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CHARACTERIZATION OF TAPIOCA STARCH PLASTICIZED BY 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE

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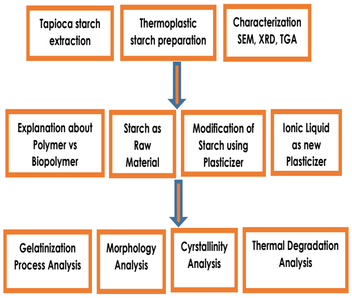
Graphical abstract



Abstract

Starch is one of natural materials that been used for producing biodegradable materials. The starch-based materials are produced through a process known as gelatinization with the presence of plasticizer and elevated temperature. Properties of starch-based materials are lacking in terms of viscosity, water absorption, thermal and mechanical properties compare with synthetic materials. Researchers are involved in finding ways for improvement of starch-based materials properties and one of that is introducing new plasticizer. 1-ethyl-3-methylimidazolium acetate, [Emim][OAc] is an ionic liquid that used as plasticizer to produce thermoplastic starch. Starch plasticized by [Emim][OAc] were prepared with different total plasticizer contents (50%,70%) and [Emim][OAc]/water ratio (1:6,1:4,2:3 wt%). The thermoplastic starches were characterized in terms of morphology, crystalline structure and thermal degradation. The results showed that 70% of total plasticizer contents were mixed well during gelatinization process. [Emim][OAc] contributed to granule disruption as shown by SEM. Based on the XRD analysis, it was shown that thermoplastic starch at 70% total plasticizer contents and 1:4 wt% ratio of [Emim][OAc]/water, caused disruption of the A-type crystalline structure, generated V_H-type crystalline structure and thus increased the mobility of the amorphous starch. The presence of [Emim][OAc] promotes the thermal degradation of starch molecules as described by TGA. Therefore, plasticizer contents and [Emim][OAc]/water ratio are vital parameters that influences the properties of thermoplastic starch.

Keywords: Starch, Ionic liquid, 1-ethyl-3-methylimidazolium acetate, Plasticizer, Gelatinization

1.0 INTRODUCTION

Due to the environmental concerns, a great interest towards the usage of biodegradable materials increasing from the last few years. Nowadays, conventional plastics are commonly used. However, major drawback arise from the usage of conventional plastics are non-biodegradability, release of toxic pollutants, litter and impact on landfills [1, 2]. The other reason apart from environmental problems is shortage of petrochemical resources. Petroleum-based are one of the main raw materials for producing conventional plastics [3]. Biodegradable plastics can be arise 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 polysaccharide derived from agricultural plants. Starch is naturally structured in a hierarchical multi-level complex form; classified as granules. The main structure of granules are amylose and amylopectin. The amylose is a linear polymer in which the repeating units are linked by a-(1-4) linkages and amylopectin has a-(1-4) linked backbone and ca. 5% of a-(1-6) linked branches [3, 5-11].

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, 12-16].

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. According to [11] Xie *et al.*, (2015), a plasticizer should preferably stable both during thermal processing and in post-processing stages, ineffective in starch macromolecular degradation, safe to environment and humans and able to provide starch-based materials with enhanced performance and new capabilities [5, 13, 15, 17-19].

Ionic liquids (ILs) consist of cations and anions. ILs also called as 'green solvents' because reusable property. ILs have good properties such as chemical and thermal stability, low vapour pressure, relatively low melting point (below than 100˚C), miscible with certain organic solvents and/or water, chemically inert, can be customized and capable of dissolving many substances including many organic polymers [11, 13, 20-23]. Many ILs such as imidazolium cation have been proved to be capable of dissolving starch [24-28]. 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 [23, 29].

Recent studies [11, 30] regarding the use of an IL, 1-ethyl-3-methylimidazolium acetate [Emim][OAc] as a plasticizer for starch shown that this IL has a significant gelatinization effect, able to reduce crystallinity and increase the mobility of amorphous phase. Gelatinization of starch by [Emim][OAc] and water play a major role in determination of thermoplastic starch characteristics. This paper focus on the preparation of starch by ILs. The effect of total plasticizer contents and ratio of [Emim][OAc]/water were evaluated on starch plasticized by [Emim][OAc]. Thus, the gelatinization effects of [Emim][OAc] on the morphology, crystalline structure and thermal degradation of the thermoplastic starch are discuss here with the aim of providing information for designing starch gelatinization processes and thermoplastic starch with

2.0 METHODOLOGY

2.1 Materials

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

2.2 Preparation of Starch

Starch were obtained according to a previously described method [31]. 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 55˚C to obtain starch powder.

2.3 Sample Preparation

Formulations for sample preparation are shown in Table 1. In Table 1 and the following text, the thermoplastic starch samples are coded in the format of "501", where "5" denotes the total of plasticizer contents and "01" indicates the ratio of IL/water in wt% (either 01, 1:6; 02, 1:4 or 03, 2:3). 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, starch powder were carefully added to the liquid mixture while slowly shaking to ensure an even distribution of starch in the liquid mixture. The mixture were heated at 50˚C under continuous stirring until the mixture gelatinized. Lastly, the mixture were dried at 55˚C to obtain powder form [1, 32].

2.4 Characterization

2.4.1 Scanning Electron Microscope (SEM)

A SEM was used to examine the morphology of thermoplastic starch; the powder of thermoplastic starch was deposited onto a carbon-coated microscopy grid.

2.4.2 X-Ray Diffraction (XRD)

The thermoplastic starch samples were analysed for crystallization structure using X-ray diffractometer (model D8 Advance, Bruker). XRD patterns were recorded for an angular range (2ϴ) of 4-40˚, with a step size of 0.02˚ and a step rate of 0.5s per step. The radiation parameters were set as 40kV and 30mA with a slit of 2mm.

2.4.3 Thermogravimetric Analysis (TGA)

A Mettler Toledo TGA/DSC1 machine (model PYRIS 1, Perkin Elmer) was used with 40 µL aluminium crucibles for thermogravimetric analysis (TGA) under nitrogen. A sample mass of about 5 mg was used for each run. The samples were heated from 25˚C to 550˚C at 3˚C/min.

3.0 RESULTS AND DISCUSSION

3.1 Starch Gelatinization Process

The gelatinization process of starch involves the complete and/or the partial destruction of the starch granules. In the presence of suitable plasticizer and elevated temperature, the molecular chains gain mobility. Gelatinization process can be done under shear and shear less condition. In the shear less condition, the process mainly depends on the water content and temperature. Water are used to break the structure of the granules which can be referred as primary plasticizer. After that, the second plasticizer is needed to complete the gelatinization process. The second plasticizer plays as determining factor in designing the properties of thermoplastic starch. Therefore, the total plasticizer contents and ratio of IL/water are plays as important role in gelatinization process. According through the sample preparation based on formulation, the samples at 50% of total plasticizer contents are hardly to mix for all of the ratio which indicate that the incomplete gelatinization process. Meanwhile, the samples at 70% of total plasticizer contents are mix properly for all of the ratio. This means that the mixtures are properly gelatinized either completely or partially.

Table 1 Sample codes and formulations of the thermoplastic starches

Sample Code	**Formulation** $_a$			
	Total Plasticizer $_b$	**Starch**	**[Emim][OAc]**	**Water**
501	50%	10	0.714	4.286
502		10	1	4
503		10	2	3
701	70%	10	1	6
702		10	1.4	5.6
703		10	2.8	4.2

$_a$Portion in dry weight
$_b$ Based on dry weight of starch (wt%)

Further characterization of the samples are needed in order to identify either the samples are completely or partially gelatinized. Based on previous research by [33] Tajuddin *et al.* (2011), sample with 70% of total plasticizer contents and 1:4 wt% ratio of glycerol/water give stronger rheological properties which is similar with the observation obtained from this research. Based on this, those parameters can be apply as a basis for processing thermoplastic starch.

3.2 Morphological Characterization

Figure 1 shows the SEM photographs of native and thermoplastic starch granules (30µm) at 2.00Kx of magnification. From SEM studies, the surface of the native starch granules are smooth without scratches while the surfaces of thermoplastic starch granules were extensively eroded with numerous cracks. The porous structure formed during the gelatinization process. The cracks were occurred from the actions of water molecules and exposed the internal structure of granules molecules [34]. During the gelatinization process, the granules will absorb water which caused the granules to swell and in the consequences lose crystallinity [35]. This produce the hole-shapes on the surface of the thermoplastic starch. Then, the second plasticizer; [Emim][OAc] are able to form hydrogen bond with starch structures that altered the whole structures into amorphous phase.

3.3 Crystallization Structure Variation

Figure 2 shows the XRD patterns of the native and different thermoplastic starches. Native starch showed a strong diffraction peak at a 2ϴ position of around 15˚ and 23˚ and unresolved doublet at 2ϴ of 17˚ and 18˚ which indicate typical A-type pattern [11, 36, 37]. After gelatinization, the samples at 50% of total plasticizer contents showed the same crystalline structure for all of the ratio. The present of the A-type crystalline structure was referred as residual crystallinity. Residual crystallinity occured because of the incomplete melting of starch during gelatinization [38].

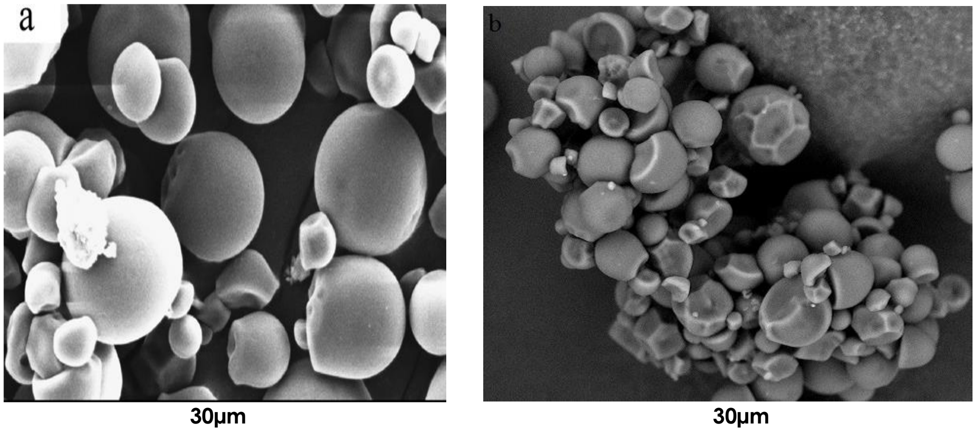


Figure 1 Scanning electron microscopy of a) native starch and b) thermoplastic starch at 2.00Kx of magnification

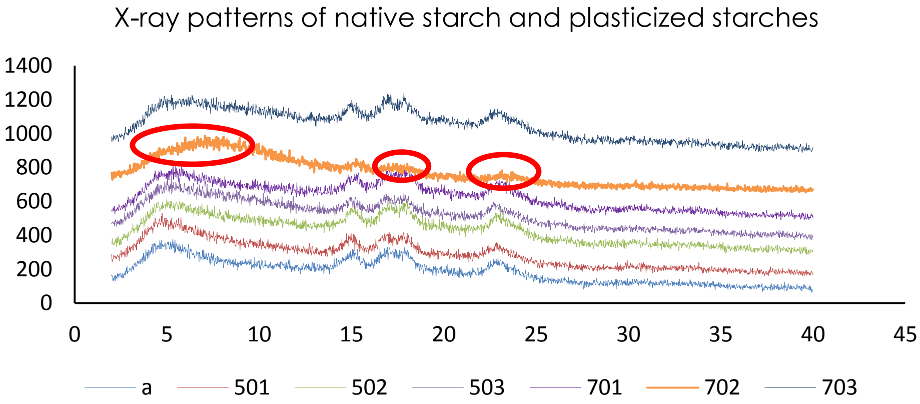


Figure 2 XRD results of native starch and the different formulation of thermoplastic starches

On the other hand, sample of 701 and 703 showed the same XRD pattern with the samples of 501, 502 and 503. Meanwhile, for the sample of 702, the doublet at2θ of 17˚ and 18˚ disappeared, suggesting a complete loss of A-type crystalline structure. Besides, the sample displayed V_H-type crystalline structure as shown by peaks at 2θ of 7˚, 17˚, 20˚ and 25˚. V_H-type crystalline structure, a single-helical amylose structure was referred as processing-induced crystallinity that formed during gelatinization [38]. From the XRD results, the present of the V_H-type crystalline structure suggest that the gelatinization process occurred in the sample of 702. Direct gelatinization process under the combined action of temperature and plasticizer, caused granular disruption, leading to a change in the characteristic profile of the native starch from A-type to V_H-type [14]. Based on this, the result obtained is indirectly same with [33] Tajuddin *et al.,* (2011), even though using different type of plasticizer.

3.4 Thermal Degradation Analysis

Thermogravimetric analysis (TGA) measurements were carried out to access the thermal stability of thermoplastic starches. The thermal decomposition of the starchy matrix occurs in three main steps as reported in the literature [3, 39-42]. The first stage corresponds to the loss of water and low-molecular weight compounds. The second stage is decomposition of the [Emim][OAc]-rich phase and starch, and the third stage refer to the oxidation of the partially decomposed starch.

Figure 3 shows the TGA results of the native and different thermoplastic starches, in terms of both percentage of weight loss and its derivative value. The results clearly suggest that by using [Emim][OAc], thermal degradation happened at a lower temperature. It can be seen from Figure 3a that thermoplastic starches exhibit a small and gradual mass loss in the range of 25-200 ˚C which is 100 ˚C lower than native starch which relate to water loss.The decomposition of [Emim][OAc]-rich phase and starch begins after 200 ˚C for thermoplastic starches and 300 ˚C for native starch.

According to [14] Lomeli-Ramirez *et al.,* (2014), degradation of tapioca starch begins after 300 ˚C. This can be confirmed from the derivative weight percentage peak in Figure 3b. It can be seen that all thermoplastic starches had a major derivative weight percentage peak between 200 ˚C and 350 ˚C, after a gentle hump ranging from 25 ˚C to 180 ˚C which is lower than the native starch. According to [30] Xie *et al.*, (2014) the [Emim][OAc] was responsible to promote the thermal degradation of starch molecules. ILs has ability to reduce starch molecular weight during processing which caused the thermal degradation to occur at a lower temperature [30, 43, 44].

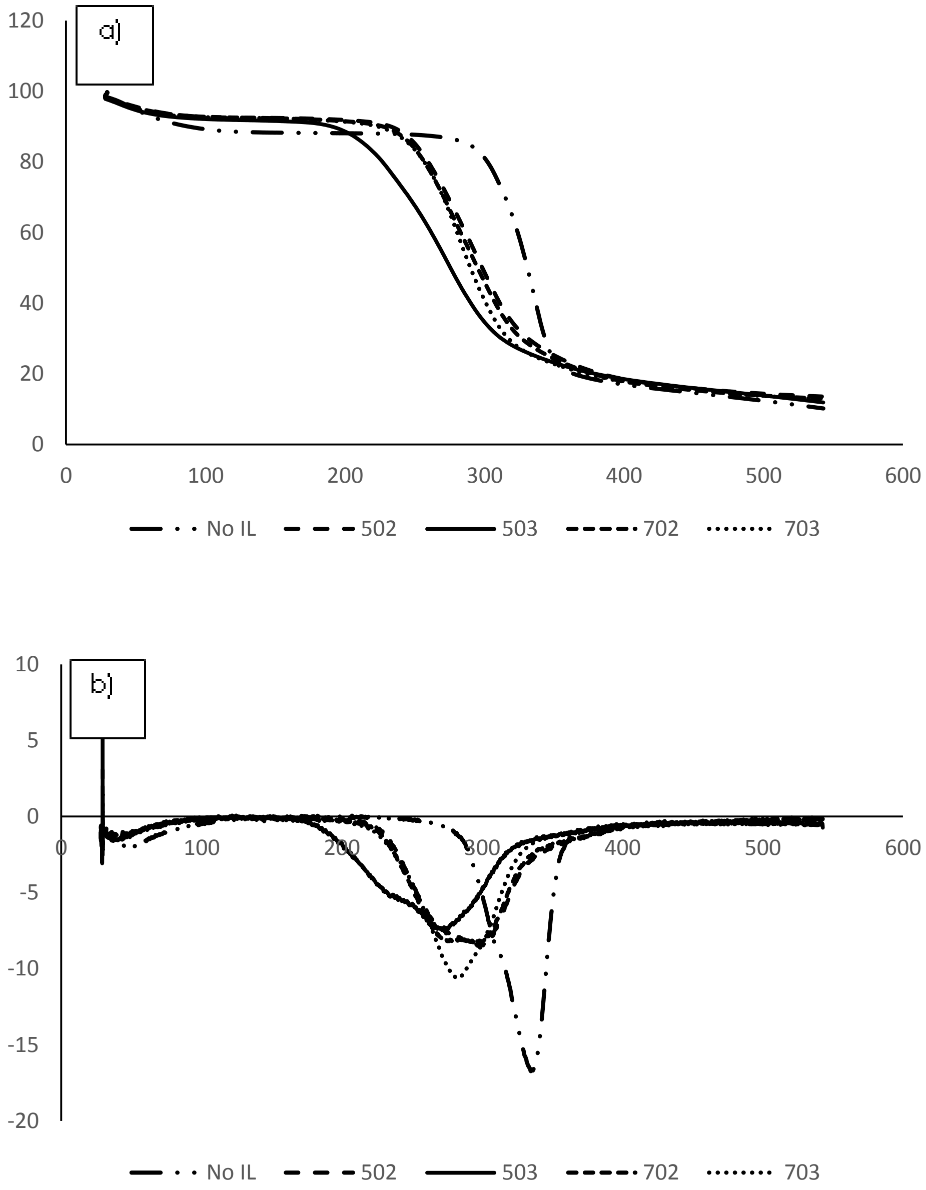


Figure 3 TGA results in term of a) weight percentage and b) derivative weight percentage of native starch and the different formulation of thermoplastic starches

4.0 CONCLUSION

In this study, the gelatinization effect of total plasticizer contents and ratio of [Emim][OAc]/water on characteristics of thermoplastic starch were investigated. [Emim][OAc] contributed to the granular disruption as observed by SEM. The XRD results revealed that at 70% total plasticizer contents and 1:4 wt% ratio of [Emim][OAc]/water, disrupted the A-type crystalline structure, generated V_H-type crystalline structure and thus increased the mobility of the amorphous starch. [Emim][OAc] also promote the thermal degradation of starch at lower temperature. Therefore, this prove that plasticizer contents and [Emim][OAc]/water ratio were vital parameters influencing the properties of thermoplastic starch. As conclusion, optimum formulation of [Emim][OAc] /water could be a promising for starch to develop thermoplastic starch with excellent rheological and physico-chemical properties to meet conventional processing standards. In this part, research is in progress.

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