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Structure and characteristics of lipase-catalyzed rosin acid starch

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ABSTRACT

Cassava starch was esterified with rosin acid, an abundant raw material from pine trees, by using lipase as catalyst. The physicochemical properties of esterified starches with degree of substitution (DS) ranging from 0.031 to 0.092 were compared with native starch. Esterification of cassava starch was confirmed by Fourier transform infrared spectroscopy. The results of scanning electron microscopy and X-ray diffraction analysis revealed that the morphology and crystallinity of the cassava starch were largely destroyed, and the esterification took place in both the non-stereotyped area and inside the crystalline regions of starch. Thermal gravimetric analysis indicated that thermal stability of rosin acid starch decreased compared with native starch. Rosin acid starch exhibited higher viscosity as well as emulsifying properties. Esterified starch decreased its swelling power, solubility and transparency in water. Rosin acid starch has potential applications in food and biomedical materials.

1. Introduction

Cassava or tapioca starch is one of the important agricultural products in warm tropical areas. Structurally, cassava starch consists of two types of molecules (Bangyekan, Aht-Ong, & Srikulkit, 2006): approximately 17% amylose, a substantially linear polymer with a molecular weight of about 10^5; and 83% amylopectin, a highly branched polymer with a molecular weight of about 10^7. Cassava starch has been tested as a thickening agent in food processing, and as binding agents in pharmaceuticals (Wickramasinghe, Takigawa, Matsuura-Endo, Yamauchi, & Noda, 2009). However, starch displays strong hydrophilicity because of the large numbers of hydroxyl groups in its structure, which accounts for some disadvantages of native starch such as high surface energy, low moisture resistance, and incompatibility with hydrophobic polymers (Cunha & Gandini, 2010; Junistia et al., 2009). The inherent drawbacks limit its applications as agricultural mulch, packaging material, or as building block for biodegradable polymers.

Many efforts have been made to improve the properties of native starch, and esterification of starch by modifying the hydroxyl groups in the anhydrous glucose unit (AUG) is one of the important methods, for the esterified starches develop specific physicochemical properties but still maintain their biodegradability (Alissandratos et al., 2011; Luo & Shi, 2012). Aliphatic acids from C_2 to C_{16} have been successfully introduced into starch molecule using fatty acid vinyl esters, fatty acid chlorides, or fatty acid methyl esters as reactants (Alissandratos et al., 2011; Muljana et al., 2010). The esterified products can be applied not only in the food but also in other industries, such as spinning, papermaking, pharmacy, packaging industries, etc. (Horchani, Chaâbouni, Gargouri, & Sayari, 2010) Previous works have reported that the properties of esterified starch are considerably affected by the degree of substitution (DS) and nature of the introduced ester group. For example, Aburto et al. (1999) have reported that the mechanical properties of starch esters differ according to the length of the grafted fatty acid chain. By comparing the mechanical properties of octanoated, decanoated and dodecanoated starch esters with the DS about 1.7, they find the octanoated and decanoated starch esters form brittle films (the mechanical properties can not be measured), the dodecanoated starch enhance its mechanical properties as: the elongation at break reaches to 49% and the tensile strength of reaches to 8.6 MPa. Therefore, more organic acid candidates should be investigated to produce novel starch esters and broaden their application.

Rosin acid, a kind of natural product obtained from conifer exudates, is a mixture consisting primarily of abietic acid, levopimaric acid, and pimaric acid, with a typical molecular formula $C_{19}H_{29}COOH$ (Maiti, Roy, & Kundu, 1989). More than 1 million tons of gum rosin is produced worldwide per year, and traditionally it is

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used as ingredients for inks, varnishes, adhesives, cosmetics, medicines, chewing gums, etc (Zheng et al., 2010). Rosin acid attracts much attention in the synthesis or modification of polymeric materials because it is inexpensive, abundant, potentially biodegradable and biocompatible, as well as its special structure (Wilbon, Chu, & Tang, 2013; Yao et al., 2011; Zheng et al., 2010). There are two chemically reactive centers in the rosin acid molecule, the double bond and the carboxyl group, which make it easy to integrate into polymers by direct esterification reaction or synthesis of rosin-maleic anhydride adduct first by Diels–Alder reaction (Jin et al., 2002). Wilbon, Zheng, Yao, and Tang (2010) have successfully placed rosin acid moiety and caprolactone segment into a block copolymer through atom transfer radical polymerization and ring-opening polymerization techniques. Besides, there is a characteristic bulky hydrophenanthrene ring structure in rosin acid molecule, similar to petroleum-based cycloaliphatic and aromatic compounds, which provides the material with substantial hydrophobicity, rigidity and chemical stability (Wilbon et al., 2013). Wang et al. (2011) have investigated the properties of rosin polymer-grafted lignin composites. They found water uptake of all rosin-modified lignin composites was below 1.0% (wt), which indicates the impartation of hydrophobicity of rosin into lignin provides excellent water resistance of the polymers. Moreover, the rosin polymer-grafted lignin composites exhibits glass transition temperatures in a broad temperature range from 20 to 100 °C. Jin et al. (2002) have prepared polyurethane foams with the rosin-based polyols. The foaming behavior is similar to that made with industrial polyester Daltolac™ P744, but the physical properties for polyurethane foams containing rosin structure, including the 10% compression strength, the thermal conductivity, and the dimensional stability, are better than those for the industrial foam. The results indicate that the important physical properties for the polyurethane foams are improved by the rigid phenanthrene nucleus of the rosin. In addition, rosin shows excellent biodegradability and biocompatibility. Satturwar, Fulzele, and Dorle (2003) report that rosin film implanted in rats did not cause necrosis or abscess in the surrounding tissues, and was completely degraded in 90 days in vivo. Approved by the U.S. Food and Drug Administration, rosin and rosin-derived esters are permitted to be used as food additives in chewing gum and beverages, etc. (Yao et al. 2011)

Duan, Fang, Ma, Li, and Cen (2009) have reported the synthesis of rosin acid starch by acylating cassava starch with maleopimaric acid chloride under microwave irradiation. Considering the conventional chemical methods involve harsh reaction conditions and hazardous reagents such as acyl-chlorides, a lipase-catalyzed synthesis of rosin acid starch method (Fig. 1) has been developed in our group recently. To the best of our knowledge, there has been no report about enzymatic synthesis of rosin acid starch until now. Therefore, it is reasonably expected that the introduction of rosin acid group would bring new properties to the starch.

In this work, rosin acid starches with DS ranging from 0.031 to 0.092 were synthesized by using Novozym 435 (immobilized *Candida arctica* lipase) as catalyst. The morphological and structural features of rosin acid starch were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared analysis (FTIR). This work also studied the physicochemical properties of rosin acid starch, including viscosity, emulsifying properties, swelling power, solubility and transparency. The application of rosin acid starch as emulsion stabilizer was also discussed.

2. Material and methods

2.1. Materials

Gum rosin was supplied by Guangxi Wuming Chaoyan Rosin Plant, China, and was used directly for esterification reaction. Cassava starch (approximately 17% amylose and 83% amylopectin) was purchased from Guangxi Cenxishi Sanjiao Food Scuffled. Novozym 435 with an activity of 10 unit/mg was purchased from Novo Industries, Denmark. DMSO and methanol were analytical grade purchased from Chengdu Kelong Chemical Reagent Co., China.

2.2. Preparation of rosin acid starch

Starch was firstly pretreated according to the literature (Geng, Chang, Yu, & Ma, 2010). Cassava starch (4 g) was dissolved in NaOH/urea solution (6 g NaOH and 3 g urea in 100 ml deionized water) completely, and then neutralized with HCl. The starch was washed with 95% ethanol twice after precipitated by the same solvent. Finally, the precipitate was dried at 70 °C for 24 h.

The pretreated cassava starch (0.25 g) was dissolved in 50 ml DMSO in a round flask, followed by the addition of 0.44 g rosin. To the mixtures, 10% immobilized lipase (mass/mass, relative to

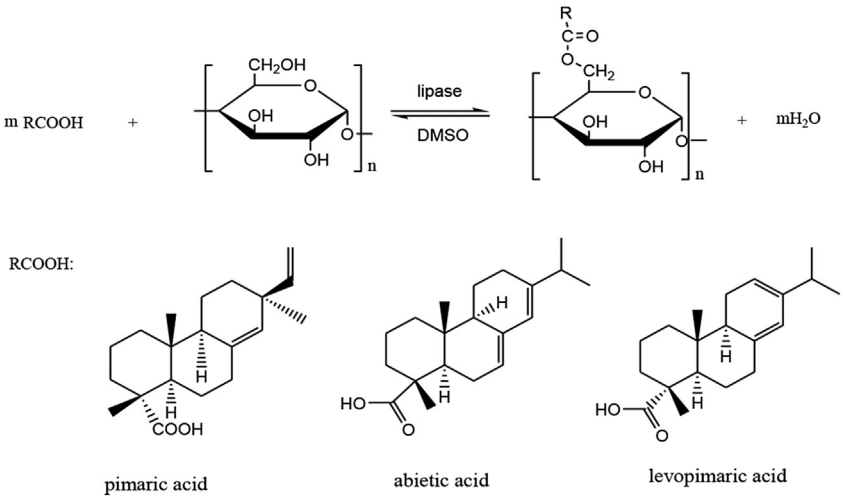

Fig. 1. Esterified starch with rosin acid catalyzed by lipase. Although in the figure the substitution was represented only on the OH in position 6, it also could occur on hydroxyl groups located at positions 2 or 3.