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Accepted Manuscript

Title: Zinc Chloride Aqueous Solution as a Solvent for Starch

Author: Meiying Lin Xiaoqin Shang Peng Liu Fengwei Xie
Xiaodong Chen Yongyi Sun Junyan Wan
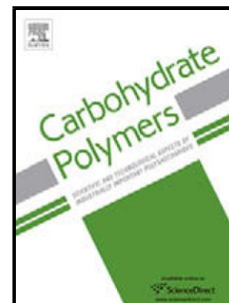
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Highlights:

✓ $ZnCl_2$ aqueous solution (>29.6 wt.%) is a non-derivatizing solvent for starch

✓ Starch can be dissolved completely and regenerated easily in $ZnCl_2$ solution

✓ The suggested dissolution mechanism was the formation of a "zinc-starch complex", not degradation by H^+.

1   **Zinc Chloride Aqueous Solution as a Solvent for Starch**

2

3   Meiying Lin [a], Xiaoqin Shang [a]*, Peng Liu [a], Fengwei Xie [b], Xiaodong Chen [a], Yongyi

4   Sun [a], Junyan Wan [a]

5

6   [a] School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou

7   510006, China

8   [b] School of Chemical Engineering, The University of Queensland, Brisbane, Qld 4072,

9   Australia

10

11   ** Corresponding author. Tel.: +86 20 13342885662; fax: +86 20 39366902; Email address:*

12   *hushanren@163.com (X.Q. Shang)*

13

1

14   **Abstract:**

15   It is important to obtain starch-based homogeneous systems for starch modification.

16   Regarding this, an important key point is to find cheap, low-cost and low-toxicity

17   solvents to allow complete dissolution of starch and its easy regeneration. This study

18   reveals that a $ZnCl_2$ aqueous solution is a good non-derivatizing solvent for starch at

19   50 °C, and can completely dissolve starch granules. The possible formation of a

20   "zinc-starch complex" might account for the dissolution; and the degradation of starch,

21   which was caused by the H^+ in$ZnCl_2$ aqueous solution, could not contribute to full

22   dissolution. From polarized light microscopic observation combined with the solution

23   turbidity results, it was found that the lowest $ZnCl_2$ concentration for full dissolution

24   was 29.6 wt.% at 50 °C, with the dissolving time being 4 h. Using Fourier-transform

25   infrared (FTIR), solid state ^{13}C nuclear magnetic resonance(NMR), and X-ray

26   diffraction (XRD), it was revealed that $ZnCl_2$ solution had no chemical reaction with

27   starch glucosides, but only weakened starch hydrogen bonding and converted the

28   crystalline regions to amorphous regions. In addition, as shown by intrinsic viscosity

29   and thermogravimetric analysis (TGA), $ZnCl_2$ solution caused degradation of starch

30   macromolecules, which was more serious with a higher concentration of $ZnCl_2$

31   solution.

32

33   *Keywords:* starch; $ZnCl_2$ aqueous solution; non-derivatizing solvent; dissolution;

34   zinc-starch complex

35

36   Chemical compounds studied in this article:

37   Starch (PubChem CID: 24836924); Water (PubChem CID: 962); Zinc dichloride

38   (PubChem CID: 5727)

2

39

1. Introduction

40

41   Starch is one of the most abundant carbohydrates in nature, and has been widely

42 used as a raw material in industry. Furthermore, native starch can be modified into

43 various derivatives to widen its applications. Modified starches such as starch sodium

44 succinate and starch phosphate ester can be used to prepare food additives; and starch

45 can also be converted into value-added chemical products, such as binders and

46 flocculants (Hanselmann & Burchard, 1996; Wu & Hakkarainen, 2014).

47   However, the modification of starch has been greatly limited by its insolubility in

48 water and most organic solvents. This is especially true if a high degree of substitution

49 (DS) is desired, and in this case modification can only occur in a heterogeneous way.

50 In order to increase the DS, starch esters, for example, were usually prepared in

51 organic solvents, where catalysts may be further added. However, these organic

52 solvents were often volatile, not recyclable, and the catalysts such as pyridine were

53 toxic. These heterogeneous systems have limited the development of starch

54 modification and the application of modified starch (Junistia, Sugih, Manurung,

55 Picchioni, Janssen, & Heeres, 2008).

56   Homogeneous systems have been reported to be beneficial to carbohydrate

57 modification (Heinze & Liebert, 2011; Gao, Luo, & Luo, 2012). As a result, efforts in

58 recent years have been focused on the search for solvents that can completely dissolve

59 starch. Solvents can be classified into derivatizing and non-derivatizing types

60 according to whether or not any chemical reaction is occurring in the dissolution

61 process. Some traditionally- and broadly-used solvents for starch include dimethyl

62 sulfoxide (DMSO) and strong inorganic alkalis (e.g., KOH and NaOH). However,

63 research has shown that alkaline solutions may induce undesirable side reactions such

3

64   as structural depolymerization and oxidation (Jackson, Choto-Owen, & Waniska,

65   Rooney, 1988; Jordan, Schmidt, Liebert, & Heinze, 2014). DMSO was found to be

66   able to dissolve starch without structural degradation (Everett & Foster, 1959).

67   However, the dissolution process with DMSO is not straight forward. Starch is heated

68   in 90% aqueous DMSO for about 24 h, followed by precipitation and re-dissolution in

69   water (with further heating); and this procedure requires intensive shear and thermal

70   treatment to starch (Chakraborty, Sahoo, Teraoka, & Gross, 2005; Han & Lim, 2004;

71   Zhong, Yokoyama, Wang, & Shoemaker, 2006).

72   Ionic liquids (IL's) represent a new class of solvents for starch, which have

73   gained much attention recently. IL's have been claimed as "green solvents" for many

74   substances including natural polymers such as starch and cellulose, because of their

75   chemical and thermal stability, low vapor pressure, and high ionic activity (Gericke,

76   Schlufter, Liebert, Heinze, & Budtova, 2009; Lu, Yan, & Texter, 2009). However, the

77   research on IL's has just been started and the toxicity of IL's remains uncertain.

78   Jastorff et al. and Matsumoto et al. (Jastorff et al., 2003; Matsumoto, Mochiduki,

79   Fukunishi, & Kondo, 2004) have preliminarily studied the toxicity of IL's and proved

80   that the commonly-accepted notion that IL's have low toxicity is incorrect. Most IL's

81   are designed with large organic cations, such as pyridinium, imidazolium and

82   pyrrolidinium while the anions are hexafluorophosphate (PF_6^-), tetrafluoroborate

83   (BF_4^-), dicyanamide ($N(CN)_2^-$), etc.. Their release to aquatic environments could

84   cause severe water and soil contamination due to the potential toxicity and

85   non-biodegradability (Gathergood & Scammells, 2002). Moreover, the high prices of

86   IL's make them difficult to be applied practically in industry. Therefore, the practical

87   application of IL's remains uncertain.

88   Another class of solvents for natural polymers is inorganic salt hydrates, which

4

89 are liquids that have a designated water-salt mole ratio close to the coordination

90 number of the strongest hydrated ion. Typical examples are liquid phases of solid salt

91 hydrates, such as $Ca(SCN)_2/H_2O$ (Warwicker, Jeffries, Colbran, & Robinson, 1966),

92 $LiSCN/H_2O$ (Lukanoff, Schleicher, & Philipp, 1983) and $ZnCl_2/H_2O$ (Letters, 1932).

93 They are inexpensive, convenient, and environmentally friendly. They are

94 non-derivatizing solvents not only being regarded as very efficient solvents for most

95 natural polymers such as cellulose (Cao, Xu, Chen, Gong, & Chen, 1994), chitin

96 (Wang, Pedersen, Deng, Qiao, & Hou, 2013), but also have been applied as a medium

97 for the chemical functionalization or derivatization, such as carboxymethylation and

98 esterification, of these natural polymers, within a short reaction time (Leipner,

99 Fischer, Brendler, & Voigt, 2000; Sen, Martin, & Argyropoulos, 2013). For example,

100 Heinze et al. used molten $LiClO_4/3H_2O$ as a solvent for homogeneous

101 carboxymethylation of cellulose with a high DS (i.e., ＜2) in a one-step synthesis

102 after a short reaction time of 4 h (Fischer, Thümmler, Pfeiffer, Liebert, & Heinze,

103 2002). Acetylation could also be carried out at a temperature of 130 °C for a short

104 reaction time (0.5-3.0 h) with DS between 1 and 2.5 (Fischer, Leipner, Thümmler,

105 Brendler, & Peters, 2003). When cellulose is dissolved in a molten salt hydrate, the

106 formation of a homogeneous phase makes cellulose hydroxyl groups completely

107 available for chemical derivatization. This allows the control of both the degree of

108 substitution and the distribution of functional groups, which can undoubtedly broaden

109 the reaction paths and the diversity of products. However, there has been no report on

110 molten salt hydrates applied as solvents or reaction media for starch.

111   Thus, the aim of the present work was to investigate the ability of $ZnCl_2$ aqueous

112 solution, a molten salt hydrate, as a solvent for starch, together with the structure and

113 properties of the regenerated starch from this solvent.

5

2. Materials and Methods

2.1. Materials

Native cassava starch (with moisture content of 14%) was obtained from Dongguan Wenying Starch Trade Co., Ltd., without further treatment. Anhydrous zinc chloride ($ZnCl_2$) and methanol (analytical grade) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Other chemicals including hydrazine sulfate and hexamethylenetetramine were of analytical grade and used as received without further purification. All solutions were prepared with distilled water.

2.2. Dissolution and regeneration of starch from zinc chloride solutions

Certain amounts of anhydrous $ZnCl_2$ were added to a three-neck, round-bottom flask equipped with an electric stirrer to obtain $ZnCl_2$ aqueous solutions of certain concentrations (65%, 43%, 35% and 29.6%). The $ZnCl_2$ solution was then mixed with a certain amount of starch (2.0 wt.%, dry weight). Then, the system was stirred at 50 °C for 4 h. In order to prevent degradation by shear force, the revolution speed was set as 60 rpm. Besides, during the dissolution process, the solution was sampled at intervals and observed under a polarized light microscope (Motic BA300POL, Motic Asia, Hongkong) equipped with a digital camera (Moticam Pro 205A, Motic Asia, Hongkong).

Regenerated starch was obtained from the above solutions by adding absolute ethanol with continuous stirring (The absolute ethanol was about 2-5 times the volume of the starch solution). The starch samples were then dried and smashed into powder for further analysis.

$ZnCl_2$ aqueous solution was acidic (pH = 4.09 for 29.6% and pH = 0.67 for 65%).

6

139   For discussing the influence of H^+ on starch, hydrochloric acid (HCl) solution with a

140   pH value of 4.09 was prepared. After that, native cassava starch was treated with the

141   HCl solution under the exactly same processes as with $ZnCl_2$ aqueous solution. And

142   regenerated starch from HCl solution was collected and compared with those from

143     $ZnCl_2$ aqueous solution.

144

145   *2.3. Characterization of starch and regenerated starch*

146   Fourier-transform infrared (FTIR) spectra for native and regenerated starches

147   were obtained in the range of 400–4000 cm^{-1} with a TENSOR27 FTIR model

148   manufactured by Burker, Germany. The samples were mixed with KBr and well

149   ground before being pressed into wafers.

150   X-ray diffraction (XRD) patterns for native and regenerated starches were

151   obtained on an PW3040/60 X'pert PRO X-ray diffractometer (PANalytical,

152   Netherlands) using the Cu-Ka X-ray source operating at 36 kV and 20 mA. The

153   scanning range and rate are 5–90° and 4°/min, respectively.

154   Solid-state ^{13}C CP/MAS spectra were collected on a Bruker Avance 500 nuclear

155   magnetic resonance (NMR) spectrometer using a 4mm MAS BB-1H probe head. The

156   spectral width used was 37.6 KHz. The acquisition time was 27 ms, together with

157   7.7 μs pre-scan delay and 13.3 μs dwell time. All solid experiments were carried out

158   at 125.8 MHz for ^{13}C with 4096 scans accumulating for each spectrum.

159   To determine the intrinsic viscosity of native and regenerated starches (Islam,

160   Mohd, & Noor, 2001), the samples were dispersed in 0.5mol/L KOH solutions and

161   stirred in a boiling water bath for 10 min. The solutions were then cooled to room

162   temperature and left overnight. The final concentrations of the solutions were

163   2.6–6.0 mg/mL. Intrinsic viscosity measurements were obtained using a Ubbelohde

164   dilution capillary viscometer (size 37, Shanghai Liangjing Glass Instrument Factory,

165   China) immersed in a water bath maintained at 25±0.1 °C. The efflux time of solvent

166   and solutions were measured in triplicate and averaged. Results were expressed as

167   relative viscosity (η_r), $\eta_r = \eta/\eta_0$; specific viscosity (η_{sp}), $\eta_{sp} = \eta_r - 1$; and intrinsic

168   viscosity ([η]). η is the solution viscosity and η_0 is the solvent viscosity. Intrinsic

169   viscosity, [η], was then calculated as the zero concentration-limit of the η_{sp}/c value

170   resulting from the plots of η_{sp}/c versus c straight lines (c represents the concentration

171   of solvent).

172   The thermal decomposition of native and regenerated starches was determined

173   by a thermogravimetric analysis (TGA) apparatus (TGA4000, PerkinElmer, USA) in

174   an open system (Liu, Yu, Liu, Chen, & Li, 2009). Starch samples were heated to

175   800 °C at 20 °C/min. The weight loss results were also converted to derivative weight

176   percentages to measure and compare the peak temperatures. The temperature

177   calibration was done by the Curie temperatures of nickel and iron.

178

179   **3. Results and discussion**

180   *3.1. Solubility of starch in ZnCl$_2$ aqueous solutions*

181   Fig. 1 showed the photos of cassava starch (2% concentration) dispersed in

182   ZnCl$_2$ aqueous solution (29.6 wt.%). Starch was seen to be fully dissolved in the

183   solution, as a clear and transparent solution was formed without any sediment

184   (Fig. 1a). In contrast, when starch was dispersed in water, it was only suspended and

185   the solution was turbid (Fig. 1b). In this case, starch granules could only partially

186   swell in water without gelatinization, as the temperature was 50 °C which is lower

187   than the gelatinization temperature of cassava starch.

8

188   Since $ZnCl_2$ aqueous solution was acidic (pH 4.09 at 29.6% concentration), it is

189   necessary to discuss the influence of H^+ on starch. Fig. 1c shows that when starch was

190   dispersed in a HCl solution (pH 4.09), the granules were also suspended in the solvent

191   and no transparent solution could be obtained.

192   The effect of H^+ on starch granules has been studied since 1885 (Lintner, 1886),

193   and different modified starch products can be produced based on it. Lintnerized starch

194   was the first water soluble starch which was prepared by treatment of starch in 7.5%

195   (w/v) HCl for one week at 22-24 °C, or for three days at 40 °C. Nowadays,

196   commercial soluble starch is still produced by this old procedure (Johnston, Mukerjea,

197   & Robyt, 2011). Besides, microporous starch can also be prepared by treatment of

198   starch in acid solution (Kimura & Robyt, 1995).

199   While the degradation of starch is inevitable with H^+ in the solution, the process

200   progresses from the amorphous region to the crystalline region (Srichuwong, Isono,

201   Mishima, & Hisamatsu, 2005; Chen, Yu, Simon, Liu, Dean, & Chen, 2011).

202   Specifically, due to the small molecular size, H^+ can penetrate into the pores on the

203   granule surface, which are the radial channels into the granule interior. Since the

204   amorphous region is looser than the crystalline region, H^+ preferably attacks the

205   amorphous region, with the crystalline region being mostly intact. Therefore, the

206   starch granules can only form a classic "Swiss cheese" appearance in acidic solution,

207   and cannot completely be dissolved. In other words, the degradation of starch

208   granules by H^+ can only result in a suspension (as shown inFig. 1c). Therefore,

209   although $ZnCl_2$ aqueous solution is acidic, the mechanism for dissolution of starch

210   granules should not be based on the H^+ in the solution.

211   Fig. 2 showed the birefringence (Maltese crosses) changes of cassava starch

212   granules during dissolution in 29.6% $ZnCl_2$ aqueous solution. It could be seen that the

9

213   starch granules exhibited clear birefringence initially after mixing (Fig. 2a). Then,

214   with the elapse of time, the amount and size of birefringence was observed to decrease

215   (Fig. 2b~2d). After an even longer time (4 h), the visual field gradually turned dark,

216   and all birefringence disappeared totally (Fig. 2d), suggesting that starch granules

217   dissolved completely. Thus, for 2% cassava starch in 29.6% $ZnCl_2$ aqueous solutionat

218   50 °C, the dissolution time was 4 h.

219   As is known, the main ions in $ZnCl_2$ aqueous solution are H^+, Zn^{2+} and Cl^-.

220   Since starch is slightly acidic in nature and is negatively charged, Cl^- is repelled by

221   starch molecules (Oosten, 1990). H^+ attacked the amorphous region initially, which

222   only resulted in partial degradation of starch granules, but not dissolution. Thus, it

223   was highly possible that the interaction between Zn^{2+} and starch molecules led to the

224   dissolution. Cao et al. (Cao, Xu, Chen, Gong, & Chen, 1994) proved the presence of a

225   zinc-cellulose complex after microcrystalline cellulose (Avicel) was treated with

226    $ZnCl_2$ aqueous solution. Since starch has the same monosaccharide (glucose) and

227   intermolecular force between molecules (hydrogen bonding) as cellulose, a similar

228   complex may be formed between Zn^{2+} and starch molecules. Furthermore, Islam et al.

229   (Islam, Mohd, & Noor, 2001) found that when starch is added to sodium chloride

230   solution, sodium ions penetrate into starch chains, replacing H^+ which migrates to the

231   water phase; as a result, "sodium salts of starch" are formed. Here in this study, it was

232   possible that a "zinc-starch complex" was formed. Specifically, Zn^{2+} can penetrate

233   into the inner structure of starch, weakening the intra- and inter-molecular hydrogen

234   bonds, disrupting the crystalline region, and forming a "zinc-starch complex" with

235   starch chains. This could be the dominant factor for starch dissolution in $ZnCl_2$

236   aqueous solution.Regarding this complexity, further research is required.

237   Turbidity was also used to determine the dissolution of starch in aqueous $ZnCl_2$

10

238   solution as it represents the cloudiness of a fluid caused by particles in suspension.

239   Turbidity is expected to keep reasonably constant as long as the solute is perfectly

240   soluble, but it will increase sharply with newly added solute remaining solid when the

241   maximum solubility is reached (Mazza, Catana, Garcia, & Cecutti, 2009). As shown

242   in Fig. 3, the starch (2 wt.%) was totally dissolved in 65% $ZnCl_2$ aqueous solution and

243   formed a clear and transparent solution without any sediment. The turbidity in this

244   case was low (about 21.9 NTU). When the $ZnCl_2$ concentration was decreased, the

245   turbidity increased very moderately. Nevertheless, when the $ZnCl_2$ concentration was

246   below 29.6%, precipitation started to appear and the turbidity increased sharply. This

247   suggests that the $ZnCl_2$ concentration needs to be $\geq$29.6 wt.% for full dissolution of

248   starch (2 wt.%).

249

250   *3.2. FTIR spectra fornative and regenerated starches*

251   The FTIR spectra of native cassava starch and regenerated starch from 29.6%

252    $ZnCl_2$ aqueous solution were shown in Fig. 4. The spectra of regenerated starch were

253   quite similar to the native counterpart and no new characteristic peaks were found,

254   indicating no chemical changes to the glucosides in the regenerated starch. Thus, the

255    $ZnCl_2$ aqueous solution can be considered as a non-derivatizing solvent for starch.

256   Nevertheless, there were also some differences in band wave numbers between

257   native and regenerated starches. As seen from Fig. 4, the O-H bending of adsorbed

258   water at 1647 cm^{-1} was shifted to 1627 cm^{-1}, indicating that the water absorption

259   function of regenerated starch became worse (Vicentini, Dupuy, Leitzelman, Cereda,

260   & Sobral, 2005). Moreover, in the adsorption band between 1100 cm^{-1} and 900 cm^{-1},

261   which indicates the interactions of hydrogen bonds, the peak at 1016 cm^{-1} was shifted

262   to 1020 cm^{-1} and the one at 929 cm^{-1} was shifted to 935 cm^{-1}. According to Ahmad et

11

263 al. and Ma et al. (Ahmad, Anuar, & Yusof, 2011; Ma, Yu, & Zhao, 2006), the peak at

264 the low wave number results from the strong hydrogen bonds that drag the relative

265 groups to a lower vibration frequency, and the peaks at the higher wave number are

266 due to the weak interaction of hydrogen bonding. Thus, the above changes in wave

267 numbers indicated less hydrogen bonding in regenerated starch.

268   All in all, aqueous $ZnCl_2$ could be considered as a non-derivatizing solvent for

269 starch without causing obvious change to the starch glucosidic structure but can

270 destroy the inter- and intra-molecular hydrogen bonding in starch.

271

272 *3.3. Solid state ^{13}C NMR study of native and regenerated starches*

273   For further understanding the effects of $ZnCl_2$aqueous solution on starch, ^{13}C

274 NMR spectra on native cassava starch and regenerated starch were obtained (Fig. 5).

275 It can be seen that both native and regenerated starches showed very similar spectra

276 which had four dominant NMR signals. The signals at 90–110 ppm and 81–85 ppm

277 were attributed to C-1 and C-4, respectively, while the signal at 59–65 ppm was

278 assigned to hydroxymethyl C-6. The large signal around 70–79 ppm was associated

279 with C-2, C-3, and C-5 (Morrison, Tester, Gidley, & Karkalas, 1993). Except these,

280 no new peaks appeared in the regenerated starch ^{13}C NMR spectrum.

281   Compared with the spectra for native and regenerated starch, two distinct

282 differences could be observed: the chemical shifts of C-1 peak (from 103.66 ppm to

283 105.18 ppm), and the increase inintensity of C-4 peak. The sharp signal intensity of

284 C-4 peak showed an increase in amorphous content (Atichokudomchai, Varavinit, &

285 Chinachoti, 2004; Fan et al., 2013), suggesting that $ZnCl_2$ aqueous solution destroyed

286 the crystalline region and changed it into amorphous starch. And the shifts of C-1

287 peak could result from the interaction between Zn^{2+} and hydroxyl groups to form a

12

288   complex (Cao, Xu, Chen, Gong, & Chen, 1994). This complex could be the

289   "zinc-starch complex" as mentioned before.

290

291   *3.4. XRD analysis of native and regenerated starches*

292   Native cassava starch and regenerated starch after treatment with $ZnCl_2$ aqueous

293   solutions of different concentrations were examined by XRD, and the results were

294   shown in Fig. 6. Native starch exhibited a typical A-type XRD pattern, giving strong

295   reflections at about $15°$, $23°$ and unresolved doublet at nearly $17°$ and $18°(2\theta)$

296   (Cheetham & Tao, 1998; Kuo & Lai, 2007). In contrast, the regenerated starch only

297   had a dispersive broad peak and showed no crystalline peaks. This suggested that the

298   crystalline region of native starch was completely damaged during the dissolution.

299   The loss of crystallinity could be attributed the penetration into starch of Zn^{2+} which

300   weakened the inter- and intra- molecular hydrogen bonds of starch (Gao, Luo, & Luo,

301   2012). These results were in agreement with the shifts in the FTIR and NMR signals.

302

303   *3.5. Intrinsic viscosity analysis ofnative starch and regenerated starch*

304   Polymer intrinsic viscosity, $[\eta]$, is an important parameter reflecting the size of a

305   macromolecule in a given solvent at a certain temperature (Liu & Budtova, 2013).

306   This parameter is determined using the classical Huggins equation (see the Materials

307   and Methods section). Fig. 7 shows the intrinsic viscosity of native starch and

308   regenerated starch. Native starch was observed to exhibit the highest intrinsic

309   viscosity (about 192 mL/g). With the increased concentration of $ZnCl_2$aqueous

310   solution, the intrinsic viscosity of regenerated starch apparently decreased, from

311   158 mL/g for 29.6% $ZnCl_2$ aqueous solution, to 126 mL/g for 65% $ZnCl_2$ solution.

312   The intrinsic viscosity of polymers is caused by the friction force between the

13

313 solvent and the solute in dilute solution, and can be used to reflect the size of the

314 macromolecular conformation in the certain solution (Wolf, 2007). For starch, no

315 matter amylopectin or amylose, the size of their macromolecular conformation was

316 caused by the degree of polymerization (DP), namely the molecular weight of

317 macromolecules (Higiro, Herald, Alavi, & Bean, 2007). Therefore, from the

318 decreased intrinsic viscosity, it can be deduced that the starch dissolution in $ZnCl_2$

319 aqueous solution was accompanied by the degradation of starch chains, which mainly

320 resulted from the attack by H^+. Since $ZnCl_2$ aqueous solution of higher concentration

321 had lower pH, the intrinsic viscosity of regenerated starch decreased correspondingly.

322 Moreover, Fig. 7 also shows the intrinsic viscosity of regenerated starch from a

323 HCl solution (pH 4.09), which was apparently lower than that of regenerated starch

324 from 29.6% $ZnCl_2$aqueous solution (pH 4.09). It was possible that the "zinc-starch

325 complex" prevented starch chains from being attacked by H^+. Nonetheless, this needs

326 further studies. Also, the accurate quantitative relationship between $ZnCl_2$ solution

327 concentration and starch molecular weight will be discussed in our ongoing research.

328

329 *3.6. Thermal decomposition of native and regenerated starches*

330 Based on previous research, the thermal decomposition temperature of starch

331 without chemical modification is mainly based on the DP of starch molecular chains,

332 and is not significantly influenced by its crystallinity or granule size (Liu et al., 2013).

333 The derivative weight percentage of starch samples (DTG) could be seen in

334 Fig. 8. There were two peaks on the DTG curves. The first one represented moisture

335 evaporation, which occurred with the increased temperature until ca.110 °C. The

336 percentage of weight loss in this step was dependent on the moisture content in starch.

337 The second weight loss peak corresponded to the thermal decomposition of starch

14

338 molecular chains. For native starch, this peak located at 337 °C. For regenerated

339 starch from 35%, 43% and 65% $ZnCl_2$ solutions, this peak located at 271 °C, 253 °C

340 and 250 °C, respectively. The decomposition temperature of native starch was

341 significantly higher than those of regenerated starch, indicating the reduction in DP of

342 starch molecular chains after dissolution in $ZnCl_2$ solutions. Moreover, the

343 decomposition temperature of regenerated starch was decreased with the increased

344 concentration of $ZnCl_2$ solution, also showing that a higher concentration of $ZnCl_2$

345 solution caused greater degradation of starch macromolecules. These results are in

346 agreement with the intrinsic viscosity results.

347

348 **4. Conclusions**

349 $ZnCl_2$ aqueous solution can be used as an effective solvent for starch at 50 °C,

350 which is inexpensive and environmentally friendly. For 2 wt.% starch, the lowest

351 $ZnCl_2$ concentration to allow full dissolution of starch was 29.6 wt.%, with the

352 dissolving time being 4 h. By characterizing the structure and properties of

353 regenerated starch, $ZnCl_2$ aqueous solution was found to be a non-derivatizing solvent

354 for starch without causing changes to starch glucosidic structure, but only destroying

355 the inter- and intra- molecular hydrogen bonds of starch and converting the crystalline

356 structure to amorphous state. This is albeit the inevitable degradation of starch chains

357 since $ZnCl_2$ aqueous solution was acidic. The partial degradation by acid could not be

358 the mechanism of dissolution as it acted mostly to the amorphous region of starch

359 granules. Instead, the dissolution was more likely to rely on the formation of a

360 "zinc-starch complex".

361 Further research will be focused on the dissolution mechanism including the

362 verification of the proposed "zinc-starch complex". Besides, it is worth to study the

15

363   interactions between starch and other salt hydrates, the accurate quantitative

364   relationship between $ZnCl_2$ solution concentration and starch molecular weight, and

365   the chemical modification of starch in a homogeneous phase with $ZnCl_2$ aqueous

366   solution as a reaction medium.

367

375

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ACCEPTED MANUSCRIPT
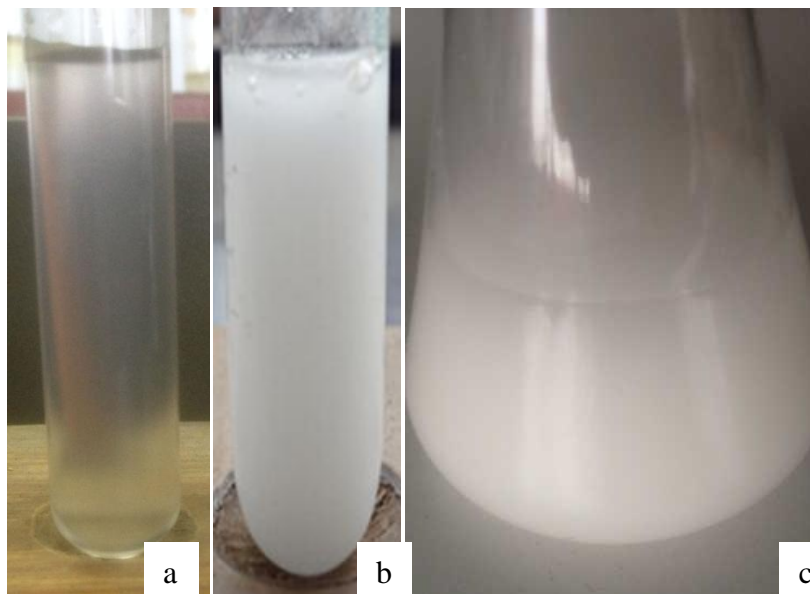
1 **Figure Captions**

2 Fig. 1. Pictures of cassava starch (2% concentration) dissolved in 29.6% $ZnCl_2$

3 aqueous solution (a), water (b) and HCl solution (c) after stirring for 4 h
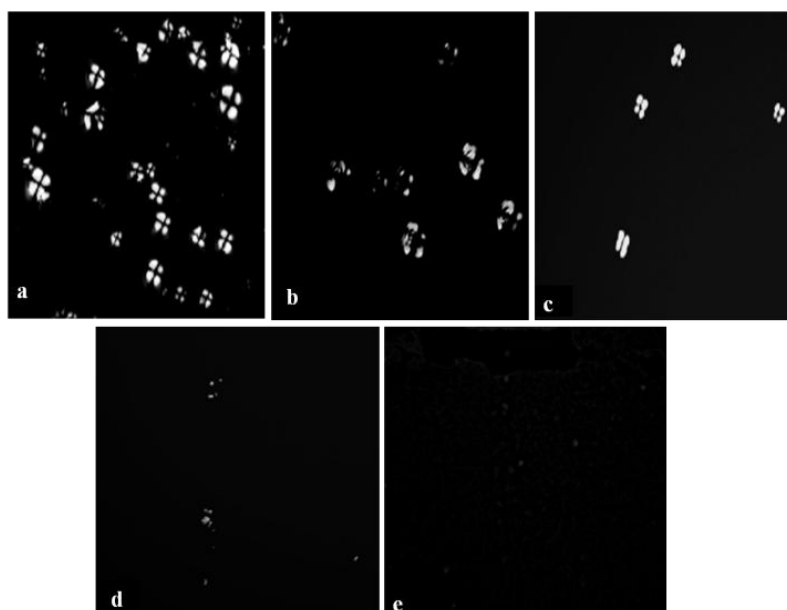
4 Fig. 2. Birefringence images for 2% cassava starch granules dissolved in 29.6%

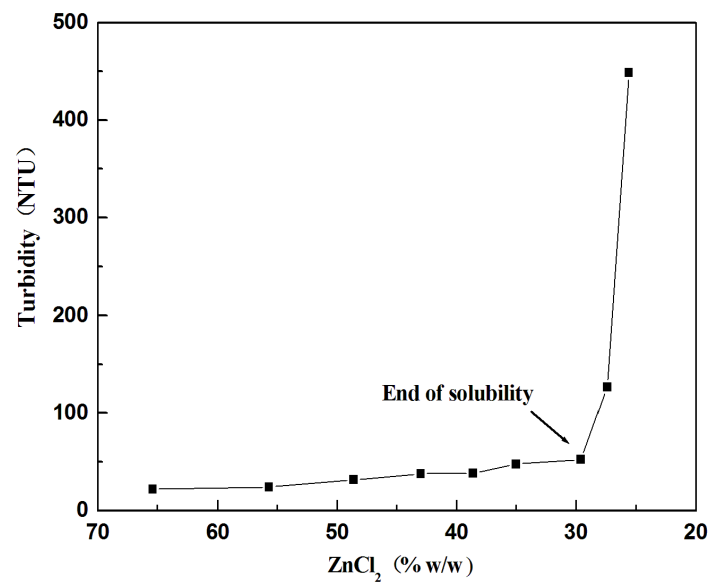5 $ZnCl_2$ aqueous solution for 0 h (a), 1 h (b), 2 h (c), 3 h (d), and 4 h (e)

6 Fig. 3. Turbidity of starch dissolved in aqueous$ZnCl_2$ of different concentrations

7 Fig. 4. FTIR spectra for native cassava starch (a) and regenerated starch from

8 29.6% $ZnCl_2$ aqueous solution (b)
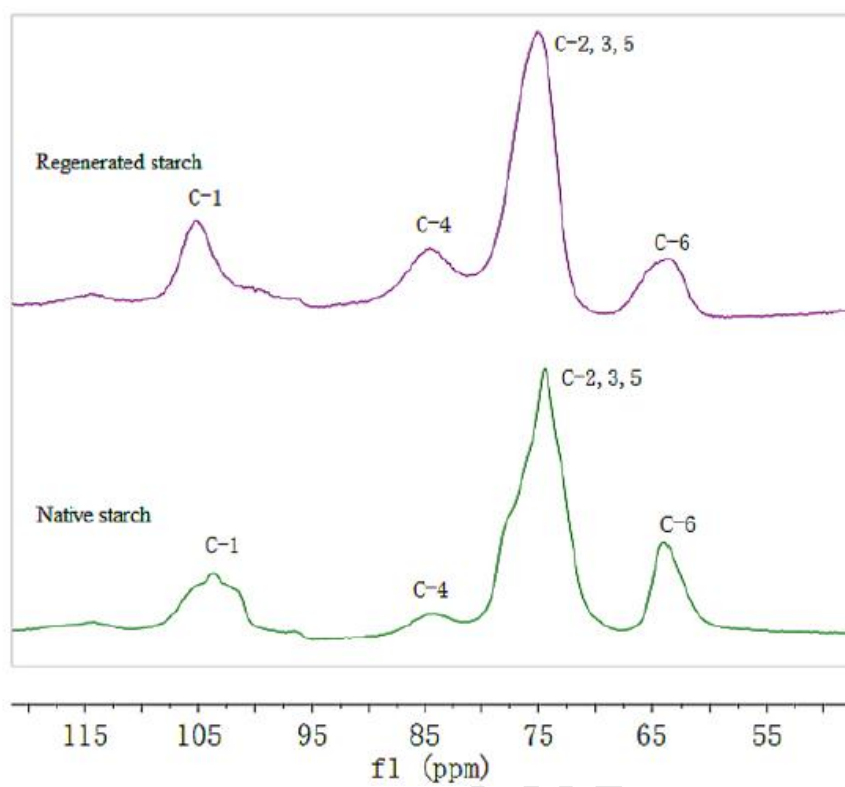
9 Fig. 5. ^{13}C NMR spectra for native starch and regenerated starch from 29.6% $ZnCl_2$

10 aqueous solution

11 Fig. 6. XRD patterns for regenerated starch samples from 35% (a), 43% (b), 65% (c)

12 $ZnCl_2$ solutions, and native starch (d)

13 Fig. 7. Intrinsic viscosity of native starch (a), and regenerated starch from 29.6% (b),

14 43% (c), 65% (d) $ZnCl_2$ solutions, and from HCl solution (pH=4.09) (e)

15 Fig. 8. TGA results for native starch (A), and regenerated starch samples from 35%

16 (B), 43% (C) and 65% (D) $ZnCl_2$ solution.

22

Fig. 1.   Pictures of cassava starch (2% concentration) dissolved in 29.6% $ZnCl_2$

aqueous solution (a), water (b) and HCl solution (c) after stirring for 4 h.

22

Fig. 2.   Birefringence images for 2% cassava starch granules dissolved in 29.6%

ZnCl$_2$ aqueous solution for 0 h (a), 1 h(b), 2 h(c), 3 h(d), and 4 h(e).

23

Fig. 3.   Turbidity of starch dissolved in aqueous ZnCl$_2$ of different concentrations.

24

Fig. 4.   FTIR spectra for native cassava starch (a) and regenerated starch from 29.6%

ZnCl$_2$ aqueous solution (b).

25

Fig. 5. ^{13}C NMR spectra for native starch and regenerated starch from 29.6% $ZnCl_2$
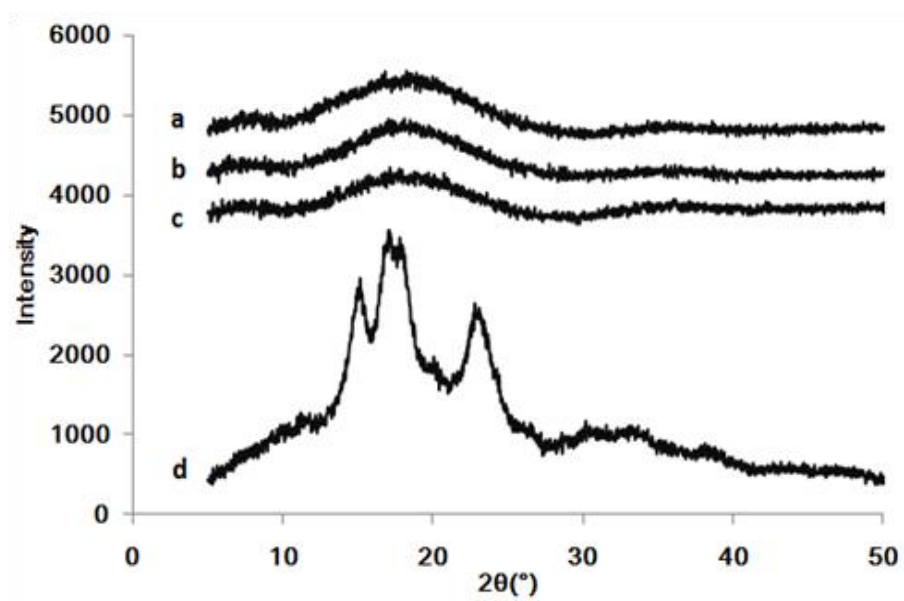
aqueous solution.

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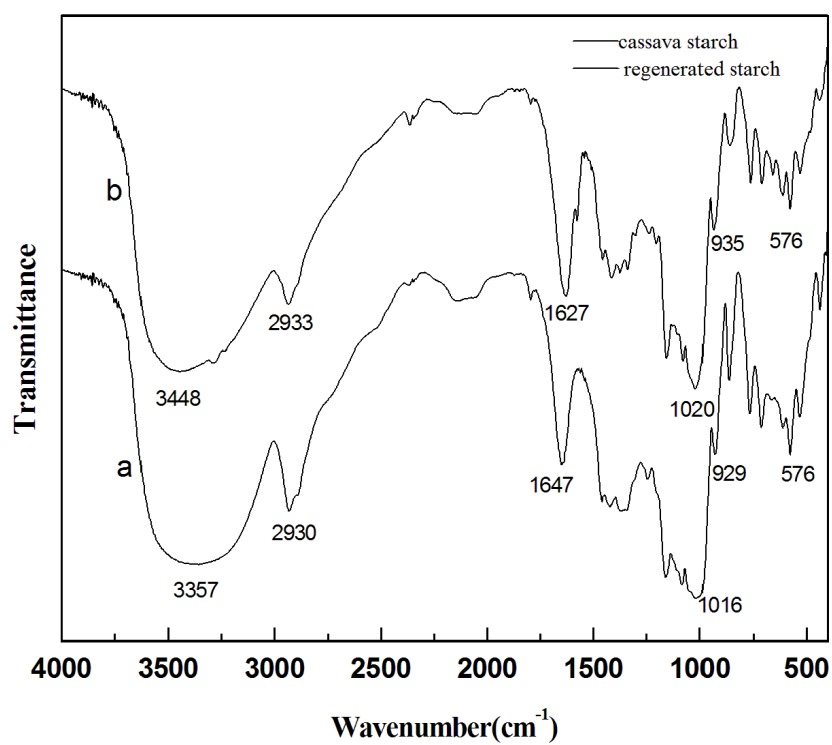
Fig. 6.   XRD patterns for regenerated starch samples from 35% (a), 43%(b), and

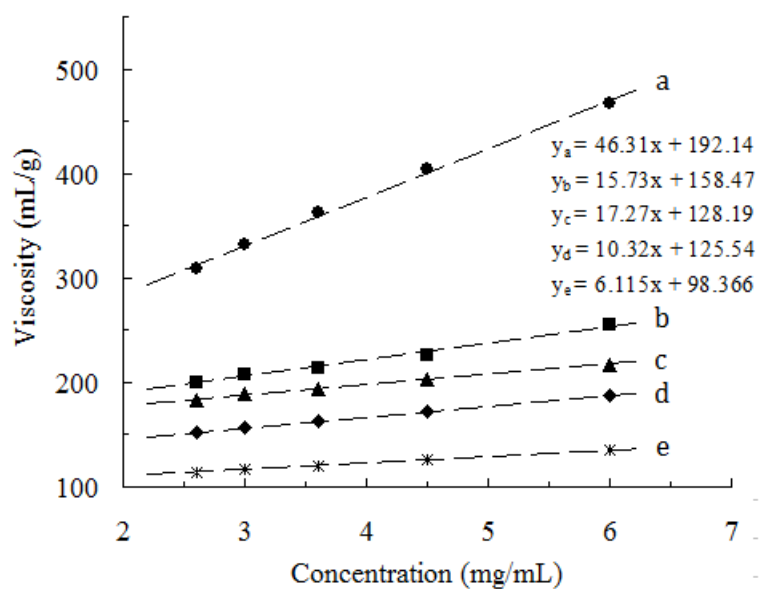65%(c) ZnCl$_2$ solutions, and native starch (d).

27

Fig. 7. Intrinsic viscosity of native starch (a), and regenerated starch samples from

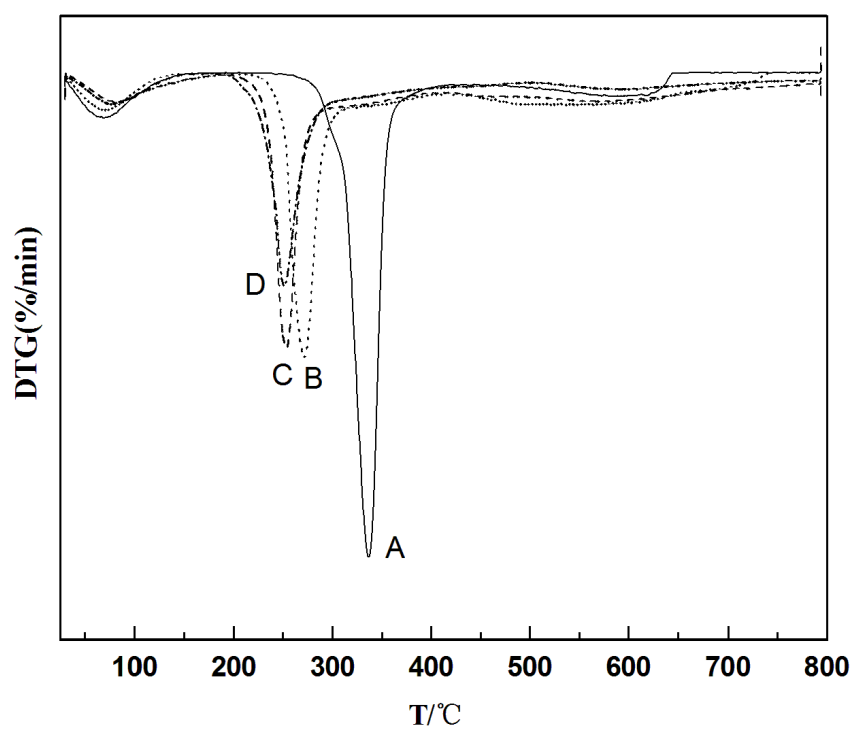29.6% (b), 43% (c), and 65% (d) $ZnCl_2$ solutions, and HCl solution (pH=4.09) (e).

28

Fig. 8.　TGA results for native starch (A), and regenerated starch samples from

35%(B), 43%(C) and 65% (D)ZnCl$_2$ solution.

29