Carbohydrate Polymers 86 (2011) 424–428

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Review

Ionic liquids: Media for starch dissolution, plasticization and modification

Katarzyna Wilpiszewska, Tadeusz Spychaj*

Polymer Institute, West Pomeranian University of Technology, ul. Pulaskiego 10, 70-322 Szczecin, Poland

ARTICLE INFO

Article history:
Received 16 March 2011
Received in revised form 6 May 2011
Accepted 1 June 2011
Available online 12 June 2011

Keywords:
Ionic liquids
Starch dissolution
Starch thermoplasticization
Chemically modified starch

ABSTRACT

A growing interest in applying ionic liquids as polysaccharide solvent has been observed. The influence of ionic liquid on native starch structure has been described. The first synthetic review of various chemical modifications of starch as well as starch plasticization using ionic liquids has been reported.

Contents

1. Introduction . . . 424
2. Ionic liquids as starch solvents . . . 425
3. Starch plasticization by ionic liquids . . . 426
4. Chemical modification of starch in an ionic liquid environment . . . 426
5. Conclusion . . . 427
References . . . 427

1. Introduction

Starch is one of the most abundant natural polymers. There has been increasing interest in manufacturing value-added products based on starch (Ma, Yu, & Kennedy, 2005; Taguet, Huneault, & Favis, 2009). Growing interest in modifying starch into thermoplastic form has been observed. Thermoplastic starch (TPS) is obtained by destructurization of semicrystalline granular structure of native starch. To process starch plasticizers mainly low molecular weight polar compounds such as glycerol, urea, formamide are normally required (Wilpiszewska & Spychaj, 2006). TPS as a biodegradable material could be used for packaging and agricultural purposes (Chaudhary, Torley, Halley, McCaffery, & Chaudhary, 2009). However, some shortcomings of conventional TPS materials such as sensitivity to water or tendency for retrogradation which causes brittleness might limit their application.

Ionic liquids (ILs) are organic salts with melting point below 100 °C. They consist only of an organic cation and 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 (El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007; Olivier-Bourbigou, Magna, & Morvan, 2010). Depending on the ions they may exhibit hydrophilic or hydrophobic properties.

ILs have been claimed as “green solvents” because of their negligible vapour pressure, non-flammability and recyclability. Recently the influence of ionic liquids on the environment was a matter of interest (Modelli, Sali, Galletti, & Samorí, 2008; Olivier-Bourbigou et al., 2010; Pretti, Chiappe, Baldetti, Brunini, Monni, & Intorre, 2009). The cation and anion structure determines the IL toxicological properties, e.g. for imidazolium-based ILs toxicity increases with the number of nitrogen atoms in the cation ring (Couling, Bernot, Docherty, Dixon, & Maginn, 2006). It is established that side chains on the imidazolium cations have strong influence on IL toxicity; the longer and more branched side chain, the more toxic IL. The effects of anions are generally more complicated (Olivier-Bourbigou et al.,

---

* Corresponding author. Tel.: +48 91 449 4684; fax: +48 91 449 4247.
E-mail address: Tadeusz.Spychaj@zut.edu.pl (T. Spychaj).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.06.001

2010). A high throughput screen based on the agar diffusion method was recently applied to test the toxicity of IL towards microorganisms and to distinguish the toxic and biocompatible ILs (Rebros, Gunaratne, Ferguson, Seddon, & Stephens, 2009).

No research concerning the influence of IL traces in starch material has been reported yet.

ILs are good solvents and can dissolve various substances including biomass (e.g. cellulose, lignin and directly wood as well as other renewable polymers such as starch and chitin). During the last few years vigorous research effort in processing biomass utilizing ILs is observed. Most papers, including some review contributions concerning biomass treatment with ILs are focused mainly on cellulose (Laus et al., 2005), cellulose and lignin (Tan & MacFarlane, 2009) or on direct wood dissolution (Fort, Remsing, Swatloski, Moyna, & Rogers, 2007).

For instance it has been noted, that 1-allyl-3-methylimidazolium chloride [AMIM]Cl is a better cellulose solvent than 1-butyl-3-methylimidazolium chloride [BMIM]Cl (Zhang, Wu, Zhang, & He, 2005). The fact is attributed to smaller size and higher polarity of $[AMIM]^+$ cation as well as ion pair dissociation mechanism above a critical temperature (42 °C in pure [AMIM]Cl) (Zhang et al., 2005). Simmons' team (Singh, Simmons, & Voegel, 2009) has evaluated that 1-ethyl-3-methylimidazolium acetate [EMIM]Ac is currently the most effective IL solvent for a rapid swelling of the secondary plant cell walls (cellulose and lignin) as based on 10 min switchgrass exposure tests at relatively mild temperature (120 °C).

Less research has been reported on other biorenewable polymers with ILs, e.g. chitin or starch (Qin, Lu, Sun, & Rogers, 2010; Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2010). Ionic liquids containing dicyanamide anion are good solvents of low molecular weight saccharides (>100 mg/ml) (Rosatella, Branco, & Afonso, 2009). The dissolving mechanism is based on hydrogen bonding formation between imidazolium salt anion and protons of carbohydrates hydroxyl group in stoichiometric ratio. The cation function is only partially understood and depends probably on its size and hydrophobicity (Remsing, Swatlowski, Rogers, & Moyna, 2006).

This review summarizes the state of art in the field of starch/IL systems concerning questions of ILs dissolving and/or plasticization abilities as well as chemical reaction environment for starch modification.

2. Ionic liquids as starch solvents

Several studies employing 1-butyl-3-methylimidazolium chloride (Lehmann & Volkert, 2009; Liu, Janssen, van Rantwijk, & Sheldon, 2005) or 1-allyl-3-methylimidazolium chloride (Wang, Zhang, Liu, & He, 2009a; Xu, Kennedy, & Liu, 2008a) for dissolving or plasticizing of starch have been reported.

Some ionic liquids (containing Cl^- anions) are able to destroy the semicrystalline structure of native starch granules (Xie, Shao, & Liu, 2010) and disrupt hydrogen bonding between hydroxyl groups of polysaccharide (Stevenson, Biswas, Jane, & Inglett, 2007). The starch solubility depends on ionic liquid structure as well as temperature. For instance, at 80 °C in [BMIM]Cl 15 wt% homogeneous solution might be prepared (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006), when in [AMIM]Cl up to 20 wt% (Xu et al., 2008a) and at 100 °C even 50 wt% still clear and transparent but viscous solution could be prepared (Xu, Wang, & Liu, 2008b); in 1-butyl-3-methylimidazolium dicyanamide starch dissolves only at 90 °C (10 wt%) but in 1-methylimidazolium tetrafluoroborate is insoluble (Biswas et al., 2006). Amylose was found to be soluble up to 20 wt% in 1-allyl-3-methylimidazolium formate at 60 °C (Fukaya, Sugimoto, & Ohno, 2006) and by heating it in 1-methoxymethyl-3-methylimidazolium bromide or 1-methoxyethyl-3-methylimidazolium bromide 30 mg/L solution could be easily prepared (Kimizuka & Nakashima, 2001).

Stevenson et al. (2007) have studied the influence of dispersing starch of different origin (corn, rice, wheat and potato) in [BMIM]Cl on amylopectin molecular weight M_w. A significant cereal amylopectin M_w value decrease has been observed; for potato starch M_w value slightly increased (this phenomenon was not noted for potato starch dispersed in hot water). The potato amylopectin M_w value increase might be attributed to the presence of phosphate derivatives in potato starch and ionic interactions between negatively charged phosphomonoesters and positively charged imidazolium ring of the ionic liquid. Moreover, the concentration of Cl^- could influence the cereal amylopectin degradation – in acidic environment hydrolysis of glycosidic bonds may occur. Phosphate groups of monoesters from potato starch may to some extent repel chloride ions, which may additionally explain different chromatographic results when compared to cereal starches (Stevenson et al., 2007). Additionally, the potato native starch granules are relatively bigger which may impede ionic liquid penetration inside.

Myllymäki and Aksela (2005) claim that using ionic liquid [BMIM]Cl might allow barley starch to be selectively depolymerised. By adjusting depolymerization process parameters (temperature, stirring time) complete amylose depolymerization could be achieved, amylopectin remaining intact (stirring for 30 min at 85 °C and 2 h at 100 °C) or complete depolymerization of both polymers (stirring for 30 min at 85 °C and 2 h at 150 °C). According to the inventors the presence of a small amount of water (<1 wt%) is significant.

Kärkkäinen, Lappalainen, Joensuu, and Lajunen (2011) heat-dispersed starch of different origin (wheat, barley, potato, rice, corn and waxy corn) in [BMIM]Cl under controlled microwave conditions and in oil bath. The effect of temperature, heating time and method on amylose as well as amylopectin molecular weight was studied. Transparent solutions were formed at 100 °C or 80 °C when starch dispersion in [BMIM]Cl was heated, respectively: conventionally and under microwave conditions. The dissolution time depended on the starch origin – when corn, rice, wheat and barley starch was fully gelatinized, waxy corn and potato starch granules were still present. Degradation of amylopectin in [BMIM]Cl was observed immediately after dispersing starch in the ionic liquid, subsequently amylose degraded as well. The molecular weight (determined using gel permeation chromatography equipped with an evaporative light scattering detector) of starch polymers decreased with increasing time and temperature. Microwave heating accelerated starch dissolution as well as degradation process when compared to conventional heating method. However, no selective depolymerization of amylose as described in the patent by Myllymäki and Aksela (2005) was detected. The starch molecular weight reduction might be an effect of the pH value determined by the ionic liquids character: in acidic conditions hydrolysis, in alkaline conditions oxidation and breaking of glycosidic bonds might occur (Stevenson et al., 2007).

A question of the most effective IL as starch solvent still seems to be open as follows from data presented in a recent bulletin issued by Iolitec GmbH company (Heilbronn, Germany) (Smiglak, 2010). Forty eight ILs composed of various cations and anions have been selected and their dissolution power tested toward three biopolymers: cellulose, lignin and starch (type of starch was not given). Criteria of ILs selection for the experiments were as follows: (i) kind of cation core (pyrrolidinium, imidazolium, aromatic, aliphatic, cyclic), (ii) length of alkyl chains, (iii) functional groups on alkyl chains, and (iv) anion kind (acetate, bromide, chloride, dimethylphosphate, dicyanamide, formate, methylsulfate, tetrafluoroborate, triflate). The biopolymer dissolution test was carried out as follows: 4–5 g ILs in a glass vial, initially heating ILs for 60 min at 80 °C, then biomass added and the system vigorously stirred for

1 min and placed back into the heating block for 60 min. The following results have been obtained based on visual analysis of the vial contents: (a) for cellulose (10 wt%) – nine ILs dissolved cellulose completely (including [EMIM]Ac, and [BMIM]Cl, (b) almost all of the ILs tested dissolved lignin (5 wt%), whereas one IL did not dissolve lignin at all, (c) only one IL (non defined) was found to dissolve starch (5 wt%) completely. From the above data it is clear that the real solubility of cellulose in ILs (and lignin as well) is substantially better than that of starch.

3. Starch plasticization by ionic liquids

Sankri et al. (2010) performed starch plasticization with ionic liquids in a twin screw extruder and in a microcompounder. It is currently the only paper relating to continuous method of starch modification using ionic liquids. More noticeable molecular weight decrease of starch extruded with [BMIM]Cl than polysaccharide plasticized with glycerol was assigned rather to thermal–mechanical treatment than interaction with ionic liquid. The polydispersity index M_w/M_n of the extruded starch material was above 3, the presence of high molecular weight fraction was noted. No short chain molecules (DP < 12) was detected thus the depolymerization mentioned by Myllymäki and Aksela (2005) has not occurred. Surprisingly, starch plasticized with [BMIM]Cl had lower hydrophilicity when compared to glycerol plasticized starch (water content 13 and 20 wt%, respectively). Moreover, the value of Young's modulus decreased by one order of magnitude (from 8.3 to 0.5 MPa), and elongation at break increased from 100 to 400%. Determined glass transition temperature T_g for [BMIM]Cl plasticized starch was lower than calculated, respectively: −13 °C and −6 °C (for glycerol plasticized polysaccharide T_g values were respectively: −21 °C and −36 °C) which suggests better plasticization efficiency with ionic liquid than with glycerol. Moreover, it indicates significant reduction of hydrogen bonds between starch chains in case of [BMIM]Cl plasticization, which was confirmed by FTIR spectroscopy. It is assumed that each ion pair: $Cl^-/[BMIM]^+$ strongly interacts with C–O–H starch group (anion interacts with the hydrogen atom, cation with the oxygen atom). As a result hydrogen and oxygen cannot form hydrogen bonds with water molecules or with other OH groups on the polysaccharide (Sankri et al., 2010). If so, starch plasticized with [BMIM]Cl would interact with water molecules less intensely than starch plasticized with glycerol. This assumption has been confirmed by the hydrophilicity decrease of the starch/[BMIM]Cl system.

In the case of starch plasticized by [AMIM]Cl Wang et al. (2009a) have observed a higher intensity of hydrogen bonding than for starch plasticized by [BMIM]Cl. It has been explained by other anion and cation interaction mechanism: ion Cl^- may interact locally with hydrogen atom of starch OH, and cation $[AMIM]^+$ interacts weaker with oxygen atom of OH group. In such a situation two OH groups are still capable of forming hydrogen bonds with other hydroxyl groups of starch or water molecules. As a result starch plasticized with [AMIM]Cl exhibits more hydrophilic character than glycerol plasticized starch. This difference is not seen for starch plasticized with [BMIM]Cl (Sankri et al., 2010).

Wang et al. (2009a) used [AMIM]Cl as a corn starch plasticizer to prepare solid biopolymer electrolytes. They obtained films by casting from aqueous solutions of electrical conductivity in a range from $10^{-3.4}$ to $10^{-1.6}$ S/cm for starch plasticized with respectively 10 and 30 wt% ionic liquid. Higher electrical conductivity value was obtained by adding sodium montmorillonite (9 wt%) to starch plasticized with [AMIM]Cl ($10^{-0.3}$ S/cm at 23 wt% water content (Wang, Zhang, & Wang, 2009b).

Wang, Zhang, Liu, and Han (2010) showed that by mixing starch with [AMIM]Cl in a presence of lithium chloride highly plasticized, homogeneous and conductive films could be prepared. An increased LiCl content enhanced the water absorption of starch material as well as the ionic conductivity. Moreover, it was also shown that high Cl^- ions concentration accelerated the thermal decomposition of starch.

Wu, Wang, Li, Li, and Wang (2009) prepared composite films from natural polymers by dissolving starch, cellulose and lignin in [AMIM]Cl (total biopolymer concentration was ~6 wt%). Subsequently biopolymer solution was cast on glass plates and coagulated in the distilled water to obtain regenerated biopolymer gel. During dissolving of starch–hydrogen bonds are formed between hydroxyl groups of biopolymers. In such a system starch, cellulose and lignin display good affinity to each other. By changing the biopolymer content films exhibiting different mechanical properties were prepared. Starch presence contributes to the film flexibility. The composite films were amorphous, transparent and had better gas permeability (oxygen and carbon dioxide) than regenerated cellulose films. This fact allows these biopolymer films to be considered as a fresh food packaging material.

Kadokawa, Murakami, Takegawa, and Kaneko (2009) prepared cellulose/starch composite gel and fibrous material from ionic liquid solution. The gel was obtained by keeping homogeneous mixture of cellulose (10 wt%) and starch (5 wt%) in [BMIM]Cl for several days at room temperature and then extracted with acetone. The fibrous material (ca. 100–200 μm in diameter) composed of cellulose and starch by regeneration from the homogeneous mixture (10 wt% each) in [BMIM]Cl was also demonstrated.

4. Chemical modification of starch in an ionic liquid environment

Many papers considering modification of starch using ILs, e.g. preparation of esterified starches reported methods performed periodically. Using IL as the reaction medium has advantages over other starch solvents, such as dimethylsulfoxide, which exhibit high toxicity and low stability during the modification process as well as difficulties with solvent recovery (Xie & Shao, 2009).

Selected parameters for the chemical modifications of starch in ILs were collected in Table 1. Obtained values of degree of substitution (DS) of ester derivatives prepared from acidic anhydrides usually exceeded 2. In case of phosphate derivatives maximal DS value was 0.55; for comparison DS of "traditionally" prepared starch phosphates was in a range of 0.01–0.2 (Xie & Shao, 2009). It has been observed that independently from starch origin susceptibility of hydroxyl groups to esterification in ionic liquid decreased in order of carbon atoms of glycosidic unit: C6 > C2 > C3 (Lehmann & Volkert, 2009). However, Shogren and Biswas (2010) observed that in case of reaction between starch (maltodextrin) and vinyl acetate the substitution position depends on a type of ionic liquid medium used. In [BMIM] dicyanamide (DCA) acetylation at C2 was preferred, while in [BMIM] acetate was more uniform.

Lehmann, Volkert, Hassan-Nejad, Greco, and Fink (2010) performed starch esterification in imidazolium salt prepared *in situ*. The imidazole derivatives were used as precursors for imidazolium salts that catalyze starch esterification reaction. The total DS value of obtained starch mixed esters was close or equal 3.

Biswas, Shogren, and Willett (2009) used ionic liquid [BMIM]DCA as a solvent and catalyst for direct esterification of starch (maltodextrin) with stearic acid or vinyl stearate. The reaction occurred even at mild temperature (40 °C). At higher temperature (75 °C) starch stearates of high degree of substitution (DS 2.4) might be obtained (Shogren, Biswas, & Willett, 2010). Xie and Wang (2011) very recently have performed starch esterification with fatty acid methyl esters in [BMIM]Cl using base catalyst; the highest DS values were close to 0.4.

Table 1
Selected parameters of starch modification reactions in ionic liquids.

Ionic liquids (IL)	Reagent	DS	Starch concentration in IL (wt%)	Ref.
Starch esters				
[BMIM]Cl	Acetic anhydride	0.3–2.6	10	Biswas et al. (2006)
	Acetic anhydride	0.9–2.9		
[BMIM]Cl	Propionic anhydride	2.1–3.0	~9	Lehmann and Volkert (2009)
	Hexanoic anydride	1.92		
	Phthalic anhydride	2.12		
[BMIM]Cl	Acetic anhydride	0.37–2.35	~5	Xie et al. (2010)
	Succinic anhydide	0.03–0.93		
[BMIM]DCA	Vinyl acetate	0.84–1.10	~6	Shogren and Biswas (2010)
[BMIM]OAc		0.75–1.8		
[BMIM]Cl	Sodium dihydrogenphosphate	0.03–0.36	~5	Xie and Shao (2009)
	Disodium hydrogenphosphate	0.06–0.55		
	Exemplary mixture:			
[MIM]Cl	Acetic anhydride	DS_{Ac} 2.28	–	Lehmann et al. (2010)
[EtIM]Cl	Propionic anhydride	DS_{Prop} 0.63		
[AcIM]Cl	Lauroyl chloride	DS_{Lau} 0.10		
[BMIM]Cl	Methyl laurate	0.06–0.38	10	Xie and Wang (2011)
	Methyl stearate	0.03–0.29		
[BMIM]DCA	Stearic acid	0.03–0.72	~6	Biswas et al. (2009)
	Vinyl stearate	<0.01–0.64		
Cationic starch				
[BMIM]Cl	Glycidyltrimethylammonium chloride	0.05–0.99	10	Wang and Xie (2010)
Starch graft copolymer				
[AMIM]Cl	ε-Caprolactone	Grafting efficiency >24%	15	Xu et al. (2008a)
[AMIM]Cl	L-Lactide	Grafting efficiency >30%	15	Xu et al. (2008b)

Xu et al. (2008a, 2008b) used ionic liquid [AMIM]Cl as a reaction media for the ring opening graft copolymerization of ε-caprolactone and L-lactide onto starch. The grafting efficiency was 24.4% and 30%, respectively.

The attempts of reusing [BMIM]Cl as another esterification reaction medium have been performed (Xie et al., 2010; Wang & Xie, 2010). The DS value after fifth cycle was on average ~20% smaller when compared to DS of product prepared with fresh ionic liquid.

5. Conclusion

Because of the unique properties ionic liquids might be applied as solvents or plasticizers for native granular starch. Various chemical reactions, such as starch esterification, acid-catalysed hydrolysis, enzymatic transformations or graft copolymerisation could be preformed in ionic liquids. Biodegradable ionic liquid–starch materials might be used e.g. for biocomposites, additives in paper industry or food packaging production. Starch systems containing ionic liquid might find application as electrically conductive materials. Despite papers concerning interactions between starch and ionic liquids that have appeared up today additional research effort including the influence of anion kind and organic cation core type (e.g. substituents on imidazolium ring) or functional groups on alkyl substituents of ionic liquids should be performed. It seems also that comparative study on dissolution properties of different origin starches in selected ionic liquids at established experimental conditions is necessary to choose those with the highest effectiveness and acceptable prices as candidates for industrial application.

References

Biswas, A., Shogren, R. L., & Willett, J. L. (2009). Ionic liquid as a solvent and catalyst for acylation of maltodextrin. *Industrial Crops and Products*, *30*, 172–175.

Biswas, A., Shogren, R. L., Stevenson, D. G., Willett, J. L., & Bhowmik, P. K. (2006). Ionic liquids as solvents for biopolymers: Acylation of starch and zein protein. *Carbohydrate Polymers*, *66*, 546–550.

Chaudhary, A. L., Torley, P. J., Halley, P. J., McCaffery, N., & Chaudhary, D. S. (2009). Amylose content and chemical modification effects on thermoplastic starch from maize – Processing and characterization using conventional polymer equipment. *Carbohydrate Polymers*, *78*, 917–925.

Couling, J. D., Bernot, R. J., Docherty, K. M., Dixon, J. K., & Maginn, E. J. (2006). Assessing the factors responsible for ionic liquid toxicity to aquatic organisms *via* quantitative structure–property relationship modeling. *Green Chemistry*, *8*, 82–90.

El Seoud, O. A., Koschella, A., Fidale, L. C., Dorn, S., & Heinze, T. (2007). Applications of ionic liquids in carbohydrate chemistry: A window of opportunities. *Biomacromolecules*, *8*, 2629–2647.

Fort, D. A., Remsing, R. C., Swatloski, R. P., Moyna, P., & Rogers, R. D. (2007). Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride. *Green Chemistry*, *9*, 63–69.

Fukaya, Y., Sugimoto, A., & Ohno, H. (2006). Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates. *Biomacromolecules*, *7*, 3295–3297.

Kadokawa, J., Murakami, M., Takegawa, A., & Kaneko, Y. (2009). Preparation of cellulose–starch composite gel and fibrous material from a mixture of the polysaccharides in ionic liquid. *Carbohydrate Polymers*, *75*, 180–183.

Kärkkäinen, J., Lappalainen, K., Joensuu, P., & Lajunen, M. (2011). HPLC-ELSD analysis of six starch species heat-dispersed in [BMIM]Cl ionic liquid. *Carbohydate Polymers*, *84*, 509–516.

Kimizuka, N., & Nakashima, T. (2001). Spontaneous self-assembly of glycolipid bilayer membranes in sugar-philic ionic liquids and formation of ionogels. *Langmuir*, *17*, 6759–6761.

Laus, G., Bentivoglio, G., Schottenberger, H., Kahlenberg, V., Kopacka, H., Röder, T., & Sixta, H. (2005). Ionic liquids: Current developments, potential and drawbacks for industrial applications. *Lenzinger Berichte*, *84*, 71–85.

Lehmann, A., & Volkert, B. (2009). Investigations on esterification reactions of starches in 1-n-buthyl-3-methylimidazolium chloride and resulting substituent distribution. *Journal of Applied Polymer Science*, *114*, 369–376.

Lehmann, A., Volkert, B., Hassan-Nejad, M., Greco, T., & Fink, H. P. (2010). Synthesis of thermoplastic starch mixed esters catalyzed by the *in situ* generation of imidazolium salts. *Green Chemistry*, *12*, 2164–2171.

Liu, Q., Janssen, M. H. A., van Rantwijk, F., & Sheldon, R. A. (2005). Room-temperature ionic liquids that dissolve carbohydrates in high concentrations. *Green Chemistry*, *7*, 39–42.

Ma, X., Yu, J., & Kennedy, J. F. (2005). Studies on the properties of natural fibers-reinforced thermoplastic starch composites. *Carbohydrate Polymers*, *62*, 19–24.

Modelli, A., Sali, A., Galletti, P., & Samorí, C. (2008). Biodegradation of oxygenated and non-oxygenated imidazolium-based ionic liquids in soil. *Chemosphere*, *73*, 1322–1327.

Myllymäki, V., and Aksela, R. (2005). Depolymerization method. Pat. No. WO2005066374.

Olivier-Bourbigou, H., Magna, L., & Morvan, D. (2010). Ionic liquids and catalysis: Recent progress from knowledge to applications. *Applied Catalysis A: General*, *373*, 1–56.

Pretti, C., Chiappe, C., Baldetti, I., Brunini, S., Monni, G., & Intorre, L. (2009). Acute toxicity of ionic liquids for three freshwater organisms: *Pseudokirchneriella subcapitata*, *Daphnia magma* and *Danio rerio*. *Ecotoxicology and Environmental Safety*, *72*, 1170–1176.

Qin, Y., Lu, X., Sun, N., & Rogers, R. D. (2010). Dissolution or extraction of crustacean shells using ionic liquids to obtain high molecular weight purified chitin and direct production of chitin films and fibers. *Green Chemistry*, *12*, 968–971.

Rebros, M., Gunaratne, H. Q. N., Ferguson, J., Seddon, K. R., & Stephens, G. (2009). A high troughput screen to test the biodegradability of water-miscible ionic liquids. *Green Chemistry*, *11*, 402–408.

Remsing, R. C., Swatlowski, R. P., Rogers, R. D., & Moyna, G. (2006). Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: A ^{13}C and $^{35/37}$Cl NMR relaxation study on model systems. *Chemical Communications*, *12*, 1271–1273.

Rosatella, A. A., Branco, L. C., & Afonso, C. A. M. (2009). Studies on dissolution of carbohydrates in ionic liquids and extraction from aqueous phase. *Green Chemistry*, *11*, 1406–1413.

Sankri, A., Arhaliass, A., Dez, I., Gaumont, A. C., Grohens, Y., Lourdin, D., Pillin, I., Rolland-Sabaté, A., & Leroy, E. (2010). Thermoplastic starch plasticized by an ionic liquid. *Carbohydrate Polymers*, *82*, 256–263.

Shogren, R. L., & Biswas, A. (2010). Acetylation of starch with vinyl acetate in imidazolium ionic liquids and characterization of acetate distribution. *Carbohydrate Polymers*, *81*, 149–151.

Shogren, R. L., Biswas, A., & Willett, J. L. (2010). Preparation and physical properties of maltodextrin stearates of low to high degree of substitution. *Starch/Staerke*, *62*, 333–340.

Singh, S., Simmons, B. A., & Voegel, K. P. (2009). Visualization of biomass solubilization and cellulose regeneration during ionic liquid pretreatment of switchgrass. *Biotechnology and Bioengineering*, *104*, 68–75.

Smiglak, M. (2010). Ionic liquids as solvents for dissolution, fractioning, cracking and reprocessing of biomass and biopolymers. In: Ionic Liquids Today 01–10, 2010. p. 12–17 www.iolitec.com.

Stevenson, D. G., Biswas, A., Jane, J., & Inglett, G. E. (2007). Changes in structure and properties of four botanical sources dispersed in the ionic liquid, 1-butyl-3-methylimidazolium chloride. *Carbohydrate Polymers*, *67*, 21–31.

Taguet, A., Huneault, M. A., & Favis, B. D. (2009). Interface/morphology relationships in polymer blends with thermoplastic starch. *Polymer*, *50*, 5733–5743.

Tan, Y. S. S., & MacFarlane, D. R. (2009). Ionic liquids in biomass processing. *Topics in Current Chemistry*, *290*, 311–339.

Wilpiszewska, K., & Spychaj, T. (2006). Starch thermoplasticization by extrusion in a presence of the plasticizers. *Polimery*, *51*, 327–332.

Wang, N., Zhang, X., Liu, H., & Han, N. (2010). Ionically conducting polymers based on ionic liquid-plasticized starch containing lithium chloride. *Polymers & Polymer Composites*, *18*, 53–58.

Wang, N., Zhang, X., Liu, H., & He, B. (2009a). 1-Allyl-3-methylimidazolium chloride plasticized-corn starch as solid biopolymer electrolytes. *Carbohydrate Polymers*, *76*, 482–484.

Wang, N., Zhang, X., & Wang, X. (2009b). Ionic liquids modified montmorillonite/thermoplastic starch nanocomposites as ionic conducting biopolymer. *Macromolecular Research*, *17*, 285–288.

Wang, Y., & Xie, W. (2010). Synthesis of cationic starch with a high degree of substitution in an ionic liquid. *Carbohydrate Polymers*, *80*, 1172–1177.

Wu, R. L., Wang, X. L., Li, F., Li, H. Z., & Wang, Y. Z. (2009). Green composite films prepared from cellulose, starch and lignin in room-temperature ionic liquid. *Bioresource Technology*, *100*, 2569–2574.

Xie, W., & Shao, L. (2009). Phosphorylation of corn starch in an ionic liquid. *Starch/Staerke*, *61*, 702–708.

Xie, W., Shao, L., & Liu, Y. (2010). Synthesis of starch esters in ionic liquids. *Journal of Applied Polymer Science*, *116*, 218–224.

Xie, W., & Wang, Z. (2011). Synthesis of high fatty acid starch esters with 1-butyl-3-methylimidazolium chloride as a reaction medium. *Starch/Staerke*,. DOI: 20.1002/star.201000126

Xu, Q., Kennedy, J. F., & Liu, L. (2008). An ionic liquid as reaction media in the ring opening graft polymerization of ε-caprolactone onto starch granules. *Carbohydrate Polymers*, *72*, 113–121.

Xu, Q., Wang, Q., & Liu, L. (2008). Ring-opening graft polymerization of L-lactide onto starch granules in an ionic liquid. *Journal of Applied Polymer Science*, *107*, 2704–2713.

Zakrzewska, M. E., Bogel-Łukasik, E., & Bogel-Łukasik, R. (2010). Solubility of carbohydrates in ionic liquids. *Energy Fuels*, *24*, 737–745.

Zhang, H., Wu, J., Zhang, J., & He, J. S. (2005). 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose. *Macromolecules*, *38*, 8272–8277.