



A comparison study on phase transition and structure of cornstarch in dimethyl sulfoxide and ionic liquid systems



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ABSTRACT

A comparison study of the phase transition and structure of waxy cornstarch in DMSO and AMIMCl systems was conducted using a differential scanning calorimeter, an optical microscope, a scanning electron microscope, X-ray diffraction and thermogravimetric analysis. A full disruption and dissolution of starch granules was completed in 10 h at room temperature in pure DMSO, which was faster and more effective than that in ionic liquid 1-allyl-3-methylimidazolium chloride (AMIMCl). When dispersed in DMSO/water and AMIMCl/water at various ratios, respectively, different phase transitions were clearly exhibited, and the appearance and crystal structure of starch granules were significantly damaged with an increase in the concentration. Basing on the study of the decomposition temperature change through TGA measurements, a decreased temperature was observed in both DMSO and AMIMCl system, meaning starch degradation occurred with different levels. The huge temperature change from 357 to 328 °C were found in AMIMCl system, which most likely induced the distinct exothermic phenomenon in the DSC observation due to a significant depolymerization of starch.

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1. Introduction

Starch is one of the most versatile natural polymers and has many advantages such as exhaustible supply, low cost, renewability and biodegradability. Generally, most native starch consists of a mixture of two polymers, amylose and amylopectin. Amylose is essentially a linear structure of α -1, 4 linked glucose units, whereas amylopectin is a highly branched structure of short α -1, 4 chains linked by α -1, 6 bonds. Physically, in their original form, starch granules contain a semi-crystalline structure with altering amorphous and crystalline regions: Amylose and the branching points of amylopectin form the amorphous regions, whereas the short-branched chains of the amylopectin construct the crystalline regions (Liu et al., 2009a; Shi et al., 1998; Tester et al., 2004; Zobel, 1988). The crystalline configuration of starch can be effectively

distinguished by X-ray powder diffraction (XRD), and it is typically classified into three types, A, B, or C (Cheetham and Tao, 1998), depending on the botanical origin of the starch.

Due to the presence of the crystalline phase in granules, starch are highly insoluble and remain virtually intact in cold water, and specific solvents are usually essential for manufacturing value-added products based on starch. With a certain plasticizer at elevated temperature, starch gelatinization or melting occurs, contributing to a disruption of starch structure; and, if preferential conditions are reached, it can lead to a homogeneous amorphous material known as thermoplastic starch (or plasticized starch), which is essential in the production of some starch-based materials (Liu et al., 2009a; Xie et al., 2015). Water is most commonly employed as a plasticizer for starch processing, and substances such as polyols (glycerol, glycol, sorbitol, etc.), compounds containing nitrogen (urea, ammonium derived, amines) have also been developed for plasticization. Undoubtedly, a suitable plasticizer for starch should be stable during thermal processing, be ineffective in macromolecular degradation of starch, and be able to provide final products with enhanced performance and new capabilities (Xie et al., 2014, 2015). However, the currently used plasticizers do not

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yet have all the desired attributes and thus finding alternative and better ones for starch is of great interest.

Because of their fascinating and unique properties, such as the negligible vapor pressure, low melting points, non-flammable nature, miscibility with other solvents and recyclability, ionic liquids (ILs) have recently been claimed to be “green solvents” and applied to dissolve highly polar compounds, including carbohydrates, posing a promising alternative that opens up a broad variety of new opportunities (Kubisa, 2009), which typically consist of an organic cation and smaller organic or inorganic anions, are essential organic salts. Many ILs, such as 1-allyl-3-methylimidazolium chloride (AMIMCl), 1-butyl-3-ethylimidazolium chloride (BMIMCl), and 1-ethyl-3-methylimidazolium acetate (EMIMAc), have been shown to be capable of dissolving starch and thus can be applied as an excellent media for starch plasticization and modification (Wilpiszewska and Szychaj, 2011; Xie et al., 2015). Moreover, a few studies also have shown that starch-based ionically conducting polymers or solid polymer electrolytes could be developed by using ILs (Leroy et al., 2012; Sankri et al., 2010; Xie et al., 2015). In these studies, the liquids were found to remarkably disrupt the hydrogen bonding between the hydroxyl groups of starch and consequently to lead to dissolution, which strongly depended on the structure of IL, the environmental temperature and the resource of starch (Lehmann and Volkert, 2009; Wang et al., 2009). Later, other researchers further reported that in the presence of water, starch gelatinization and dissolution occurred simultaneously, depending on the ratio of IL and water in the mixed solvent system (Mateyawa et al., 2013; Sciarini et al., 2015; Zhang et al., 2015; Zhao et al., 2015). Such mixed system decreases the higher cost of IL and brings some unique characters for starch, providing a new way to tailor starch-based products with controlled structures.

Dimethyl sulfoxide (DMSO) is the polar aprotic solvent most frequently used for SEC analysis. Although it is less directly related to applications, a few studies have been conducted on the structural configuration and behavior of starch in the system. Moreover, binary DMSO-water mixtures have been widely used to dissolve starch molecules without degrading them (Jackson, 1991). In fact, starch could be gelatinized and solubilized by dispersion in aqueous DMSO solutions, a process that is radically different from gelatinization in boiling water (Mukerjea et al., 2006). However, to the best of our knowledge, no studies have compared the phase transitions of starch in the solvent systems of DMSO and IL, particularly in terms of their aqueous solvents at various concentrations, and the inherent mechanisms have not been fully understood.

Therefore, the main focus in present research was to conduct a thorough study and comparison of the effect of DMSO and ionic liquid AMIMCl on the fine structure, morphology and phase transition of starch, in particular focusing on the changes in gelatinization, dissolution and degradation. Using an aqueous solution of DMSO and AMIMCl at various ratios, an intermediate rather than a complete destruction of the starch granules was designed. Waxy cornstarch, which is primarily composed of amylopectin, was applied in current work as a model material to simplify the understanding and the interpretation of the results obtained. Evidence collected from a differential scanning calorimeter (DSC), an optical microscope, a scanning electron microscope (SEM) and X-ray diffraction (XRD) was used to elucidate the corresponding mechanism of phase transition and evaluate the relative characters, which, in turn, will be helpful in the comprehension of the fine structure of starch at the molecular level, including both the double helices of amylopectin and the complexes of amylose-lipid, and provided knowledge for understanding starch-solvent interactions and for designing starch-based materials with desired properties.

2. Materials and methods

2.1. Materials

The waxy cornstarch, which contained primarily amylopectin (>99.6%, manufacturer's data), used in this work is commercially available and was supplied by Penford Food Ingredients Company (Australia). The initial moisture content of the starch was about 13.5%, measured by heating samples to 110 °C for 20 min by an infrared heating balance (Model DHS-20).

DMSO with a purity of 99.7% and AMIMCl with a purity of 99.5% were provided by the Lanzhou Institute of Chemical Physics (Lanzhou, China). The two solvents were also diluted with deionized water to create solvent mixtures with different ratios (w/w: approximately 0/100, 20/80, 50/50, 80/20 and 100/0), which were generated before usage; they are labeled as control, 20% DMSO (AMIMCl), 50% DMSO (AMIMCl), 80% DMSO (AMIMCl) and 100% DMSO (AMIMCl) in the following descriptions. All reagents were used as received.

2.2. Microscope

A polarization microscope (BHS-2, Olympus Vanox, Japan) equipped with a MicroPulisher 3.3 RTV camera and a hot-stage (THMS600, Linkam, UK) thermo-system was applied in this work. The magnification was 500 × (50 × 10). Suspensions of 0.5 wt% starch (with respect to the total amount) in the different solvents were initially prepared in glass vials, and then, one drop of sample was transferred onto a glass cover-slip and sealed using silicon adhesive before subsequent measurements using the hot stage. As starch suspensions were heated, both normal light and polarized light were used to capture the microscopic images of the granules dispersed in the solvent. Each sample was heated from room temperature (25 °C) to 100 °C at 2 °C/min. The camera interval timer was set as 30 s so that an image was captured at each 1 °C temperature increase. The measurements were performed in triplicate to ensure consistent results.

To monitor the series of changes of starch granules with an increasing storage time, the starch samples were first prepared following the method described above, and then sealed with silicon adhesive to prevent water evaporation, finally each sample was fixed onto the microscope stage for continuous observation (up to 52 h) under the same visual field. The integral optical density (IOD) method was used to compare the change in the birefringence brightness in the solvent as described in the previous work (Zhao et al., 2015). The IOD value of each digital image, which is defined as the sum of the optical density (OD) values of all pixels within the area under birefringence light, was calculated using Image-Pro Plus 5.0 software. Degree of dissolution (DD) based on the IOD value was calculated as follows:

$$\text{Background correction : } C = A - B \quad (1)$$

$$\text{DD (\%)} = (1 - C/C_0) \times 100\% \quad (2)$$

where A is the original IOD value at specific point, B is the background IOD value, which was calculated from the original digital image when all birefringence disappeared, and C_0 is the initial real IOD value.

2.3. Differential scanning calorimeter (DSC)

A Perkin-Elmer DSC Diamond-8000 with a refrigerated cooling system and nitrogen purge gas was used in the experimental work. The melting point and enthalpies of indium were used to calibrate

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