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Defatted cashew nut shell starch as renewable polymeric material: Isolation and characterization

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ABSTRACT

Starch attracts public attention as a replacement of fossil fuel in polymer industries because it is renewable, biodegradable and nontoxic. In this study, the isolation of starch from defatted cashew nut shell (CNS) using wet milling was reported. A product that contains 85.01 wt.% starch was recovered from the defatted CNS. Various analyses were performed on the starch to characterize its physicochemical properties. It was found that the starch obtained possesses high amylopectin content (75.35 wt.%), which supports the results of thermal analysis that proved the high crystallinity of starch. Morphological study of the starch showed that bonded resins were found attached to the starch granules. Due to high crystallinity, the presence of bonded resins and low cost, starch from defatted CNS can be considered as a prospective renewable material in polymer industries, with potential to compete with current feedstock such as potato and corn.

1. Introduction

The use of fossil fuels such as naphtha and natural gas for producing plastic resins accounts for about 4–5% of the world's oil consumption, with the increasing demand in the future. A challenge comes from the society to reduce the exploitation of fossil fuel and to protect the climate through the reduction of CO_2 released, as well as to preserve the environment from the harmful effects of the indiscriminate plastic disposal. These issues, especially the disposal of plastic wastes in the environment, stimulated a demand for harmless, eco-friendly and biodegradable materials. This then evolved to the adoption of the recycling concept through mechanical recovery and composting of wastes or energy production by plastic incineration, which directly contribute towards the reduction of the consumption of fossil raw materials in industry [1]. However, the focus soon began to shift to the plastic production using the renewable materials as a replacement of the petrochemical substances.

Starch, cellulose, sugar, vegetable oil, and wood are the most frequently used natural and renewable raw materials in the direct manufacturing of biodegradable plastics (hereafter will be called as bioplastics) or its bio-intermediaries. Queiroz and Collares-Queiroz (2009) reported that starch-based bioplastic production covered around 20% of the total world production of bioplastic. The properties of natural polymers derived from starch, which are biodegradable, usually can be modified by blending with polycaprolactone (PCL), polyvinyl alcohols (PVOH), and other chemicals.

Starch serves as the major source of polysaccharide in plants that provides the bulk nutrient and energy source in human diet (Galliard, 1987; Shelton & Lee, 2000). It finds wide applications not only in food but also in pharmaceutical, biomedical and polymer industries because of its biocompatibility, biodegradability, nontoxicity, and abundant sources. Naturally, starch is semicrystalline substance with varying levels of crystallinity. The crystallinity is associated with the amylopectin compound, while the amorphous regions mainly represent amylose (Zobel, 1988a,b). Behavior of starch in aqueous systems depends on the physical and chemical characteristics of the starch granules, such as mean granule size, granule size distribution, amylose/amylopectin ratio and mineral content (Madsen & Christensen, 1996). Interest in new value-added starch products to the industry has resulted in many studies being carried out on the morphological, rheological, thermal and textural properties of starches. Identification of native starch sources is required for determine its desired functionality and unique properties.Cashew (*Anacardium occidentale* L.) is an indigenous tree of Brazil and grows well in some tropical countries in Asia and Africa, such as Mozambique, Vietnam, Sri Lanka, Malaysia, India and Indonesia (Assunção & Mercadante, 2003; Michodjehoun-Mestres, Souquet, Fulcrand, Bouchut, Reynes & Brillouet, 2009;

Abbreviation: CNS, cashew nut-shell.

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Shobha, Krishnaswamy, & Ravindranath, 1992). The nut is considered as the most important part in international market due to its widespread acceptance and demand (MacLeod & Troconis, 1982; Maia, Andrade, & Zoghbi, 2000). Cashew nut comprises the kernel, which is edible and nutritionally valuable, and the shell, which is known as inedible by-product of cashew nut production and a well-known source for unsaturated long-chain phenols, such as anacardic acids, anacardols, cardols and their isomers. However after the removal of the phenols and lipids, defatted cashew nut-shell (CNS) may cause an environmental problem if it is not handled properly. Utilizing the defatted CNS as a starch source for bioplastic production is a way to reduce the waste disposal from the cashew nut production. Moreover, the use of defatted CNS, due to its existence as by-product, may provide the cost reduction of raw material in the bioplastic production, which is currently dominated by higher price feedstock such as potato and corn.

There has been no report published on the isolation of starch from defatted CNS and to date, no data is available on the starch properties of the defatted CNS. This study focused on the isolation and characterization of starch from defatted CNS. The feasibility of this starch as a renewable material for commercial application such as starch-based bioplastic production was also observed.

2. Materials and methods

2.1. Materials

CNSs were obtained from the waste of cashew (variety *Venguria-4*) nut production in a factory in Solo, Indonesia. They were grounded, sieved, and stored at −4 °C to minimize the degradation of its compounds. Defatting of CNSs was carried out using methanol at 65 °C for 10 h followed by n-hexane at 69 °C for another 10 h in a soxhlet extractor.

The two solvents used for defatting CNSs were of HPLC grade. n-Hexane (95% purity) was purchased from Tedia (OH, USA) while methanol (99.5% purity) was obtained from Echo Chemical (Miao Li, Taiwan). Standards for glucose, amylose from potato starch and amylopectin from maize were purchased from Sigma–Aldrich (St. Louis, MO). Enzymes for starch analysis, namely α-amylase (EC 3.2.1.1), protease (EC 3.4.23.18) and amyloglucosidase (EC 3.2.1.3) were also obtained from Sigma–Aldrich.

2.2. Purification of starch from defatted CNS

The isolation of starch from defatted CNS was carried out using the modified method of Fabian, Ayucitra, Ismadji, and Ju (2011). CNS (10 g) was soaked in water with a CNS to water ratio of 1–5 (w/w) for 3 h at 30 °C. The mixture was blended for 5 min and screened using a 60-mesh sieve. The residue was re-blended with 50 ml 70% ethanol for 5 min, passed through a 60-mesh sieve and then the residue was re-blended with 50 ml 0.1 M NaOH for another 5 min, and screened using a 60-mesh sieve. The filtrates obtained were combined and centrifuged at 11,000 × *g* for 15 min. The supernatant was then decanted carefully and the residue was re-slurried with 100 ml of water, re-filtered twice through a 200 mesh screen and a Whatman analytical grade no.5 filter paper with 2.5 μm pore size and then washed successively with 0.1 M NaOH and deionized water. The residue restrained at the filter paper was dried by using a freeze drier (Labconco Free Zone 2.5 Benchtop freeze dry system model 7670520, Kansas City, MO). The dried starch was kept at −5 °C prior to analysis. All purification and analysis experiments were done at least in duplicates.

2.3. Starch analysis

2.3.1. Total starch analysis

Total starch content was analyzed using the modified method of AOAC Official Method 996-11 (1996). In spite of using glucose oxidase–peroxidase–aminoantipyrine buffer mixture as the reagent mentioned in the official method, 3,5-dinitrosalicylic acid or popularly known as DNS was chosen since this reagent is unaffected by the interference of xylose presence in the sample and has a good stability of color development.

2.3.2. Protein, ash and total dietary fiber analysis (TDF)

The protein and ash content were determined by AOCS Official Methods Ba 4a-38 (1997) and Ba 52-49 (1997), respectively. Total dietary fiber was analyzed by using the modified method of Prosky, Asp, Scheweizer, de Vries, and Furda (1988) which is discussed by Fabian et al. (2011). The TDF content was measured as the weight of residue less its protein and ash.

2.3.3. Total amylose content analysis

Amylose content in starch was determined by using the method of Sadasivam and Manickam (1996). Total amylose content was analyzed using a Jasco UV–vis spectrophotometer (UV–V 550) at 590 nm.

2.3.4. Swelling and solubility

The study of swelling and solubility were adapted from Singh, Okadome, Toyoshima, Isobe, and Ohtsubo (2000). Defatted CNS (0.5 g) was mixed with 20 ml water and the mixture was heated from 30 °C to 90 °C in 30 min. The sample-water mixture was then weighed and more water was added until the weight of the mixture reached 25 g. Centrifugation at 11,000 × *g* for 15 min was performed to separate the solid residue and the supernatant. Swelling power was determined by using the following formula:

$$\text{Swelling power} = \frac{\text{Wet residue weight (g)} - \text{dry deffated CNS (g)}}{\text{dry deffated CNS (g)}}$$

For determining the solubility of starch, about 10 ml of supernatant was freeze dried using a freeze drier (Labconco Free Zone 2.5 Benchtop freeze dry system model 7670520, Kansas City, MO). The dried soluble starch was then weighed and the solubility was calculated by the equation proposed by Singh et al. (2000)

$$\text{Solubility\%} = \frac{\text{dry residue starch}}{\text{dry defatted CNS}} \times \frac{25\text{ ml}}{10\text{ ml}} \times 100$$

2.3.5. Thermal analysis

Retrogradation property of defatted CNS starch was analyzed using DSC Jade (Perkin Elmer, Japan). About 6 mg defatted CNS starch was weighed and put in a 40 μl aluminum pan (TA instrument, USA). The sample was sealed and kept for 1 h at 30 °C prior to analysis. The DSC was calibrated by indium and an empty aluminum pan was used as the reference. Sample pans were heated from 25 °C to 200 °C at 10 °C/min. The onset temperature (T_o), peak temperature (T_p) and enthalpy of gelatinization (ΔH_{gel}) were calculated automatically by Pyris thermal data analysis software. The sample was then cooled down to 4 °C for 7 days and re-heated from 25 °C to 200 °C at 10 °C/min to measure the retrogradation. The enthalpy of retrogradation (ΔH_{ret}) was determined by the software and the percentage of retrogradation was calculated using the following equation:

$$\%\text{retrogradation} = \frac{\Delta H_{ret}}{\Delta H_{gel}}$$

On the other hand, the thermal stability of starch was studied using Diamond TG/DTA instrument (Perkin Elmer, Japan). A 6 mg