Industrial Crops & Products 105 (2017) 231–237

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Research paper

Increased water resistance of paper treated with amylose-fatty ammonium salt inclusion complexes

George F. Fanta[a], Frederick C. Felker[b,*], William T. Hay[a], Gordon W. Selling[a]

[a] USDA, Agricultural Research Service, National Center for Agricultural Utilization Research, Plant Polymer Research, 1815 N. University Street, Peoria, IL 61604, USA
[b] USDA, Agricultural Research Service, National Center for Agricultural Utilization Research, Functional Foods Research, 1815 N. University Street, Peoria, IL 61604, USA

ARTICLE INFO

Keywords:
Starch
Coatings
Packaging
Biodegradable
Cellulose
Polysaccharides

ABSTRACT

Amylose inclusion complexes were prepared from high amylose cornstarch and hexadecyl- and octadecylammonium chloride. The complexes were applied to paper at concentrations of 2–4%. After drying the papers, a sodium hydroxide solution was applied to convert the complexes to the insoluble amine form, rendering the paper hydrophobic. SEM showed that the complexes were uniformly deposited onto the paper with no visible particles. Increased resistance of papers to water penetration was indicated by an increase in the contact angles of water droplets from not measurable to as much as 113°, and by longer times for total absorption of the droplets. Treated papers also absorbed less water than untreated papers, with the C_{16} amylose-hexadecylammonium chloride complex providing the greatest water resistance (81.2% less water absorbed than untreated paper). Unlike other technologies widely used for rendering paper hydrophobic, the materials used for this novel method are water soluble, non-toxic, biobased, and biodegradable.

1. Introduction

Although certain uses for paper call for high wettability and rapid absorbency of water, many applications require treatment or coating to impart a more hydrophobic or water resistant surface (Geissler et al., 2014). In particular, paper used for printing with water-based inks must allow drying of the ink on the surface without bleeding into the paper (Koskela and Hormi, 2003). The use of paper for packaging is increasing, and many of these applications also require water resistance (Challener, 2011). Consequently, a great deal of research is aimed at exploring various approaches to developing better coating technologies. Methods for imparting water resistance to cellulosic materials have been reviewed (Samyn, 2013).

In this report, we describe the increased water resistance obtained when paper is treated with aqueous solutions of amylose inclusion complexes prepared from jet cooked high amylose corn starch and the HCl salts of fatty amines with hydrocarbon chain lengths of C_{16} and C_{18}. Starch is a high molecular weight, carbohydrate polymer comprised of glucose units joined by glycosidic bonds, and is a two component mixture containing varying amounts of un-branched amylose and highly-branched amylopectin, depending on the plant source. Steam jet cooking was used in this study to prepare aqueous solutions of starch for the preparation of amylose inclusion complexes, and this inexpensive, continuous process is widely used to prepare starch solutions for commercial applications such as incorporation into paper products (Klem and Brogley, 1981). In the jet cooking process, an aqueous dispersion of granular starch is pumped through a hydroheater where it is heated with steam at high temperature and pressure. The intense turbulence and mechanical shear that results from instantaneous heating and the passage of excess steam through the hydroheater promotes the dissolution of starch granules and can also result in the reduction of starch molecular weight (Dintzis and Fanta, 1996; Byars, 2003). When jet cooked solutions of starch are cooled, retrogradation of amylose occurs (Miles et al., 1985; Orford et al., 1987) causing the amylose component to precipitate from solution. However, when water-soluble ligands such as the HCl salts of fatty amines are added to the hot jet cooked solutions, amylose assumes a helical conformation, and stable water-soluble inclusion complexes are formed in which the hydrophobic hydrocarbon chain of the fatty amine salt is complexed within the hydrophobic central cavity of the helix formed from the amylose polymer in solution (Putseys et al., 2010; Obiro et al., 2012). The amine salt groups, however, remain exterior to the amylose helix and therefore are available to interact with other substances, such as the hydroxyl groups of cellulose. Since the amylose inclusion complexes are water soluble and do not retrograde, the dried complexes can be easily re-dissolved in water by heating, and remain soluble at room

---

[*] Corresponding author.
E-mail address: frederick.felker@ars.usda.gov (F.C. Felker).

http://dx.doi.org/10.1016/j.indcrop.2017.04.060
Received 1 February 2017; Received in revised form 7 April 2017; Accepted 30 April 2017

0926-6690/ Published by Elsevier B.V.

temperature.

Although the amylose complexes prepared from fatty ammonium salts are soluble in water, the complexes precipitate from solution when sodium hydroxide solution is added to convert the acidic fatty ammonium salts within the amylose helix to the corresponding water insoluble fatty amine form. This treatment does not cause the dissociation of the complex. When a dilute solution of the amylose complex prepared from the HCl salt of hexadecylamine was titrated with sodium hydroxide, the viscosity of the solution increased between pH 8.35 and 8.5, and the amylose-fatty amine complex precipitated from solution at pH 9.4 (Fanta et al., 2013). When composite films were prepared from mixtures of polyvinyl alcohol (PVOH) and amylose-fatty amine salt complexes (Fanta et al., 2016b), the properties of these films suggested that associations had taken place between the cationic amine groups of the amylose complexes and the hydroxyl groups of PVOH. Solution rheology indicated that the cationic amine groups of the amylose-fatty amine complex formed a close interaction with hydroxyl groups of PVOH, as shown by dramatic alterations in solution rheological properties of the amylose complexes when blended with PVOH (Hay et al., 2017). Based on these studies, it was reasonable to assume that similar associations would also occur between the exposed cationic ammonium groups of the amylose-amine salt complexes and the cellulose hydroxyl groups of paper. Subsequent addition of sodium hydroxide solution to convert the complexed amine salts to the corresponding water insoluble amines would then cause the amylose-fatty amine complexes to precipitate onto the cellulose fibers of the paper and thus increase the water resistance of the treated paper. In contrast to current industrial methods, this procedure would yield paper with increased resistance to the penetration of water using materials that are water soluble, nontoxic, biobased, and biodegradable.

Alkene ketene dimer and alkenyl succinic anhydrides have been used for this purpose (Geissler et al., 2014), however alkene ketene dimer requires the use of hazardous, water-reactive ketenes, and water-reactive alkenyl succinic anhydrides can cause skin/eye damage. Ketenes and anhydrides are also costly ingredients and require tight pH controls during their application steps. Dellinger et al. (2014) produced water resistant paper by applying an amide wax combined with a cellulose ester, shellac and rosin, and phospholipids or medium-chain length triglycerides were used to improve properties. However, these compounds require the use of volatile, flammable solvents for the coating process. Koskela and Hormi (2002) used long-chain fatty amine quaternary salt derivatives to modify the surface properties of paper, but these compounds often require the use of hazardous materials for their synthesis. Geissler et al. (2014) used nanoparticles prepared from cellulose stearoyl esters to improve water resistance, and high contact angles for water were obtained. However, the hazardous reagents and wastes produced could negate any benefits due to biodegradability of the final particles. Cellulosic materials such as paper or cotton have also been treated with silanes to impart water resistance (Oyola-Reynoso et al., 2015; Oh et al., 2011), and cellulosic articles with improved hydrophobic properties have also been prepared by plasma-induced deposition of fluorocarbons or acrylate monomers onto cellulose (Vaswani et al., 2005; Song et al., 2013). Hu et al. (2009) used a three component system of precipitated calcium carbonate, stearic acid, and a copolymer of styrene and acrylate to prepare a cellulosic article with a water contact angle exceeding 130°. Yan et al. (2013) developed cross-linked cationic latexes that contained epoxy and quaternary ammonium groups that imparted improved water resistance to paper, and the latex was combined with polymers prepared from styrene, butyl acrylate, dimethylaminoethyl methacrylate, stearyl methacrylate, and epichlorohydrin. Wang et al. (2015) and Zhu et al. (2016) developed polyurethane systems that imparted increased water resistance to paper. Knaup and Gasafi-Martin (2016) used fluorinated polyacrylate compositions to impart increased water resistance, and these compositions were comprised of up of at least three different acrylic and methacrylic acid esters, a paraffin wax, and other ingredients such as isocyanates, polysiloxanes or melamine resins. Iselau et al. (2015) used nanometer sized organic particles that provided increased water resistance after deposition onto paper; however, these particles were prepared from a mixture of styrene, t-butyl acrylate and n-butyl acrylate coupled with a complex cationic surfactant composed of styrene, dimethylaminopropyl methacrylamide and 2-dimethylaminoethyl methacrylate. A common feature of the methods cited above is that the chemicals used for the treatment or those used for their synthesis are toxic, hazardous, non-biobased, non-biodegradable, non-renewable, expensive, or some combination of these. In a review article by Gaikwad and Ko (2015), the use of clays to provide improved water resistance has also been described, but a non-biobased, non-biodegradable latex was used to bind the clay to the paper. Finally, Yoon and Deng (2006) observed that amylose complexes prepared from starch and palmitic acid increased the hydrophobicity of paper when they were applied to the surfaces of clay particles. However, these complexes have limited solubility in water and precipitated from solution at temperatures lower than 70 °C. It was therefore necessary to precipitate the complexes onto clay particles in order to incorporate the complexes into paper formulations.

The objectives of this investigation were therefore to (1) prepare water soluble amylose inclusion complexes from jet-cooked high amylose starch and the HCl salts of hexadecylamine (C_{16}), and octadecylamine (C_{18}); (2) apply water solutions of these complexes to paper at a range of concentrations, and then treat the papers with sodium hydroxide solution to precipitate the water insoluble amylose-amine complexes onto the cellulose fibers of the paper; and (3) determine the resistance of the treated papers to the penetration of water, and compare the results obtained with the two amylose complexes.

2. Materials and methods

2.1. Materials

High amylose corn starch was purchased from Cargill, Minneapolis, MN and contained 68% amylose and 32% amylopectin, as determined by iodine binding (Jane et al., 1999). Hexadecylamine (98%) and octadecylamine (97%) were purchased from Sigma-Aldrich, St. Louis, MO. The moisture content of starch was 9.4% and was determined by measuring weight loss after heating under vacuum at 100 °C.

2.2. Preparation of amylose-fatty ammonium salt complexes

Steam jet cooking of high amylose starch was carried out as previously reported (Fanta et al., 2010). High Amylose starch (50.0 g) was dispersed in 900 mL of water, and the granule dispersion was passed through a Penick & Ford laboratory model steam jet cooker (Penford Corp., Englewood, CO). Jet cooking was carried out under excess steam conditions (Klem and Brogley, 1981). The hydroheater temperature was 140 °C, the steam back pressure was 380 kPa (40 psig), the steam line pressure was 550 kPa (65 psig), and the pumping rate through the jet cooker was approximately 1 L/min.

To prepare aqueous solutions of the HCl salts of hexadecylamine and octadecylamine, 2.6 g of insoluble fatty amine was dispersed in 100 mL of an aqueous solution at 90 °C containing an amount of HCl required to convert the amine to the soluble HCl ammonium salt. The weight of fatty amine used to prepare the amylose complexes was equal to 7.5% of the weight of amylose in 50.0 g of high amylose corn starch. The hot solutions of amine salts were added to the hot solutions of jet cooked starch and stirred for 1 min, and then cooled in ice to 25 °C. The amylose complexes were then freeze dried for further experimental use, although it would not be necessary to dry them for commercial production. The amylopectin component of high amylose corn starch (not complexed due to its highly branched structure) was not removed from the amylose complexes, since separation and removal of amylopectin would not be practical in a commercial process.