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Effect of the ionic liquid 1-ethyl-3-methylimidazolium acetate on the phase transition of starch: Dissolution or gelatinization?

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ABSTRACT

This work revealed that the interactions between starch, the ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]), and water might contribute to the phase transition (gelatinization, dissolution, or both) of native starch at reduced temperature. Using mixtures of water and [Emim][OAc] at certain ratios (7.2/1 and 10.8/1 mol/mol), both the gelatinization and dissolution of the starch occur competitively, but also in a synergistic manner. At lower [Emim][OAc] concentration (water/[Emim][OAc] molar ratio $\geq$ 25.0/1), mainly gelatinization occurs which is slightly impeded by the strong interaction between water and [Emim][OAc]; while at higher [Emim][OAc] concentration (water/[Emim][OAc] molar ratio $\leq$ 2.8/1), the dissolution of starch is the major form of phase transition, possibly restricted by the difficulty of [Emim][OAc] to interact with starch.

1. Introduction

Starch is a natural polymer with particular properties unlike those of traditional polymers. As a heterogeneous material, it has macromolecular structures bound in a granular superstructure; it normally has both linear (amylose) and branched (amylopectin) molecules; and it contains both amorphous and crystalline regions within its granules (Pérez & Bertoft, 2010). When native starch granules are heated in water, their semicrystalline nature and three-dimensional architecture are gradually disrupted, resulting in a phase transition from the ordered granular structure into a disordered state in water, which is known as "gelatinization" (Atwell, Hood, Lineback, Varrianomarston, & Zobel, 1988; Lelievre, 1974; Ratnayake, Jackson, & Steve, 2008). Gelatinization is an irreversible process that includes several, often sequential steps, such as granular swelling, native crystalline melting (loss of birefringence), and molecular solubilization (Russo et al., 2009). The gelatinization process is essential in the processing of foods and emerging biodegradable starch-based materials.

For improving starch's processibility and product properties, adding new functionalities, and expanding the current applications, it is not uncommon to carry out processing of starch in environments containing substances other than water. Various plasticizers and additives for starch processing that have been used include polyols (glycerol, glycol, sorbitol, etc.) and nitrogen-containing compounds (urea, ammonium derived, and amines) (Liu, Xie, Yu, Chen, & Li, 2009; Xie, Halley, & Avérous, 2012). However, these plasticizers or additives either are not stable under normal processing conditions, can be lost from the final product, or are hydroscopic. An alternative class of materials known as ionic liquids (ILs), now commonly defined as salts which melt below 100 °C, has recently attracted much interest for the processing of biopolymers including starch. Many ILs, especially ones based on the imidazolium cation, outperform other plasticizers and additives as they directly dissolve polysaccharides such as starch and thus can be used as an excellent media for polysaccharide plasticization and modification (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006; El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007; Wilpiszewska & Spychaj, 2011; Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2010; Zhu et al., 2006). Furthermore,

Abbreviations: WMS, waxy maize starch; RMS, regular maize starch; G50, Gelose 50; G80, Gelose 80; [EMIM][OAc], 1-ethyl-3-methylimidazolium acetate; T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔT, temperature range, i.e. $T_c - T_o$; ΔH, enthalpy.

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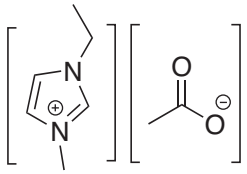

Fig. 1. Chemical structure of 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]).

studies have shown that starch-based ionically conducting polymers or solid polymer electrolytes could be developed by using ILs as plasticizers, such as 1-allyl-3-methylimidazlium chloride ([Amim][Cl]), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]), or 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][CF_3SO_3]) (Liew, Ramesh, Ramesh, & Arof, 2012; Ramesh, Liew, & Arof, 2011a; Ramesh, Shanti, Morris, & Durairaj, 2011b; Ramesh, Shanti, & Morris, 2012; Wang, Zhang, Liu, & He, 2009a; Wang, Zhang, Wang, & Liu, 2009b; Wang, Zhang, Liu, & Han, 2010b). Sankri et al. (2010) and Leroy, Jacquet, Coativy, Reguerre, & Lourdin (2012) have already done pioneering work using 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) as a new plasticizer in melt processing of starch-based materials and improvements in plasticization, electrical conductivity, and hydrophobicity were demonstrated.

It is worth noting that many of the ILs used previously to plasticize starch contained the corrosive [Cl^-] anion (e.g. [BMIM][Cl]) (Wilpiszewska and Spychaj, 2011). By heat dispersion in this type of IL, macromolecular degradation of starch could be observed (Kärkkäinen, Lappalainen, Joensuu, & Lajunen, 2011; Stevenson, Biswas, Jane, & Inglett, 2007), due to acidic hydrolysis of glycosidic bonds in starch-based materials. Specifically, the reason for this degradation is the formation of HCl (as a result of the protonation of [Cl^-] anion in the presence of moisture), which can catalyze the depolymerization of starch (Kärkkäinen et al., 2011). Considering these issues, it has been suggested that ILs with non-halogen-containing anions such as 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) (see Fig. 1 for chemical structure) may be more suitable for the development of high-performance functional starch-based materials. [Emim][OAc] has a very low vapor pressure, high thermal stability, and relatively low viscosity at room temperature (Liu & Budtova, 2012), which enables it to be used with starch in a wide range of processing conditions.

Very recently, Liu and Budtova (2012) carried out a quality study of gelatinization/dissolution of waxy maize starch in water/[Emim][OAc] mixtures of different ratios by microscopy. Compared with pure water or neat [Emim][OAc], the water/[Emim][OAc] mixtures of certain ratios produced better gelatinization and dissolution of starch at elevated temperature (Liu and Budtova, 2012). Their results also showed that the dependence of gelatinization/dissolution parameters on the ratio of water/[EMIM][OAc] was quite complex. However, the mechanism of such gelatinization/dissolution was not well understood and it is unlikely that starch–IL gelatinization is best revealed using solely microscopy.

This paper focuses on understanding the role of water/[Emim][OAc] mixtures in starch gelatinization/dissolution and the establishment of the corresponding mechanisms. Maize starches with different amylose contents have been used. They are interesting because that they can be directly provided by nature and the varied amylose content has an impact on the native granular structures, processing behaviors, and final product properties (Chaudhary, Miler, Torley, Sopade, & Halley, 2008; Chaudhary, Torley, Halley, McCaffery, & Chaudhary, 2009; Li et al., 2011; Tan, Flanagan, Halley, Whittaker, & Gidley, 2007; Wang, Yu, Xie, Chen, Li, & Liu, 2010a; Xie et al., 2009, 2012).

The three most recognized techniques for starch gelatinization characterization were used; namely differential scanning calorimetry (DSC), rapid visco analysis (RVA), and microscopy. DSC provides the possibility of analyzing the transition temperatures as well as the transition enthalpies, which correspond to the melting of crystalline structures in starch during heating. RVA, which is used as an industrial standard, detects the viscosity change of starch slurries during a pre-set controlled heating and cooling, where the gelatinization process (which results in viscosity changes) can be revealed. Microscopy is a simple but reliable method in the study of starch as it reveals the morphology (under normal light) and crystalline structures (under polarized light) of starch. To the best of our knowledge, this is the first work involving the use of these different techniques in the study of starch phase transitions in ionic liquid–water environments and the exploration of the possibility to dissolve starch at reduced temperature. Basic knowledge related to the use of ILs in starch processing is thus provided, which is valuable for future work.

2. Materials and methods

2.1. Materials

Four varieties of commercially available maize starches were used in this work, including waxy maize starch (Mazaca 3401X) (WMS), regular maize starch (Avon Maize Starch) (RMS), Gelose 50 (G50), and Gelose 80 (G80). RMS was supplied by New Zealand Starch Ltd. (Onehunga, Auckland, New Zealand) and the other three starches were supplied by National Starch Pty Ltd. (Lane Cove NSW 2066, Australia). All starches were chemically unmodified and the amylose contents for these four types of starches were 3.4%, 24.4%, 56.3% and 82.9%, respectively, as measured by Tan et al. (2007) using the iodine colorimetric method. The original moisture contents of the four starches were 12.4%, 14.1%, 13.6%, and 14.4%, respectively. Deionized water was used in all instances. [Emim][OAc] of purity ≥90%, produced by BASF, was supplied by Sigma–Aldrich. [Emim][OAc] was used as received without further purification but the purity was considered for molar ratio calculation. As [Emim][OAc] was in liquid form at room temperature, different ratios of water/[Emim][OAc] mixture could be easily prepared in vials for subsequent studies. Water and [Emim][OAc] were completely miscible according to the [Emim][OAc] specifications provided by BASF. The mass ratios of water/[Emim][OAc] used were 10/0, 9/1, 7/3, 5/5, 4/6, 2/8, and 0/10; and the related molar ratios were 1/0 (pure water), 96.0/1, 25.0/1, 10.8/1, 7.2/1, 2.8/1, 0.1/1 (also in Appendix A). Molar ratio will be used in Sections 3 and 4.

2.2. DSC

A TA Q2000 DSC (TA Instruments, Inc., New Castle, DE 19720, USA) was used to investigate the thermal transition of native starches in water/[Emim][OAc] mixtures. 1.5–3 mg of starch was weighed into the 40 μL Tzero aluminium pan (TA Instruments), to which was then added, by a microsyringe, the water/[Emim][OAc] mixture, in the amount 10 times that of the starch. Then, a pin was used to gently mix starch with the plasticizer. After sealing, the pan was gently shaken for a few seconds. The mixing and shaking were to ensure the starch granules were completely immersed and equally dispersed in the liquid but did not sediment at the bottom of the pan. The pans thus prepared were transferred into the DSC machine for immediate analysis to avoid sedimentation of starch granules or time effects of the water/[Emim][OAc] mixture on starch. An empty pan was used as a reference. The pans were heated from 20 °C to 120 °C at a scanning rate of 5 °C/min. The instrument was calibrated using indium as a standard. At least two runs were carried out for each sample to ensure the consistency of the results. The Universal Analysis 2000 (TA Instruments–Waters LLC) software