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ScienceDirect

Procedia Engineering 184 (2017) 567 – 572

Procedia Engineering

www.elsevier.com/locate/procedia

Advances in Material & Processing Technologies Conference

A Study on Thermal Behaviour of Thermoplastic Starch Plasticized by [Emim] Ac and by [Emim] Cl

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Abstract

Thermoplastic starch (TPS) is a material that's been produced through a gelatinization process at elevated temperature in the presence of plasticizers. However, the hydrophilic properties of structural starch may decrease the thermal behaviour of TPS. Therefore, the effect of 1-ethyl-3-methylimidazolium acetate ([Emim] Ac) and 1-ethyl-3-methylimidazolium chloride ([Emim] Cl) as plasticizers on the thermal behaviour of TPSs was investigated in this paper. The TPSs were prepared with two different ILs/water ratios; 1:4 and 2:3. The addition of [Emim] Ac as plasticizer shows lower onset temperature of the thermal degradation than [Emim] Cl. The presence of [Emim] Ac promotes the thermal degradation of starch molecules, leaving an amount of around 13% of residue. The results indicated that TPS plasticized by [Emim] Ac improved the thermal behaviour of TPSs than [Emim] Cl. Therefore, this can conclude that [Emim] Ac is more suitable than [Emim] Cl as a plasticizer for TPS.

Peer review under responsibility of the organizing committee of the Advances in Materials & Processing Technologies Conference

Keywords: Starch, Ionic liquids, Plasticizer, Gelatinization process, [Emim] Ac, [Emim] Cl

1. Introduction

There have been huge interests in the utilization of renewable resources as biopolymer due to its environmental sustainability nature and reduced carbon impact. Biopolymers are referred as polymers derived from biomass, a natural source of renewable materials such as cellulose, starch and lignin [1]. Starch is a polysaccharide preferable

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Peer review under responsibility of the organizing committee of the Advances in Materials & Processing Technologies Conference
doi:10.1016/j.proeng.2017.04.138

as source of renewable materials due to availability in large quantities, biocompatibility and biodegradability [2, 3]. It is also known as a semi-crystalline polymer consists of glucose units joined together by glycosidic bonds. The structure of starch is divided into linear structure called as amylose and amylopectin; branched structure [4]. TPS is a homogenous amorphous material derived through a process known as gelatinization. Through gelatinization process, the structure of native starch may be disrupted in the presence of plasticizers at elevated temperature [5-7]. Various type of plasticizers have been used including water and mostly used as a primary plasticizer in starch gelatinization. Besides that, a second plasticizer was required to complete the gelatinization process. Many other substances such as glycerol, sorbitol and others have been used to plasticized starch. However, those substances have caused problems to the TPS such as recrystallization phenomena.

Ionic liquids (ILs) are salts consist of anions and cations. Anions and cations can be fine-tuned in according to the desired properties. ILs is also called as 'green solvents' due to reusable property. In recent studies, the use of ILs such as 1-allyl-3-methylimidazolium chloride;[Amim] Cl [8, 9], 1-butyl-3-methyl imidazolium chloride; [Bmim] Cl [10] and 1-ethyl-3-methylimidazolium acetate; [Emim] Ac [1, 7, 11] as a plasticizer have been reported. However many of the ILs used contained the corrosive [Cl^-] anion that caused depolymerization of starch due to the formation of HCl. Therefore another type of ILs with non-halogen containing anions such as [Emim] Ac may be more suitable as it has a low vapor pressure and viscosity and high thermal stability at room temperature. The presence of salts are affecting the gelatinization process following the Hofmeister series. Anions gave greater influenced than cations. Acetate and chloride are called as kosmotropes (structure making, salting-out) that act as gelatinizing agent and could promote the starch gelatinization by rupturing the hydrogen bond between starch chains [12-14]. The anions are gelatinizing agent that promote the gelatinization process by rupturing the hydrogen bond between starch chains [13]. Therefore as acetate is better kosmotropes, [Emim] Ac should be better plastizer for starch. Further analysis towards the four samples was able to prove [Emim] Ac as a good plasticizer. The TGA analysis was done in order to identify the thermal behaviour of TPSs as that property was one of important property for polymer materials. The thermal behaviour of TPSs will give some information regarding the interaction between the ILs and starch.

In this study, two different of ILs; [Emim] Ac and [Emim] Cl were used as plasticizer for starch gelatinization at a ratio of ILs/water; 1:4 and 2:3. The influence of anions on starch gelatinization was investigated by comparing the thermal behaviour of TPSs. Although many studies concerning the effects of various ILs as plasticizer on starch gelatinization have been reported, no studies have been investigated on comparison between [Emim] Ac and [Emim] Cl.

2. Materials and Methods

2.1 Materials

Tapioca was purchased from local supplier at Kulim, Kedah. [Emim] Ac and [Emim] Cl were purchased from Sigma-Aldrich.

2.2 Preparation of Starch

Starch were attained according to a previously described method [15]. 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 starches were dried in an oven for 24 hrs at 60˚C to obtain starch powder.

2.3 Sample Preparation

Table 1 shows the compositions for TPSs preparation. TPSs samples are coded in the format of "SWIL", where "S" denotes as starch, "W" denotes as water and "IL" denotes as either [Emim]Ac (Ac) or [Emim]Cl (Cl).Starch powder was blended with a mixture of [Emim] Ac and water based on the Table 1. Firstly, [Emim] Ac and water were mixed for 5 minutes. Then, the liquid mixtures were added into starch powders while mixing to ensure a