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Ionic liquids as starch plasticizers or solvents

RAPID COMMUNICATION

Summary — The article presents results of application of ionic liquids {1-allyl-3-methylimidazolium chloride ([AMIM]Cl) as well as deep eutectic solvents: choline chloride/urea, choline chloride/citric acid, choline chloride/succinic acid} as plasticizers and solvents for potato starch. Rheometric measurements and morphology changes of thermoplasticized starch/ionic liquid systems and solubility tests for 5 wt. % starch solutions in ionic liquids have been performed. Dry starch was dissolved in ionic liquids at high temperatures (80—135 °C). [AMIM]Cl, choline chloride/urea and choline chloride (for moisturized starch) displayed best plasticizing abilities.
Keywords: starch, ionic liquid, deep eutectic solvent, choline chloride, plasticizer, solvent.

CIECZE JONOWE JAKO PLASTYFIKATORY LUB ROZPUSZCZALNIKI SKROBI
Streszczenie — W artykule przedstawiono wyniki badań nad zastosowaniem cieczy jonowych {chlorku 1-allilo-3-metyloimidazoliowego ([AMIM]Cl) oraz mieszanin eutektycznych: chlorek choliny/mocznik, chlorek choliny/kwas cytrynowy, chlorek choliny/kwas bursztynowy} jako plastyfikatorów i rozpuszczalników skrobi ziemniaczanej. Badania obejmowały analizę zmian reologicznych i morfologii termoplastyfikowanych układów skrobiowych oraz testy rozpuszczalności 5 % mas. roztworów skrobi w cieczach jonowych. W badanych cieczach jonowych sucha skrobia ulegała rozpuszczeniu w temperaturze należącej do przedziału 80—135 °C. Najlepsze właściwości plastyfikujące wykazały [AMIM]Cl, chlorek choliny/mocznik oraz sam chlorek choliny (tylko dla skrobi wilgotnej).
Słowa kluczowe: skrobia, ciecz jonowa, mieszanina eutektyczna, chlorek choliny, plastyfikator, rozpuszczalnik.

Ionic liquids (ILs) are organic salts with melting point below 100 °C. They consist only of an organic cation and a smaller organic or inorganic anion. Because of unique properties, such as non-flammability, non-volatility, ionic conductivity, catalytic activity, thermal, chemical as well as electrochemical stability and recyclability ILs have attracted much interest in the last years [1—3].

Term „deep eutectic solvent" (DES) is used to a type of ionic solvent comprising a mixture which forms an eutectic with a melting point significantly lower than that of its individual components. The deep eutectic phenomenon was first described in 2003 [4] for a mixture of choline chloride (ChCl) and urea in a 1:2 molar ratio. The charge delocalization occurring through hydrogen bonding between the halide anion with hydrogen donor moiety is responsible for the decrease of the freezing point of the mixture relative to the melting points of individual components. Compared to ionic liquids which share many characteristics but are ionic compounds and not ionic mixtures, DESes are cheaper to produce, much less toxic and sometimes biodegradable.

During the last few years vigorous research effort in biomass processing utilizing ILs is observed. Most papers, including some review contributions concerning biomass treatment with ILs are focused mainly on cellulose and lignin, or direct wood dissolution [2, 3]. Less attention is paid to research of ILs and starch systems. Very recently a review contribution about the starch/IL systems concerning questions of ILs dissolving and/or plasticization abilities and environment for starch chemical modification, has appeared [5].

Among conventional ILs: 1-allyl-3-methylimidazolium chloride [AMIM]Cl is one of the most efficient starch solvents and plasticizers [5]. DESes based on choline chloride (ChCl) are good candidates for starch modification because they interact strongly with OH groups of glycosidic units, decrease chain interaction and plasticize the polymer. They can also wet the surface of

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individual grains and bind them together [6]. ChCl is nontoxic and readily available as a bulk commodity chemical (vitamin B4) [7].

This work presents results of comparative evaluation of ILs, *i.e.* conventional [AMIM]Cl as well as some deep eutectic salts based on ChCl as plasticizers and solvents of potato starch (both are called here ionic liquids).

EXPERIMENTAL

Materials

In this work potato starch (Nowamyl S.A.) was used. To prepare ILs for investigation of their starch plasticizing or/and dissolution abilities there were applied: choline chloride (ChCl, Sigma-Aldrich, purity ≥98 %), urea (U, pure, Chempur), succinic acid (SA, pure, Reanal) and citric acid (CA, pure, Chempur).

Molar ratios of eutectic mixtures were as follows: ChCl/urea (ChCl/U) 1:2, ChCl/succinic acid (ChCl/SA) 1:1, ChCl/citric acid (ChCl/CA) 2:1. These eutectic mixtures acting as DESes were prepared by stirring the components at 100 °C, until transparent colorless liquid was obtained. Then the temperature was slowly decreased and DES was poured into a hermetic vessel.

[AMIM]Cl has been synthesized according to the method described in [8]. *N*-methyl imidazole was placed in a glass reactor and allyl chloride (to reach the molar ratio 1:1.2) was added dropwise during stirring followed by the temperature increase up to 55 °C. The reaction system was kept for 24 h under continuous stirring. The transparent amber liquid was washed few times with ethyl acetate and then placed in a vacuum drier for 12 h at 85 °C.

Methods

Rheometric behavior of IL/starch systems was investigated with ARES rheometer (Rheometric Scientific) equipped with parallel plate system. Samples for these measurements were prepared by mixing IL with dried (with 3 wt. % of water, dS) or undried potato starch (with 14 wt. % of water, mS) in mass ratio 30:100. After that starch pastes were kept in hermetic vials for 48 h. Pressed material from ARES was analyzed in terms of morphology (crystallinity) by X-ray diffraction (X'pertPro, PANalytical, operated at the CoKα wavelength 1.78901 A).

In order to study plasticizing abilities of ILs hot compression molding tests for IL/starch systems with mass ratio 30:100 have been performed using Testchem laboratory hand press.

Vials containing 5 wt. % of dried starch in ILs were prepared and kept initially at 80 °C for 1 h and when the sample was still heterogeneous with visible granules, the temperature was respectively increased. Visual as well as laser scanning microscopy (LSM) using Keyence VK-9710 observations of vials content was performed for solubility evaluation.

RESULTS AND DISCUSSION

Rheometric behavior

Rheometric behavior of IL/starch systems in a function of temperature was evaluated. Rheometric curves for the systems based on dried or moist starch were collected in Figure 1. Figure 1a presents dry and moist starch/[AMIM]Cl systems ([AMIM]Cl/dS and [AMIM]Cl/mS, respectively). The sample [AMIM]Cl/dS exhibited sharp decrease of viscosity (η) from 10^4 to 50 Pa · s in the temperature range 25—40 °C, whereas [AMIM]Cl/mS within the same range of temperature showed η above 10^4 Pa · s. Above 45 °C η of the former system increased reaching the level of *ca.* $2 \cdot 10^4$ Pa · s at 65 °C. Both rheometric curves showed viscosity increase at 80—105 °C (with maximum at 10^5 Pa · s at 105 °C).

DES/starch materials have been investigated using dry starch (DES/dS) only because water negatively influences

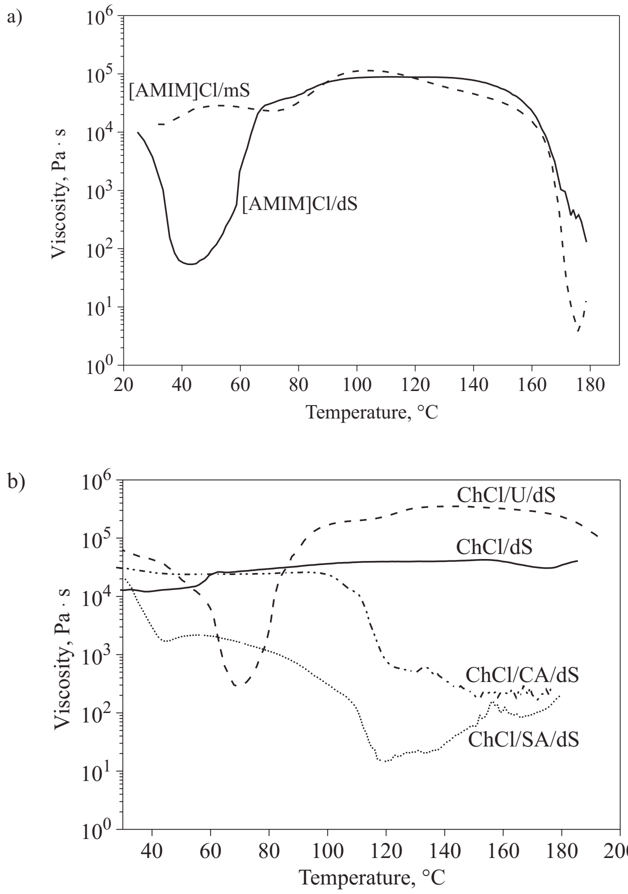

Fig. 1. Rheometric curves for ILs/starch systems with mass ratio 30:100: a) with [AMIM]Cl and dry starch (dS, 3 wt. % of water) or moist starch (mS, 14 wt. % of water); b) based on dry starch with ChCl itself or with deep eutectic mixtures of ChCl with urea (ChCl/U 1:2 mol/mol), citric acid (ChCl/CA 2:1 mol/mol) or succinic acid (ChCl/SA 1:1 mol/mol)

interaction between components of DES pairs. Practically flat rheometric curve has been found for ChCl/dS system (Fig. 1b). It might mean that no plasticization of dry starch in the presence of high melting ChCl (205 °C) takes place. Rheometric behavior of ChCl/U/dS composition is similar to that of [AMIM]Cl/dS, *i.e.* fast viscosity drop in the range 30—70 °C ($7 \cdot 10^4$—$3 \cdot 10^2$ Pa·s) and then sharp increase up to 10^5 Pa·s (70—100 °C) (Fig. 1b).

Different rheology was observed for starch systems with DES based on ChCl and carboxylic acids (CA) (Fig. 1b). The sample ChCl/CA/dS revealed viscosity decrease from 10^4 to $4 \cdot 10^2$ Pa · s above *ca*. 100 °C. Even deeper viscosity drop exhibited the sample with ChCl/SA from $2 \cdot 10^4$ Pa · s (30 °C) to 15 Pa · s (120 °C). Runs of the two rheometric curves for DES/dS materials based on carboxylic acids (differences above 100 °C in comparison with the other dependences in Fig. 1) — might be caused by esterification reaction of carboxylic groups with polysaccharide hydroxyls.

Crystallinity of thermoplasticized starches

IL/starch materials after rheometric investigations have been analyzed using X-ray diffraction to evaluate crystallinity changes. The respective diffractograms are presented in Figure 2. Intensity of pattern in the range 18—20° characteristic for B-type crystallinity has been greatly diminished in cases of starch materials plasticized with [AMIM]Cl (moist starch) and ChCl/carboxylic acid (dry starch). It may show high amorphization degree of these samples. XRD curves for dry starches with [AMIM]Cl and ChCl/U are similar to that of native starch (most starch).

Hot compression molding tests

Hot comparison molding tests were performed to study plasticizing abilities of various ILs/starch systems. Samples were molded in the laboratory hand press using the pressure of 20 MPa at 140 °C during 10 min. Eight discs were investigated. Appearance of the pressed thermoplasticized discs was described in Table 1.

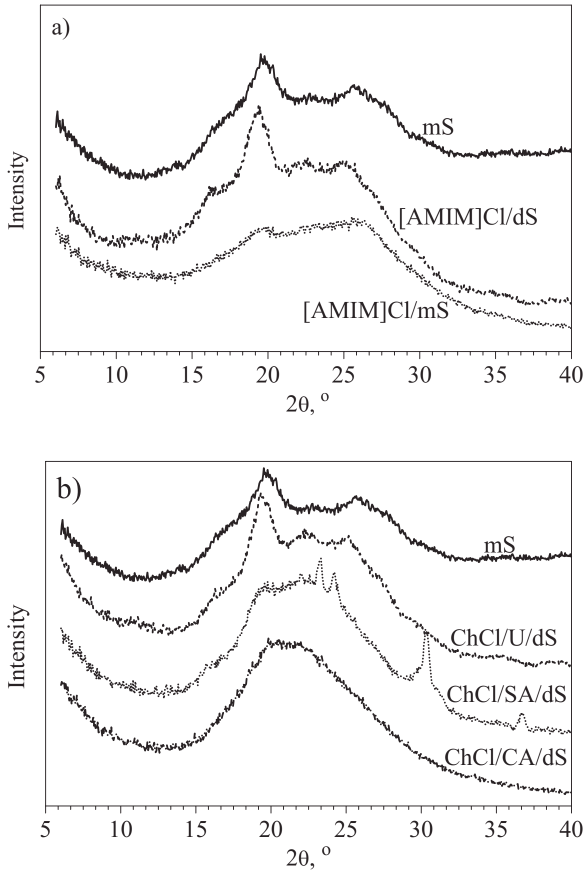

Fig. 2. Comparison of XRD diffractograms of native starch (mS) with that obtained for residues after thermoplasticization in rheometric test conditions of ILs/starch systems with mass ratio 30:100: a) [AMIM]Cl and dry or moist starch, b) based on dry starch with ChCl itself and deep eutectic mixtures of ChCl with urea (ChCl/U 1:2 mol/mol), citric acid (ChCl 2:1 mol/mol) and succinic acid (ChCl/SA 1:1 mol/mol)

Solubility tests

Table 1 contains description of experiments in which the starch granules were fully dissolved. Except of the system with [AMIM]Cl in which polysaccharide was fully dissolved at 80 °C, all starch samples with DESes are soluble above 100 °C. Starch dissolves in ChCl/U at

T a b l e 1. Results of comparison of molding and solubility tests of starch/ILs systems

Sample acronym	Compression molding test		Solubility test (5 wt. % starch solutions)	
	temperature/pressure/ time, °C/MPa/min	remarks	temperature/ time, °C/min	remarks
[AMIM]Cl/dS	140/20/10	cream-colored, semitransparent	80/60	clear, amber gel
[AMIM]Cl/mS		cream-colored, transparent	80/60	clear amber liquid
ChCl/dS		not flowing	—	—
ChCl/mS		transparent, colorless	—	—
ChCl/U/dS		colorless, semitransparent	118/60	colorless very viscous liquid
ChCl/U/mS		colorless, transparent	118/60	swollen, semitransparent gel particles
ChCl/CA/dS		sticky, transparent, porous, yellowish	120/60	brown very viscous liquid
ChCl/SA/dS		colorless, transparent porous	135/60	brown very viscous liquid

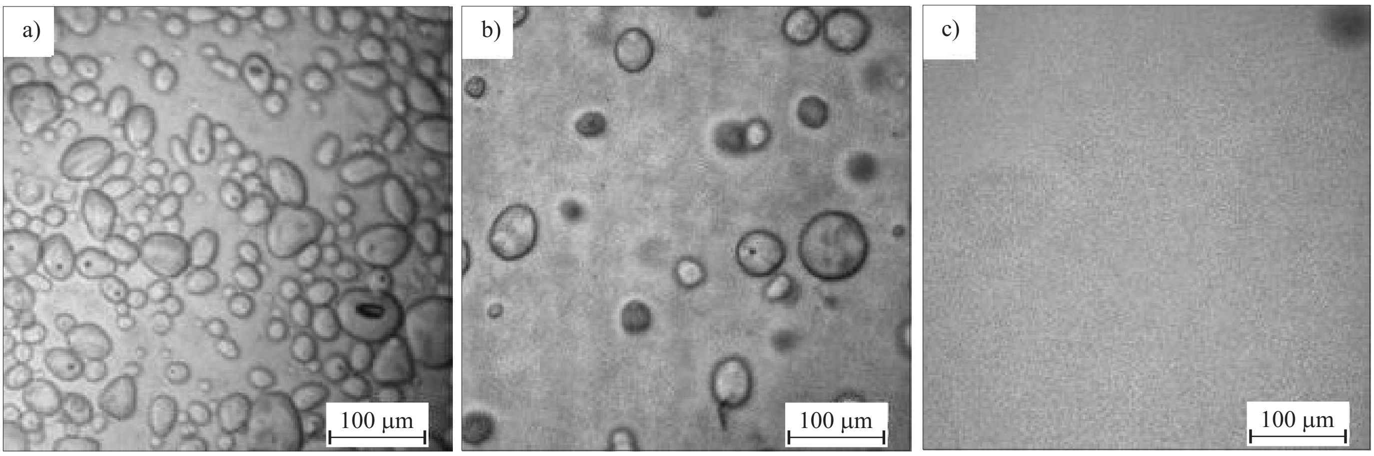

Fig. 3. LSM micrographs for 5 wt. % dry potato starch in ChCl/U eutectic mixture after 1 h solubility tests at: a) 80 °C, b) 100 °C, c) 118 °C

118 °C and forms a transparent colorless gel. In cases of DESes with acids the solution temperatures are 120 °C for ChCl/CA and 135 °C for ChCl/SA. During long time high temperature treatment the last two samples became brown. Figure 3 presents laser scanning microscopy pictures of starch/ChCl/U system during its gradual heating up to 118 °C. Starch granules still present at 80 °C are disrupted and just some left at 100 °C and fully disappeared at 118 °C.

CONCLUSIONS

Investigated ionic liquids both conventional 1-allyl-3-methylimidazolium chloride and eutectic mixtures based on choline chloride can be used as starch solvents, *e.g.* for chemical and enzymatic transformations. The best plasticizing properties besides the mentioned IL exhibited also choline chloride (with moisturized starch) and choline chloride/urea eutectic mixture. To evaluate tendency for retrogradation and mechanical properties of thermoplasticized starches further investigations are necessary.

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