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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 ($\eta_{20\,^\circ C} = 9.5$ 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,

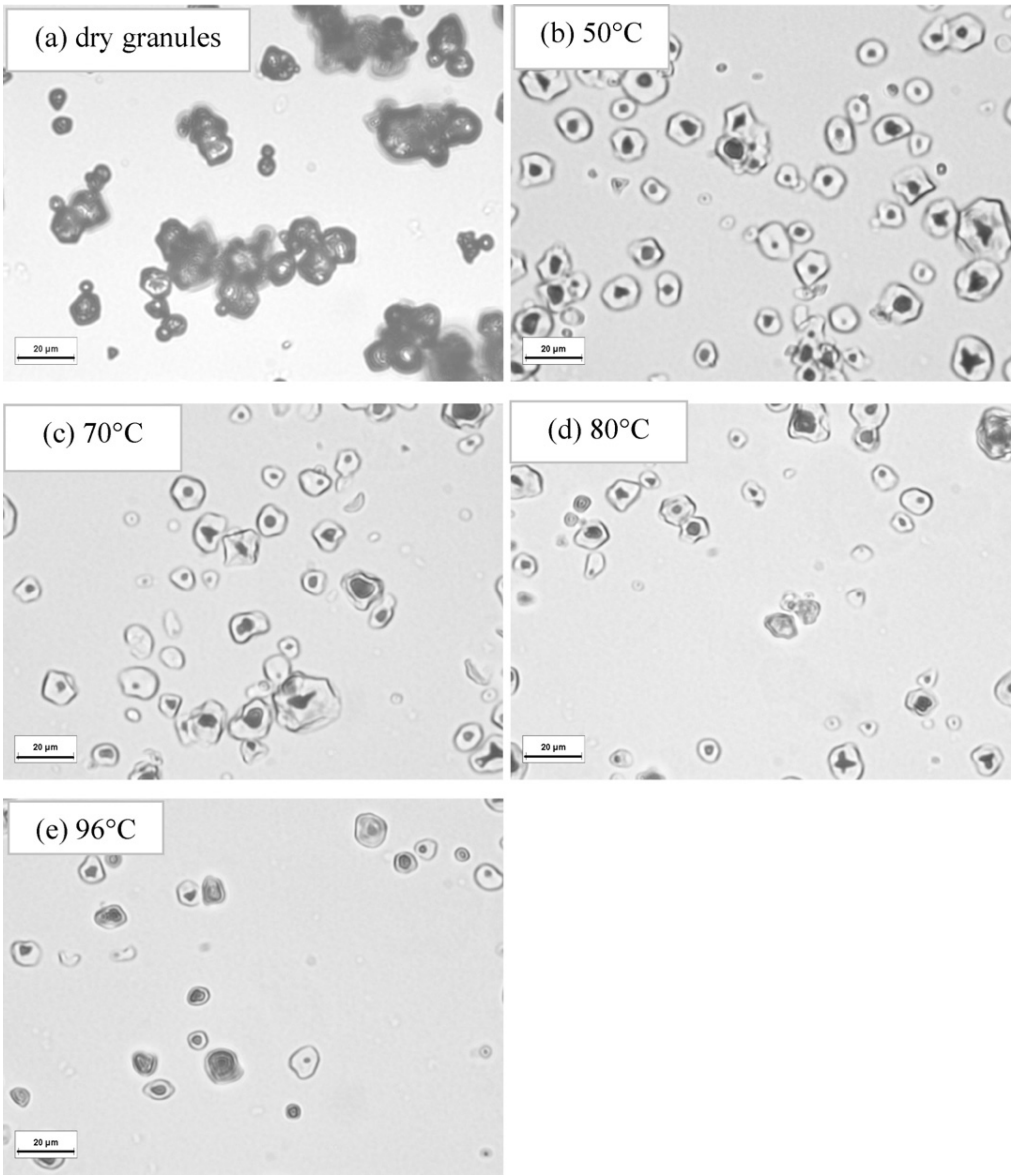

Fig. 1. Evolution of waxy corn starch granules in EMIMAc during heating. The scale in all optical micrographs is 20 μm.

several other factors such as the interactions between EMIMAc and water should also be taken into account.

The presence of water in EMIMAc strongly accelerates the dissolution as compared with pure EMIMAc (Table 1): for example, in 75%EMIMAc–25%water the dissolution is visually completed at 78 °C in 8 min vs. 16 min in pure EMIMAc. Several reasons can be given to explain this result. Water, being much less bulky than EMIMAc, penetrates the granule first, swells the outer layer and facilitates ionic liquid penetration and starch dissolution. The viscosity of "new solvent", 75%EMIMAc–25%water, is much lower than the one of pure EMIMAc, as shown in a recent article of Le, Sescousse, & Budtova, 2012). The decrease in solvent viscosity increases polymer diffusion coefficient and allows quicker homogenisation of the whole system and thus quicker dissolution. Finally, EMIMAc and water are interacting (Le, Sescousse, & Budtova, 2012) and EMIMAc–water may become a more powerful solvent. Whilst the last reason is a speculation, the first two can indeed explain the acceleration of starch dissolution in the presence of water. When the major component in EMIMAc–water mixture is water (25%EMIMAc–75%water system, Fig. 4), gelatinisation process occurs: granules first swell and then start bursting at 75–77 °C. Surprisingly, this temperature is almost ten degrees

Table 1
Parameters characterising dissolution and gelatinisation of waxy starch in EMIMAc, water and EMIMAC–water mixtures.

	Beginning of dissolution or gelatinisation (°C)	Temperature of complete dissolution (°C)	Total dissolution time (min)
100% EMIMAc	75–80	100	16
75%EMIMAc–25%water	54–56	76–78	8
50%EMIMAc–50% water	54–56	76–78	8
25%EMIMAc–75%water	75–77	100	12
100% water	65–70	95–100	12

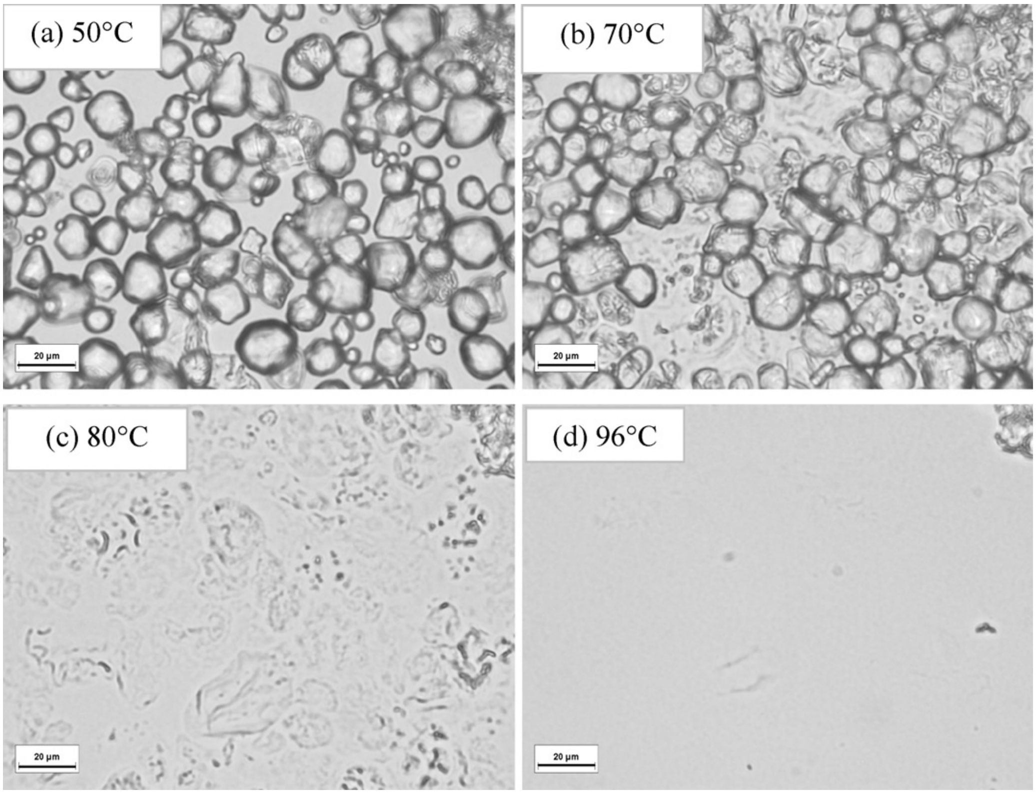

Fig. 2. Swelling and burst of waxy corn starch in water at different temperatures.

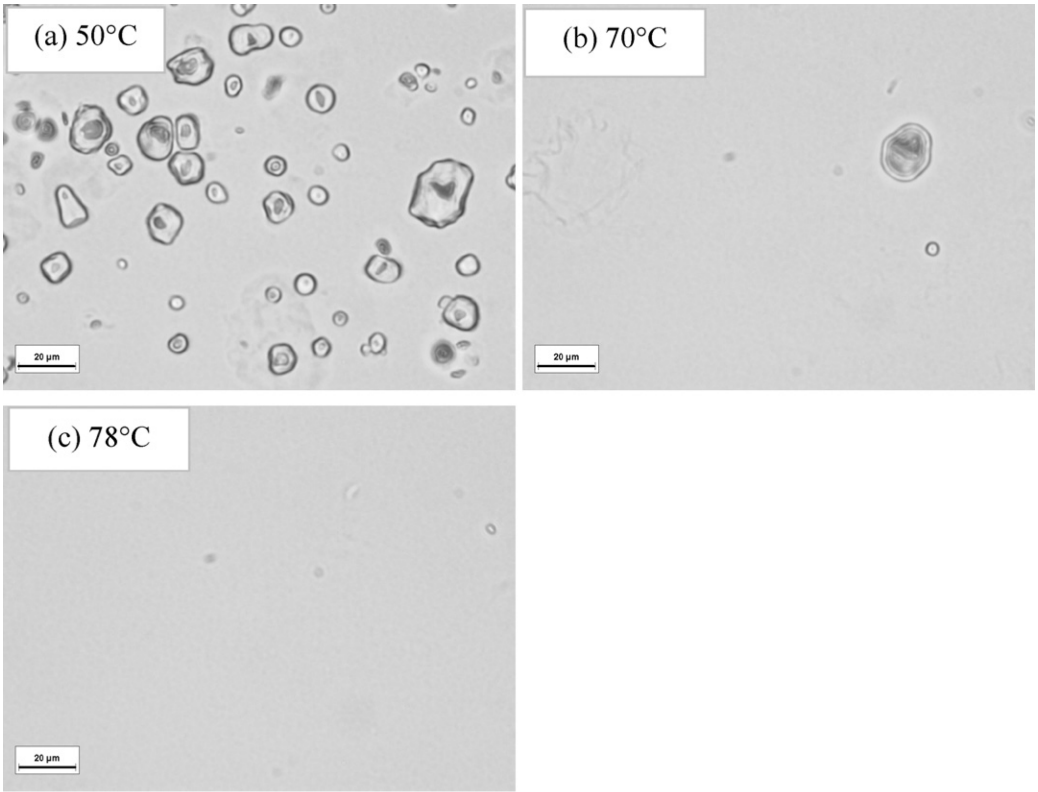

Fig. 3. Behaviour of waxy corn starch granules in 75%EMIMAc–25%water at different temperatures.

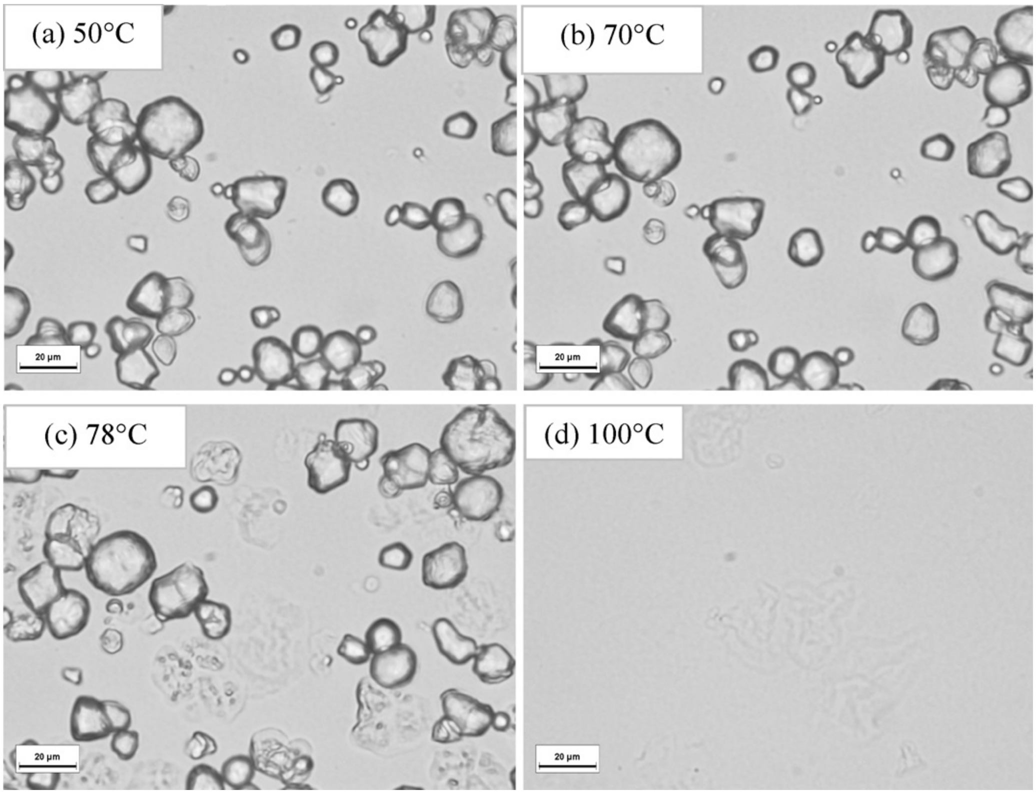

Fig. 4. Swelling and burst of waxy corn starch granules in 25%EMIMAc–75%water at different temperatures.

higher that the equivalent one in water; gelatinisation is "delayed" as compared with pure water. The dissolution in 25%EMIMAc–75%water is visually completed at 100 °C. To interpret this result the interactions between EMIMAc and water should be first understood. What can be concluded from this qualitative study is that (a) starch dissolution in EMIMAc proceeds in time with very low swelling of granules, with temperature increase speeding up the dissolution and (b) the presence of water up to 50% strongly accelerates dissolution.

3.2. Rheological proprieties of amylopectin starch solution in EMIMAc

3.2.1. Flow curves

The examples of steady state viscosity of starch–EMIMAc solutions at various concentrations and temperatures are presented in Fig. 5. At high polymer concentrations the flow is shear-thinning. Such behaviour is different from microcrystalline cellulose–EMIMAc solution which was found Newtonian over several shear rate decades (Gericke et al., 2009) and can be explained by higher molecular weight of amylopectin. The shear-thinning behaviour of amylopectin has also been reported in other solvents as water, DMSO and NMMO (De Vasconcelos, Pereira, & Fonseca, 2001; Koganti et al., 2011).

In order to perform further analysis of starch–EMIMAc solutions on the molecular level, zero-shear rate viscosities, η_0, were determined for each polymer concentration and temperature. The values of η_0 were obtained by fitting the flow curves with the Carreau–Yasuda model according to Eq. (1) (Yasuda, Armstrong, & Cohen, 1981):

$$\frac{\eta(\dot{\gamma})-\eta_\infty}{\eta_0-\eta_\infty}=\left[1+(\lambda\dot{\gamma})^{\alpha}\right]^{(m-1)/\alpha} \qquad (1)$$

where $\eta(\dot{\gamma})$ is viscosity measured at a certain steady shear rate, η_∞ is solvent viscosity, λ is the relaxation time, m is power law index and α is the fitting parameter. Solid lines in Fig. 5 show that calculated viscosity-shear rate dependences are fitting well the experimental data. Contrary to starch–water pastes, amylopectin–EMIMAc solutions behave like a classical polymer solution allowing further analysis of macromolecule hydrodynamic properties.

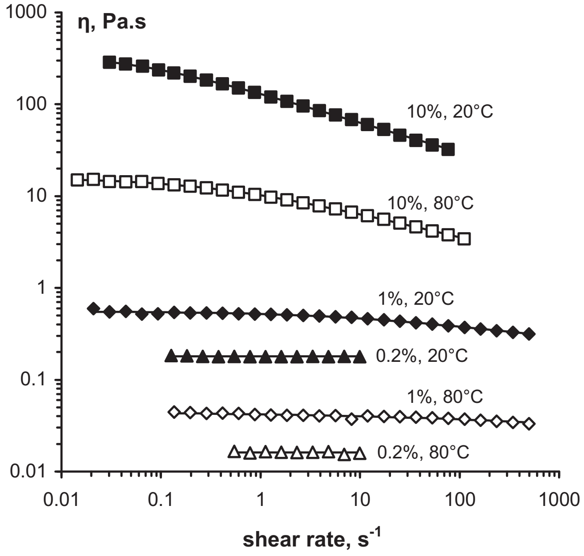

Fig. 5. Viscosity-shear rate dependence for starch–EMIMAc solutions of various concentrations at different temperatures. Lines are approximations calculated according to Eq. (1).

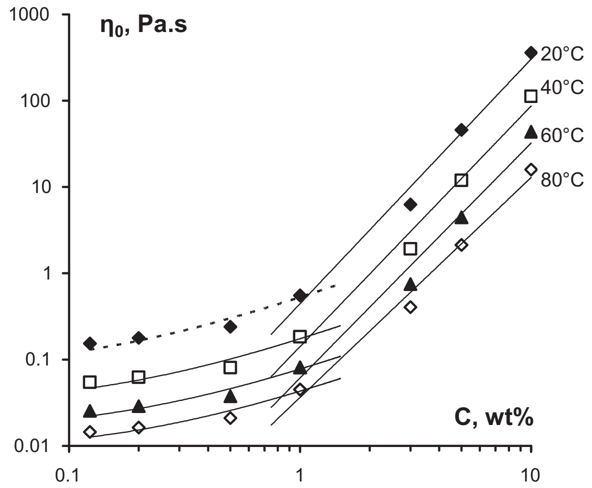

Fig. 6. Zero-shear rate viscosity vs. concentration for amylopectin-EMIMAc solutions at different temperatures. Dashed lines are linear dependence for dilute solutions, solid lines correspond to power-law approximation (Eq. (2)) calculated above the overlap concentrations.

3.2.2. Viscosity-concentration dependence, intrinsic viscosity and overlap concentration

The examples of zero-shear rate viscosity as a function of polymer concentration for amylopectin–EMIMAc solutions at four selected temperatures are shown in Fig. 6. In dilute region, the viscosity increases linearly with starch concentration. Once in the semi-dilute region, we found the classical power law viscosity-concentration dependence for polymer solutions:

$$\eta_0 \sim C^n \tag{2}$$

The power law coefficient n decreases from 2.84 to 2.53 when temperature increased from 20 °C to 100 °C, as demonstrated in Fig. 7. The values of n are in the same range as for other polysaccharides in EMIMAc and also for amylopectin in other solvents (Gericke et al., 2009; Sescousse et al., 2010; Yang et al., 2006); however, the influence of temperature on amylopectin macromolecule is much less pronounced as compared with cellulose dissolved in the same solvent (Gericke et al., 2009; Sescousse et al., 2010).

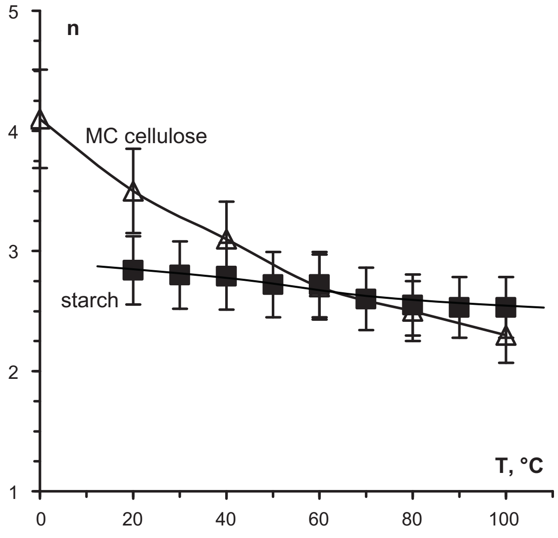

Fig. 7. Power law coefficient from Eq. (2) as a function of temperature for semi-dilute starch–EMIMAc solutions, with error bars of 10%. Data for microcrystalline cellulose (DP = 300) are taken from reference Gericke et al. (2009). Lines are to guide the eye.

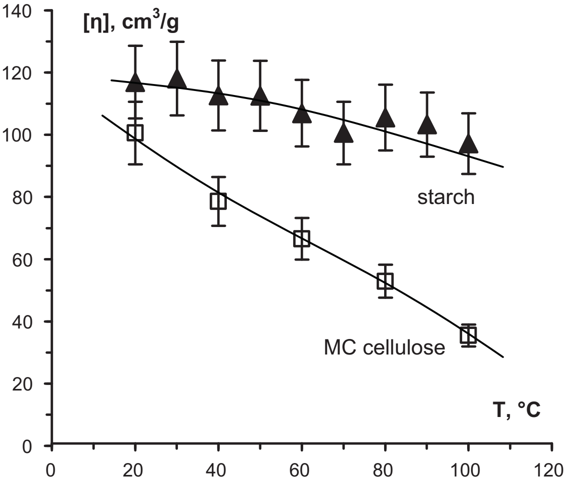

Fig. 8. Intrinsic viscosity of amylopectin and MC cellulose in EMIMAc as a function of temperature, with error bars of 10%. Data on cellulose are taken from Gericke et al. (2009). Lines are to guide the eye.

Polymer intrinsic viscosity, $[\eta]$, is an important parameter which reflects the size of the macromolecule in a given solvent at a certain temperature. Usually $[\eta]$ is obtained from solution dilution with the solvent in Ubbelohde capillary viscometer. The procedure then consists of plotting $(\eta_{\mathrm{rel}} - 1)/C$ vs. C and deducing $[\eta]$ as limiting value at $C = 0$, where relative viscosity $\eta_{\mathrm{rel}} = \eta_{\mathrm{sol}}/\eta_{\mathrm{solv}}$, η_{sol} and η_{solv} are solution and solvent viscosity, respectively, and polymer concentration C is expressed in mass per volume units. In order to recalculate amylopectin concentration in g/cm^3, we used solvent (EMIMAc) density equal to 1.1 g/cm^3 which is a mean value between 1.08 at 90 °C and 1.12 g/cm^3 at 20 °C (Sescousse et al., 2010). This small variation of density with temperature can be neglected in the calculation of the intrinsic viscosity in the view of all other accumulated errors.

In the case studied here it was not possible to perform measurements in a capillary Ubbelohde viscometer because EMIMAc is too viscous and too hygroscopic to be studied in contact with the air. Thus we used solution and solvent zero-shear rate viscosities obtained from the flow curves as described above at various starch concentrations and solution temperatures. We applied Wolf approach (Eckelt et al., 2011; Wolf, 2007) to calculate amylopectin intrinsic viscosity as far as data presented in the classical Huggins plot, $(\eta_{\mathrm{rel}} - 1)/C$ vs. C, were somewhat scattered and do not allow an adequate $[\eta]$ determination. Briefly, Wolf approach consists in the calculation of the limiting slope of $\ln(\eta_{\mathrm{rel}})$ vs. C which, according to phenomenological considerations, is identical to the intrinsic viscosity (Wolf, 2007). Indeed, both Huggins and Wolf approaches gave the same cellulose intrinsic viscosity values for cellulose dissolved in NMMO monohydrate (Eckelt et al., 2011).

Amylopectin intrinsic viscosity as a function of temperature is shown in Fig. 8. It slightly decreases with temperature increase. The trend obtained can again be compared with $[\eta]$ of microcrystalline cellulose (DP 300) in EMIMAc as a function of temperature (Gericke et al., 2009). Fig. 8 shows that cellulose macromolecule is much more sensitive to temperature as compared with amylopectin; however, for both polysaccharides temperature increase leads to solvent (EMIMAc) thermodynamic quality decrease. Considering the fact that amylopectin is a branched high molecular weight polymer and its intrinsic viscosity is close to the one of microcrystalline cellulose at room temperature, it can be assumed that amylopectin has a very compact conformation, probably solvent impenetrable, like oblate ellipsoid in water and in DMSO (Callaghan & Lelievre, 1985; Durrani & Donald, 2000). Amylopectin is thus much less affected by temperature as compared with cellulose, a linear

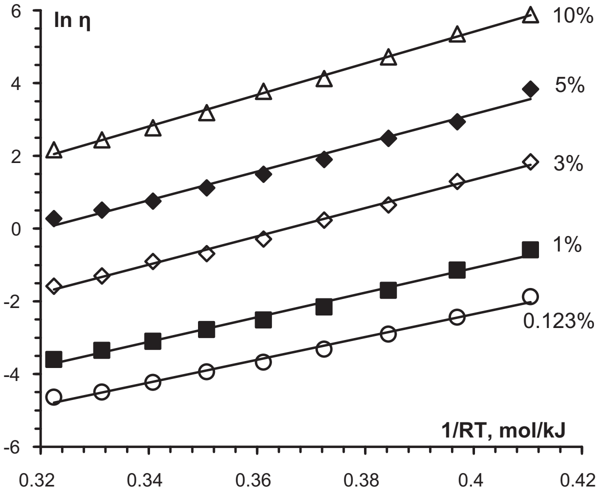

Fig. 9. Arrhenius plots for starch–EMIMAc solutions at different concentrations; error bars are smaller than or equal to the point size.

polymer, which can adopt more conformations as a reaction to external conditions.

Another proof that amylopectin conformation in EMIMAc is similar to the one in water can be deduced from the analysis of the overlap concentration, C^*, which can be determined as the inverse value of $[\eta]$. C^* of amylopectin in EMIMAc varies from 0.8 to 1 wt% for temperatures from 20 °C to 100 °C. The value of about 1 wt% could be roughly guessed from the viscosity-concentration dependence (Fig. 6). Our value of C^* of amylopectin in EMIMAc is in the same range as the $C^* = 0.9$ wt% of waxy starch in water at 25 °C as reported by Ring et al. (1987) and higher than the $C^* = 0.46$ wt% in 0.5 M NaOH–water at 25 °C obtained by Yang et al. (2006). This means that 0.5 M NaOH–water is thermodynamically better solvent for amylopectin than EMIMAc. It should be noted that the comparison of the exact values of overlap concentrations cited above should be taken with care as far as they were obtained with different methods: in 0.5 M NaOH it was with light scattering technique, in water with Ubbelohde viscometer and in EMIMAc (this case) with viscosity measured with rotational rheometer. As far as amylopectin C^* values in water and in EMIMAc are practically the same (0.9 and 0.8, respectively), this confirms that amylopectin conformation in EMIMAc is similar to the one in water.

3.2.3. Viscosity-temperature dependence and activation energy

The viscosity-temperature dependence of amylopectin-EMIMAc solution was analyzed with the classical Arrhenius approach: $\eta \sim \exp(E_a/RT)$, where E_a is the activation energy, R is the universal gas constant and T is temperature in K. The values of $\ln\eta$ plotted as a function of the inverse temperature are shown in Fig. 9. The experimental dependence of $\ln\eta$ vs. $1/RT$ can be considered linear within the experimental errors (standard deviation $R^2 > 0.985$) despite the fact that data for EMIMAc and low-concentrated solutions have a slightly concave shape. This has also been observed for cellulose solutions in EMIMAc and in BMIMCl and is due to the unique behaviour of the ionic liquids (Gericke et al., 2009; Sescousse et al., 2010).

The values of E_a obtained are comparable with the ones of microcrystalline cellulose dissolved in EMIMAc (Gericke et al., 2009) as well as with amylose dissolved in BMIMCl (Horinaka, Yasuda, & Takigawa, 2011). The activation energy increases with polymer concentration increase, as shows Fig. 10. A power law correlation between solution activation energy and polymer concentration C was suggested for cellulose–ionic liquid solutions (Sescousse et al., 2010): $E_a = E_a(0) + pC^x$, where $E_a(0)$ is solvent activation energy and p and x are adjustable constants. A far as at low polymer concentrations E_a vs. C can be approximated by a straight line (see inset Fig. 10), we suggest a more general correlation:

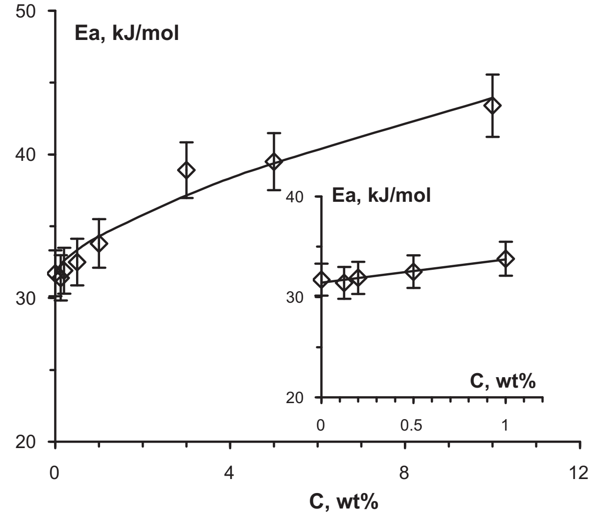

Fig. 10. Activation energy of starch–EMIMAc solutions at different concentrations: symbols are experimental data with 10% error bars; solid line is calculated according to Eq. (3). Inset: the same data below the overlap concentration, line is a linear approximation.

$$E_a = E_a(0) + aC + bC^x \quad (3)$$

Indeed, at $C < C^*$ E_a vs. C is linear; and at $C > C^*$, the least squares approximation gives $a = 0$, $b = 49.5$ and $x = 0.61$, see line in Fig. 10. The result obtained shows that activation energy-polymer concentration power law dependence works well for polysaccharides dissolved in ionic liquids.

4. Conclusions

The dissolution of waxy corn starch in ionic liquid, EMIMAc, and solution properties were investigated. The dissolution process in EMIMAc is different from starch gelatinisation in water. Starch granules in EMIMAc were gradually dissolved in time without swelling. The presence of water accelerates the dissolution probably due to granules partial swelling in water and facilitating EMIMAc diffusion.

The flow of waxy corn starch–EMIMAc solution at various temperatures and starch concentrations were studied. Above the overlap concentration (~1 wt%) the solutions are shear-thinning. Carreau–Yasuda model was used to fit experimental flow curves. Zero shear viscosity vs. starch concentration was examined; in semi-dilute region power law exponents varied from 3 to 2.5 for temperatures from 20 °C to 100 °C, respectively. Power law exponent decrease with temperature increase obtained for starch is much less pronounced as compared with microcrystalline cellulose dissolved in the same solvent (from 4 to 2 for the same temperature interval).

Amylopectin intrinsic viscosity slightly decreases with temperature increase indicating the decrease of solvent quality. As compared with cellulose intrinsic viscosity in the same solvent, this decrease for starch is much less pronounced: from 120 to 100 cm^3/g for starch vs. 100 to 30 cm^3/g for cellulose, for temperatures from 20 °C to 100 °C, respectively. The fact that amylopectin intrinsic viscosity is the same as the one of microcrystalline cellulose at room temperature, and also that amylopectin overlap concentration practically coincides with the one in water means that starch conformation is most probably a compact ellipsoid. This finding may explain low amylopectin sensitivity to temperature as compared with cellulose dissolved in the same solvent. The activation energy of the viscous flow of waxy corn starch–EMIMAc solutions was obtained for various polymer concentrations and successfully approximated by power law dependence.

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