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Iron chelating active packaging: Influence of competing ions and pH value on effectiveness of soluble and immobilized hydroxamate chelators

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ABSTRACT

Many packaged foods utilize synthetic chelators (e.g. ethylenediaminetetraacetic acid, EDTA) to inhibit iron-promoted oxidation or microbial growth which would result in quality loss. To address consumer demands for all natural products, we have previously developed a *non-migratory* iron chelating active packaging material by covalent immobilization of polyhydroxamate and demonstrated its efficacy in delaying lipid oxidation. Herein, we demonstrate the ability of this hydroxamate-functionalized iron chelating active packaging to retain iron chelating capacity; even in the presence of competing ions common in food. Both immobilized and soluble hydroxamate chelators retained iron chelating capacity in the presence of calcium, magnesium, and sodium competing ions, although at pH 5.0 the presence of calcium reduced immobilized hydroxamate iron chelation. A strong correlation was found between colorimetric and mass spectral analysis of iron chelation by the chelating packaging material. Such chelating active packaging may support reducing additive use in product formulations, while retaining quality and shelf life.

1. Introduction

In foods, beverages, and consumer products, the presence of even trace concentrations of transition metals (e.g. Fe, Cu) can cause degradative reactions and support microbial growth which leads to unacceptable changes in product quality. Lipid oxidation, natural color degradation, and nutrient loss are examples of such degradative reactions that ultimately lead to product loss (Goddard, McClements, & Decker, 2012). To inhibit such metal promoted degradation reactions, synthetic chelators (e.g. ethylenediaminetetraacetic acid, EDTA) are commonly incorporated into products (Hart, 1985). However, as consumers are increasingly demanding products free of synthetic additives in the food and consumer products industries, alternative technologies are needed. Active packaging, in which the packaging performs a role beyond containment, may offer a solution by performing the functional role of additives. Many reported technologies on antioxidant active packaging rely on migration of an active component from the package into the product. For example, common antioxidants, including butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), rosemary extract, and δ-tocopherol, were added to low-density polyethylene (LDPE) to preserve color by migration from LDPE film to the surface of fresh beef (Moore et al., 2003). In addition, a multilayer packaging, where the innermost layer composed of LDPE with either BHT, BHA, or α-tocopherol designed for antioxidant migration into the food product, demonstrated inhibition of lipid oxidation in whole milk powder (Soto, Peralta, Cano, Martinez, & Granda, 2011). While effective, such *migratory* active packaging technologies (as it pertains to food packaging regulations) would still fall under the classification of direct additive, as the functional agent is intended to become a part of the food product (Koontz, 2012). Recently, our and other groups have explored the concept of *non-migratory* active packaging, in which the active agent is covalently bound to the packaging material such that it retains activity but is unlikely to migrate to the food product (Arrua, Strumia, & Nazareno, 2010; Tian, Decker, & Goddard, 2013a).

We have recently reported on the development of novel non-migratory active packaging materials capable of chelating iron ions at a capacity similar to that of the maximum legal limit of EDTA in beverages (Roman, Tian, Decker, & Goddard, 2014; Tian, Decker, & Goddard, 2012, 2013b; Tian, Decker, McClements, & Goddard,

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2014; Tian, Roman, Decker, & Goddard, 2015). Such materials are designed for application in liquid and semi-liquid foods that are susceptible to oxidation, such as citrus beverages, salad dressing, sauces, and mayonnaise. First generation materials utilized carboxylic acid derived functional groups grafted from the surface of polymer films (i.e.: polyacrylic acid grafted from polypropylene). While effective in both chelating iron ions and significantly delaying the onset of lipid oxidation at pH values of 5.0 and above, these materials had reduced effectiveness at lower pH values (Tian et al., 2014). This result was to be expected due to the pK_a of the chelating moiety ($pK_a \sim 6.45$), as further explored in detailed studies on their dissociation behavior (Roman, Decker, & Goddard, 2014). To expand the potential application of our non-migratory iron chelating active packaging materials, we then grafted polyhydroxamic acid from the surface of polypropylene films (noted PP-*g*-PHA) and demonstrated greatly improved performance at pH values down to 3.0 (Tian et al., 2013b). What is unique about the hydroxamate chelating moiety compared to other chelating compounds is the well characterized high specificity to iron compared to other ions, as well as its low effective charge (Fig. 1) (Farkas, Enyedy, & Csóka, 1999; Roman, Decker, et al., 2014). These characteristics suggest that a chelating active packaging material prepared using hydroxamic acid chelators would be effective even in the presence of complex matrix components (e.g. proteins, lipids, carbohydrates, and competing ions) typical of food and consumer products. The goal of the present work was to demonstrate the ability of our PP-*g*-PHA iron chelating non-migratory active packaging materials to perform in the presence of competing ions (calcium, magnesium, and sodium) at a range of pH values typical of food and consumer products. Additionally, the performance of the PP-*g*-PHA iron chelating packaging material was compared to a soluble analog, deferoxamine (DFO).

2. Materials and methods

2.1. Materials

Polypropylene (PP, isotactic, pellets) was purchased from Scientific Polymer Products (Ontario, NY). Isopropanol, acetone, heptane, methanol, sodium acetate trihydrate, ferric chloride hexahydrate, hydrochloric acid, nitric acid (trace metal grade), sodium hydroxide, calcium chloride, and sodium chloride were purchased from Fisher Scientific (Fair Lawn, NJ). Hydroxylamine hydrochloride, magnesium chloride hexahydrate (99%) and imidazole (99%) were purchased from Acros Organics (Morris Plains, NJ). Benzophenone (BP, 99%), deferoxamine mesylate salt (⩾92.5%, DFO) and methyl acrylate (MA, 99%) were purchased from Sigma-Aldrich (St. Louis, MO). All the chemicals and reagents were used without further purification.

2.2. Preparation of polyhydroxamic acid grafted polypropylene iron chelating materials

Polyhydroxamic acid was grafted from the surface of polypropylene (resulting material denoted PP-*g*-PHA) using a method previously reported by Tian et al. (2015) (Fig. 1b), in which polymethyl acrylate (PMA) is grafted from PP via UV initiated graft polymerization, followed by conversion of methyl acrylate groups to hydroxamate chelating moieties by exposure to hydroxylamine. PP pellets were cleaned by sonication in isopropanol, acetone, and deionized water twice for each solvent. Cleaned PP pellets were then pressed into films using Carver Laboratory Press (Model B, Fred S. Carver Inc., NJ) at 170 °C with a loaded force of 9000 lbs. PP were cut into 8×8 cm^2 squares and cleaned by same procedure as cleaned PP pellets. Cleaned PP were dried in a desiccator (25 °C and 15% relative humidity) until use.

A two-step photografting process was used to introduce PMA to the surface of PP. In the first step, the photoinitiator BP was covalently grafted to the PP surface. BP (5 wt% in heptane) was spin coated on both sides of the PP. BP coated PP were cut into 2×8 cm^2 pieces and placed in septum-fitted screw cap bottles. Nitrogen gas was purged into the bottles for 5 min to remove oxygen. Then, PP were exposed to ultraviolet (UV) irradiation (Dymax, Model 5000 flood, 320-395 nm, 200 mW/cm^2, Dymax Corporation, Torrington, CT) for 90 s. The BP-functionalized PP (PP-BP) were washed three times in acetone for 5 min for each time to remove non-covalently grafted BP. In the second step of the graft polymerization procedure, PP-BP were cut into 1×2 cm^2 and submerged in MA solution (70 wt% in acetone) in glass vials with septum-fitted screw caps. Vials were nitrogen purged for 5 min to remove oxygen, then PP-BP were exposed to UV irradiation for 3 min. The resulting PP-*g*-PMA were extensively cleaned by Soxhlet extraction (150 mL acetone, 12 h) to remove any residual monomer and non-covalently grafted PMA homopolymers (Abu-Ilaiwi et al., 2004).

Ester groups on the surface of PP-*g*-PMA were converted to hydroxamic acid by reaction with hydroxylamine, to produce the final PP-*g*-PHA iron chelating active packaging materials (Lutfor et al., 2001; Wen et al., 2012). Hydroxylamine reagent was prepared by neutralizing hydroxylamine hydrochloride solution (20 wt% in 5:1 methanol:water) to pH 13 by sodium hydroxide followed by removal of sodium chloride precipitate by Buchner filtration. PP-*g*-PMA were submerged in hydroxylamine solution in a flask equipped with a reflux condenser, and the hydroxyamidation

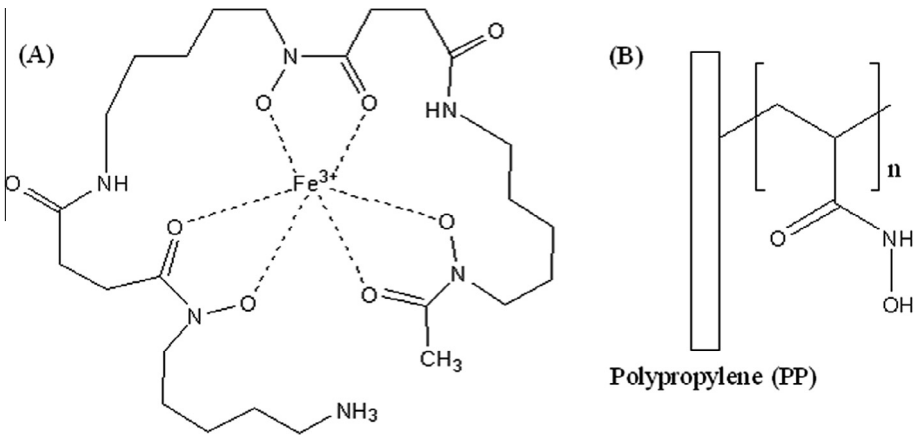

Fig. 1. Chemical structure of (A) soluble DFO/Fe^{3+} complex and (B) PP-*g*-PHA non-migratory iron chelating active packaging material.