

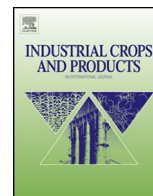


ELSEVIER

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop



Physico-chemical properties of solvent based etherification of sago starch

M.A. Misman, A.R. Azura*, Z.A.A. Hamid

School of Material and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300, Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:

Received 17 June 2014

Received in revised form 3 November 2014

Accepted 8 November 2014

Available online xxx

Keywords:

Sago starch

Etherification

Benzyl chloride

Degree of substitution

Ethanol

ABSTRACT

The etherification process of sago starch was done with benzyl chloride in ethanol (solvent based) and conventional method (water based). Fourier transform infrared (FTIR) analysis confirmed the benzylation process of sago starch in both preparation techniques. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) technique was performed to determine the elements presented on the surface of modified and un-modified sago granules. The process of solvent based etherification produced larger sago granules compared to etherification in conventional method and native sago granules (control). The starch degree of substitution (DS), thermal and rheological properties were determined from results of elemental analysis, DSC, TGA–DTA and viscograms, respectively. Prior to the viscosity test, both benzylation sago starch powders were gelatinized at a temperature of 80 °C. The process of etherification of sago starch in solvent based produces starch with a higher DS, high thermal stability and better flow abilities.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Recently, much effort has been made to reduce the dependency on petroleum based products. This is attributed to the resource scarcity as well as the waste generated which is potentially harmful towards the environment. Starch, which occurs in abundance, cheap, and a renewable material is a viable option as a potential replacement material. Despite its traditional usage in paper making, pharmaceutical, and food industries, starch has a potential to be used in production of several elastomeric composite (Carvalho et al., 2003; You-Ping et al., 2006).

For example, You-Ping et al. (2006) have successfully reinforced the starch/styrene butadiene rubber (SBR) composite via modification of corn starch with resorcinol formaldehyde and N-β(aminoethyl)-γ-aminopropyl trimethoxy silane (KH792). The modified corn starch able to mixed homogeneously with the SBR blend based on a single glass transition temperature obtained in dynamic mechanical and thermal analyzer (DMTA) analysis. They stated that it is due to the improvement of the starch/rubber interfacial adhesion. In this research, the same strategy was used where benzylation starch in high DS was prepared to explore the potential to be used in the production of elastomeric products.

Etherification of starch by benzyl chloride was first reported in 1922 (Gomberg and Buchler, 1922). Since then, many researchers have studied the characteristics of the benzylation starch intensively. The process is an S_N2-nucleophilic substitution process (Williamson reaction) at the hydroxyl functional group of starch (Berkhout and Guns, 1973; Cho and Lim, 1998; Pieters et al., 2003; Bohrisch et al., 2004; Jaspreet et al., 2007; Sarka et al., 2012). Prior to etherification process, the starch was protonated by aqueous alkaline metal hydroxide, e.g., sodium hydroxide or potassium hydroxide, to form an alkoxide ion (RO⁻) (Banks and Greenwood, 1975; Pieters et al., 2003).

During the process, alkoxide ion was formed as a transition state with sodium ion (Maher, 1983). This nucleophile reacts with benzyl chloride to produce benzylation starch. As reported by Pieters et al. (2003), the reaction rates are very dependent on the concentration of alkoxide ion (transition states) produced during the first stage of reaction (dissociation of proton from hydroxide ion in the starch main chain). This can be achieved via reducing the amount of water during reaction. The proposed reaction mechanism for maximum DS (DS = 3) is shown in Fig. 1.

As reported by Pieters et al. (2003), benzyl chloride consumption can be determined by measuring the rates of hydroxide consumption in the reaction mixture. They found that, as the concentration of hydroxyl ion (contributed by sodium hydroxide) increases, the consumption of benzyl chloride also increases which reflecting an increase in the formation of benzylation starch.

* Corresponding author. Tel.: +60 4 5996111.
E-mail address: srazura@usm.my (A.R. Azura).

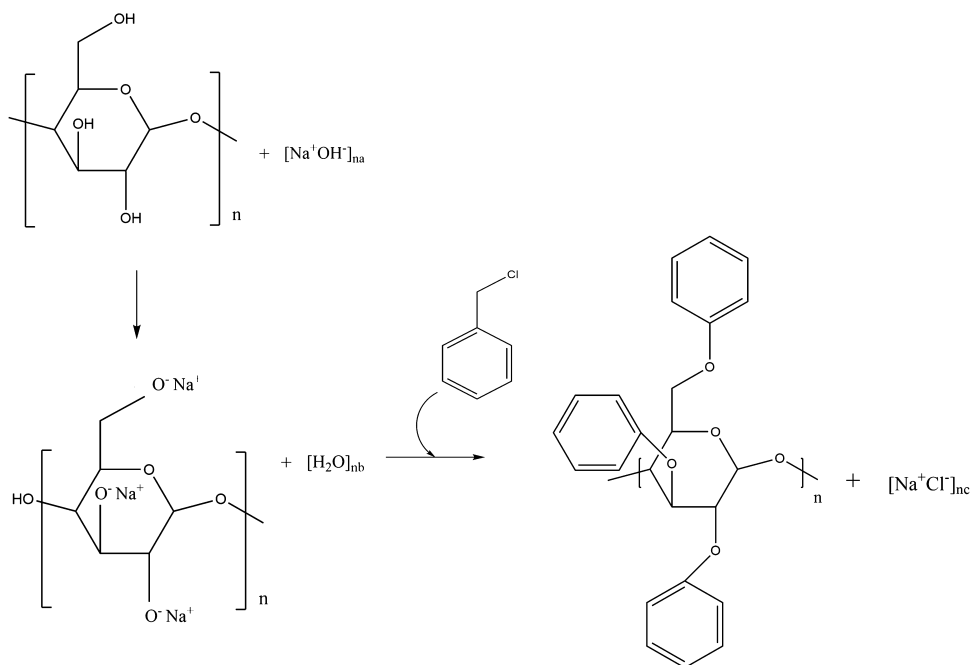


Fig. 1. Proposed mechanism of starch benzoylation process.

However, as the concentration of sodium hydroxide solution increases, gelatinization of starch molecule could occur (Maher, 1983; Han and Lim, 2004; Junli et al., 2012). Bohrisch et al. (2004) reported that, even though benzoylation of starch could occur in gelatinized states (paste), the final starch dispersion will have lower substitution degree. Thus, an inhibitor such as inorganic salt was used to minimize the gelatinization process (Foster, 1965; Hjerstad et al., 1969; Kaur et al., 2011).

As reported by Jane (1993), the used of sodium sulfate as an inhibitor gives the highest reaction efficiency compared to other salts. This finding was supported by Kurtis and James (2005) which found out that sulfate anions, restricts the absorption or neutralization of hydroxide ion. This is due to the divalent properties of sulfate anions which give more concentrated source of electro-negativity. This phenomenon leads into formation of Donnan potential which repels anions from the granules and thus effectively protecting the granules from gelatinization.

Apart from that, the rates of benzoylation also could be increased via increasing of reaction temperature (Pieters et al., 2003). Even though subjecting the starch at high temperature could lead into starch gelatinization (Ahmad et al., 1999; Karim et al., 2008; Suriani, 2002), the used of sulfate salt (sodium sulfate) could increased the initial gelatinization temperature, T_{gel} (Sandstedt et al., 1960; Evans and Haisman, 1982) and hence prolong the gelatinization process to occur.

Thus in this study, higher DS of benzoylated sago starch are produced by using solvent based etherification process using ethanol as its medium. As the DS of benzoylated starch increases, the degree of hydrophobicity of the materials were expected to increase which contributes towards prolonged starch shelf life. Furthermore, better interaction between solvent were expected as well as increased in miscibility with elastomeric latex compound.

The strategies are to reduce the amount of water and increase the presence of hydroxide ions in the reaction medium. This will increase the tendency of formation of alkoxide ions which can further increase the reaction rates of the ionic species with benzyl chloride. In order to prolong the granules to gelatinize, sodium sulfate was used as inhibitor.

2. Methodology

2.1. Etherification of sago starch

Dissolve 0.5 moles of sodium sulfate per anhydroglucose units (AGU) in 600 ml of water, followed with addition of 1 mol per AGU of sago starch powder and 0.08 mol per AGU of aqueous sodium hydroxide solution. The process was carried out in the reactor complete with condenser and internal thermometer. The dispersion was heated up to 60 °C where the benzyl chloride was added subsequently. The dispersion was stirred for 24 h and cooled down under room temperature for about 60 min. The pH was adjusted to neutral by the addition of acetic acid. The benzoylated starch was precipitated by 80% v/v methanol, washed by 90% ethanol and filtered by the vacuum suction filtration system. The residue was dried in a convection oven at 45 °C for 96 h and the dried residue was sieved by a wire mesh with an opening diameter of 0.425 mm.

For solvent based etherification process, the process was carried out in 70% ethanol solution. Sago starch powder was first pre-dispersed in water and the ethanol was added after the temperature of the reactor reached 60 °C before the addition of benzyl chloride.

2.2. Fourier transform infra-red (FTIR) analysis

FTIR analysis was carried out with Perkin Elmer Spectrum One spectrometer (Shelton, USA), with wave number ranging from 550 to 4000 cm^{-1} with resolution of 0.5 cm^{-1} . The parameter was set with wave characteristics (peaks intensities and area) of aromatics, carbonyl, hydroxyl and doubly bonded carbon groups. Each sample was scanned for four times.

2.3. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) analysis

SEM-EDX analysis was carried out by using a Zeiss Supra 35 VP SEM machine (Oberkochen, Germany). The magnification was set at 1000 \times and 3000 \times . The voltage acceleration was set at 10 kV. Both samples were mounted on aluminium specimen stubs and

Download English Version:

<https://daneshyari.com/en/article/6376235>

Download Persian Version:

<https://daneshyari.com/article/6376235>

[Daneshyari.com](https://daneshyari.com)