

Influence of [Emim][OAc] and Water on Gelatinization Process and Interactions with Starch

Shajaratuldur Ismail, Nurlidia Mansor, Zakaria Man

Abstract—Thermoplastic starch (TPS) plasticized by 1-ethyl-3-methylimidazolium acetate [Emim][OAc] were obtained through gelatinization process. The gelatinization process occurred in the presence of water and [Emim][OAc] as plasticizer at high temperature (90°C). The influence of [Emim][OAc] and water on the gelatinization and interactions with starch have been studied over a range of compositions. The homogenous mass was obtained for the samples containing 35, 40 and 43.5 % of water contents which showed that water plays important role in gelatinization process. Detailed IR spectroscopy analysis showed decrease in hydrogen bonding intensity and strong interaction between acetate anion in [Emim][OAc] and starch hydroxyl groups in the presence of [Emim][OAc]. Starch-[Emim][OAc]-water mixture at 10-3-8.7 presented homogenous mass, less hydrogen bonding intensity and strong interaction between acetate anion in [Emim][OAc] and starch hydroxyl groups.

Keywords—Starch, ionic liquid, 1-ethyl-3-methylimidazolium acetate, plasticizer, gelatinization, IR spectroscopy.

I. INTRODUCTION

IN recent years there is growing interest regarding the use of biodegradable materials due to the environmental problems associated with conventional plastics including non-biodegradability, the release of toxic pollutants, litter and impact on landfills [1], [2]. The other reason apart from environmental problems are shortage of oil and petrochemical resources. Conventional plastics are mostly made up from the petroleum-based plastics [3], [4]. There are many sources of biodegradable plastics from synthetic to natural polymers. Natural polymers like polysaccharides and proteins, are preferable due to availability in large quantities from annually renewable resources, biocompatibility and biodegradability [5], [6].

Starch is an important productive, low cost polysaccharide derived from agricultural plants [7]. Starch exists in granular form and the granules are broadly composed of alternating amorphous and semi-crystalline shells (growth rings) (100-400 nm). The semi-crystalline shell is stacked crystalline and amorphous lamellae (periodicity) (9-10 nm) with all structures based on two major macromolecules called amylose and amylopectin.

Native starch is difficult to process because of its brittleness. This is due to the many hydrogen bonds between the starch macromolecules which reduce the movement of these molecules [7]. To improve the starch process ability, the semi

crystalline granular structure of native starches need to disrupt and melt [8]. The destruction of native starch granules formed material called as thermoplastic starch (TPS). This irreversible order-disorder transition termed gelatinization can be either obtained by solubilizing starch in water or by treating starch granules thermo-mechanically in the presence of water [9]. The transformation of granular starches into TPS is influenced by processing conditions such as temperature and plasticizer content. The most commonly used plasticizers in TPS materials are water and glycerol [8] but several other compounds like compounds containing nitrogen (urea, ammonium derived, amines) and citric acid have also been successfully employed. Those plasticizers are reported to be effective in the plasticization of starch [6], [10]-[15].

Ionic liquids (ILs) consist of cations and anions are low melting point salts, often referred to as 'green solvents' since ILs are non-volatile and reusable. ILs can be used to dissolve solutes of a wide-range of polarities and show varied miscibility with other solvents by modifying chemical structure of cation and anion moieties [9], [16], [17]. Starch can be processed with ILs to give materials with tuneable properties [18]. Gelatinization of starch by ILs is less hygroscopic than a corresponding sample plasticized by glycerol due to a rather strong interaction between starch and ILs which in turn limits the interaction between starch and water molecules [9], [19].

Previous study showed that gelatinization of starch occurs at 70% of total plasticizer contents and 1:4 w/w% ratio of [Emim][OAc]/water. The present study is to investigate the influence of [Emim][OAc] and water on the gelatinization process and interactions with starch over a range of compositions.

TABLE I
SAMPLE PREPARATIONS OF THE TPS BASED ON THE DRY WEIGHT OF STARCH

Sample	Starch (g)	[Emim][OAc] (g)	Water (g)
S10-IL3-W5.6	10	3	5,6
S10-IL3-W7	10	3	7
S10-IL3-W8.7	10	3	8,7
S10-IL3-W10	10	3	10
S10-IL1.4-W5.6	10	1,4	5,6
S10-IL1.6-W6.4	10	1,6	6,4

Shajaratuldur Ismail is with the Department of Chemical Engineering, Universiti Teknologi Petronas, Bandar Seri Iskandar 31750 Tronoh, Perak, Malaysia (e-mail: shaishhaja@gmail.com).

II. MATERIALS AND METHODS

A. Materials

Tapioca were purchased from local farmer (Kulim, Kedah). [Emim][OAc] was purchased from Sigma-Aldrich. Deionised water was used in all experiments.

B. Preparation of Starch

Starch were obtained according to a previously described method [20]. Briefly, the fresh root of tapioca was washed, cut and crushed into small pieces. The crushed roots were mixed with water and blended to obtain starch slurry. The mixtures were filtered using filter cloth and the filtrates were left for 24 hrs for the starch to fully settle at the bottom. After complete sedimentation, the extract starch were dried in an oven for 24 hrs at 60°C to obtain starch powder.

C. Sample Preparation

Starch was well blended with a mixture of [Emim][OAc] and water based on the Table I. Firstly, [Emim][OAc] and water were mixed for 5 minutes. Then, the liquid mixtures were added into starch powders while slowly shaking to ensure an even distribution. The mixture was heated at 90°C under continuous stirring until the mixture gelatinized. Lastly, the mixture were dried at 60°C to obtain powder form [1], [21].

D. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analyses were carried out by using Shimadzu FTIR-8400 Series to determine the presence of functional groups in the TPS materials and to reveal the interaction among [Emim][OAc], water and starch. The sample was mixed with KBr and pressed using PIKE Technologies CrushIR to form disc. Then, the disc was scan from 400 to 4000 cm⁻¹.

TABLE II
COMPOSITION AND OBSERVATION OF TPS

Sample	Plasticizer Content (%)	[Emim] Content (%)	Water
S10-IL3-W5.6	46,2	30	Heterogenous, partially plasticized
S10-IL3-W7	50	35	Homogenous mass
S10-IL3-W8.7	53,9	40	Homogenous mass
S10-IL3-W10	56,5	43,5	Homogenous mass
S10-IL1.4-W5.6	70	32,9	Unplasticized in powder form
S10-IL1.6-W6.4	80	35,6	Unplasticized in powder form

III. RESULTS AND DISCUSSION

A. Gelatinization

The gelatinization process of starch involves the complete and/or the partial destruction of the initial crystalline order. By processing at high temperature and suitable plasticizer, the molecular chains gain mobility. Gelatinization process can be done under shear and shearless condition, where the shearless condition mainly depends on the water contents and temperature. In the presence of water, structure of starch granules was disrupted, breaking the bonds of hydrogen chains and acts as primary plasticizer in which the second plasticizer is needed to complete the gelatinization process.

From the previous study, the gelatinization process occurred at 70% of total plasticizer contents and 1:4 w/w% ratio of [Emim][OAc]/water. These parameters were used as basis to design optimization experiment. However, the experiments did not go well because all the samples did not mix together and retained in the powder form. Therefore, new formulations were tested in order to observe the gelatinization process. Based on the literature review, the starch-glycerol-water mixture was in the range of 100:30:11.2 and 100:30:40 in percentage [22]. The preparations of TPS were carried out using the above range as basis. Table II shows the composition and observation of the TPS during the gelatinization process. In gelatinization process, the range of temperature is between 90 to 180°C [23]. The minimum temperature was chosen in the experiment. From the observation, at high % of plasticizer contents the gelatinization did not occurred. The samples were remained in the powder form. When the amounts of [Emim][OAc] were increase to 3g, the samples were mixed well. Increasing the % of water contents at the constant mass of [Emim][OAc], the samples showed homogenous mass. This is because TPS can be obtained at below the excess of water, usually less than 66% according to van Soest *et al.*, [8]. This show that water content give influence on the disruptive of starch granules. Besides, water acts as primary plasticizer to disrupt the starch granules before the second plasticizer i.e [Emim][OAc] to break through and interact with starch hydroxyl groups.

B. Interactions Among [Emim][OAc], Water and Starch

Fig. 1 show the infrared absorption spectra for TPS samples and Table III gives the position of the maximum of the most significant peaks. Capron *et al.*, have been reviewed the main characteristics of the Mid-infrared spectra of starch[17]. The three ranges of wavenumbers are:

- The 3000-3600 cm⁻¹ region in which a broad absorption peak is associated with the stretching mode of the hydrogen bonded O-H groups of starch and absorbed water
- The 950-1200 cm⁻¹ region where are located the absorption peaks of the C-C and C-O stretching vibration modes and of the C-O-H bending modes
- The 950-700 cm⁻¹ region where are located the C-O-C $\alpha(1-6)$ and $\alpha(1-4)$ stretching modes and the C-O-C ring breathing modes

According to Ma *et al.*, the peaks at 1080 and 1050 cm⁻¹ are attributed to the C-O bond stretching in the C-O-H groups of starch while the peaks at 1000 and 1020 cm⁻¹ are attributed to the C-O bonds stretching in the C-O-C group of the anhydroglucose rings. This is characteristic peaks use to compare the strength of the hydrogen bonds formed by different plasticizers with the oxygen atoms of starch [24].

The shift of peaks toward lower wavenumbers indicates an increase of the hydrogen bonding to which the oxygen atoms of the C-O bonds in starch are submitted. A similar shift toward lower wavenumbers of the maximum of broad peak in 3000-3600 cm⁻¹ range will indicate an increase of hydrogen bonding to which the hydrogen atoms of O-H bonds in starch are submitted. Meanwhile a shift toward higher wavenumbers will indicate a decrease of hydrogen bonding [9], [25].

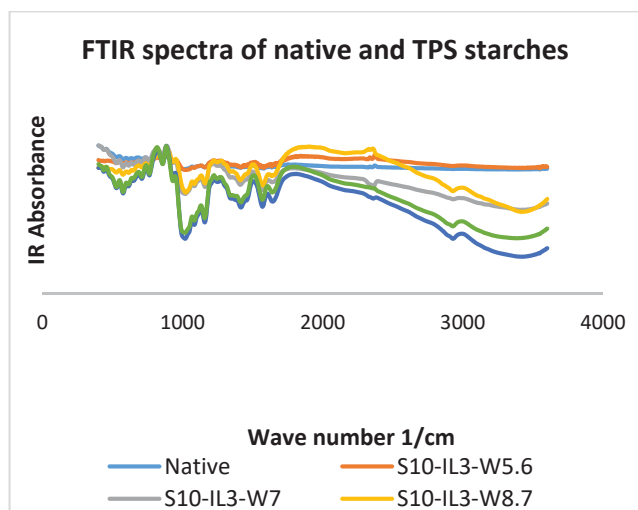


Fig. 1 FTIR spectra of native starch and TPS

The positions of the maximum of the main infrared absorption peaks in Table III were calculated using the LabSolutions software identification routine. Based on the Table III, only stretching vibration mode of hydrogen bonded O-H groups, stretching vibration mode of C-O bonds of C-O-C and C-O-C α (1-6) links between anhydroglucose rings shows significant variations.

TABLE III
POSITIONS OF THE MAXIMUM OF THE MAIN INFRARED ABSORPTION PEAKS OF
FIG. 1

Sample	O-H Stretch	C-O stretch (C-O-C groups of anhydroglucose rings)	C-O stretch (C-O-H groups)	C-O stretch (C-O-C links n(1-6))
S10-IL3-W5.6	None	1012,56	None	856,34
S10-IL3-W7	3548,78	None	1081,99	854,41
S10-IL3-W8.7	3436,91	1018,34	1083,92	856,34
S10-IL3-W10	3425,34	None	1083,92	856,34
S10-IL1.4-W5.6	3400	1016,42	1083,92	858,26
S10-IL1.6-W6.4	3400	1016,42	1083,92	856,34

For the stretching mode of hydrogen bonded O-H groups, only the samples containing 35, 40 and 43.5 % of water contents were shifted to the higher wavenumbers and sample at 35% of water contents show the highest wavenumbers. This show that the global strength of hydrogen bonds to which the hydrogen atoms of the O-H groups were submitted become lower in the presence of [Emim][OAc] which explained by Yang *et al.*, [25]. The stretching vibration mode of C-O bonds of C-O-C groups of starch were shifted to the higher wavenumbers at samples containing 32.9, 35.6 and 40% of water contents. However, there were no gelatinization occurred at samples containing 32.9 and 35.6% of water contents, which can be negligible. The shifted of peaks towards higher wavenumbers indicate a decrease of hydrogen bonding. Absorption peaks of all the samples (except sample containing 32.9% of water contents) were shifted towards lower wavenumbers at the stretching vibration mode of the C-O bonds stretching in the C-O-C group of the anhydroglucose rings. This is due to the strong interaction between acetate anion in [Emim][OAc] and starch hydroxyl groups, disrupting hydrogen bonding in starch polymer and

cause difficulty for amylose molecules to form single (and double) helices [26].

The decrease of hydrogen bonding intensity and strong interaction between acetate anion in [Emim][OAc] and starch hydroxyl groups indicate that TPS was less hydrophilic. This is because TPS plasticized by [Emim][OAc] have less interactions with water molecules. Among all those samples, only starch-[Emim][OAc]-water mixture at 10-3-8.7 show all those criteria.

IV. CONCLUSION

In this study, the influence of [Emim][OAc] and water in gelatinization process and interactions with starch over a range of compositions were investigated. Gelatinization process occurred at samples containing 35, 40 and 43.5% of water contents which showed homogenous mass. A detailed analysis by infrared spectroscopy showed the strong formation of strong hydrogen bonds between acetate anion in [Emim][OAc] and starch hydroxyl groups and decrease of hydrogen bonding intensity in the presence of [Emim][OAc]. From the study, the ideal starch-[Emim][OAc]-water mixture is 10-3-8.7. As conclusion, 10-3-8.7 will be use as a new basis to for optimization experiment in order to develop TPS with excellent rheological and physico-chemical properties to meet conventional processing needs. In this regard, research is still under way.

REFERENCES

- [1] N. Johar and I. Ahmad, "Morphological, thermal, and mechanical properties of starch biocomposite films reinforced by cellulose nanocrystals from rice husks," *BioResources*, vol. 7, pp. 5469-5477, 2012.
- [2] G. Wu, E. Sun, H. Huang, Z. Chang, and Y. Xu, "Preparation and properties of biodegradable planting containers made with straw and starch adhesive," *BioResources*, vol. 8, pp. 5358-5368, 2013.
- [3] N. L. Garcia, L. Ribba, A. Dufresne, M. Aranguren, and S. Goyanes, "Effect of glycerol on the morphology of nanocomposites made from thermoplastic starch and starch nanocrystals," *Carbohydrate Polymers*, vol. 84, pp. 203-210, 2011.
- [4] S. Tajuddin, F. Xie, T. M. Nicholson, P. Liu, and P. J. Halley, "Rheological properties of thermoplastic starch studied by multipass rheometer," *Carbohydrate Polymers*, vol. 83, pp. 914-919, 2011.
- [5] L. Yu, K. Dean, and L. Li, "Polymer blends and composites from renewable resources," *Progress in polymer science*, vol. 31, pp. 576-602, 2006.
- [6] R. Zullo and S. Iannace, "The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure," *Carbohydrate Polymers*, vol. 77, pp. 376-383, 2009.
- [7] R. Shi, Z. Zhang, Q. Liu, Y. Han, L. Zhang, D. Chen, *et al.*, "Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending," *Carbohydrate Polymers*, vol. 69, pp. 748-755, 2007.
- [8] J. J. van Soest, R. C. Bezemer, D. de Wit, and J. F. Vliegthart, "Influence of glycerol on the melting of potato starch," *Industrial Crops and Products*, vol. 5, pp. 1-9, 1996.
- [9] A. Sankri, A. Arhaliass, I. Dez, A. C. Gaumont, Y. Grohens, D. Lourdin, *et al.*, "Thermoplastic starch plasticized by an ionic liquid," *Carbohydrate Polymers*, vol. 82, pp. 256-263, 2010.
- [10] K. Krogars, J. Heinämäki, M. Karjalainen, J. Rantanen, P. Luukkonen, and J. Yliruusi, "Development and characterization of aqueous amylose-rich maize starch dispersion for film formation," *European Journal of Pharmaceutics and biopharmaceutics*, vol. 56, pp. 215-221, 2003.
- [11] H. Liu, F. Xie, L. Yu, L. Chen, and L. Li, "Thermal processing of starch-based polymers," *Progress in Polymer Science*, vol. 34, pp. 1348-1368, 2009.

- [12] S. A. McGlashan and P. J. Halley, "Preparation and characterisation of biodegradable starch-based nanocomposite materials," *Polymer International*, vol. 52, pp. 1767-1773, 2003.
- [13] K. Poutanen and P. Forssell, "Modification of starch properties with plasticizers," *Trends in polymer science*, vol. 4, pp. 128-132, 1996.
- [14] F. Xie, P. J. Halley, and L. Avérous, "Rheology to understand and optimize processibility, structures and properties of starch polymeric materials," *Progress in Polymer Science*, vol. 37, pp. 595-623, 2012.
- [15] F. Xie, B. M. Flanagan, M. Li, R. W. Truss, P. J. Halley, M. J. Gidley, *et al.*, "Characteristics of starch-based films with different amylose contents plasticised by 1-ethyl-3-methylimidazolium acetate," *Carbohydrate polymers*, vol. 122, pp. 160-168, 2015.
- [16] J. L. Anderson, J. Ding, T. Welton, and D. W. Armstrong, "Characterizing ionic liquids on the basis of multiple solvation interactions," *Journal of the American Chemical Society*, vol. 124, pp. 14247-14254, 2002.
- [17] I. Capron, P. Robert, P. Colonna, M. Brogly, and V. Planchot, "Starch in rubbery and glassy states by FTIR spectroscopy," *Carbohydrate Polymers*, vol. 68, pp. 249-259, 2007.
- [18] M. Isik, H. Sardon, and D. Mecerreyes, "Ionic liquids and cellulose: Dissolution, chemical modification and preparation of new cellulosic materials," *International journal of molecular sciences*, vol. 15, pp. 11922-11940, 2014.
- [19] A. A. Shamsuri and R. Daik, "Plasticizing effect of choline chloride/urea eutectic-based ionic liquid on physicochemical properties of agarose films," *BioResources*, vol. 7, pp. 4760-4775, 2012.
- [20] K. Saengchan, M. Nopparatana, and W. Songkasiri, "Influence of Feed Flow Rate on Tapioca Starch Perforation through Filter Medium in a Conical-Screen Centrifuge," in *International Conference on Chemical, Ecology and Environmental Sciences (ICCEES'2011) Pattaya*, 2011.
- [21] N. S. Mohd Makhtar, M. N. Muhd Rodhi, M. Musa, and K. H. Ku Hamid, "Thermal Behavior of Tacca leontopetaloides Starch-Based Biopolymer," *International Journal of Polymer Science*, vol. 2013, 2013.
- [22] S. H. Hulleman, F. H. Janssen, and H. Feil, "The role of water during plasticization of native starches," *Polymer*, vol. 39, pp. 2043-2048, 1998.
- [23] A. Curvelo, A. De Carvalho, and J. Agnelli, "Thermoplastic starch-cellulosic fibers composites: preliminary results," *Carbohydrate Polymers*, vol. 45, pp. 183-188, 2001.
- [24] X. Ma, J. Yu, and K. He, "Thermoplastic starch plasticized by glycerol as solid polymer electrolytes," *Macromolecular Materials and Engineering*, vol. 291, pp. 1407-1413, 2006.
- [25] J. h. Yang, J. g. Yu, and X. f. Ma, "Preparation of a novel thermoplastic starch (TPS) material using ethylenebisformamide as the plasticizer," *Starch-Stärke*, vol. 58, pp. 330-337, 2006.
- [26] F. Xie, B. M. Flanagan, M. Li, P. Sangwan, R. W. Truss, P. J. Halley, *et al.*, "Characteristics of starch-based films plasticised by glycerol and by the ionic liquid 1-ethyl-3-methylimidazolium acetate: A comparative study," *Carbohydrate polymers*, vol. 111, pp. 841-848, 2014.