flowed directly into capped quartz fluorescence cuvettes holding the slides. The cuvette was flushed for at least 30 min at 50 °C before each set of measurements. The cuvette was capped with a lid having inlet and outlet ports for the gas line, so all experiments were performed at constant pressure. Each phosphorescence intensity decay was an average of 50 cycles. For each cycle, data were collected from a single lamp flash with a delay of 0.04 ms, a 0.05 ms gate, and 10.0 ms total decay time. Phosphorescence and delayed fluorescence emission scans were collected over the range from 540 to 800 nm with an excitation wavelength of 520 nm. The excitation and emission monochromators were both set at 20 nm band pass. For phosphorescence emission scans, each data point (collected at 1 nm intervals with a 0.1 s averaging time) was collected from a single flash with 0.2 ms delay and 5 ms gate time.

For lifetime measurements, because intensity decays were non-exponential, a stretched exponential function was selected to analyze the intensity decays:

$$I\left(t\right) = I\left(0\right)\exp\left[-\left(t/\tau\right)^{\beta}\right] + \text{constant} \tag{1}$$

where $I(0)$ is the initial intensity, τ is the stretched exponential lifetime, and β is an exponent varying from 0 to 1 that characterizes the lifetime distribution. The use of a stretched exponential model provides an analysis in terms of a continuous distribution of lifetimes, which is appropriate for describing a complex glass possessing a distribution of relaxation times for dynamic molecular processes. The smaller the β value, the more non-exponential the intensity decays and the broader the distribution of lifetimes (You & Ludescher, 2009).

The energy of the emission maximum (ν_P) and the full-width-at-half maximum (FWHM) of the emission band were determined by using a log-normal line shape function,

$$I(\nu) = I_0 \exp\left\{-\ln\left(2\right)\left(\frac{\ln\left[1+2b\left(\nu-\nu_P\right)/\Delta\right]}{b}\right)^2\right\} \tag{2}$$

where I_0 is the maximum emission intensity, ν_P is the peak frequency (cm^{-1}), Δ is a linewidth parameter, and b is an asymmetry parameter. The bandwidth Γ (FWHM) is calculated according to the following equation: