

Original citation:

Zhang, Binjia, Xie, Fengwei, Shamshina, Julia L., Rogers, Robin D., McNally, Tony, Halley, Peter J, Truss, Rowan W, Chen, Ling and Zhao, Si-ming. (2017) Dissolution of starch with aqueous ionic liquid under ambient conditions. ACS Sustainable Chemistry & Engineering. doi : [10.1021/acssuschemeng.7b00784](https://doi.org/10.1021/acssuschemeng.7b00784)

Permanent WRAP URL:

<http://wrap.warwick.ac.uk/87612>

Copyright and reuse:

The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions. Copyright © and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable the material made available in WRAP has been checked for eligibility before being made available.

Copies of full items can be used for personal research or study, educational, or not-for profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

Publisher's statement:

This document is the Accepted Manuscript version of a Published Work that appeared in final form in ACS Sustainable Chemistry & Engineering, copyright © American Chemical Society after peer review and technical editing by the publisher.

To access the final edited and published work see link to Published Work, see: <https://doi.org/10.1021/acssuschemeng.7b00784>

A note on versions:

The version presented here may differ from the published version or, version of record, if you wish to cite this item you are advised to consult the publisher's version. Please see the 'permanent WRAP URL' above for details on accessing the published version and note that access may require a subscription.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk

Dissolution of Starch with Aqueous Ionic Liquid under Ambient Conditions

*Binjia Zhang^{a,b}, Fengwei Xie^{*b}, Julia L. Shamshina^{c,d}, Robin D. Rogers^d, Tony McNally^e, Peter J. Halley^b, Rowan W. Truss^b, Ling Chen^f, Siming Zhao^a*

^a Key Laboratory of Environment Correlative Dietology (Ministry of Education), College of Food Science and Technology, Huazhong Agricultural University, Wuhan, Hubei 430070, China

^b School of Chemical Engineering, The University of Queensland, Brisbane, Qld 4072, Australia

^c 525 Solutions, Inc., 720 2nd Street, Tuscaloosa, AL 35401, USA

^d Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, QC H3A 0B8, Canada

^e International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, CV4 7AL, UK

^f Guangdong Province Key Laboratory for Green Processing of Natural Products and Product Safety, South China University of Technology, Guangzhou, Guangdong 510640, China

KEYWORDS: Starch; Dissolution; Aqueous ionic liquid; 1-Ethyl-3-methylimidazolium acetate; Solvent effects

* Corresponding Author. Email: f.xie@uq.edu.au, fwhsieh@gmail.com (F. Xie)

1
2
3
4 ABSTRACT: With increased awareness of global sustainability, there has been growing interest
5
6 in the preparation of materials from natural, eco-friendly polymers (*i.e.*, biopolymers).
7
8 Nonetheless, despite their enormous application potential, biopolymers (starch, *etc.*) have a
9
10 native semi-crystalline structure with strong hydrogen bonding, and require use of solvents to
11
12 improve their processibility. However, the dissolution/processing of natural biopolymers such as
13
14 starch often requires heating and thus significant energy input. Herein, we report an aqueous
15
16 ionic liquid for fast and facile dissolution of starch, a typical semi-crystalline natural polymer,
17
18 under ambient conditions. The ionic liquid used is 1-ethyl-3-methylimidazolium acetate
19
20 ([C₂mim][OAc]). In particular, it is revealed that 0.15:1 mol/mol [C₂mim][OAc]:water mixture
21
22 disintegrates the sophisticated granule structure of native starch without apparently decreasing
23
24 the molecular mass within 1 h at room temperature (*i.e.*, 28 °C). In addition, this process did not
25
26 result in any undesired derivatization. The discovery of this phenomenon could provide guidance
27
28 for rationally designing ‘green’ processes for chemical and biological engineering for the
29
30 utilization of promising natural biopolymers.
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Currently, biopolymers are increasingly selected for reasons of global sustainability, as they are renewable, widely available, biodegradable and biocompatible.¹ Therefore, biopolymers have become important alternatives to petroleum-based polymers for fabricating eco-friendly materials. Starch, a semi-crystalline biopolymer in the native form of granules growing in plants, has attracted huge interest.² Considerable efforts have been devoted to improving the processes to convert starch into desirable forms³⁻⁴ and thus to design starch-based materials.⁵⁻⁷ However, the use of starch is often hindered by its low solubility in conventional solvents resulting from strong hydrogen bonding between starch chains within starch semi-crystalline structure. While the starch structure may be disrupted to some extent in excess water with significant energy input (*viz.* the “gelatinisation” process), there are always granule remnants in the gelatinised products.⁸ Other solvents known for dissolving starch include dimethylsulfoxide (DMSO) containing LiBr,⁹ and dimethylacetamide with LiCl.¹⁰ These solvents, nonetheless, are toxic, and/or expensive, presenting drawbacks for the dissolution and modification of starch. Also, the dissolution of starch using these solvents still requires high temperatures and/or other special conditions. To address the sustainability issue, it is important to develop new solvents or processes that can transform starch into homogeneous amorphous forms with reduced energy consumption.

Recently, intense research has been focused on using ionic liquids (ILs) as alternative solvents for aiding biopolymer processing. ILs containing acetate [OAc]⁻ or chloride [Cl]⁻ anions and alkyimidazolium cations were identified most effective at dissolving biopolymers including starch.¹¹⁻¹⁴ Compared with mild [OAc]⁻, corrosive [Cl]⁻ in an IL prominently depolymerises starch polymer chains, because of the acid hydrolysis of glycosidic bonds.¹⁵⁻¹⁶ Consequently, acetate-based imidazolium ILs such as 1-ethyl-3-methylimidazolium acetate [C₂mim][OAc] are recognised as excellent media for the dissolution and modification of starch.¹⁷⁻²¹ [C₂mim][OAc]

1
2
3 has a very low vapour pressure, high thermal stability and a relatively low viscosity at room
4 temperature.²² Nonetheless, significant energy (or heating) is still required to achieve a complete
5 starch dissolution in pure [C₂mim][OAc] or its water solutions.^{17, 23}
6
7

8
9
10 Very recently, we found that the hydrogen bonding between starch hydroxyls and [OAc]⁻
11 anions might be enhanced by addition of water in [C₂mim][OAc],²⁴ though the amount of [OAc]⁻
12 anions in the solvent was reduced by water. With inspiration of this finding, we hypothesised
13 that aqueous [C₂mim][OAc] at a certain concentration might dissolve starch even under ambient
14 conditions. To this end, this work was focused on the effect of [C₂mim][OAc] mixing with
15 different amounts of water on the starch dissolution at room temperature (RT, *ca.* 28 °C).
16
17 Regular maize starch, with an amylose content of 24.4 wt% and an initial moisture content of
18 13.36 wt%, was obtained from New Zealand Starch Ltd. (Onehunga, Auckland, New Zealand).
19
20 [C₂mim][OAc], of ≥ 95% purity with a moisture content of *ca.* 1200 ppm, was produced by
21
22 IoLiTec Ionic Liquids Technologies GmbH (Salzstraße184, D-74076 Heilbronn, Germany).
23
24 Milli-Q water was used in all instances. Table S1 (SI) shows the formulations of
25
26 [C₂mim][OAc]:water mixtures containing 10 wt% starch used in this work.
27
28

29
30 Here, we used aqueous [C₂mim][OAc] as a solvent for the starch. Different
31
32 [C₂mim][OAc]:water ratios were used including 0:1 (pure water), 0.10:1, 0.15:1, and 0.38:1,
33
34 mol/mol. It is known that the dissolution of native starch granules in a solvent could result in an
35
36 increase in viscosity. Here, we studied the viscosity changes with time of the starch (10 wt%) in
37
38 [C₂mim][OAc]:water mixtures (Figure 1) using a Rapid Visco Analyser (RVA) 4 (Newport
39
40 Scientific Pty Ltd., Warriewood, NSW 2102, Australia). Approximately 28 g of the biopolymer
41
42 suspensions were contained in standard RVA canisters for viscosity measurements. The viscosity
43
44 *vs.* time was recorded at 28 °C.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

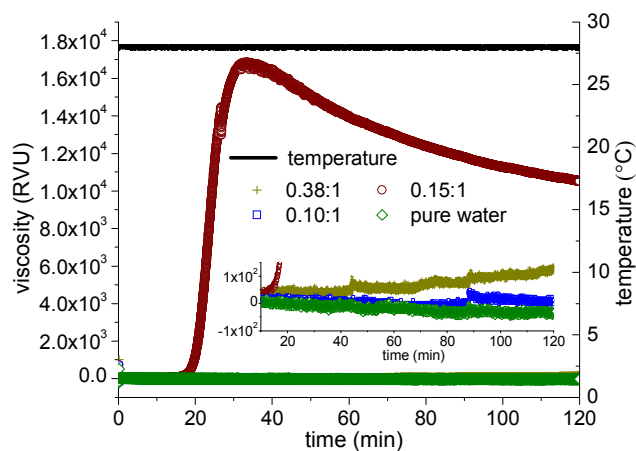


Figure 1. Viscosity profiles measured by a Rapid Visco Analyser (RVA) of 10 wt% starch (dry basis) in pure water (green rhombuses), and in 0.10:1 (blue squares), 0.15:1 (wine circles) and 0.38:1 (dark yellow crosses) mol/mol [C₂mim][OAc]:water mixtures at room temperature (28 °C). The viscosity in RVA is expressed in rapid visco units (RVU).

The viscosities of pure water and 0.10:1, 0.15:1 and 0.38:1 mol/mol [C₂mim][OAc]:water mixtures were *ca.* 0.1 RVU, 0.5 RVU, 0.9 RVU and 2.0 RVU, respectively, which would not change with time. As the dissolution time prolonged to 120 min, there was no apparent change in viscosity for up to 2 h for 10 wt% starch in pure water or 0.10:1 mol/mol [C₂mim][OAc]:water mixture from the initial viscosity of the suspension (25 RVU or 45 RVU, respectively). This constant viscosity suggested that at RT the starch structure could not be disrupted in pure water or 0.10:1 mol/mol [C₂mim][OAc]:water mixture. When 0.15:1 mol/mol [C₂mim][OAc]:water mixture was used for the starch, the initial viscosity was *ca.* 55 RVU, which started to rise rapidly at *ca.* 18 min, and at *ca.* 34 min the maximum of viscosity (*ca.* 16700 RVU) was achieved. This drastic viscosity change with time clearly showed the effectiveness of the 0.15:1 mol/mol mixture to rapidly disorganise native starch granules at RT. The starch molecules liberated from the compact native granules dramatically increased the viscosity of the solution.

1
2
3 Interestingly, a further increase in the [C₂mim][OAc]:water ratio from 0.15:1 to 0.38:1 mol/mol
4
5 did not enhance the destructuration of starch. The treatment with the 0.38:1 mol/mol mixture for
6
7 120 min just slightly increased the system viscosity from *ca.* the initial value of *ca.* 70 RVU to
8
9 *ca.* 120 RVU. Thus, the 0.15:1 mol/mol [C₂mim][OAc]:water mixture performed most
10
11 effectively for rapidly dissolving starch under ambient conditions.
12
13
14

15 The native starch structure has a hierarchical organisation containing crystallites and semi-
16
17 crystalline lamellae. To check the effect of the aqueous [C₂mim][OAc] on the crystallites, we
18
19 further studied polarised light images and time-resolved wide-angle X-ray scattering (WAXS)
20
21 patterns for the starch (10 wt%) during dissolution in the 0.15:1 mol/mol mixture at RT
22
23 (Figure 2). In the initial period (10 min) of dissolution, the starch displayed strong birefringence
24
25 (Figure 2A) and WAXS peaks (Figure 2B). However, both the birefringence and WAXS
26
27 intensities were rapidly weakened with the increased dissolution time; and they completely
28
29 disappeared within 60 min. Moreover, the 2D SAXS patterns (Figure S1, SI) revealed that the
30
31 typical scattering circle for the semi-crystalline lamellar structure of starch on the nanoscale
32
33 became invisible after treatment with the 0.15:1 mol/mol mixture for 60 min. All these results
34
35 clearly indicated the 0.15:1 mol/mol mixture could easily destroy and dissolve the native starch
36
37 structure.
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

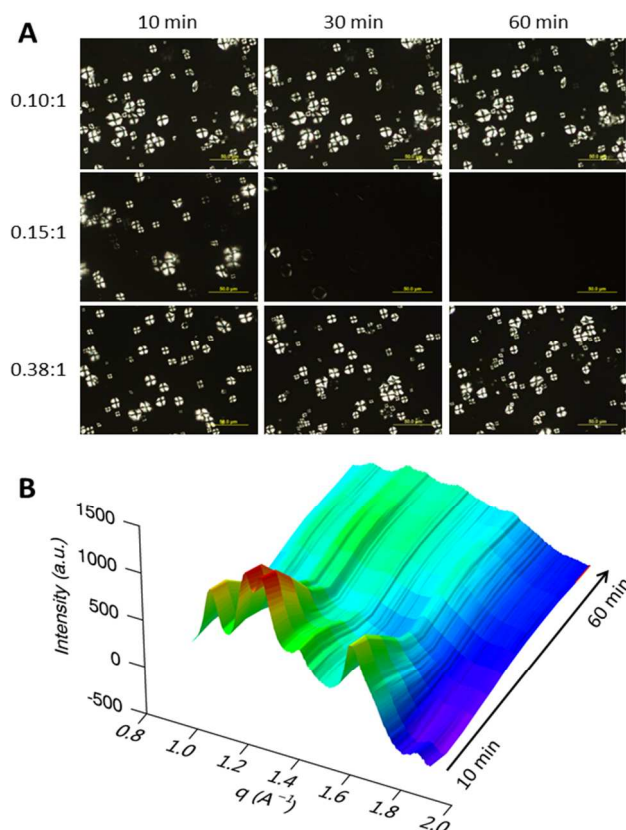


Figure 2. Polarised-light micrographs (A) of 10 wt% starch (dry basis) in 0.10:1, 0.15:1 and 0.38:1 mol/mol [C₂mim][OAc]:water mixtures at room temperature (28 °C); Time-resolved WAXS pattern (B) of 10 wt% starch (dry basis) in 0.15:1 mol/mol [C₂mim][OAc]:water mixture at room temperature (28 °C).

To help understanding the mechanism of starch dissolution at RT, the attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of [C₂mim][OAc]:water mixtures and those containing 10 wt% starch are shown in Figure 3. Two intense and broad IR absorption peaks at 1390–1405 cm⁻¹ and at 1550–1560 cm⁻¹ were observed for the [OAc]⁻ anion in the [C₂mim][OAc]:water mixtures (Figure 3A and B). These peaks were ascribed to the symmetric and asymmetric O–C–O stretching, respectively.²⁴⁻²⁵ At low IL concentrations (*i.e.*, 0.10:1 and 0.15:1 mol/mol [C₂mim][OAc]:water), the addition of starch led to slight reductions in intensity

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

and small shifts in position for the two acetate stretches. These changes were confirmed with repeated tests and indicated that the acetate ions interacted with the starch hydroxyl groups *via* hydrogen bonding²⁴ at RT and weakened the [C₂mim][OAc]-water interactions. Also, the hydration of [OAc]⁻ weakened the kosmotropic effect of this anion on its interaction with a polyol hydrogen bond network.²⁶ Consequently, the addition of starch to the [C₂mim][OAc]:water mixture increased the water hydroxyl stretching at *ca.* 3400 cm⁻¹ (Figure 3), resulting from the weakened solvation of [OAc]⁻ with water molecules. It was noteworthy that in the 0.38:1 mol/mol mixture, there was no change observed for the acetate stretches contrary to those in 0.10:1 and 0.15:1 mol/mol mixtures. Further investigation is needed to understand the interactions between starch, the IL and water in this tertiary system.

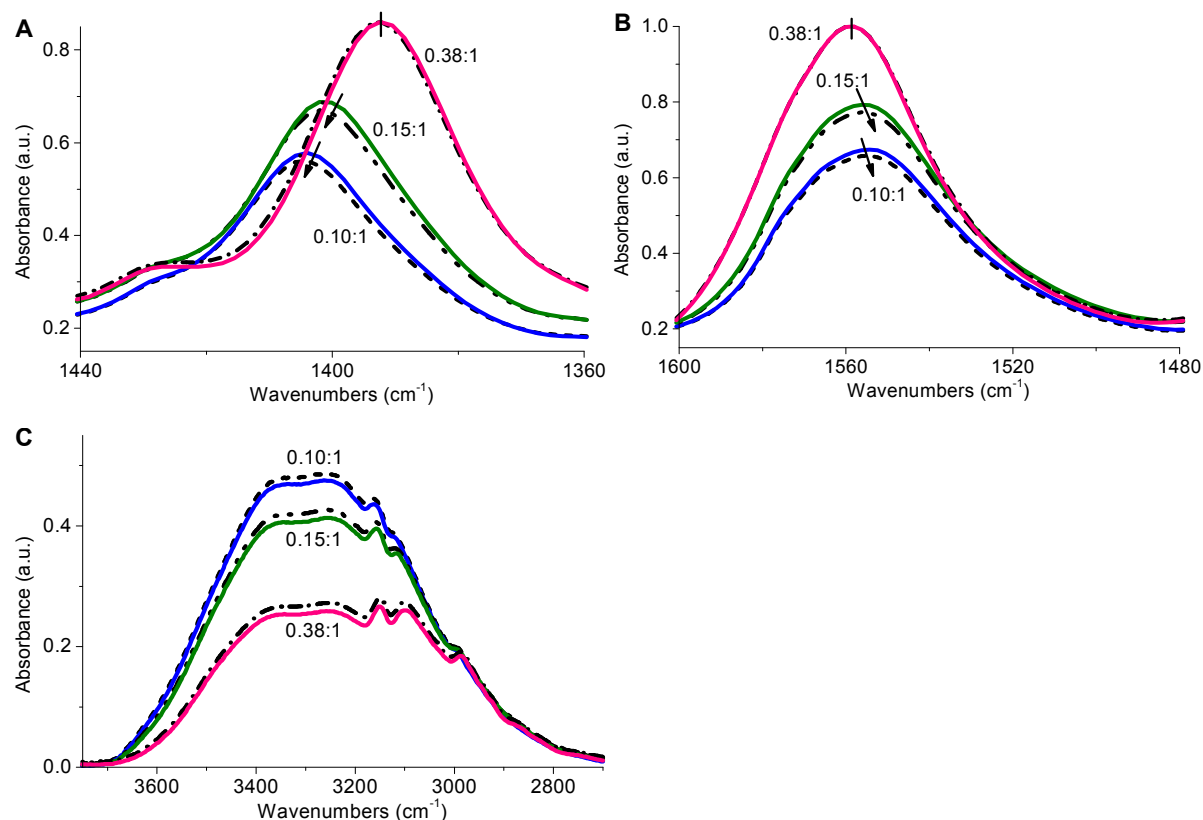


Figure 3. FTIR spectra for 0.10:1, 0.15:1 and 0.38:1 mol/mol [C₂mim][OAc]:water mixtures before (real line) and after (dash line) adding 10 wt% starch (dry basis) at room temperature (28 °C) for 60 min.

1
2
3 Aqueous NaOH solution is known as a cheap solvent for starch.²⁷ Nonetheless, a strict control
4 of conditions is required for the starch dissolution, including the use of a very low NaOH
5 concentration (*e.g.* 2%, w/v), low temperature (35 °C) and a very long time (≥ 7 days). Even so,
6 only a small amount of starch (*e.g.* 1.5 wt% and 2 wt%) can be dissolved. These drawbacks
7 restrict the alkali solution from being used as a solvent for starch. In contrast, our work
8 demonstrated that 0.15:1 mol/mol [C₂mim][OAc]:water mixture could easily dissolve an
9 evidently higher amount (*e.g.* 10 wt%) of starch under ambient conditions.
10
11

12
13 We also checked the chemical difference of the starch before and after dissolution at 10 wt% in
14 10 mL 0.15:1 mol/mol [C₂mim][OAc]:water mixture at RT. After dissolution for 60 min, the
15 starch was regenerated by 20 mL of ethanol. The resulted starch was washed with 10 mL of
16 water and then 20 mL of ethanol, followed by filtration, for three times. The solution ¹³C nuclear
17 magnetic resonance (NMR) spectra for the starch before and after dissolution exhibited the same
18 resonance peaks between 100 to 60 ppm, which originated from the carbons of starch glucan
19 units (Figure 4). The dissolved starch also had very weak resonances especially at *ca.* 15, 36, 44,
20 122, and 124 ppm, corresponding to the C8', C3', C7', C6', and C5' of [C₂mim][OAc],
21 respectively (see Figure S2, SI). These weak resonances indicated the presence of a slight
22 amount of IL residue in the regenerated starch after washing for three times, as also shown by the
23 solution ¹H NMR spectra in Figure S3 in SI. Thus, the solvent did not induce any derivatisation
24 of starch during the dissolution process at RT. The absence of starch derivatisation was further
25 confirmed by FTIR and Raman spectroscopic analyses (see Figure S4, SI).
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

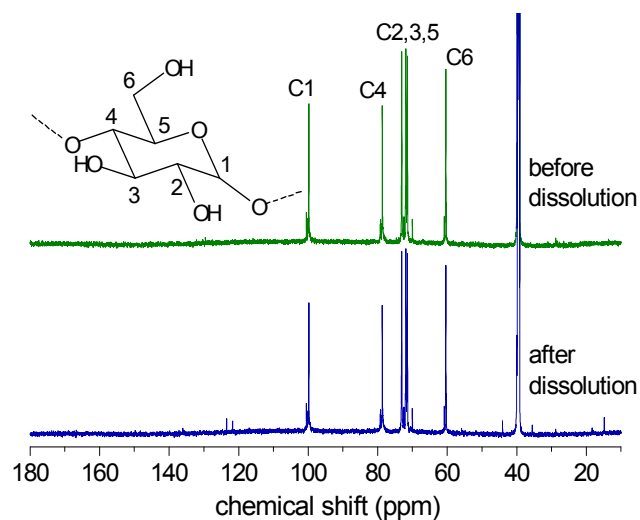


Figure 4. Solution ^{13}C NMR spectra of starch before and after dissolution at 10 wt% (dry basis) in 0.15:1 mol/mol $[\text{C}_2\text{mim}][\text{OAc}]$:water mixture at room temperature (28 °C) for 60 min in $\text{DMSO}-d_6$.

A very recent finding shows that heating pure $[\text{C}_2\text{mim}][\text{OAc}]$ with cellulose, another polysaccharide, at a high temperature (*e.g.* 120 °C) for an extended time (*e.g.* 48 h) transforms a certain proportion of $[\text{C}_2\text{mim}]^+$ into an imidazolium adduct 1-ethyl-2-(hydroxymethyl)-3-methylimidazolium ($[\text{C}_2\text{C}_1(\text{HO})\text{C}_1^2\text{im}]^+$).²⁸ This transformation potentially hinders the complete dissolution of cellulose but can be suppressed at a reduced temperature. Therefore, the dissolution under modest conditions (at RT for a short time) could serve as a strategy to dissolve polysaccharides without undesired derivatisation.

To understand the molecular structure of starch before and after dissolution, we further used gel permeation chromatography coupled with multi-angle light scattering (GPC-MALS) (Figure S5). It was revealed that the molar mass profile showed very slight variations for the starch before and after dissolution at 10 wt% in 0.15:1 mol/mol $[\text{C}_2\text{mim}][\text{OAc}]$:water mixture at RT. Specifically, there was no apparent change in the molar mass distribution of the starch after

1
2
3 dissolution, indicating the negligible molecular degradation of the starch. This result was
4
5 somewhat different from a previous report where certain molecular degradation of starch
6
7 occurred during dissolution in pure [C₂mim][OAc] or its aqueous forms on dynamic heating
8
9 from 20 °C to 120 °C.¹⁷ Our results here suggested that 0.15:1 mol/mol [C₂mim][OAc]:water
10
11 mixture could be used for facile and rapid dissolution of starch at RT with minimal molecular
12
13 degradation.
14
15

16
17 In summary, aqueous [C₂mim][OAc] could disrupt semi-crystalline starch at RT. In particular,
18
19 0.15:1 mol/mol [C₂mim][OAc]:water mixture effectively dissolved starch under ambient
20
21 conditions, without derivatisation and apparent degradation of starch. The discovery here could
22
23 be helpful for rationally designing ‘green’ chemical and biological engineering processes for the
24
25 processing of natural polymers. More research, *e.g.*, the dissolution kinetics, the molecular
26
27 interactions of starch-IL-water, is underway for in-depth understanding the dissolution of starch
28
29 with aqueous [C₂mim][OAc] at RT.
30
31
32
33
34
35

36 ASSOCIATED CONTENT

37
38
39 **Supporting Information (SI)** is available free of charge on the ACS Publications website at
40
41 DOI: xxx. See SI for Experimental details, and supplementary Table and Figures.
42
43
44

45 AUTHOR INFORMATION

46 47 48 **Corresponding Author**

49
50
51 * Fengwei Xie. Email: f.xie@uq.edu.au, fwhsieh@gmail.com
52
53
54

55 **Author Contributions**

1
2
3 The manuscript was written through contributions of all authors. All authors have given approval
4 to the final version of the manuscript.
5
6
7

8 9 **Notes**

10
11 The authors declare no competing financial interest.
12
13

14 15 **ACKNOWLEDGMENT**

16
17 The authors acknowledge the Australian Research Council (ARC) Discovery Project (No.
18 120100344), the Hubei Provincial Natural Science Foundation of China (2016CFB142), the
19 Fundamental Research Funds for the Central Universities (2662016QD008), and the Open
20 Project Program of Provincial Key Laboratory of Green Processing Technology and Product
21 Safety of Natural Products (201602). The SAXS/WAXS measurements were performed at the
22 Australian Synchrotron, Victoria, Australia. This research was undertaken, in part, thanks to
23 funding from the Canada Excellence Research Chairs Program.
24
25
26
27
28
29
30
31
32

33 34 35 **ABBREVIATIONS**

36
37 IL, ionic liquid; [C₂mim][OAc], 1-ethyl-3-methylimidazolium acetate; DMSO, dimethylsulfoxide;
38
39 RVA, Rapid Visco Analyser; WAXS, wide-angle X-ray scattering; SAXS, small-angle X-ray
40 scattering; ATR-FTIR, attenuated total reflectance-Fourier transform infrared; NMR, nuclear
41 magnetic resonance; GPC-MALS, gel permeation chromatography coupled with multi-angle
42 light scattering.
43
44
45
46
47
48

49 50 **REFERENCES**

- 51
52 1. Yu, L.; Dean, K.; Li, L., Polymer blends and composites from renewable resources. *Prog.*
53 *Polym. Sci.* **2006**, *31* (6), 576-602.
54
55
56
57
58
59
60

- 1
2
3 2. Shogren, R. L.; Fanta, G. F.; Doane, W. M., Development of starch based plastics - A
4 reexamination of selected polymer systems in historical perspective. *Starch/Stärke* **1993**, *45* (8),
5 276-280.
6
7
- 8
9
10 3. Gallezot, P., Process options for converting renewable feedstocks to bioproducts. *Green*
11 *Chem.* **2007**, *9* (4), 295-302.
12
13
- 14
15 4. Gandini, A., The irruption of polymers from renewable resources on the scene of
16 macromolecular science and technology. *Green Chem.* **2011**, *13* (5), 1061-1083.
17
18
- 19
20 5. Liu, H.; Xie, F.; Yu, L.; Chen, L.; Li, L., Thermal processing of starch-based polymers.
21 *Prog. Polym. Sci.* **2009**, *34* (12), 1348-1368.
22
23
- 24
25 6. Xie, F.; Halley, P. J.; Avérous, L., Rheology to understand and optimize processibility,
26 structures and properties of starch polymeric materials. *Prog. Polym. Sci.* **2012**, *37* (4), 595-623.
27
28
- 29
30 7. Xie, F.; Liu, P.; Yu, L., Processing of plasticized starch-based materials: State of the art
31 and perspectives. In *Starch Polymers: From Genetic Engineering to Green Applications*, 1st ed.;
32 Halley, P. J.; Avérous, L. R., Eds.; Elsevier: Amsterdam, 2014; pp 257-289.
33
34
- 35
36 8. Debet, M. R.; Gidley, M. J., Why do gelatinized starch granules not dissolve completely?
37 Roles for amylose, protein, and lipid in granule “ghost” integrity. *J. Agric. Food Chem.* **2007**, *55*
38 (12), 4752-4760.
39
40
- 41
42
43 9. Schmitz, S.; Dona, A. C.; Castignolles, P.; Gilbert, R. G.; Gaborieau, M., Assessment of
44 the extent of starch dissolution in dimethyl sulfoxide by H-1 NMR spectroscopy. *Macromol.*
45 *Biosci.* **2009**, *9* (5), 506-514.
46
47
- 48
49
50 10. Striegel, A.; Timpa, J. D., Molecular characterization of polysaccharides dissolved in
51 Me2NAc-LiCl by gel-permeation chromatography. *Carbohydr. Res.* **1995**, *267* (2), 271-290.
52
53
54
55
56
57
58
59
60

- 1
2
3 11. Lappalainen, K.; Kärkkäinen, J.; Lajunen, M., Dissolution and depolymerization of
4
5 barley starch in selected ionic liquids. *Carbohydr. Polym.* **2013**, *93* (1), 89-94.
6
7
- 8 12. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D., Dissolution of cellulose with
9
10 ionic liquids. *J. Am. Chem. Soc.* **2002**, *124* (18), 4974-4975.
11
12
- 13 13. Tan, S.; MacFarlane, D., Ionic Liquids in Biomass Processing. In *Ionic Liquids*, Kirchner,
14
15 B., Ed.; Springer Berlin Heidelberg: Berlin, 2010; Vol. 290, pp 311-339.
16
17
- 18 14. Pinkert, A.; Marsh, K. N.; Pang, S.; Staiger, M. P., Ionic liquids and their interaction with
19
20 cellulose. *Chem. Rev.* **2009**, *109* (12), 6712-6728.
21
22
- 23 15. Stevenson, D. G.; Biswas, A.; Jane, J.-l.; Inglett, G. E., Changes in structure and
24
25 properties of starch of four botanical sources dispersed in the ionic liquid, 1-butyl-3-
26
27 methylimidazolium chloride. *Carbohydr. Polym.* **2007**, *67* (1), 21-31.
28
29
- 30 16. Kärkkäinen, J.; Lappalainen, K.; Joensuu, P.; Lajunen, M., HPLC-ELSD analysis of six
31
32 starch species heat-dispersed in [BMIM]Cl ionic liquid. *Carbohydr. Polym.* **2011**, *84* (1), 509-
33
34 516.
35
36
- 37 17. Sciarini, L. S.; Rolland-Sabate, A.; Guilois, S.; Decaen, P.; Leroy, E.; Le Bail, P.,
38
39 Understanding the deconstruction of starch in water-ionic liquid mixtures. *Green Chem.* **2015**,
40
41 *17* (1), 291-299.
42
43
- 44 18. Biswas, A.; Shogren, R. L.; Stevenson, D. G.; Willett, J. L.; Bhowmik, P. K., Ionic
45
46 liquids as solvents for biopolymers: Acylation of starch and zein protein. *Carbohydr. Polym.*
47
48 **2006**, *66* (4), 546-550.
49
50
- 51 19. El Seoud, O. A.; Koschella, A.; Fidale, L. C.; Dorn, S.; Heinze, T., Applications of ionic
52
53 liquids in carbohydrate chemistry: A window of opportunities. *Biomacromolecules* **2007**, *8* (9),
54
55 2629-2647.
56
57
58
59
60

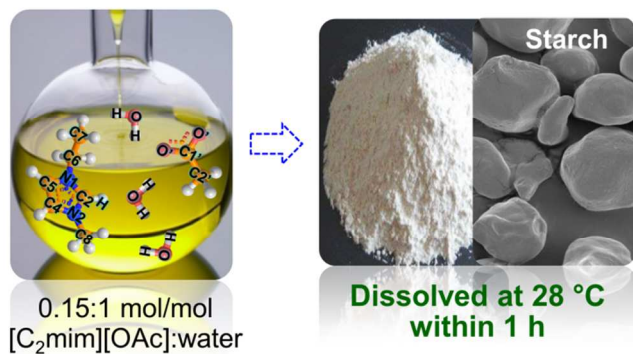
- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
20. Zakrzewska, M. E.; Bogel-Łukasik, E.; Bogel-Łukasik, R., Solubility of carbohydrates in ionic liquids. *Energy Fuels* **2010**, *24* (2), 737-745.
21. Wilpiszewska, K.; Spychaj, T., Ionic liquids: Media for starch dissolution, plasticization and modification. *Carbohydr. Polym.* **2011**, *86* (2), 424-428.
22. Liu, W.; Budtova, T., Dissolution of unmodified waxy starch in ionic liquid and solution rheological properties. *Carbohydr. Polym.* **2013**, *93* (1), 199-206.
23. Mateyawa, S.; Xie, D. F.; Truss, R. W.; Halley, P. J.; Nicholson, T. M.; Shamshina, J. L.; Rogers, R. D.; Boehm, M. W.; McNally, T., Effect of the ionic liquid 1-ethyl-3-methylimidazolium acetate on the phase transition of starch: dissolution or gelatinization?. *Carbohydr. Polym.* **2013**, *94* (1), 520-530.
24. Zhang, B. J.; Chen, L.; Xie, F. W.; Li, X. X.; Truss, R. W.; Halley, P. J.; Shamshina, J. L.; Rogers, R. D.; McNally, T., Understanding the structural disorganization of starch in water-ionic liquid solutions. *Phys. Chem. Chem. Phys.* **2015**, *17*, 13860-13871.
25. Delgado, J. M.; Rodes, A.; Orts, J. M., B3LYP and in situ ATR-SEIRAS study of the infrared behavior and bonding mode of adsorbed acetate anions on silver thin-film electrodes. *J. Phys. Chem. C* **2007**, *111* (39), 14476-14483.
26. Papanyan, Z.; Roth, C.; Wittler, K.; Reimann, S.; Ludwig, R., The dissolution of polyols in salt solutions and ionic liquids at molecular level: Ions, counter ions, and hofmeister effects. *ChemPhysChem* **2013**, *14* (16), 3667-3671.
27. Praznik, W.; Buksa, K.; Ziobro, R.; Gambuś, H.; Nowotna, A., The effect of long - term alkali treatment on the molecular characteristics of native and extruded starches at 35° C. *Starch - Stärke* **2012**, *64* (11), 890-897.

- 1
2
3 28. Clough, M. T.; Geyer, K.; Hunt, P. A.; Son, S.; Vagt, U.; Welton, T., Ionic liquids: not
4 always innocent solvents for cellulose. *Green Chem.* **2015**, *17* (1), 231-243.
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table of Contents

Dissolution of Starch with Aqueous Ionic Liquid under Ambient Conditions

*Binjia Zhang^{a,b}, Fengwei Xie^{*b}, Julia L. Shamshina^{c,d}, Robin D. Rogers^d, Peter J. Halley^b, Tony McNally^e, Rowan W. Truss^b, Ling Chen^f, Siming Zhao^a*



An aqueous ionic liquid (1-ethyl-3-methylimidazolium acetate, [C₂mim][OAc]) is reported for fast and facile dissolution of a natural biopolymer, *i.e.*, starch, under ambient conditions.