



4th International Conference on Process Engineering and Advanced Materials

Effect of Water and [Emim][OAc] as Plasticizer on Gelatinization of Starch

Shajaratuldur Ismail*, Nurlidia Mansor ,Zahid Majeed , Zakaria Man

Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Tronoh ,Perak, Malaysia

Abstract

As the depletion of petroleum source and environmental concerns been arises, a new polymer defined as biodegradable material had been extensively study in order to replace the synthetic one. Starch is one of natural materials that been used for producing biodegradable materials. Through gelatinization process, native starches were changed into thermoplastic starch (TPS) in the presence of water and [Emim][OAc] as plasticizers at high temperature (90°C). The structure and interaction of starch/water/[Emim][OAc] have been study using differential scanning calorimetry (DSC). DSC analysis is used to analyse the onset temperature (T_o), the peak temperature (T_p), the melting temperature (T_m) and melting enthalpy (ΔH) of samples over a wide range of starch/water/[Emim][OAc] contents. Gelatinization peak shift to higher temperature as the value of [Emim][OAc] is increasing. The values of T_o , T_p and ΔH are influenced by the hydrogen bonding capacity of plasticizers. Thus, showed that composition of water/[Emim][OAc] is effectively influence the gelatinization process.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of ICPEAM 2016

Keywords: Starch; plasticizer; 1-ethyl-3-methylimidazolium acetate; gelatinization;

1. Introduction

Due to the environmental concerns, a great interest towards the usage of biodegradable materials arise from the last few years. Nowadays, conventional plastics are commonly used. However, major drawback come from the usage of conventional plastics are non-biodegradability, release of toxic pollutants, litter and impact on landfills [1] [2]. The other reason is shortage of petrochemical resources. Petroleum-based are one of the main raw materials for

* Corresponding author. Tel.: +06-011-16424192.
E-mail address: shaisshaja@gmail.com

producing conventional plastics [3]. Biodegradable plastics can be produce from many sources either synthetic or natural polymers. Natural polymers are mostly used, such as polysaccharides and proteins due to availability in large quantities, renewable resources, biocompatibility and biodegradability [4, 5].

Starch is preferable among the groups of polysaccharides. Starch has versatility, low price and availability. Starch is a semi crystalline polymer which is derived from plants. It consist of glucose units joined together by glycosidic bonds [6]. Starch is naturally structured in a hierarchical multi-level complex form; classified as granules. The main structure of granules are amylose; a linear structure and amylopectin; branched structure [3, 5, 7-11].

Native starch has difficult process ability and need to undergo modification. This can be achieved by destroying the molecular order within the granules. This process called as 'gelatinization' occurred in the present of plasticizer and elevated temperature. Through this process, the 3D structure of starch were disrupted and in the preferential conditions, produced a homogenous amorphous material known as 'thermoplastic starch' or plasticised starch'. Gelatinization process caused the changes from crystalline to an amorphous structure. This structure is needed in production biodegradable materials that can be applied in conventional technology such as hot press and injection moulding [3, 5, 11-16].

Plasticizer is an important substance in gelatinization process. The most commonly used plasticizers are polyols such as glycerol and water which is excellent in the plasticization of starch. However, certain plasticizer caused problems to the thermoplastic starch. The sole used of water as a plasticizer caused hygroscopic property. The others for the example, a plasticizer from polyols caused recrystallization phenomena due to the small size and can easily be separated from the starch macromolecular chains.

Ionic liquids (ILs) consist of cations and anions. ILs also called as 'green solvents' because reusable property [11, 17, 18]. Many ILs such as imidazolium cation have been proved to be capable of dissolving starch [19-23]. Gelatinization of starch by ILs are less hygroscopic than starch plasticized by glycerol due to a rather strong interaction between starch and ILs. This strong interaction limits the interaction between starch and water molecules [18, 24].

Previous study showed that at 40% w/w of water contents enhanced the starch gelatinization process. In this study, the amount of [Emim][OAc] is been manipulated while the water content is fixed at 40% w/w. Therefore, the focus is to study the effect of water and [Emim][OAc] as plasticizer on gelatinization of starch using the Differential Scanning calorimetry (DSC) analysis.

2. Materials and Methods

2.1 Materials

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

2.2 Preparation of Starch

Starch were obtained according to a previously described method [25]. Briefly, the fresh root of tapioca were 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.

2.3 Sample Preparation

Starch was well blended with a mixture of [Emim][OAc] and water based on the Table 1. 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 were heated at 90°C under continuous stirring until the mixture gelatinized. Lastly, the mixture were dried at 60°C to obtain powder form [1, 26].

Table 1. Sample preparations of the TPS based on the dry weight of starch

Sample	Starch(g)	Water(g)	[Emim][OAc](g)
SWE1	10	7.33	1.0
SWE2	10	7.67	1.5
SWE3	10	8.00	2.0
SWE4	10	8.33	2.5
SWE5	10	9.00	3.0

2.4 Differential Scanning Calorimetry (DSC)

The DSC measurement were carried out using DSC instrument at a heating rate of 5°C/min from 30 to 150°C with an empty pan as the reference. TA Universal Analyses software was used to determine the onset temperature (T_o), the peak temperature (T_p), the melting temperature (T_m) and melting enthalpy (ΔH).

3. Results and Discussion

DSC is one of the analysis tools used to help understanding the structure and interaction between starch/water/[Emim][OAc] mixtures. DSC analysis is used to analyse the onset temperature (T_o), the peak temperature (T_p), the melting temperature (T_m) and melting enthalpy (ΔH) of samples over a wide range of starch/water/[Emim][OAc] mixtures. The DSC characteristics of starch/water/[Emim][OAc] mixtures are shown in Table 2 and graphically in Figure 1.

Table 2. DSC characteristics of starch/water/[Emim][OAc] mixtures

Sample	T_o (°C)	T_p (°C)	T_m (°C)	ΔH (J/g)
SWE1	39.5	93.1	148.3	248.5
SWE2	66.6	115.1	148.1	157.4
SWE3	42.8	96.1	148.3	226.1
SWE4	46.7	101.0	148.3	219.8
SWE5	45.4	98.9	148.3	286.9

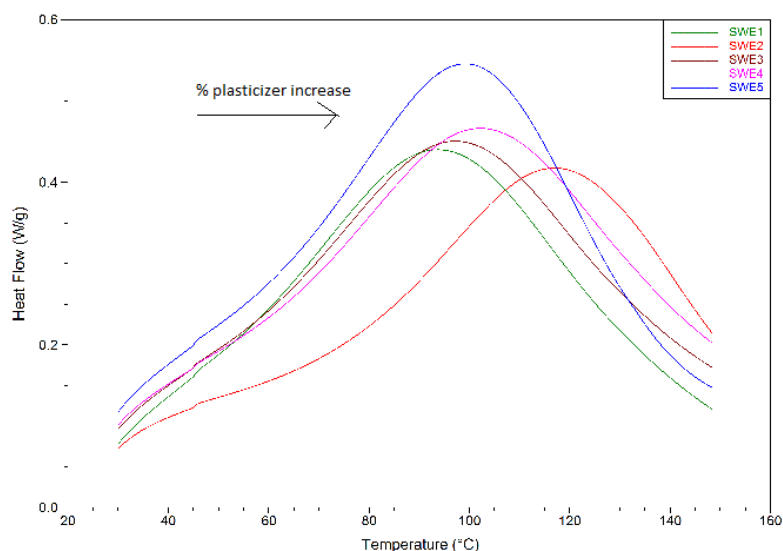


Fig. 1. DSC traces of gelatinization for starch/water/[Emim][OAc] system

As shown in the above figure, all the samples exhibited a single endothermic transition, corresponding to the melting process of the matrix crystalline phase as proven by [27]. Based on the Table 2, the T_m for all the samples are in the range of 148.1 to 148.3 °C, in which didn't showed any significant changes. However, there are significant changes in the T_o , T_p and ΔH as the amount of [Emim][OAc] increasing. The values of T_o , T_p and ΔH are influenced by the hydrogen bonding capacity of plasticizers. According to [28], the crystallinity of starch is disrupted in two distinct steps independent to the type of plasticizer which are plasticization and gelatinization steps. Plasticization step involved the diffusion of the plasticizer into the amorphous part of starch granules. During this step, the amorphous parts of starch gain a certain degree of freedom and molecular activity. In this step, water have played the main roles as water is known as primary plasticizer to destruct the starch granules. Water penetrated into starch granules caused the outer layers to swelled and facilitated penetration of second plasticizer. Next in the second step, the gain mobility initiates the helix-coil irreversible transition and disruption of crystalline structure. During this step, the starch-starch hydrogen bonds should be disrupted and starch-plasticizer hydrogen bonding should be built. This bonding between starch-plasticizer hydrogen bond is referred to the hydrogen bonding between starch and second plasticizer which in this study is [Emim][OAc]. As the hydrogen bonding capacity increasing, the values of T_o and T_p happened at lower temperature and need less thermal energy uptake in which the value of ΔH also lowered. Low value of ΔH is due to the higher interaction between starch-plasticizer hydrogen bonding, causing a higher mobility during heating and increasing kinetic energy.

According to the previous study, 40% w/w of water composition enhanced the starch gelatinization process. Therefore in this study, only the amount of [Emim][OAc] been manipulated in order to identify the influence of [Emim][OAc] as second plasticizer in gelatinization process. Based on Figure 1, the gelatinization peak shift to higher temperature as the amount of [Emim][OAc] increased which proven by [29]. This is due to the presence of salts in the solutions. The effect of salts in gelatinization of starch were found to follow the Hofmeister series. In Hofmeister series, kosmotropes delaying gelatinization and chaotropes accelerating gelatinization. Acetate is a well-known kosmotropes, so caused the gelatinization toward higher temperature [29, 30]. Based on Table 2, the values of T_o , T_p and ΔH seems fluctuations, not too much different among the 5 samples and only SWE2 show significant change. SWE2 have high value of T_o and T_p but low values of ΔH . This might be because of structure-making effects on water and electrostatic interactions between salts and hydroxyl groups of starch. Even though the gelatinization peak increase as [Emim][OAc] increasing at certain ratio of water-[Emim][OAc], water compete with starch in bonding with [Emim][OAc]. Interaction between water-ionic liquid mixture ([Emim][OAc]) is quite

complex. Water is a key factor in gelatinization process and at certain ratio, water can become the limiting factor [31]. To better understand water-[Emim][OAc] interaction, an optimization analysis using Response Surface Methodology (RSM) will be used.

4. Conclusion

In this study, effect of water and [Emim][OAc] as plasticizer on gelatinization of starch had been studied. DSC analysis is used to better understand the structure and interaction between starch/water/[Emim][OAc] mixtures. All the samples showed a single endothermic transition. Gelatinization peak shift to higher temperature as the value of [Emim][OAc] is increasing. The values of T_o , T_p and ΔH are influenced by the hydrogen bonding capacity of plasticizers. Better gelatinization process occurred at lower value of T_o , T_p and ΔH . Improvement in water/[Emim][OAc] ratio are needed to enhance the starch gelatinization process and producing TPS with excellent properties. The optimization analysis using Response Surface Methodology (RSM) is still under way.

Acknowledgements

The financial support by a FRGS grant through Universiti Teknologi Petronas are greatly appreciated.

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. García, 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] L. Yu, K. Dean, and L. Li, "Polymer blends and composites from renewable resources," *Progress in polymer science*, vol. 31, pp. 576-602, 2006.
- [5] 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.
- [6] Z. Majeed, N. Mansor, and Z. Man, "Lignin Effect on Tensile Properties of Biodegradable Urea-Crosslinked Starch in Aerobic Soil Microcosm," in *Advanced Materials Research*, 2016, pp. 45-49.
- [7] Z.-q. Fu, L.-j. Wang, D. Li, Q. Wei, and B. Adhikari, "Effects of high-pressure homogenization on the properties of starch-plasticizer dispersions and their films," *Carbohydrate Polymers*, vol. 86, pp. 202-207, 2011.
- [8] J. Jane, "Structural features of starch granules II," *Starch: Chemistry and technology*, vol. 3, 2009.
- [9] S. Pérez and E. Bertoft, "The molecular structures of starch components and their contribution to the architecture of starch granules: A comprehensive review," *Starch-Stärke*, vol. 62, pp. 389-420, 2010.
- [10] D. Thomas and W. Atwell, "Starches," *American Association of Cereal Chemists*, 1997.
- [11] 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 plasticized by 1-ethyl-3-methylimidazolium acetate," *Carbohydrate polymers*, vol. 122, pp. 160-168, 2015.
- [12] L. Avérous, "Biodegradable multiphase systems based on plasticized starch: a review," *Journal of Macromolecular Science, Part C: Polymer Reviews*, vol. 44, pp. 231-274, 2004.
- [13] 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.
- [14] M. G. Lomeli-Ramírez, S. G. Kestur, R. Manríquez-González, S. Iwakiri, G. B. de Muniz, and T. S. Flores-Sahagun, "Bio-composites of cassava starch-green coconut fiber: Part II—Structure and properties," *Carbohydrate polymers*, vol. 102, pp. 576-583, 2014.
- [15] 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.
- [16] F. Xie, E. Pollet, P. J. Halley, and L. Avérous, "Starch-based nano-biocomposites," *Progress in Polymer Science*, vol. 38, pp. 1590-1628, 2013.
- [17] A. A. Shamsuri and D. K. Abdullah, "Isolation and characterization of lignin from rubber wood in ionic liquid medium," *Modern Applied Science*, vol. 4, p. p19, 2010.
- [18] 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.
- [19] A. Biswas, R. Shogren, D. Stevenson, J. Willett, and P. K. Bhowmik, "Ionic liquids as solvents for biopolymers: Acylation of starch and zein protein," *Carbohydrate Polymers*, vol. 66, pp. 546-550, 2006.
- [20] O. A. El Seoud, A. Koschella, L. C. Fidale, S. Dorn, and T. Heinze, "Applications of ionic liquids in carbohydrate chemistry: a window of opportunities," *Biomacromolecules*, vol. 8, pp. 2629-2647, 2007.
- [21] K. Wilpiszewska and T. Spychaj, "Ionic liquids: Media for starch dissolution, plasticization and modification," *Carbohydrate*

- Polymers*, vol. 86, pp. 424-428, 2011.
- [22] M. E. Zakrzewska, E. Bogel-Lukasik, and R. Bogel-Lukasik, "Solubility of carbohydrates in ionic liquids," *Energy & Fuels*, vol. 24, pp. 737-745, 2010.
- [23] S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, et al., "Dissolution of cellulose with ionic liquids and its application: a mini-review," *Green Chem.*, vol. 8, pp. 325-327, 2006.
- [24] 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.
- [25] K. Saengchan, M. Nopharatana, 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.
- [26] 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.
- [27] O. Lopez, M. Garcia, M. Villar, A. Gentili, M. Rodriguez, and L. Albertengo, "Thermo-compression of biodegradable thermoplastic corn starch films containing chitin and chitosan," *LWT-Food Science and Technology*, vol. 57, pp. 106-115, 2014.
- [28] P. Perry and A. Donald, "The role of plasticization in starch granule assembly," *Biomacromolecules*, vol. 1, pp. 424-432, 2000.
- [29] L. Sciarini, A. Rolland-Sabaté, S. Guilois, P. Decaen, E. Leroy, and P. Le Bail, "Understanding the destructureation of starch in water-ionic liquid mixtures," *Green Chemistry*, vol. 17, pp. 291-299, 2015.
- [30] F. B. Ahmad and P. A. Williams, "Effect of salts on the gelatinization and rheological properties of sago starch," *Journal of agricultural and food chemistry*, vol. 47, pp. 3359-3366, 1999.
- [31] A. Taghizadeh and B. D. Favis, "Effect of high molecular weight plasticizers on the gelatinization of starch under static and shear conditions," *Carbohydrate polymers*, vol. 92, pp. 1799-1808, 2013.