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Effect of mechanical activation on physico-chemical properties and structure of cassava starch

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Abstract

Cassava starch was mechanically activated with a stirring ball mill and subsequently studied for cold-water solubility and rheological characteristics. In addition, the crystal structure, thermal properties, functional groups, granular morphology and size distribution of the activated cassava starch were further characterized using granularity analysis, scanning electron microscopy, X-ray diffractometry, Fourier transform infrared spectroscopy and differential scanning calorimetry. It was found that the crystal structure and granular morphology of cassava starch were significantly altered. Specifically, the crystalline structure of the cassava starch was significantly degraded, and the resulting amorphous particles were seen to agglomerate during the process of mechanical activation. Also, the gelatinization temperature and enthalpy, apparent viscosity and shear thinning of cassava starch were reduced, resulting in enhancement of cold-water solubility of the starch. Infrared spectroscopy showed no new functional groups produced during the mechanical activation process.

Keywords: Cassava starch; Mechanical activation; Modification; Structure; Physico-chemical property

1. Introduction

Starch is a morphologically complex polymer substance, consisting of loose amorphous regions that are interspersed with highly regular crystalline regions, resulting from the formation of hydrogen bonds between the starch molecules. The crystalline composition consists of around 15–45% of the starch granules (Christopher, 1997; Tang, Mitsunaga, & Kawamura, 2004). The scope of starch application is both enhanced and limited by its unique molecular structure. For instance, the compact arrangements of molecules in the crystalline regions inhibit water or chemical reagents from making contact with the molecules in the crystalline region. As a result, the gelatinization temperature is higher and chemical reactivity of starch is decreased. Meanwhile, the relative large molecular weight and the extensive network formed by hydrogen bonds lead to high gelatinization temperature and lower fluidity. For many purposes, the market prefers starch with less extensive crystalline regions, resulting in improved physico-chemical properties and increased reactivity for planned applications. Therefore, there is great interest in methods to modify the structure in the crystalline region, or decrease the size of crystalline regions (Fiedorowicz, Tomasik, & Lii, 2001; Liang, Zhang, Yang, & Gao, 2004). The main methods of decreasing starch crystalline regularity include chemical processes, such as acidolysis (Nakazawa & Wang, 2003), oxidation (Wang & Wang, 2003), enzymatic degradation processes (Zhang & Oates, 1999) and physical processes, such as heat-moisture treatment (Gunaratne & Hoover, 2002), radioactive degradation (Bertolini, Mestres, Colonna, & Raffi, 2001), microwave degradation (Lewandowicz, Jankowski, & Fornal, 2000), ultrasonic degradation (Renata, Bozena, Salah, Piotr, & Janusz, 2005) and extrusive degradation processes (Cai, Diosady, & Rubin, 1995). In addition, mechanical activation refers to the use of friction, collision, impingement, shear or other mechanical actions to modify the crystalline structures and properties of the starch granules. During

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mechanical activation the chemical reactivity is enhanced because some mechanical energy is converted into internal energy of the substance (Boldyrev, 1986). Currently, mechanical activation is used in a variety of applications, including nanomatrix composites, dispersed alloy materials, metallic refinery, ore treatment, waste disposal and synthesis of organic materials (Mulak, Balaz, & Chojnacka, 2002; Ren, Yang, & Shaw, 1999; Sim, Xue, & Wang, 2004; Suryanarayana, Ivanov, & Boldyrev, 2001; Takacs, 1998). In this paper, we report on the application of mechanical activation in modification of starch.

The study involved the use of a customized high-efficiency stirring mill to activate cassava starch, followed by investigation of the crystalline structures and physico-chemical properties of the resulting mechanically activated cassavas starch (MACS). The cold-water solubility and viscosity of the MACS were determined. Further characterization of the MACS's crystal structure, thermal properties, granular morphology and size distribution were studied using granularity analyzer, scanning electron microscopy (SEM), X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). The mechanism of activation was also explored.

2. Experimental

2.1. Ball mill used in the mechanical activation of cassava starch

The mechanical activation in this study was achieved with a customized stirring mill driven by a commercial available drill press equipped with a variable speed motor. The motor turned a shaft that was fitted with four paddles for mixing the cassava starch (acquired from Mingyang Biological Inc. Ltd, Guangxi, China) and 6 mm mill balls inside a stainless 1200 ml steel chamber whose temperature was maintained at constant level. The mill was stopped and the balls removed after the designated time. The resulting samples were sealed for storage and analysis immediately.

2.2. Cold-water solubility

An approximately 2.0000 g (dry weight basis) sample of MACS was dissolved in 100 ml deionized water. Then the solution was heated to a constant temperature (30 °C or 40 °C) for 20 min, with continuous stirring in order to avoid agglomeration. The solution was centrifuged at 3000 rpm for 20 min. The supernatant was removed and evaporated to dryness at room temperature. The resulting residue was placed in a drying oven at 110 °C until constant was obtained. The solubility of the starch was calculated by the weight of the resident divided by the original starch weight × 100%.

2.3. Rheological properties

The rheological properties were determined by adding deionized water to an accurately sample of starch to form 10% (w/v) starch paste. The paste was heated in boiling water bath for 15 min, and then cooled to room temperature. An aliquot of sample was analyzed using a rotational viscosity meter (Precise Scientific Instrument Co. Ltd., Shanghai, China) for its apparent viscosity at different shear rates.

2.4. Granule size distribution

Alcohol, as dispersing reagent, was added to a MACS sample which was then ultrasonically dispersed for 2 min. The particle size distribution was then determined using a granularity analyzer (SA-CP3 granularity analyzer, Shimadzu, Japan).

2.5. Scanning electron microscopy

The starch sample was fixed on a sample bench using a double glue tape for spraying gold powder. The morphological changes of the sample were examined using a SEM (S-570 SEM, Hitachi, Japan) before and after mechanical activation.

2.6. X-ray diffractometry

The X-ray diffraction patterns of the starch samples were measured using a Rigaku D/MAX 2500 V diffractometer (Japan) under the following conditions: Cu-Kα radiation, Ni filter disk, 40 kV, 30 mA and measurement range $2\theta = 3–40°$.

2.7. IR spectroscopy

KBr-pelletized starch samples analyzed using a Nicolet Nexue 470 FTIR (Nicolet Co., USA).

2.8. Differential scanning calorimetry

The starch samples were studied using a DSC-6200 differential scanning calorimetry (Perkin-Elmer Co., USA). A 4.0 mg (dry basis) sample was placed in an aluminum case and deionized water added to obtain a starch/water ratio of 1:4 by weight. The sample was sealed and equilibrated for 4 h. Then it was scanned from 30 °C to 150 °C using a scanning rate of 10 °C/min, while nitrogen gas flowed through the sample chamber at the rate of 30 ml/min. The characteristic temperatures of the transitions were recorded as onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c).

3. Results and discussion

3.1. Cold-water solubility

The effect of mechanical activation on the cold-water solubility of cassava starch is shown in Fig. 1. The data show that the longer the mechanical activation time, the