



Polysaccharide-based materials and their adsorption properties in aqueous solution



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ABSTRACT

Polysaccharides (PS) of cellulose, soluble, corn- and maize-derived starches with variable amylose/amylopectin content were cross-linked with epichlorohydrin (EPI) to form polymeric adsorbents. The properties of the cross-linked PS–EPI materials were prepared by varying the synthesis conditions (nature of polysaccharide, temperature, and reagent ratios) to afford network polymer materials with tunable properties. The optimized polymers were obtained at a reaction temperature (50–54 °C) according their yield were characterized using spectroscopic (IR and NMR) methods, and thermal gravimetric analysis (TGA). The textural and adsorptive properties of the polymers were evaluated using nitrogen gas and dye-based methods using *p*-nitrophenol. Solvent uptake, nitrogen adsorption, and aqueous dye sorption show that the amylose and amylopectin content in the PS–EPI copolymers display a complex relationship with their physicochemical properties. Polymers with greater cross-linking did not show incremental changes in water or dye uptake. Structural variation of the polysaccharide (i.e. branching, molecular weight, and relative amylopectin/amylose content) contributed to the sorption properties by modifying their textural properties and surface chemistry.

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1. Introduction

Polysaccharides such as starch and cellulose from plant sources are relatively abundant, naturally occurring, nontoxic, inexpensive and economically important biomaterials. They are amenable to chemical modification which make them especially attractive biomaterial platforms to produce value-added materials in technologies such as in drug delivery (Hamdi, Ponchel, & Duchêne, 2001; Onofre & Wang, 2010; Sandra, 2009), biomedical devices (Marques, Reis, & Hunt, 2002), tissue engineering scaffolds (Gomes, Ribeiro, Malafaya, Reis, & Cunha, 2001), dispersions (da Sil Va, Oliveira, & Rao, 1997), waste water treatment (Crini, 2005) and bio-refineries (Kamm & Kamm, 2004).

Starch and cellulose are abundant plant-based biopolymers, where the former serves as the plant's main energy reserve while the latter provides structural stability to plant cell walls (Scheller & Conrad, 2005). Starch may occur as granules (small compact form of starch molecules) which are composed mainly of two biopolymers, where the main component is amylopectin (70–80%), a branched polymer comprised of α -1,4-linked glucose units with α -1,6 branching links. The secondary component is

amylose, a linear polymer consisting mainly of α -1,4-linked D-glucose units (Copeland, Blazek, Salman, & Tang, 2009; Kubo et al., 2010; Richardson & Gorton, 2003; Varum & Smidsrod, 2005). X-ray structural analysis of starch granules indicates a model of repeating amorphous and crystalline domains (Varum & Smidsrod, 2005). The crystalline domains of starch are associated with amylopectin while the amorphous regions are associated with amylose interspersed with amylopectin (Singh, Singh, Kaur, Singh Sodhi, & Singh Gill, 2003). By comparison, cellulose is much more crystalline in nature due to its β -1,4 linked D-glucose units arranged in a linear chain with no coiling or branching (Varum & Smidsrod, 2005). These biopolymer components adopt a relatively linear and rigid conformation where the monomer units undergo extensive intramolecular and intermolecular H-bonding (Richardson & Gorton, 2003).

The tertiary structure of starch and cellulose impact their physicochemical properties. For example, the relative ease that cellulose chains form stabilizing intra- and intermolecular interactions result in a self-assembled material with high tensile strength and relatively low solubility in water and many organic solvents. Such properties that contribute to its suitable function as a plant cell wall structural component but limit its industrial use due to material processing challenges (Richardson & Gorton, 2003). On the other hand, the variable crystalline properties of starch granules due to the amylose and amylopectin content affect its structure and physicochemical properties. As in the case of

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cellulose, the crystalline domains of starch makes it less soluble in water but the presence of the amorphous regions impart lower structural rigidity and greater water solubility. This variability affinity of such biopolymers to water is useful in the food industry for improving food texture but may attenuate the sorption properties with xenobiotics due to competitive water sorption in aquatic environments (Delval, Crini, Bertini, Filiatre, & Torri, 2005). Mixed biopolymers of starch may limit a detailed understanding of their structure and properties but such materials may display unique physicochemical properties that are nonlinear with respect to their composition. For example, starch with high amylose content is commonly associated with high viscosity due to increased interactions and entanglement of the linear amylose chains (Copeland et al., 2009). Enhanced interaction between amylose chains is relevant for preparing starch-based derivatives with high thermal and mechanical stability (Xie et al., 2009). Starch with high amylopectin content favors swelling whereas starch with high amylose content display decreased swelling capacity (Copeland et al., 2009; Sasaki & Matsuki, 1998; Tester & Morrison, 1990). Swelling is a property closely associated with expansion of the polymer network and is important in drug delivery or for entrapment of guest molecules of a suitable size. Therefore, materials with well-defined swelling properties are important in sorption-based applications. In a recent study, Kyzas, Bikiaris, and Lazaridis (2008) demonstrated that sorbents that undergo pre-swelling exhibit rapid dye adsorption.

To expand the range of applications of starch and cellulose, cross-linking is a versatile strategy that affords materials with tunable mechanical and chemical properties (Ayoub & Rizvi, 2009; Crini, 2005; Delval et al., 2005; Hamdi et al., 2001; Kaur, Ariffin, Bhat, & Karim, 2012; Onofre & Wang, 2010). The cross-linker introduces intermolecular bridges between biopolymer units which may alter the overall textural properties and surface chemistry of the polymer framework. For example, Ghosh Dastidar and Netravali (2013) cross-linked waxy maize starch to obtain an environmentally friendly resin that has improved toughness and water resistance than native starch. Hamdi et al. (2001) cross-linked soluble starch to form microspheres with controlled particles with narrow size distribution for drug delivery applications. The physicochemical properties of the polymers are varied by the reaction parameters (e.g. temperature, solvent, and prepolymer composition) (Ayoub & Rizvi, 2009). For example, Ashish, Khanderao, and Deelip (2013) employed high amylose starch to form biodegradable implants for sustained drug delivery. Kaur et al. (2012) studied the effects of cross-linker content on the physicochemical properties of starch and attributed their observations to cross-linking of the starch polymer chains. Onofre and Wang (2010) used cross-linked starch with variable amylose/amylopectin content to study the rates of sustained drug release and reported its influence on the degree of cross-linking.

In this study, starch with variable amylose and amylopectin content along with cellulose were modified by chemical cross-linking with epichlorohydrin at variable reaction conditions. The resulting polysaccharide-epichlorohydrin (PS-EPI) copolymers were studied by evaluating their sorptive uptake properties in aqueous solutions with a model organic dye adsorbate (*p*-nitrophenol; PNP). The results of this systematic study will contribute to a greater understanding of the relationship of the sorption properties and structure of such copolymer materials in aqueous solutions.

2. Experimental

2.1. Preparation of PS-EPI copolymers

Different sources of starch (corn, maize, high amylose, high amylopectin), cellulose and epichlorohydrin were obtained from

Sigma-Aldrich (Oakville, ON, Canada) and used as received. The synthesis of starch-epichlorohydrin copolymer materials employed a modified procedure are described elsewhere (Pratt, Wilson, Kozinski, & Mohart, 2010). Briefly, an aqueous solution of NaOH (2 M) was used to dissolve and ionize the polysaccharide hydroxyl groups prior to the addition of variable amounts of epichlorohydrin (EPI) to produce cross-linked polymers. The effect of temperature on the cross-linking reaction was evaluated at 40, 50, 60 and 70 °C.

2.2. Characterization of PS-EPI copolymers

The products were characterized using ¹³C solid NMR spectroscopy with a wide-bore (89 mm) 8.6T Oxford superconducting magnet system equipped with a 4 mm CP-MAS (cross polarization with magic angle spinning) solids probe. Operating parameters were controlled using an Avance DRX360 console and workstation running TopSpin 1.3 (Bruker Bio Spin Corp; Billerica, MA, USA). Standard pulse programs utilized were included in the TopSpin 1.3 software. Samples were packed in 4 mm outer diameter zirconium oxide rotors capped with Teflon MAS rotor caps. Acquisition was carried out using MAS at a rotational speed of 5 kHz, 2-s recycle delay and 750 μs cross polarization time. The chemical shift of adamantane ($\delta = 38.6$ ppm) was used as an internal shift reference.

Fourier transform infrared (FTIR) spectra were obtained with a BIO-RAD FTS-40 spectrophotometer operating in diffuse reflectance mode. Multiple scans were obtained with a 4 cm⁻¹ resolution and corrected against spectroscopic grade KBr background as the sample matrix over the spectral range of 400–4000 cm⁻¹. Thermogravimetry analysis (TGA) was performed using a TGA Q50 (New Castle, DE) operated at a heating rate of 5 °C min⁻¹ up to a maximum temperature of 500 °C under a N₂ (carrier gas) atmosphere.

2.3. Solvent swelling properties of copolymer materials

The swelling properties of the sorbent materials were studied by use of approximately 40 mg of material was equilibrated in 6 ml of solvent (either Millipore water or neat ethanol for 48 h). The weight of hydrated polymer (w_s) was determined after tamping dry with filter paper by weighing, and then drying in an oven at 60 °C for 12 h to a constant dry weight (w_d). The swelling ratio was calculated using the following Eq. (1):

$$S_w = \frac{w_s - w_d}{w_d} \times 100\% \quad (1)$$

2.4. Dye adsorption studies

The textural properties were evaluated using nitrogen adsorption and a dye-based sorption method with UV-vis detection. Aqueous dye solutions of *p*-nitrophenol (PNP) were prepared at pH 6, below the pK_a value (7.14) of PNP (Mohamed, Wilson, & Headley, 2010; Mohamed, Wilson, Headley, & Peru, 2011). Approximately 20 mg of the powdered and sieved (40 mesh) copolymers were mixed in 10 ml of solution containing PNP at variable concentration (0.1–25 mM) in 10 mM potassium phosphate monobasic buffer solution (pH 6) in 4 dram glass vials. The vials were sealed with parafilm between the cap and the glass bottle, followed by equilibration on a horizontal mechanical shaker (Poly Science, Dual Action Shaker) for 24 h at 180 rpm. The samples were then centrifuged (Precision Micro-Semi Micro Centricone, Precision Scientific Co.) at 1800 rpm for 30 min. The UV-vis absorbance of PNP in the supernatant solutions was measured at $\lambda_{max} = 318$ nm using a Varian CARY 100 double beam spectrophotometer at room temperature (295 ± 0.5 K). An absorbance calibration curve was obtained from standard solutions of PNP and the molar absorptivity of PNP

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