



Rheological characterization of solutions and thin films made from amylose-hexadecylammonium chloride inclusion complexes and polyvinyl alcohol[☆]



William T. Hay^a, Jeffrey A. Byars^b, George F. Fanta^a, Gordon W. Selling^{a,*}

^a Plant Polymer Research Unit, USDA, Agricultural Research Service, National Center for Agricultural Utilization Research, 1815 N, University Street, Peoria, IL 61604, USA

^b Functional Foods Research Unit, USDA, Agricultural Research Service, National Center for Agricultural Utilization Research, 1815 N, University Street, Peoria, IL 61604, USA

ARTICLE INFO

Article history:

Received 19 September 2016

Received in revised form 3 January 2017

Accepted 4 January 2017

Available online 5 January 2017

Keywords:

Amylose complex

Starch rheology

Polyvinyl alcohol

Composite films

DMA

ABSTRACT

The rheological properties of aqueous solutions and films made from blends of polyvinyl alcohol (PVOH) and amylose-hexadecylammonium chloride inclusion complexes (Hex-Am) were investigated to better understand the polymer interactions and processing parameters. Aqueous solutions of Hex-Am displayed non-Newtonian shear thinning characteristics, becoming highly viscous at 4.2% solids and forming a strong mechanical gel at 10% solids. Cationic Hex-Am was observed to have dramatically different rheological temperature response profiles from anionic amylose-sodium palmitate inclusion complexes, displaying a precipitous increase in viscosity upon cooling from 95 °C to 50 °C. Aqueous solution blends of 1:1 PVOH/Hex-Am lack this precipitous increase in viscosity, indicating that PVOH reduces amylose-chain entanglement. Films cast from varying blends of Hex-Am and PVOH were thermostable to 200 °C, and displayed decreasing storage modulus with increasing concentrations of PVOH in film blends. Films cast from Hex-Am/PVOH absorb water vapor at lower rates than their constitutive polymers.

Published by Elsevier Ltd.

1. Introduction

Starch is an inexpensive, biodegradable plant based polysaccharide that has a large number of applications in food and material science. Starch is composed of repeating glucose units and is comprised of two fractions, amylose and amylopectin. The amylose fraction is a linear polysaccharide with α -(1 \rightarrow 4)-glucan linkages, while the amylopectin fraction is a highly branched α -(1 \rightarrow 4)-glucan with α (1 \rightarrow 6)-branch points (Tester, Karkalas, & Qi, 2004). Amylopectin is typically the major component of normal food grade corn starch, with amylose typically constituting 15–30% of the starch. Starches containing greater than 40% amylose are defined as high-amylose starches, while starches containing <1% amylose are defined as waxy starches (Bates, French, & Rundle, 1943; Tester et al., 2004).

[☆] Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

* Corresponding author.

E-mail address: gordon.selling@ars.usda.gov (G.W. Selling).

When dissolved, amylose can form inclusion complexes with hydrophobic ligands such as fatty acids and fatty amines (Godet, Bouchet, Colonna, Gallant, & Buleon, 1996; Helbert & Chanzy, 1994; Immel & Lichtenthaler, 2000; Obiro, Sinha Ray, & Emmambux, 2012). The left-handed helices formed by amylose in solution have a hydrophobic internal cavity where hydrophobic ligands can reside (Saenger, 1984). Structurally, the inner surface of the helix is comprised of methylene groups and glycosidic linkages, while the hydrophilic hydroxyl groups are located on the outer surface (Immel & Lichtenthaler, 2000; Obiro et al., 2012). In the presence of suitable ligands amylose-inclusion complexes can form when the hydrophobic portion of a ligand associates with the hydrophobic internal cavity of the amylose helix by van der Waals forces (Nimz, Gessler, Usón, Sheldrick, & Saenger, 2004). A minimum chain length of 10 carbons is necessary for complex formation, with an ideal chain length between 14 and 18 carbons (Godet et al., 1995; Krog, 1971). Amylose-inclusion complexes are categorized into two main types, type I and type II. Type I complexes are randomly oriented structures with no distinct crystalline regions. They are typically formed at lower temperatures (<90 °C) and are partially ordered. Type II complexes are semicrystalline with distinct crystalline and amorphous regions and are formed at temperatures near

90 °C (Biliaderis & Seneviratne, 1990; Tufvesson & Eliasson, 2000). Due in part to their crystalline structure, amylose-lipid inclusion complexes have increased resistance to starch degrading enzymes, with highly crystalline Type II complexes being even more resistant (Gudmundsson, 1992; Putseys et al., 2009). Amylose-inclusion complexes can be produced using the commonly used industrial method of steam jet cooking (Klem and Brogly, 1981). Using this technique, water dispersions of granular starch are heated at high temperature with high-pressure steam under high-shear conditions to dissolve the starch. The desired ligand is then added to the resulting starch solution to form the amylose inclusion complex (Fanta et al., 1999). While fatty acid inclusion complexes produced in this fashion will form insoluble spherulites when cooled, amylose-fatty acid salt inclusion complexes are water soluble and can be dried and easily re-dissolved in water (Fanta, Kenar, Byars, Felker, & Shogren, 2010; Fanta, Kenar, & Felker, 2013).

Starch is used in many industrial applications, including the production of paper and as components in polymer composites to improve biodegradability (Fanta, Felker, Selling, Hay, & Biswas, 2016; Nachtergaele, 1989; Rahmat, Rahman, Sin, & Yussuf, 2009; Tang & Alavi, 2011). Cationic starches are widely used as flocculating agents in paper production to enhance filtration and improve mechanical strength (Nyström, Backfolk, Rosenholm, & Nurmi, 2003). Cationic amylose-fatty amine salt inclusion complexes produced by excess steam jet cooking have been suggested for use as flocculants and retention aids in paper production (Fanta et al., 2013). The rheological properties of amylose-inclusion complexes produced using steam jet cooking of high amylose corn starch and the salts of long chain fatty acids have been studied (Byars, Fanta, Kenar, & Felker, 2012; Fanta et al., 2010, 2013, 1999). In these solutions, the rheology was found to vary significantly with temperature and pH. Starch is extensively used by industry as an important functional ingredient to form viscous dispersions to prepare valued products (Banerjee & Bhattacharya, 2012; Saha & Bhattacharya, 2010). When the fatty acid salt was used, at low pH's the viscosity changed dramatically (Byars et al., 2012). This may limit its utility in products having lower pH.

The formation of amylose inclusion complexes with hexadecylammonium chloride using steam jet cooking and isolation using freeze drying has been previously described (Fanta et al., 2013). A 6₁V x-ray diffraction pattern is observed after complex formation, as well as an inhibition of retrogradation due to electrostatic repulsion between amylose helices. Blending the water soluble amylose hexadecylammonium chloride complexes (Hex-Am) with polyvinyl alcohol (PVOH) has been demonstrated to produce composite films with high tensile strength, high% elongation and increased water contact angle (Fanta, Felker, Selling et al., 2016; Fanta, Felker, Selling, 2016). Additional rheological characterization is required in order to define the solution properties of these compositions. In addition, developing an understanding of how the blended film's properties change with temperature will be of use in defining potential markets for the polymer blends.

The rheological properties of Hex-Am solutions and films formed from Hex-Am have not been fully characterized, and have a different rheological response with pH and temperature relative to previously generated complexes (Byars et al., 2012). Composite films prepared from PVOH and Hex-Am have been demonstrated to have a better balance of properties such as, tensile strength, elongation and water contact angles, than control films (Fanta, Felker, Selling et al., 2016; Fanta, Felker, Selling, 2016). Dynamic mechanical analysis (DMA) techniques would be a useful technique to fully define the thermal properties of these films.

The objectives of this investigation were therefore to (1) determine solution rheological properties of amylose-hexadecylammonium chloride inclusion complexes (Hex-Am), (2) determine the rheological properties of films prepared from Hex-

Am and PVOH blends with varying concentration of plasticizer, (3) define the thermal properties of films made from various blends of PVOH and Hex-Am. By accomplishing these objectives, the overall value of the technology will be better understood and the processing parameters for the production of the complex will be better defined.

2. Materials and methods

2.1. Materials

High-amylose corn starch (~68% amylose, AmyloGel 03003) was a product of Cargill (Minneapolis, MN). Hexadecylamine (98%); sodium palmitate (98.5%); and hydrochloric acid (HCl, 37%) were purchased from Sigma (St. Louis, MO); PVOH (MW 133,000, 99 mol% hydrolyzed) was purchased from Polysciences, Warrington, PA; glycerol (Certified A.C.S); and sodium hydroxide pellets (Certified A.C.S) was purchased from Fisher Scientific, Pittsburg, PA. Deionized water was used for the preparation of all solutions.

2.2. Preparation of Hex-Am

The procedure for producing the amylose-inclusion complexes was the same as that reported earlier (Fanta et al., 2010). A high-amylose starch dispersion was prepared by adding 1800 mL of deionized water to 100 g of high-amylose corn starch in a 2 L stainless steel Waring blender (Waring Products division, New Hartford, CT). The dispersion was subsequently passed through a Penick & Ford (Penford Corp., Englewood, CO) laboratory model steam jet cooker operating at excess steam conditions (Klem & Brogly, 1981). Temperature in the hydroheater was 140 °C, steam back pressure was 380 kPa, and the steam line pressure was 550 kPa. The starch dispersion was pumped through the jet cooker at a rate of 1 L/min, and the hot starch solution was collected in a 4 L stainless steel Waring blender container (Waring Products division, New Hartford, CT). A solution of hexadecylammonium chloride was prepared by dispersing 5.25 g of hexadecylamine in 217.42 g of 0.1 N HCl, and then heating to 90 °C. This solution was then added to the hot starch dispersion in the Waring blender container immediately after jet-cooking. The solution was stirred for 1 min, and then rapidly cooled in an ice bath to 25 °C. The cooled dispersion was then freeze dried using a Labconco Freezone 6 L freeze dryer (Labconco, Kansas City, MO). Amylose-sodium palmitate inclusion complexes (Na-Palm) were similarly prepared, albeit exchanging hexadecylammonium chloride with sodium palmitate and the 0.1N HCl with deionized water.

2.3. Preparation of sample solutions

Solutions of Hex-Am, Na-Palm, PVOH, and blends of PVOH/Hex-Am were prepared by dispersing the polymers in deionized water, heating the dispersions to 80 °C and then immediately cooling the dispersions in an ice bath to 25 °C.

2.4. Solution titration

Solutions of 100 g of 2% Hex-Am, 2% PVOH, and 4% 1:1 blend of PVOH/Hex-Am were titrated at 25 °C with 0.1 N NaOH. The pH was measured with an Orion Star A215 pH/millivolt meter (Orion Research, Inc., Cambridge, MA), using a glass electrode (Number 8157BNUMD from Thermo Orion, Thermo Fisher Scientific, Waltham, MA).

Download English Version:

<https://daneshyari.com/en/article/5157736>

Download Persian Version:

<https://daneshyari.com/article/5157736>

[Daneshyari.com](https://daneshyari.com)