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Physicochemical properties of starch dispersed in 1-allyl-3-methylimidazolium chloride

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ABSTRACT

In recent years, considerable concerns have arisen over new efficient and environmentally friendly way for utilizing ionic liquids to dissolve starch. In this study, corn, wheat, potato, rice, and mung bean starches were dispersed in 1-allyl-3-methylimidazolium chloride (AMIMCl). The maximum solubilities of corn, wheat, rice, mung bean, and potato starches measured by turbidimetry were 11.75, 11.25, 11.00, 10.50, and 9.00 g/100 g of AMIMCl, respectively. And steady shear behavior of starch–AMIMCl mixtures, morphology, thermal properties, and molecular weight of native starch, and starch dissolved in AMIMCl were analyzed. All the starch/AMIMCl solutions were typical pseudoplastic fluids. Thermal properties showed that all starches dispersed in AMIMCl had no endotherm except potato starch. Scanning electron microscopy (SEM) and gel permeation chromatography (GPC) revealed that shapes and structures of native starch granules were destroyed, and starch molecules endured different degrees of degradation during dissolution process.

1. Introduction

Starch is one of the most abundant natural polymers, which is renewable, biodegradable and modifiable. As an excellent industrial material, it has generated a wide interest in manufacturing value-added products (Ma et al., 2005; Malafaya et al., 2001; Taguet et al., 2009; Thiebaud et al., 1997). Chemical modification, which is based on reactions of hydroxyl groups in the anhydroglucose units (AGU), is one method for producing starch derivatives (Liu et al., 1997; Raina et al., 2006; Rudnik et al., 2005). However, native starch molecules tend to exist in semi-crystalline structure, which generates low solubility in most conventional solvents, such as water, ethanol, acetone, and so on (Chen et al., 1997). It brings about drawbacks in reaction process including low reaction efficiency and low degree of functionalization. Therefore, finding excellent starch solvents is crucial in improving chemical reaction, which can enhance its processability and change its compatibility with thermoplastics, mechanical properties and resistance to decay.

Ionic liquids (ILs) are organic salts with low melting points (below 100 °C), which have unique properties of high thermal stability, low vapor pressure, electrochemical stability, and recyclability (El Seoud et al., 2007; Olivier-Bourbigou et al., 2010). Due to all these advantages, ILs are considered to be green solvents, which have a potential of substituting for volatile organic solvents (Rogers and Seddon, 2003; Sheldon, 2001; Welton, 1999). As a result, there is an increasing interest in application of ILs as alternative solvent and reaction media for a variety of synthetic processes.

Since less than a decade, ILs have been found to be capable of dissolving various polymers. However, the most published articles for polysaccharide chemistry mainly focus on use of ILs as solvent for cellulose (Laus et al., 2005; Zhu et al., 2006), lignin (Tan and MacFarlane, 2009) or on direct wood dissolution (Fort et al., 2007; Kilpelainen et al., 2007; Yuan et al., 2010). Swatloski et al. had studied dissolution of cellulose using a range of ionic liquids containing 1-butyl-3-methylimidazolium cations, in which chloride containing solvents were found to be the most effective solvents for solubilizing cellulose (Swatloski et al., 2002, 2004). In contrast, studies on investigating the potential of using ionic liquids to disperse or modify starch are limited. And 1-butyl-3-methylimidazolium chloride (BMIMCl) is the commonly used ionic liquid for dissolving starch. Stevenson et al. (2007) have studied the influence of dispersing starch of different origin (corn, rice, wheat, and potato) in BMIMCl on amylopectin molecular weight (M_w). Kärkkäinen et al. (2011) studied the effect of temperature, heating time, and method on amylose as well as amylopectin molecular weight by heat-dispersing starch of different origin (wheat,

Abbreviations: AMIMCl, 1-allyl-3-methylimidazolium chloride; SEM, scanning electron microscopy; GPC, gel permeation chromatography; AGU, anhydroglucose units; ILs, ionic liquids; BMIMCl, 1-butyl-3-methylimidazolium chloride; NTU, nephelometric turbidity units; M_w, molecular weight; DSC, differential scanning calorimetry.

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barley, potato, rice, corn, and waxy corn) in BMIMCl under controlled microwave conditions and in oil bath. It is found that the Cl^- anions in BMIMCl are capable of destroying the semi-crystalline structure of native starch granules and disrupting hydrogen bonding between hydroxyl groups of starch molecules (Xie et al., 2010).

It is worth noting that the ionic liquid 1-allyl-3-methylimidazolium chloride (AMIMCl) was synthesized in 2003 and proved to be a better cellulose solvent than BMIMCl (Zhang et al., 2005). One substituent on nitrogen of AMIMCl molecule is alkenyl instead of saturated alkyl, which attributed to smaller size and higher polarity of $[AMIM]^+$ cation as well as ion pair dissociation mechanism above a critical temperature (Zhang et al., 2005; Wu et al., 2004). Recently, Lappalainen et al. (2012) have prepared water-soluble starch oligomers from variable starch species in 1-allyl-3-methylimidazolium chloride with p-toluenesulfonic acid as the catalyst.

Starch is a mixture of amylose and amylopectin macromolecules. When viewed under polarized light, starch granules show birefringence, which originated from the concentric pattern of semi-crystalline layers in native starch granules (Donald et al., 2001). Hence, the loss of birefringence in starch granules could be used as an assessment for starch dissolution (Souza and Andrade, 2002). However, this method could only provide qualitative assessment in the dissolution of starch. Moreover, the evaluation process is based on a tiny quantity of samples, which contain the risk of inaccuracy at sometimes. In this study, we proposed that the quantitative solubility of starch in ionic liquid was determined by turbidimetric measurement. Turbidimetry was selected as a simple technique with high accuracy and reproducibility.

The aim of our study was to investigate the physicochemical properties of starch of five botanical sources dispersed in AMIMCl. Steady shear behavior of starch/AMIMCl mixtures, morphology, thermal properties and molecular weight of starch heat-dispersed in AMIMCl were analyzed to determine if AMIMCl could provide suitable chemical reaction environment for starch modification. In particular, turbidimetric measurement in combination with polarized light microscope was selected as an alternative method to determine the solubility of starch in AMIMCl.

2. Materials and methods

2.1. Material

Corn and wheat starches were obtained from ChangChun DaCheng Corn Products Co., ChangChun, China. Potato, mung bean, and rice starches were obtained from DongGuan DongMei Food Co., Dongguan, China. These starches were oven dried at 105 °C for 24 h prior to use. 1-Allyl-3-methylimidazolium chloride (AMIMCl, >99%) was provided from Lanzhou Institute of Chemical Physics (Lanzhou, China). Other chemicals and solvents were commercially available and of analytical grade.

2.2. Starch dispersion in 1-allyl-3-methylimidazolium chloride

100 mg of starch sample was added to AMIMCl (2 g) in a three-necked flask, which was continuously purged with gaseous N_2. The mixture was heated at 90 °C for 2 h to dissolve starch with stirring throughout. Starch was then precipitated with sufficient anhydrous ethanol and centrifuged at 4500 rpm for 20 min. Pellet was washed with deionized water then precipitated again using anhydrous ethanol to eliminate IL. Finally, starch was filtered and dried in vacuum at 40 °C for 48 h. The same starches had the entire procedure conducted using deionized water instead of ionic liquid as a control. The prepared samples were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

2.3. Turbidimetric measurements

Turbidity was measured according to the method of Mazza et al. (2009) with some modifications. Turbidimetric clear glass vials containing a precise quantity of ionic liquid (40 mL) and a magnetic stirrer were placed into a heating oil bath. Small precise amounts of starch (50 mg) were added discretely into the vials. The mixture was heated at 90 °C with stirring throughout. In between each addition, at least 30 min was allowed for dissolution and turbidity was measured with a nephelometer (2100AN, Hach Company, Loveland, CO, USA) until a stable nephelometric turbidity units (NTU) value was reached. In the meantime, a polarized light microscope (Olympus BX51, Tokyo, Japan) was used to investigate the granular structure of each starch heated in AMIMCl during the turbidimetric measurement.

2.4. Steady shear properties

Steady shear properties were analyzed by a rheometer (RS600, HAAKE) equipped with a parallel-plate system (4 cm diameter) at 90 °C. The gap size was set at 1 mm. Starch dispersions with 1, 5, and 9% (dry weight basis) of total solids were prepared by heating starch at 70, 80, 90, and 100 °C for 2 h and then transferred to the rheometer platen (9% of potato starch dispersion was not studied because of its solubility at 90 °C). The exposed sample edge was covered with a thin layer of light paraffin oil to prevent evaporation during measurements. For each test, the dispersion was sheared at a programmed rate linearly increasing from 0 to 500 s^{-1} in 120 s to describe the flow behavior, and the data were fitted to the power law:

$$\tau = K\gamma^n \quad (1)$$

where τ is the shear stress (Pa), γ is the shear rate (s^{-1}), K is the consistency coefficient (Pa S^n), and n is the flow behavior index (dimensionless). The well-known power law model (Eq. (1)) is used extensively to describe the flow properties of non-Newtonian liquids in theoretical analysis as well as in practical engineering applications (Barnes et al., 1989).

The effect of temperature on the apparent viscosity of five native starch dispersions at a specified shear rate can be determined using an Arrhenius model (Eq. (2)), in which the apparent viscosity (η) decreases exponentially with temperature:

$$\eta = K_0 \exp(\mathrm{Ea}/RT) \quad (2)$$

where η is the apparent viscosity (Pa s) at 100 s^{-1}, K_0 is a constant (Pa s), T is the absolute temperature (K), R is the gas constant (8.3144 J mol^{-1} K^{-1}), and Ea is the activation energy (kJ mol^{-1}).

2.5. SEM

The morphology of the starch granules was observed by scanning electron microscopy. Starch samples were mounted on circular aluminum stubs with double sticky tape and then coated with 20 nm of gold and examined and photographed in a scanning electron microscope (model 1530VP, LEO, Oberkochen, Germany) at an accelerating potential of 20 kV.

2.6. Differential scanning calorimetry (DSC)

Gelatinization properties were measured and recorded on a Perkin-Elmer DSC-8000 (Norwalk, CT, USA) differential scanning calorimeter, equipped with a thermal analysis data station. Water