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Dissolution of unmodified waxy starch in ionic liquid and solution rheological properties

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ABSTRACT

Dissolution of waxy corn starch in 1-ethyl-3-methylimidazolium acetate (EMIMAc) was qualitatively studied and compared with gelatinisation process in water. The rheological properties of starch–EMIMAc solutions were investigated in dilute and semi-dilute regions, from 0.1 to 10 wt% over temperature range from 20 °C to 100 °C. The values of zero shear viscosity were obtained by applying Carreau–Yasuda model to shear-thinning flow curves and plotted vs. polymer concentration. Power law exponents in viscosity-concentration dependence in semi-dilute region were compared with the ones reported previously for microcrystalline cellulose. Intrinsic viscosity was obtained as a function of temperature and compared with the one of microcrystalline cellulose; starch was found to be much less temperature sensitive than cellulose. Amylopectin overlap concentration in EMIMAc was compared with the one in water and 0.5 M NaOH–water. Based on these comparisons it was suggested that starch conformation in EMIMAc is similar to the one in water (compact ellipsoid). The activation energy was calculated for starch–EMIMAc solutions and demonstrated to obey power-law concentration dependence.

1. Introduction

Starch is a major component in many food plants such as wheat, potatoes, maize, rice and peas. It is renewable, biodegradable, cheap, and mainly used in food, paper and pharmaceutical applications. Mixing starch with cellulose, another abundant polysaccharide, can bring new interesting ways of making polysaccharide-based materials with tuned properties. To achieve this, a common solvent is needed, as far as cellulose does not melt. Unlike starch, which could be readily gelatinised and dissolved once heated in water, the solvent options for cellulose are quite limited (Liebert, 2009). Researchers have been exploring different solvent systems for blending cellulose and starch (or starch derivative), from sodium hydroxide–water (Builders, Bonaventure, Tiwalade, Okpako, & Attama, 2010; Chang, Jian, Zheng, Yu, & Ma, 2010; Wang, Chang, & Zhang, 2010) and N-methylmorpholine-N-oxide monohydrate (NMMO) (Nechwatal, Michels, Kosan, & Nicolai, 2004; Wendler et al., 2010, 2011) to various ionic liquids (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006; Kadokawa, Murakami, Takegawa, & Kaneko, 2009; Wu, Wang, Li, Li, & Wang, 2009). All these solvents have certain advantages and weakness. NaOH–water is economic, “green” and easy to operate, whilst it is hard to ignore the limited amount of cellulose that can be dissolved in this solvent and the inevitable gelation of solution (Egal, Budtova, & Navard, 2007; Roy, Budtova, & Navard, 2003). Bringing urea and/or thiourea into the solvent system (Cai & Zhang, 2006; Zhou, Chang, Zhang, & Zhang, 2007) or adding zinc oxide (Liu, Budtova, & Navard, 2011) improves solution stability but does not solve both problems (Egal, Budtova, & Navard, 2008; Liu et al., 2011). Despite the fact that NMMO is used as cellulose solvent on the industrial level, it is not easy to operate because of specific temperature regime and reaction by-products.

Ionic liquids (ILs), especially but not limited to imidazolium based ones, have been proved quite efficient solvents for polysaccharides. Numerous kinds of ILs have been applied to dissolve cellulose of different origins and molecular weights. The maximum concentration of cellulose dissolved is much higher as compared to NaOH–water system, making it possible to build objects of various shapes and structures, for example, fibres, films and aerogels (Cai, Zhang, Guo, Shao, & Hu, 2010; Sescousse, Gavillon, & Budtova, 2011; Turner, Spear, Holbrey, & Rogers, 2004; Wendler, Kosan, Krieg, & Meister, 2009). ILs have also been designed and developed as a media to carry out chemical modifications of polysaccharides (El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007; Murugesan & Linhardt, 2005). 1-Ethyl-3-methylimidazolium acetate (EMIMAc) is a commercialised imidazolium-based ionic liquid with very low vapour pressure, high thermal stability and a relatively low viscosity at room temperature, which enables

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cellulose dissolution by simple heating and stirring. The properties of cellulose–EMIMAc solutions has been intensively investigated in the past decade (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Heinze et al., 2008; Li et al., 2011; Lovell et al., 2010; Maki-Arvela, Anugwom, Virtanen, Sjoholm, & Mikkola, 2010; Sescousse, Le, Ries, & Budtova, 2010). The dissolution of starch in ILs such as 1-butyl-3-methylimidazolium chloride (BMMCl) or 1-allyl-3-methylimidazolium chloride (AMIMCl) has also been reviewed recently (Wilpiszewska & Spychaj, 2011), however, the information on solution properties is rather scarce. In addition to the use of ionic liquids as a common solvent of polysaccharides, there is another interest in studying starch–IL solution properties: it is the possibility to perform chemical reactions in the homogeneous conditions. The properties of IL may be tuned by varying anions and cations, which lead to new routes of starch modifications. The understanding of starch–IL solution properties on the molecular level is thus a prerequisite for a successful processing of mixed polysaccharides and for starch chemical derivatisation as well.

The goal of this work is to provide a fundamental background on solution and hydrodynamic properties of starch–ionic liquid. We use EMIMAc as a solvent of unmodified waxy corn starch. This starch is pure amylopectin which simplifies the understanding and interpretation of the results obtained. First we use optical microscope to monitor starch granules dissolution in EMIMAc, and we compare this process with starch gelatinisation in water. Then we examine the rheological properties of both dilute and semi-dilute starch–EMIMAc solutions. Using Carreau–Yasuda model, we obtain zero-shear rate viscosities at various temperatures and starch concentrations and use them to build viscosity-concentration dependences. This allows us to determine starch intrinsic viscosity at different temperatures and to compare the trend obtained with the one known for cellulose dissolved in EMIMAc. Finally, we calculate starch activation energy and show that it is power-law dependent on starch concentration.

2. Experimental

2.1. Materials

Unmodified waxy corn starch (amylose-free, “starch” in the following) was purchased from Sigma–Aldrich. Starch was dried before use in vacuum oven at 50 °C for 1 h to remove water residues. Ionic liquid, 1-ethyl-3-methylimidazolium acetate (EMIMAc) of purity $\geq$90% was from BASF. A fresh bottle of EMIMAc was used as received without further purification.

2.2. Methods

2.2.1. Dissolution of starch in IL

Except for optical microscope observations, starch–EMIMAc solutions of different concentrations (from 0.123 wt% to 10 wt%) were prepared by mixing starch and IL in a sealed reaction vessel at 80 °C for 24–48 h to ensure complete dissolution. The reaction vessel was filled with nitrogen during the dissolution process.

2.2.2. Optical microscope for dissolution/gelatinisation observation

Optical microscope (Leica, Germany) was used to observe and compare the behaviour of starch granules in EMIMAc, water and EMIMAc/water mixtures (in wt%). Dry starch was dispersed in each solvent to reach 5 wt% and stirred for 10 min at room temperature. Within this duration the granules remained intact. One drop of sample was placed between glass slides, quickly heated to 40 °C and then heated from 40 °C to 100 °C at 5 °C/min using Linkam hot stage with Peltier plate for temperature control. Photos of 500× magnification were taken with Archimedes software at every 2 °C during the heating. Each experiment was repeated at least two to three times; the difference in dissolution/gelatinisation temperature for the same system from one experiment to another was 2–3 °C.

2.2.3. Rheological measurement of starch/IL solutions

Rheological measurements were performed on a Bohlin Gemini^{TM} 150 rheometer (Malvern Instruments, UK) with a Peltier temperature control system. Measuring system was cone-plate geometry with 4° angle and 40 mm diameter. For each solution, steady state viscosity was recorded as a function of shear rate, from 0.001 s^{-1} to 500 s^{-1}, at a constant temperature. Each shear rate sweep was performed at various temperatures, from 20 °C to 100 °C, with 10 °C increment. Silicone oil (DC 200, Sigma–Aldrich) was placed around the edge of the measuring cell to prevent water absorption. Silicone oil is not miscible with polysaccharide solutions and had a relatively lower viscosity ($\eta_{20\,^{\circ}\mathrm{C}} = 9.5$ mPa s) thus not perturbing the measurements. A solvent trap covering the measuring cell and wrapped with Parafilm® (Pechiney Plastic Packaging, US) was also used to prevent water absorption.

3. Results and discussion

3.1. Dissolution/gelatinisation process of starch in EMIMAc, water and EMIMAc/water

The goal of this part is to qualitatively analyse the behaviour of starch granules in ionic liquid and compare with the known starch-in-water gelatinisation process. Only one heating rate, at 5 °C/min, was used to qualitatively demonstrate the difference in starch behaviour in EMIMAc vs. water.

The evolution of 5% starch dry granules dispersed in EMIMAc under heating from 40 °C is shown in Fig. 1 for some representative temperatures. For comparison, the same process but in water is demonstrated in Fig. 2. In EMIMAc, starch dissolution gradually proceeds with time and temperature. Solvent penetrates granule, making outer layer slightly swollen (and thus transparent); however, most of the granules kept their initial shape up to 80 °C. Above 80 °C quick dissolution occurs (Fig. 1d) and less and less granules can be seen, up to complete visual disappearance at 100 °C after a few minutes of storage at this temperature. Total (visual) dissolution time in these conditions was about 16 min. A similar behaviour was observed for normal maize starch (23% amylose content) in 78%NMMO–22%water system (Koganti, Mitchell, Ibbett, & Foster, 2011). Starch dissolution in EMIMAc also occurs at room temperature but kinetics is very slow. Such dissolution process is clearly very different from starch gelatinisation in water (see Fig. 2). In water, waxy corn starch granules first swell with temperature increase and then burst around 65–70 °C (Fig. 2b) under heating conditions. Whilst there is a large amount of liquid around dissolving starch granules in EMIMAc (Fig. 1b–e), in water granules are highly swelling absorbing almost all water around (Fig. 2a and b). The viscosities of these systems are thus very different.

It was interesting to check what type of behaviour, dissolution or gelatinisation, “dominates” in a mixed solvent, EMIMAc–water. Here again, only qualitative conclusions were made based on granule evolution monitored with optical microscopy. Three solvent mixtures were prepared, with 25, 50 and 75 wt% of EMIMAc, the rest being water. We found that dissolution similar to the one in pure EMIMAc occurs for 75%EMIMAc–25%water system (Fig. 3) and gelatinisation was detected for 25–75% (Fig. 4) and 50–50% EMIMAc–water. The characteristic temperatures of the beginning and the end of gelatinisation or dissolution, and of the total time needed to dissolve granules as depicted from optical micrographs, are shown in Table 1. The availability of water molecules can be one of the factors controlling gelatinisation vs. dissolution, however,