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Formation of starch-guest inclusion complexes in electrospun starch fibers

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ABSTRACT

We have demonstrated a method of fabricating starch fibers with an average diameter in the order of micrometers. In the present study, the formation of starch-guest inclusion complexes in the electrospun starch fibers was evaluated. Two methods were used to electrospin starch fibers with starch-guest inclusion complexes: a dope mixing method, where guest material was mixed into the starch dispersion prior to electrospinning, and a bath mixing method, where guest material was mixed into the coagulation bath into which starch dispersions were electrospun. Three selected guest compounds, palmitic acid, ascorbyl palmitate, and cetyl-trimethylammonium bromide, formed inclusion complexes with starch in the electrospun starch fibers. The presence of native lipids was not necessary to induce the inclusion complex formation. Encapsulation of these molecules in electrospun starch fibers may increase their stability during processing and storage, while providing controlled release properties.

1. Introduction

Starch, especially its amylose component, is well known to form inclusion complexes with a variety of small molecules, e.g. iodine (Bluhm & Zugenmaier, 1981), alcohols (Whittam et al., 1989), fatty acids (Biliaderis, Page, Slade, & Sirett, 1985), aromas (Pozo-Bayon, Biais, Rampon, Cayot, & Le Bail, 2008), salicylic acid (Oguchi, Yamasato, Limmatvapirat, Yonemochi, & Yamamoto, 1998) and its analogues (Uchino, Tozuka, Oguchi, & Yamamoto, 2002), and ibuprofen (Yang et al., 2013). In the presence of many guest molecules, amylose forms a 6-fold left-handed single helix stabilized by hydrogen bonds (Conde-Petit, Escher, & Nuessli, 2006). The amylose helices may then pack together forming a crystalline structure known as the V-type. The amylose helix has a hydrophilic outer surface and a hydrophobic helical channel that accommodates the guest molecules (intrahelical association). Crystals of such intra-helical inclusion complexes are known as sub-type V_{6I} (aka V-hydrate or V_h), or anhydrous V (V_a) on losing water from between the helices (Winter & Sarko, 1974). Alternatively, guest molecules can also be entrapped between amylose helices (interhelical association) in sub-type V_{6II} (or $V_{butanol}$) and V_{6III} (or $V_{isopropanol}$), which have larger inter-helical space than V_{6I} (Helbert & Chanzy, 1994; Rondeau-Mouro, Bail, & Buléon, 2004). In the absence of inclusion complex formation, materials may be simply entrapped in the starch matrix in a process known as microencapsulation (Shimoni, 2008).

Amylose-guest inclusion complexes may be useful as a delivery system for guest molecules. For instance, amylose complexed with conjugated linoleic acid (Lalush, Bar, Zakaria, Eichler, & Shimoni, 2004), genistein (Cohen, Orlova, Kovalev, Ungar, & Shimoni, 2008), esters of vitamin and fatty acid (Lay Ma, Floros, & Ziegler, 2011), and long chain unsaturated fatty acids (Lesmes, Barchechath, & Shimoni, 2008; Lesmes, Cohen, Shener, & Shimoni, 2009) have been produced for controlled release purposes. By forming an inclusion complex with amylose or starch, it is expected that the active ingredients, such as essential fatty acids, lipophilic vitamins, and soy isoflavones, can be protected against the acidic environment of the stomach, and their bioavailability may be increased, since the bioactive guest compounds can be released in the small intestine by the action of enzymes (Yang, Gu, & Zhang, 2009).

There are mainly three methods to prepare amylose-guest inclusion complexes: the high temperature method, the dimethyl sulfoxide (DMSO) method and the alkali method (Putseys, Lamberts, & Delcour, 2010). The general idea is to first obtain random coils or loose helices of amylose molecules by dissolution in water (e.g. at 160 °C), in DMSO (e.g. 95% (v/v) DMSO) or in alkali (e.g. 0.01 M potassium hydroxide) solutions, respectively. After which the desired guest can be mixed into the amylose dispersion. In the high temperature method, the mixture is allowed to cool

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down slowly and the inclusion complexes formed will crystallize. In the DMSO method, the solution is diluted with water at an elevated temperature and allowed to cool slowly. The inclusion complexes formed will then crystallize and precipitate. In the alkali method, the solution is neutralized and slowly cooled prior to precipitation.

We have recently fabricated starch fibers by an electrospinning method and studied the effect of solution rheological properties and spinning parameters on fiber formation (Kong & Ziegler, 2012a, 2012b, 2013, 2014). These electrospun starch fibers showed V-type X-ray diffraction patterns, especially when using a coagulation bath with ethanol concentrations above 50% (v/v) suggesting this may be a new method to prepare starch-guest complexes (Kong & Ziegler, 2014).

A nonwoven starch fiber mat may find use in biomedical applications, especially wound dressings and drug delivery. Fibers have a greater surface area compared with current wound dressings and delivery matrices based on foams, films and hydrogels. The high effective surface area promotes hemostasis, extrudate absorption, and cell proliferation (Zahedi, Rezaeian, Ranaei-Siadat, Jafari, & Supaphol, 2010). The porous 3-dimensional structure and small pore size enable the respiration of cells as well as protect the wound from bacterial infection, and compared with traditional petroleum-based synthetic dressing materials, such as nylon and polystyrene, starch is lower in cost and biodegradable, with a sustainable supply. Starch fibers can be absorbed by the human body without any allergic or toxic side effects. Hence the opportunity to develop active wound dressings and drug delivery systems if drugs, nutrients or bioactive compounds can be complexed inter-helically or intra-helically within the starch fibers.

The objectives of the present study were to investigate the formation of inclusion complexes of high amylose starch with palmitic acid (PA), ascorbyl palmitate (AP), and cetyltrimethylammonium bromide (CTAB) in electrospun starch fibers. AP is an ester form of ascorbic acid (vitamin C) with palmitic acid and has been used as a source of vitamin C and an antioxidant food additive. CTAB can be used as a cationic surfactant and an effective antiseptic agent against bacteria and fungi. All of these three guest compounds have 16-carbon alkyl chains and have been shown to readily form complexes with starch using conventional methods (Bhosale & Ziegler, 2010; Eliasson, 1988; Lay Ma et al., 2011). Two inclusion forming methods during electrospinning were evaluated, namely a dope mixing method and a bath mixing method. For each compound, the effects of guest concentration and ethanol concentration in the coagulation bath were also studied. Complementary techniques were employed to determine whether the guest molecules were molecularly included into the starch helices.

2. Materials and methods

2.1. Materials

High amylose maize starch (Hylon VII) was kindly provided by Ingredion Incorporated (Bridgewater, NJ). Dimethyl sulfoxide (DMSO) and Ethanol (200 proof) were obtained from VWR International (Radnor, PA). Guest material cetyl trimethylammonium bromide (CTAB) was obtained from J. T. Baker (Philipsburg, NJ), palmitic acid (PA) from Eastman Kodak Company (Rochester, NY), and ascorbyl palmitate (AP) from Sigma–Aldrich, Inc (St. Louis, MO). Lipid-free Hylon VII starch was produced by dispersing the starch in 90% DMSO aqueous solution followed by ethanol precipitation (Klucinec & Thompson, 1998). Electrospinning of lipid-free starch with and without AP was conducted as a control experiment to exclude native lipids as the sole guest in inclusion complex formation.

2.2. Electrospinning

The electrospinning setup (Fig. 1) used in this study contained a high voltage generator (ES40P, Gamma High Voltage Research, Inc., Ormond Beach, FL), a syringe pump (81620, Hamilton Company, Reno, NV), and a grounded metal mesh immersed in an ethanol/water mixture. A 10 mL syringe (Becton, Dickinson and Company, Franklin Lakes, NJ) with a 20 gage blunt needle was used to extrude the starch dispersion for electrospinning (Kong & Ziegler, 2012b). This electrospinning configuration can also be referred to as "electro-wet-spinning". Electrospinning was conducted at room temperature in this study. Feed rate was set at 4 mL/h, spinning distance at 7.5 cm and voltage at 7.5 kV. The fibrous mat deposited in the coagulation bath was kept for 5 min and then washed using ethanol (~50 mL for first wash and ~10 mL for second wash) and dried in a desiccator containing Drierite under vacuum.

2.3. Inclusion complex formation during electrospinning

Two different means of including guest material were evaluated in this study (Fig. 1). **Dope mixing method**: in this method, the guest material was mixed with the starch dispersion prior to

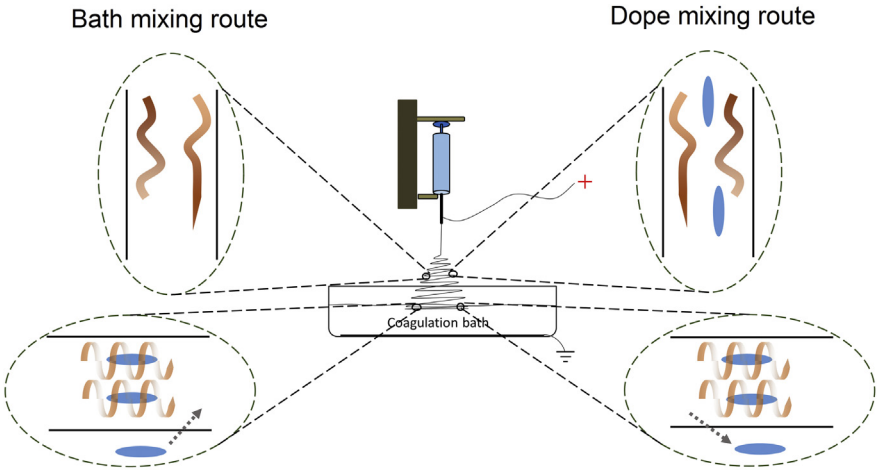

Fig. 1. Schematic drawing of the electro-wet-spinning setup and two routes of starch-guest inclusion complex formation during electrospinning. Orange curves show the conformation of starch molecules and blue ovals stand for guest molecules. Gray arrows show the diffusion of guest molecules either into or out of the precipitated fibers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)