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Influence of antioxidant structure on local molecular mobility in amorphous sucrose

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ABSTRACT

The effect of the antioxidants gallic acid and methyl, propyl, and octyl gallate on the molecular mobility and hydrogen bond network in amorphous sucrose was studied. Solid amorphous sucrose films with and without the addition of antioxidants at a mole ratio of 1:5 (antioxidant/sucrose) were cast from solution onto quartz slides. Local molecular mobility from 0 to 70 °C was measured using tryptophan amino acid as a luminescent probe dispersed in the films. Phosphorescence from the tryptophan probe provides spectroscopic characteristics—emission spectrum and lifetime—that are sensitive to changes in molecular mobility induced by the addition of antioxidants. Local molecular mobility detected by tryptophan increased in the following order: sucrose < sucrose–octyl gallate < sucrose–propyl gallate ⩽ sucrose–methyl gallate ⩽ sucrose–gallic acid. The antioxidants also modulated the activation energy for matrix motions that quench the tryptophan phosphorescence in a structure-dependent manner. IR measurements as a function of temperature indicated that hydrogen bond strength in these amorphous films followed a rank order (sucrose–methyl gallate > sucrose–gallic acid > sucrose–propyl gallate > sucrose > sucrose–octyl gallate) that was nearly the reverse of that seen in matrix mobility. Analysis of the differential effects of the antioxidants suggests that the presence of the hydroxyl benzoyl head group increased matrix molecular mobility and hydrogen bond strength while the saturated carbon chain decreased mobility and bond strength. The influence of the carboxyl group on matrix properties was comparable to that of the formyloxy group. These results indicate that the addition of specific functional ingredients such as antioxidants may significantly affect the physical properties and consequently functional properties of amorphous edible films in ways that might condition their use. The observed changes are closely related to the chemical structure of the added species.

1. Introduction

The shelf life of a food product depends upon maintaining sensory, nutritional, and safety (microbiological and toxicological) attributes throughout production, storage, and commercialization.[1] Food products are typically developed to address consumer demand for convenience, appearance, and storage stability. Lipid oxidation, one of the main causes for food deterioration during storage, occurs in oil-containing foods when lipid molecules, activated by a catalyzing agent such as heat, light, the presence of metal ions, or other factors,[2–4] react with molecular oxygen to form a highly reactive species (endoperoxide radical, hydroperoxide, etc.). These peroxides break down to a variety of organic compounds, including alcohols, aldehydes, ketones, and acids, resulting in the off odors and flavors often associated with rancidity.[5] Antioxidants are thus commonly added to foods to prevent or delay lipid oxidation.

Lipid oxidation in solid foods normally starts from the surface of the product. The oxygen diffuses into the interior of the food and lipid oxidation subsequently propagates throughout the product. Antioxidants incorporated throughout a food matrix are less efficient in controlling oxidation.[6–8] It is possible to limit surface lipid oxidation by selectively applying an antioxidant at food surfaces. However, this possibility presents technological difficulties. Systems are thus needed that can carry and protect the antioxidant until application and appropriate methodologies need to be tested to adequately and evenly deliver the antioxidant onto the food surface.

Food packaging is a standard requirement for commercialization. It is thus possible to delay or prevent lipid oxidation on food surfaces using packaging that directly incorporates antioxidants or adding an edible coating material containing antioxidants. Sweetened food products such as cereals, cookies, pastries, snack foods, nuts, or roasted nuts and candies often include a thick sugar coating. Such a surface coating will not only provide sweetening but may also act as a functional layer that protects the food from physical, chemical, biological, and environmental damage resulting

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from shear, oxygen, moisture, light, or microbial contamination.[9] Sucrose is one of the most widely used disaccharides in coatings for long-term storage due to its propensity to form an amorphous, non-crystalline solid by rapid drying from aqueous solution or cooling from a melt and, as a non-reducing sugar, its low reactivity with amino acids in Maillard browning.[10] Thus, coatings of sucrose or sucrose derivatives containing antioxidants may provide a promising freshness-retaining tool to the food industry particularly for cereal mixes, nuts, and flakes.[11]

The performance of antioxidants in packaging or coating films is highly influenced by the physical properties of the primarily amorphous matrix.[12–14] The importance of molecular mobility in the stability of amorphous solid foods and other biomaterials is widely recognized. Physical processes such as molecular diffusion[15] and crystallization[16] are directly modulated by molecular mobility. Despite extensive research on the potential usage and performance of antioxidants in edible films, data on the effect of antioxidants on the film's matrix mobility have been rarely reported. In a previous study on the effect of propyl gallate and octyl gallate on zein films,[17] we have shown that the addition of specific functional ingredients such as antioxidants may significantly modify the physical properties, structure, and thus functional properties in a manner that will affect the applicability of the films for commercial use. Since antioxidants have low molecular weight they have the potential of behaving as plasticizers in films. Polar and hydrophobic groups of the antioxidant can affect the formation of the hydrogen bond network, directly influencing the molecular mobility of the matrix and thus the coating's stability and the release rate of the incorporated antioxidants into the food. This work specifically investigates how the structure of antioxidants modulates the material properties of an amorphous sucrose matrix.

Gallic acid, methyl gallate, propyl gallate, and octyl gallate (Fig. 1) are four important antioxidants widely used in keeping food fresh and preventing lipid oxidation. They possess identical hydroxyl benzoyl head groups and differ only in the presence of and length of alkyl groups esterified to the carboxyl group. The hydroxyl benzoyl head group, carboxyl group, and the hydrocarbon chain will interact differently with the hydroxyls in the sugar film, although all groups should contribute to the overall plasticizing effect. The hydroxyl benzoyl and the carboxyl groups can form hydrogen bonds with the hydroxyl groups in the sugar matrix and consequently they will become intercalated into the hydrogen bond network, changing its structure and continuity. On the other hand, the alkyl chains can prevent the formation of hydrogen bonds by steric interference. The different number of methylene groups in the methyl, propyl, and octyl chains may also contribute to distinctive behavior and mobility of the films. Previous work on zein films indicates that the hydroxyl benzoyl head group and the saturated carbon chains act in distinct ways on the film properties. While the presence of the hydroxyl benzoyl group increases zein matrix mobility, the saturated carbon chains affect the aggregation of the zein complex, thus increasing oxygen permeability within the zein films.[17]

Phosphorescence techniques have been shown to provide detailed information about interrelations among local molecular mobility, dynamic heterogeneity, and oxygen permeability in amorphous solid biomaterials.[18–22] In this study we have monitored the phosphorescence of tryptophan, a triplet state molecular probe, to assess the local molecular properties and mobility of sucrose films containing gallate-based antioxidants. Measurements of the tryptophan excited-state lifetime provide information about how the gallate derivatives influence matrix mobility. Samples under the same conditions were also measured by FTIR to monitor hydrogen bonding network integrity. By studying the relation between mobility and hydrogen bond network strength, we can better understand the molecular mechanisms by which antioxidants modulate the physical and functional properties of edible barriers; such insights should improve our ability to engineer edible food films with the desired antioxidant functionality.

2. Results and discussion

2.1. Tryptophan phosphorescence in sucrose-based films

The usefulness of tryptophan phosphorescence in this study depends on the sensitivity of the phosphorescence emission spectrum and decay to the local molecular properties of the sucrose-based films. To show the tryptophan sensitivity to differences in film properties, tryptophan phosphorescence spectra, and decay in sucrose and sucrose–gallate derivatives films are compared in Figure 2.

The phosphorescence spectrum of tryptophan in all sucrose-based matrices showed a single peak which shifted as the matrix composition changed. The phosphorescence peak energy, a measure of average energy of emission, has been related to the polarity[23] and flexibility[24] of the indole side chain environment in proteins. In the solid sugar films, the matrix mobility in sucrose will be influenced by the structure of the additives (gallate derivatives). At 25 °C, the phosphorescence peak frequency (Fig. 2A) followed the rank order of sucrose < sucrose–octyl gallate < sucrose–propyl gallate ⩽ sucrose–methyl gallate ⩽ sucrose–gallic acid. In protein matrices of comparable albeit more heterogeneous polarity, lower emission energy reflects an increase in the matrix flexibility around Trp.[24] Thus, the emission data suggest that the mobility in these matrices followed the same rank order.

The tryptophan phosphorescence decay at 20 °C was relatively long lived in the dry sucrose films, decaying over a time scale ranging from 10 to 0.5 s depending on matrix composition (Fig. 2B). The tryptophan lifetimes in these samples were unaffected by ambient oxygen (determined from data collected from films equilibrated against dry air) indicating that oxygen could not significantly

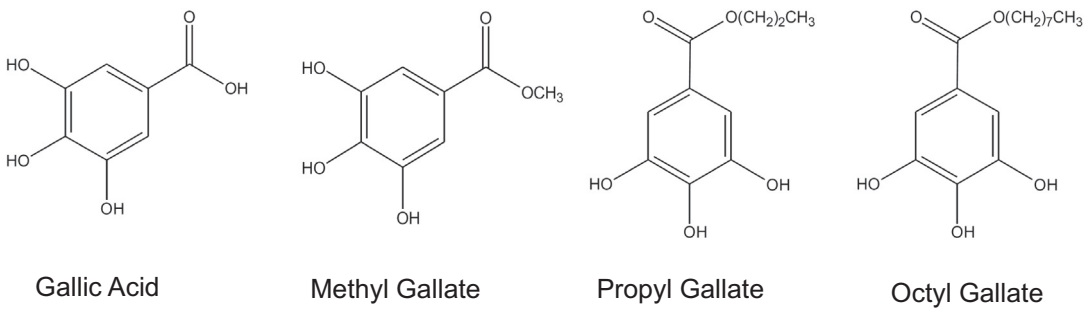

Figure 1. Chemical structure of the gallate antioxidants.