A Green Technology for the Preparation of High Fatty Acid Starch Esters: Solid-Phase Synthesis of Starch Laurate Assisted by Mechanical Activation with Stirring Ball Mill as Reactor

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Ⓢ Supporting Information

ABSTRACT: Starch laurate, a kind of high fatty acid starch ester, was directly produced by mechanical activation (MA)-assisted solid-phase synthesis (MASPS) technology with a customized stirring ball mill as reactor. The starch laurates with different degrees of substitution (0.0148−0.0412) were obtained under different reaction conditions. Fourier transform infrared spectroscopy confirmed that starch ester had been successfully produced by MASPS attributed to active hydroxy groups induced by MA. X-ray diffractometry and scanning electron microscopy showed that MA and esterification significantly disrupted the morphology and crystal structure of starch. Water absorption of starch was increased by MA but decreased by the introduction of laurate groups. Viscosity of starch was obviously reduced after both the processes of MA pretreatment and MASPS. The successful synthesis of starch laurate without the use of solvent and additives suggested that MASPS was a fast, simple, and green method for the production of high fatty acid starch esters.

1. INTRODUCTION

Starch is an abundant, inexpensive, biodegradable, and naturally renewable polysaccharide that plays an important role in the food industry and is also used as raw material to prepare different products for various applications.[1−3] However, native starches have limited industrial uses.[4] Chemical modifications, such as etherification, esterification, oxidation, and grafted and cross-linked reactions, were developed to expand the usefulness of starch for industrial applications.[5−9] Starch esters are the esterification products synthesized by reacting starch with different esterifying agents. High fatty acid starch esters (chain length of fatty substituent ≥C8), which have special thermoplasticity, hydrophobicity, and biodegradability properties, are one kind of the most important starch derivatives.[10]

Generally, high fatty acid starch esters are synthesized by dispersing starch and esterifying agent in organic solvents such as pyridine, toluene, dimethyl sulfoxide (DMSO), or LiCl/N,N-dimethyl acetamide (DMAC).[11−14] The use of volatile, toxic, and expensive organic solvents has economic, environmental, and safety problems and may limit further commercialization of the technology, particularly for food and pharmaceutical applications. Recently, room-temperature ionic liquids have been considered as desirable green solvents for the homogeneous synthesis of starch esters.[10,15,16] However, the solubility of starch in ionic liquids is not very high, limiting the production capacity and efficiency of starch esters. Additionally, ionic liquids are commonly expensive, and an effective and mature recovery process is difficult to obtain, which restrict the industrial production and economic feasibility for using ionic liquids as homogeneous reaction medium. So, there is a strong incentive to develop a simple, green, and efficient method for the synthesis of starch esters.

Currently, solid-phase synthesis (SPS) has attracted a substantial amount of attention for the advantages of simplification of reaction process and product isolation without the use of solvent, specificity of reaction, high selectivity and efficiency, and saving resources, and it is considered as an efficient procedure for green chemistry.[17−19] SPS has been successfully used for the preparation of inorganic and organic products, such as barium hexaaluminate,[20] barium titanate,[21] polyprenols,[22] pyridine derivatives,[23] cellulose derivatives,[24] and polypropylene graft copolymers.[25,26] Undoubtedly, SPS can be used for the production of high fatty acid starch esters. However, the reagents are difficult to penetrate into the interior of the starch granules, for the special semicrystalline structure of native starch resulted from the formation of hydrogen bonds between the starch molecules. In addition, the esterifying agents with long chain length exhibit a steric effect when they react with starch. As a consequence, SPS of high fatty acid starch esters hardly takes place under common conditions, and it is necessary to enhance the reaction efficiency of SPS by assisted means. Mechanical activation (MA) refers to the use of mechanical actions to change the crystalline structures and physicochemical properties of the solids carried out by high-energy ball-milling and has been successfully used for the pretreatment of starches, sugar cane bagasse, and cassava stillage residue in our previous works.[27−30] When suffering from enough mechanical energy, the chemical bonds in solids can be significantly broken up, along with the collapse of their

crystal structure, phase transformation, and the changes in surface characteristics.[1,31] The destruction of stable hydrogen bond and crystalline structure induced by MA could efficiently increase the accessibility and reactivity of solids. Additionally, MA is a simple and environmentally friendly procedure attributing to the use of simple and cheap equipment and the operations without the use of solvents, intermediate fusion, etc.[32] Generally, MA is used for the pretreatment of solid materials, and then the reaction of the pretreated materials is carried out in other equipment. In order to make full use of the mechanical energy induced by MA and improve the conditions of SPS, we combine the MA pretreatment of starch and the SPS of high fatty acid starch esters in the same equipment, which can also simplify the technological process and improve the production efficiency. In this MA-assisted SPS (MASPS) process, the intense ball-milling directly acts on all the materials in the reaction system, and the steric effect of long chain fatty substituents could be weakened under strong mechanical actions, resulting in the improvement of reaction efficiency.

In this study, starch laurate, a kind of high fatty acid starch ester, was prepared by MASPS technology in a customized stirring ball mill. The effects of the critical MASPS parameters, including the molar ratio of esterifying agent/anhydroglucose unit (AGU), mass ratio of catalysis/starch, reaction time, and reaction temperature on degree of substitution (DS), were investigated, respectively. In addition, comparative analyses of the property changes among native starch, MA-pretreated starch, and MASPS-produced starch laurates were also performed by using Fourier transform infrared spectroscopy (FTIR), X-ray diffractometry (XRD), scanning electron microscopy (SEM), water absorption determination, and viscosity measurement, respectively.

2. MATERIALS AND METHODS

2.1. Materials. Cassava starch was used as native starch, which was kindly supplied by Minyang Biological Inc. Ltd. (Guangxi, China). Lauric acid (analytical grade) was purchased from Xilong Chemical Co., Ltd. (Guangdong, China). All other chemical reagents were of analytical grade without further purification and obtained commercially. Deionized water was used throughout the work.

2.2. MASPS of Starch Laurate. MASPS of starch laurate was performed in a customized stirring ball mill driven by a commercial available drill press equipped with a speed-tuned motor. A fixed amount of milling balls (300 mL, 6 mm diameter) was first added into a jacketed stainless steel chamber (1200 mL), and then 10.0 g of cassava starch, designated dosages of esterifying agent (lauric acid), and catalyst (K_2CO_3) were added into the chamber. The mixture was subjected to milling at the speed of 375 rpm and reacted at a constant temperature (40, 50, 60, 70, and 80 °C). When the mixture was milled for different desired reaction times (0.5, 0.75, 1.0, 1.5, and 2.0 h), the balls were removed from the resulting sample, which was then purified by washing four times with sufficient 75% aqueous alcohol to eliminate unreacted reagents. Finally, the solid was dried in vacuum at 50 °C for 24 h. The products obtained were used for testing.

2.3. Determination of Degree of Substitution. The DS value of modified starch is defined as the average number of substituent of hydroxyl groups per D-glucopyranosyl structural unit of the biopolymer. DS values of starch laurates were determined according to the reported titration method with minor modification.[10,33] About 1.0 g (precision 0.1 mg) of dry

starch ester was placed into a 250 mL Erlenmeyer flask with 60 mL of 50% aqueous alcohol and agitated with a magnetic stirrer at a constant temperature of 50 °C for 1 h. Then 20 mL of 0.5 mol/L NaOH solution was added, followed by vigorously magnetic stirring at room temperature for 4 h. Excess NaOH was then back-titrated with standard 0.2 mol/L HCl solution using phenolphthalein as an indicator. The DS value of starch ester was calculated by using the following equation

$$DS = 162M(V_0 - V)/1000W \tag{1}$$

where 162 is the molecular weight of the AGU, V_0 is the volume in milliliters of the HCl solution used for blank titration, V is the volume in milliliters of the HCl solution used for sample titration, M is the exact molarity of the used HCl solution, and W is the sample weight in grams as dry substance.

2.4. MA Pretreatment of Native Starch. MA pretreatment was performed in the same equipment of MASPS. For each milling experiment, the native starch sample (10.0 g in each batch) was added into a jacketed stainless steel chamber with 300 mL milling balls and then the sample was subjected to dry milling with a speed of 375 rpm at a fixed temperature of 60 °C and no other additives were used during the milling. The balls were removed after the sample was milled for 1 h, and then the chamber and milling balls were thoroughly cleaned and dried before the next milling experiment. The resulting samples were sealed for the next analysis.

2.5. FTIR Analysis. FTIR spectra of native starch, pretreated starch, and starch laurates were acquired on an 8400S Fourier transform infrared spectrometer (Shimadzu) using the KBr disk technique. For FTIR measurement, the samples were mixed with anhydrous KBr and then compressed into thin, disk-shaped pellets. The spectra were obtained with a resolution of 4 cm^{-1} and a wavenumber range of 4000−400 cm^{-1}.

2.6. XRD Analysis. XRD patterns were recorded on a D/MAX 2500 V diffractometer (Rigaku) operating at 40 kV and 30 mA by using Cu Kα radiation (λ = 0.154 nm). The scattering angle (2θ) was varied from 5° to 50° with a step width of 0.02°.

2.7. Morphology Observation. Morphologies of the samples were performed using an S-570 scanning electron microscope (Hitachi). The sample was fixed on a sample bench using double-sided tape, and then a thin layer of gold (about 10 nm) was coated on the sample prior to measurement to improve the conductivity. SEM micrographs with different magnifications were obtained to observe the surface morphologies of different samples.

2.8. Water Absorption Capacity Determination. The samples were dried in an oven at 120 °C until constant weights were reached, and then they were stored in a sealed container with a constant relative humidity (RH) of 75% at 25 °C. The samples were weighed after being stored for a period of time. The equilibrium of water absorption was considered to be reached when their weight gain was less than 1% since the last weighing. The water content (α) was determined by using the following equation

$$\alpha = \frac{(\omega_t - \omega_0)}{\omega_0} \times 100\% \tag{2}$$

where ω_t is the weight of the sample after stored for a period of time, and ω_0 is the weight of dry sample.

2.9. Viscosity Measurement. Different samples were dispersed in distilled water to prepare 12% slurries (dry matter basis) and then were gelatinized in a boiling water bath. After being cooled to room temperature, the viscosity values of the pastes were tested by a SNB-1 rotating viscometer (Shanghai Precision Scientific Instrument Co., Ltd.).

2.10. Statistical Analysis. All tests were replicated three times, and the results were calculated and analyzed by Microsoft Excel (2003). The curves were obtained by drawing (OriginPro 7.5).

3. RESULTS AND DISCUSSION

3.1. Influence of Reaction Parameters on DS of Starch Laurate. Native starch has the special semicrystalline structure, which makes it difficult for the reagents to penetrate into the granules, leading to low reaction efficiency in traditional heterogeneous conditions. For SPS of high fatty acid starch esters, the esterification hardly takes place without any assisted means because of the highly regular and stable crystalline structure of native starch and the steric hindrance of the long carbon chain in high fatty acids. With the use of MA as assisted means for the SPS process, starch laurate has been successfully produced by MASPS, and the effects of different reaction parameters on DS of the products are presented in the Supporting Information (Table S1). Samples A1−A5 indicate the effect of the molar ratio of lauric acid/AGU on the DS of starch laurate, showing that the DS value rose steadily with the molar ratio of lauric acid/AGU upon increasing from 1:10 to 3:10. However, the DS value of the product increased slightly by increasing the molar ratio beyond 3:10, which implies that excess esterifying agent had little effect on the reaction. Therefore, the optimal molar ratio of lauric acid/AGU was 3:10, which could get a relatively high DS value of 0.0398 and avoid ineffective consumption of reagent. The proper amount of catalyst was also investigated, and the effect of mass ratio of K_2CO_3/starch on DS of the products is shown in samples B1−B5. The addition of catalyst could effectively enhance the synthesis of starch laurate, and the DS value reached 0.0398 when the mass ratio of K_2CO_3/starch was 0.25:10. However, it can be observed that the DS value of starch laurate decreased as the mass ratio of K_2CO_3/starch increased beyond 0.25:10. This may be because the excess dosage of K_2CO_3 could lead to the degradation of the molecular chain of starch, and the alkaline hydrolysis of starch esters could also took place, which had negative effect on the synthesis of starch esters and significantly decreased the DS of starch laurate. So, it can be concluded that the optimal mass ratio of K_2CO_3/starch was 0.25:10.

Reaction time is a very important parameter for the MASPS of starch laurate, because it represents both the activation time and synthesis time. The data in samples C1−C5 indicate the influence of reaction time on DS of the products. With the reaction time increasing from 0.5 to 1 h, the DS value of starch laurate increased noticeably. By combining MA and esterification in the same equipment, the active hydroxyl groups in starch induced by intense mechanical actions could rapidly react with esterifying agent under the solid state without other additives. However, when the reaction lasted for more than 1 h, the decline in DS value was observed. One reason for this phenomenon may be that the hydrolysis of starch ester occurred at longer reaction time. Another reason is due to the degradation of starch under intense milling, and adverse and side reactions may become dominant beyond 1 h, which could

hamper the esterification. Thus, the optimum reaction time was 1 h.

The influence of reaction temperature on the esterification efficiency was investigated by setting different temperatures, and the results are shown in samples D1−D5. As observed, reaction temperature had both positive and negative effects on DS of the products. An increase in reaction temperature from 40 to 60 °C resulted in a rise of the DS value of starch laurate. But further increase on temperature from 60 to 80 °C caused a decrease of the DS value. Reaction temperature has positive effect on the increase of active sites in starch and the penetration speed of reagents, which will raise the esterification rate and efficiency. However, esterification is an exothermic reaction, and relatively high temperature could hinder the formation of starch ester and cause the degradation of the product. So, the appropriate reaction temperature for MASPS of starch laurate was determined to be 60 °C.

Starch laurates with different DS values were produced successfully and directly by MASPS under different reaction conditions with the absence of solvent and additives, and the reaction time could decline from hours for conventional methods to only 1 h or less. With the combination of MA and esterification in the same equipment, the active hydroxyl groups generated from the destruction of stable crystalline structure and strong hydrogen bonding of starch induced by intense milling could be directly contacted with esterifying agents, and the steric effect of long chain fatty acids was also weakened, as attributed to the enhancement of diffusivity and mobility of long chain fatty acid and the improvement of contact state between reactants under intense mechanical actions, which resulted in the synthesis of high fatty acid starch esters under solid-phase state.[34] At present, it is difficult to use MASPS for the production of the high fatty acid starch esters with high DS values, which have been commonly produced by homogeneous synthesis in organic solvents.[13,15,16,35] However, compared with conventional synthetic methods, the presented method could be considered as a fast, facile, and pollution-free method, making MASPS technically feasible for industrial scale-up production of high fatty acid starch esters. Hopefully, the high fatty acid starch esters with high DS values can be produced by further improvement of MASPS technology.

3.2. FTIR Analysis. The FTIR spectra of native starch, MA-pretreated starch, and starch laurates with different DS values are presented in Figure 1. Compared with the spectrum of natural starch, it can be observed that no new absorption peaks appear in the spectra of MA-pretreated starch, indicating that no new functional groups were generated during MA pretreatment. However, the peak at 3426 cm^{-1}, which is assigned to the O−H hydrogen bonding stretching vibration, becomes wide and its intensity decreases after ball-milling. This could be due to the breakage of intermolecular and intramolecular hydrogen bonds under the intensive impact of mechanical actions and the increase of free and active hydroxy groups in amorphous phase.[27] As seen in Figure 1c,d, new bands at 1720 and 2853 cm^{-1} were detected and attributed to the stretching vibration of carbonyl group (C=O) and characteristic absorption peak of methylene, respectively,[36] which indicate that starch doubtlessly reacted with lauric acid to form ester carbonyl groups and introduce the methylene in long chain fatty acid. With the increase in DS of the products, the absorption peaks at 1720 and 2853 cm^{-1} gradually increased. Additionally, the C−H stretching vibration at 2930 cm^{-1} in Figure 1c,d increased in intensity compared with Figure

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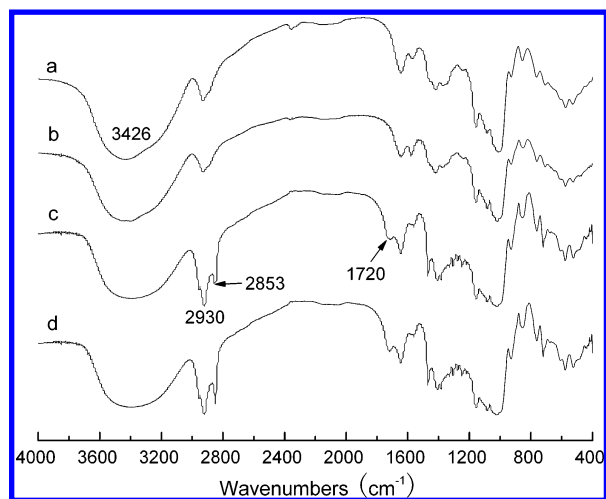dx.doi.org/10.1021/ie403186h | *Ind. Eng. Chem. Res.* 2014, 53, 2114−2120

Figure 1. FTIR spectra of (a) native cassava starch, (b) MA-pretreated starch ($t = 1$ h), (c) starch laurate (DS = 0.0256, $t = 1$ h), and (d) starch laurate (DS = 0.0398, $t = 1$ h).

1a,b, owing to the C—H band of lauric acid upon esterification.[37] These phenomena prove that starch laurate had been successfully produced by MASPS.

3.3. XRD Analysis. Figure 2 illustrates the XRD patterns of different samples, which can intuitively reflect the change in the
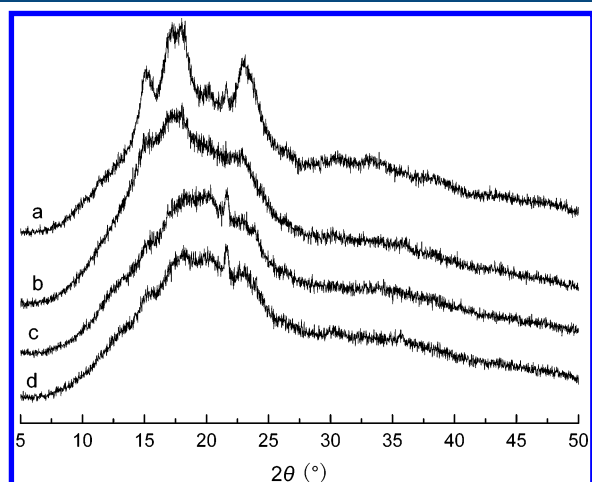

Figure 2. XRD patterns of (a) native cassava starch, (b) MA-pretreated starch ($t = 1$ h), (c) starch laurate (DS = 0.0256, $t = 1$ h), and (d) starch laurate (DS = 0.0398, $t = 1$ h).

crystallinity of native starch, MA-pretreated starch, and starch laurates. In the XRD pattern of native starch (Figure 2a), the strong reflection (2θ) are found at about 15.2°, 17.2°, 18.1°, and 23.1°, indicating that native cassava starch belongs to C-type crystalline structure.[27,38] The spectrum of native starch shows definite diffraction peaks, which reflect the crystalline regions in starch. After 1 h of MA pretreatment, the loss of peak resolution (widening and reduced altitude) can be clearly observed in Figure 2b, revealing that ball-milling significantly disrupted the inter- and intramolecular hydrogen bonds in starch and caused the distortion of crystalline structure, the decrease in crystallinity, and the variation of crystallite size.[39,40] When subjected to intense milling, the destruction of stable hydrogen bonds and crystal structure of starch could result in

the generation of active and free hydroxy groups, which help to increase the reactivity of starch.

In the XRD patterns of starch laurates produced by MASPS (Figure 2c,d), a decrease in peak intensity and broadening of diffraction peaks can be seen obviously compared with native starch and MA-pretreated starch with the same milling time, and the peak intensity of starch laurate decreased with the increase of DS value. Moreover, a small sharp peak at ~22° in Figure 2c,d can be also observed, which is associated with the crystalline structure of ordered laurate chains in the non-cross-linked amylose.[41,42] The introduction of laurate groups in starch can lead to the decrease of crystallinity, which reduced the peak intensity of starch laurate with the increase of DS value. During the process of MASPS, intense mechanical actions induced the disruption of strong hydrogen bonding in starch, generation of metastable active sites, and weakening of the steric effect of long chain fatty substituents, which have positive effects on esterification and result in the synthesis of starch laurate under solid-phase state.

3.4. Morphology Modification. The surface morphologies of different samples can be clearly observed from SEM micrographs, which are illustrated in Figure 3. Native starch granules are essentially spherical with smooth surfaces, which can be seen in Figure 3a. After the processes of MA pretreatment and MASPS, the starch granules were remarkably damaged and fractured, contributing to the generation of small irregular particles with rough and fresh surfaces, and the small particles easily agglomerated due to physical forces during ball-milling.[1,43] These indicate that the damage of starch granules, increase in specific surface area, and split and destruction of stable crystal structure were induced by mechanical milling, providing a facile access of reagents to the hydroxy groups of starch, which increased the chemical reactivity of starch and thus enhanced the esterification with lauric acid. As shown in Figure 3c,d, the combined action of MA and esterification had more considerable effects on the destruction of granules compared with the independent action of MA pretreatment, and the degree of damage increased with the increase of DS value, indicating that esterification could result in the destruction of the crystal structure of starch, which is consistent with the XRD analysis. Furthermore, the corrosion occurred as penetration or rupture from the granules surface to core during MASPS, indicating that the internal crystalline region of starch was also damaged by ball-milling to form an amorphous region, and the esterification reaction took place not only in the surface amorphous region but also in the internal damaged region.[29] This is because the destruction of compact surface coatings and crystal structure of starch induced by intense milling during MASPS built new paths for esterifying agent to enter into the interior of starch, which led to the direct synthesis of starch laurate under solid-phase state.

3.5. Water Absorption. Water absorptions of native starch, MA-pretreated starch, and starch laurates with different DS values are depicted in Figure 4. The rate of water absorption was fast in the early stage of storage, but it decreased when gradually closed to the equilibrium of water absorption. All the samples reached the equilibrium of water absorption when they were stored at an environment of RH = 75% for about 24 h. It can be observed that the MA-pretreated starch with the milling time of 1 h showed the highest water absorption among these samples. During the processing of MA pretreatment, strong mechanical actions between milling balls destroyed the starch granules repeatedly, resulting in the degrading of crystalline
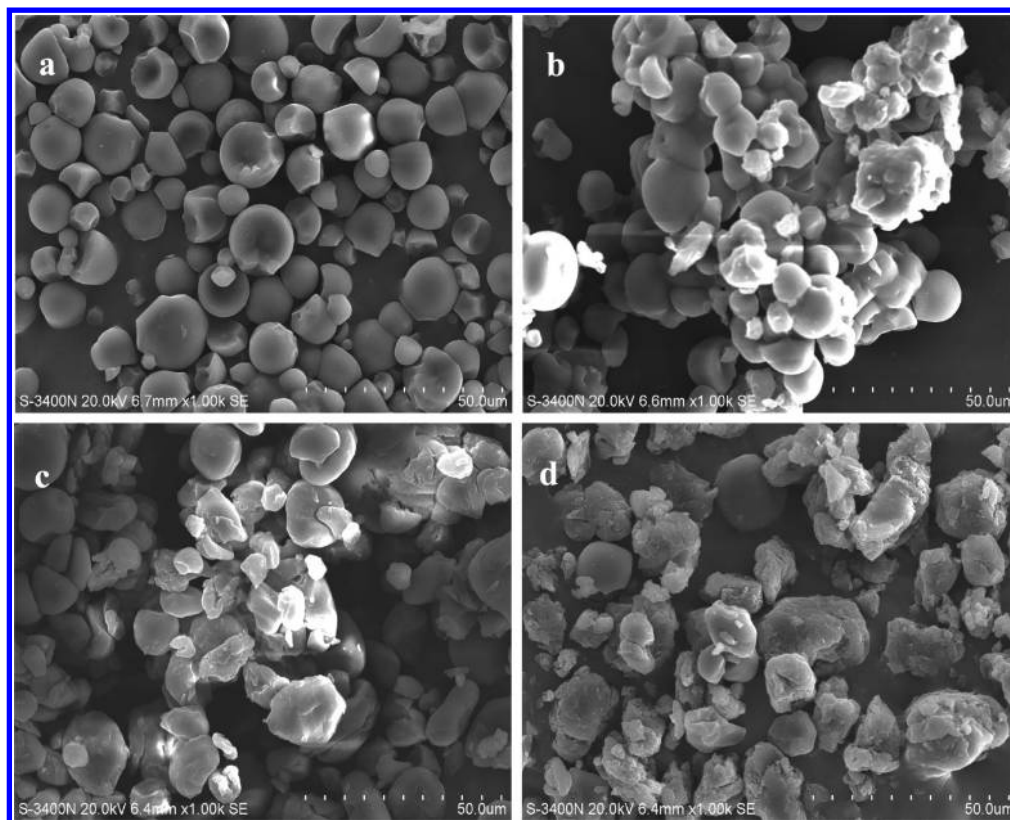
Figure 3. SEM micrographs of (a) native cassava starch, (b) MA-pretreated starch (t = 1 h), (c) starch laurate (DS = 0.0256, t = 1 h), and (d) starch laurate (DS = 0.0398, t = 1 h).
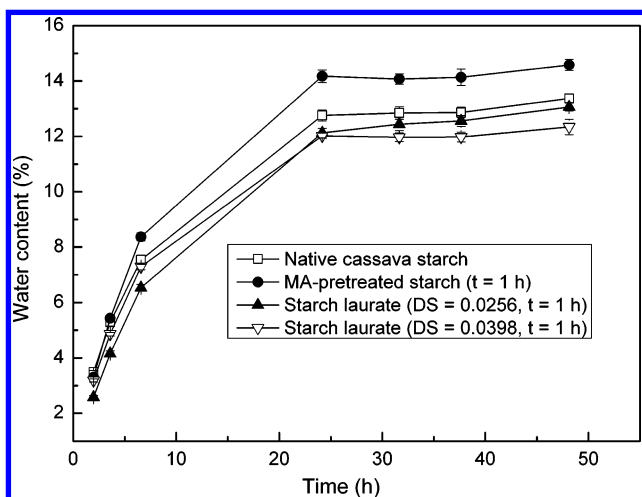

Figure 4. Water absorption versus time of native cassava starch, MA-pretreated starch, and starch laurates with different DS values.

regions, the destruction of stable inter- and intramolecular hydrogen bonds, and the increase of free hydroxyl groups.[39,44] The damage of starch granules and the increase of amorphization allowed greater entry of water into the interior of the granules and the free hydroxyl groups also enhanced the hydrophilicity of starch, which contribute to the increase in water absorption of MA-pretreated starch. For the starch laurates produced by MASPS, the water absorption at the balance decreased, and it also decreased with the increase of DS value. Since the hydrophilic hydroxyl groups of starch were partially replaced with hydrophobic ester groups, the water binding capacity of starch ester decreased and the starch

laurates exhibited lower water absorption, especially the one with higher DS value.[33,45]

3.6. Viscosity Measurement. The apparent viscosity of starch can be increased or reduced by applying different modification methods, and the pasting behavior of starch pastes is mainly governed by critical factors, such as modification method, reaction conditions, and starch source.[5] The viscosity values of native cassava starch, MA-pretreated starch, and starch laurates with different DS values are presented in Table 1,

Table 1. Viscosity of Native Cassava Starch, MA-Pretreated Starch, and Starch Laurates with Different DS Values

sample	viscosity[a] (mPa·S)
native cassava starch	84.2 ± 4.3
MA-pretreated starch (t = 1 h)	41.8 ± 2.6
starch laurate (DS = 0.0256, t = 1 h)	36.7 ± 1.7
starch laurate (DS = 0.0398, t = 1 h)	31.4 ± 1.3

[a]Data represent the mean ± standard deviation.

which shows that the viscosity of starch was obviously reduced after MA pretreatment and MASPS. Under the intensive impact of ball-milling, the physicochemical properties of starch could be changed significantly, including the breakage of inter- and intramolecular hydrogen bonds, the rupture of starch molecular chains, the destruction of tight starch granule structure, and the decrease of crystalline region in starch granules, which lead to the reduction of viscosity.[1,27] In the MASPS of starch laurate, the introduction of long-chain fatty substituent may cause the steric effect in starch molecules and weaken the association and hydrogen bonding in starch molecules. In addition, the addition of K_2CO_3 in the process of MASPS may help to accelerate the

rupture of starch molecular chains under intense milling, contributing to the decrease in molecular weight and crystallinity of starch. Therefore, the viscosity of starch laurate produced by MASPS was lower than that of native cassava starch and MA-pretreated starch, and it decreased with the increase of DS value. The modified starch with lower viscosity has better flowability, which can effectively improve the processability of starch-based materials in some applications.

4. CONCLUSIONS

The present study showed that starch laurate could be directly produced by the process of MASPS with a customized stirring ball mill as reactor in an environmentally friendly way. Lauric acid successfully reacted with starch because of the increase in the reactivity of hydroxyl groups in starch and the weakening of the steric effect of long chain fatty acids attributed to the combination of MA and esterification in the same equipment without the use of organic solvent and additives. The formation of starch laurate and the effect of ball-milling in the processes of MA pretreatment and MASPS were confirmed with comparative analyses of the property changes among native cassava starch, MA-pretreated starch, and MASPS-produced starch laurates carried out by FTIR, XRD, SEM, water absorption determination, and viscosity measurement, respectively. This simple, efficient, and environmentally friendly synthetic method would be particularly beneficial for industrialization. Hopefully, MASPS can be used for synthesis of various esters of starches or other polysaccharides from various sources to enhance the added values of farm products or even wastes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Table S1 lists DS of the starch laurates prepared by MASPS under different reaction conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Chen, C.; Shen, Y.; Yeh, A. Physico-chemical characteristics of media-milled corn starch. *J. Agric. Food Chem.* **2010**, *58*, 9083−9091.

(2) Wu, Q.; Wu, Z.; Tian, H.; Zhang, Y.; Cai, S. Structure and properties of tough thermoplastic starch modified with polyurethane microparticles. *Ind. Eng. Chem. Res.* **2008**, *47*, 9896−9902.

(3) Bhandari, P. N.; Hanna, M. A. Continuous solventless extrusion process for producing sodium carboxymethyl starch suitable for disintegrant applications in solid dosage forms. *Ind. Eng. Chem. Res.* **2011**, *50*, 12784−12789.

(4) Luo, Z.; Shi, Y. Preparation of acetylated waxy, normal, and high-amylose maize starches with intermediate degrees of substitution in aqueous solution and their properties. *J. Agric. Food Chem.* **2012**, *60*, 9468−9475.

(5) Xu, J.; Zhou, C.; Wang, R.; Yang, L.; Du, S.; Wang, F.; Ruan, H.; He, G. Lipase-coupling esterification of starch with octenyl succinic anhydride. *Carbohydr. Polym.* **2012**, *87*, 2137−2144.

(6) Liu, Z.; Li, Y.; Cui, F.; Ping, L.; Song, J.; Ravee, Y.; Jin, L.; Xue, Y.; Xu, J.; Li, G.; Wang, Y.; Zheng, Y. Production of octenyl succinic anhydride-modified waxy corn starch and its characterization. *J. Agric. Food Chem.* **2008**, *56*, 11499−11506.

(7) Kim, H.; Choi, H.; Kim, B.; Baik, M. Characterization of acetylated corn starch prepared under ultrahigh pressure (UHP). *J. Agric. Food Chem.* **2010**, *58*, 3573−3579.

(8) Chan, H. T.; Bhat, R.; Karim, A. A. Physicochemical and functional properties of ozone-oxidized starch. *J. Agric. Food Chem.* **2009**, *57*, 5965−5970.

(9) Tolvanen, P.; Sorokin, A.; Mäki-Arvela, P.; Murzin, D. Y.; Salmi, T. Oxidation of starch by H_2O_2 in the presence of iron tetrasulfophthalocyanine catalyst: The effect of catalyst concentration, pH, solid−liquid ratio, and origin of starch. *Ind. Eng. Chem. Res.* **2013**, *52*, 9351−9358.

(10) Lu, X.; Luo, Z.; Yu, S.; Fu, X. Lipase-catalyzed synthesis of starch palmitate in mixed ionic liquids. *J. Agric. Food Chem.* **2012**, *60*, 9273−9279.

(11) Aburto, J.; Alric, I.; Thiebaud, S.; Borredon, E.; Bikiaris, D.; Prinos, J.; Panayiotou, C. Synthesis, characterization, and biodegradability of fatty-acid esters of amylose and starch. *Starch/Stärke* **1999**, *74*, 1440−1451.

(12) Junistia, L.; Sugih, A. K.; Manurung, R.; Picchioni, F.; Janssen, L. P. B. M.; Heeres, H. J. Synthesis of higher fatty acid starch esters using vinyl laurate and stearate as reactants. *Starch/Stärke* **2008**, *60*, 667−675.

(13) Junistia, L.; Sugih, A. K.; Manurung, R.; Picchioni, F.; Janssen, L. P. B. M.; Heeres, H. J. Experimental and modeling studies on the synthesis and properties of higher fatty esters of corn starch. *Starch/Stärke* **2009**, *61*, 69−80.

(14) Fang, J. M.; Fowler, P. A.; Tomkinson, J.; Hill, C. A. S. The preparation and characterisation of a series of chemically modified potato starches. *Carbohydr. Polym.* **2002**, *47*, 245−252.

(15) Xie, W.; Wang, Y. Synthesis of high fatty acid starch esters with 1-butyl-3-methylimidazolium chloride as a reaction medium. *Starch/Stärke* **2011**, *63*, 190−197.

(16) Gao, J.; Luo, Z.; Luo, F. Ionic liquids as solvents for dissolution of corn starch and homogeneous synthesis of fatty-acid starch esters without catalysts. *Carbohydr. Polym.* **2012**, *89*, 1215−1221.

(17) Blaney, P.; Grigg, R.; Sridharan, V. Traceless solid-phase organic synthesis. *Chem. Rev.* **2002**, *102*, 2607−2624.

(18) Kaupp, G.; Schmeyers, J.; Boy, J. Waste-free solid-state syntheses with quantitative yield. *Chemosphere* **2001**, *43*, 55−61.

(19) Loupy, A. Solvent-free microwave organic synthesis as an efficient procedure for green chemistry. *C. R. Chim.* **2004**, *7*, 103−112.

(20) Nugroho, S.; Chen, Z.; Kawasaki, A.; Jarligo, M. O. D. Solid-state synthesis and formation mechanism of barium hexaaluminate from mechanically activated Al_2O_3−$BaCO_3$ powder mixtures. *J. Alloys Compd.* **2010**, *502*, 466−471.

(21) Senna, M. Smart mechanochemistry—Charge transfer control for tailored solid-state reaction under minimum external energy. *J. Alloys Compd.* **2007**, *434−435*, 768−772.

(22) Chang, Y.; Liu, C.; Guo, C.; Wang, Y.; Fang, J.; Cheng, W. Solid-phase organic synthesis of polyisoprenoid alcohols with traceless sulfone linker. *J. Org. Chem.* **2008**, *73*, 7197−7203.

(23) Sanchez, L. M.; Sathicq, Á. G.; Jios, J. L.; Baronetti, G. T.; Thomas, H. J.; Romanelli, G. P. Solvent-free synthesis of functionalized pyridine derivatives using Wells−Dawson heteropolyacid as catalyst. *Tetrahedron Lett.* **2011**, *52*, 4412−4416.

(24) Zhang, W.; Li, C.; Liang, M.; Geng, Y.; Lu, C. Preparation of carboxylate-functionalized cellulose via solvent-free mechanochemistry and its characterization as a biosorbent for removal of Pb^{2+} from aqueous solution. *J. Hazard. Mater.* **2010**, *181*, 468−473.

(25) Rätzsch, M.; Arnold, M.; Borsig, E.; Bucka, H.; Reichelt, N. Radical reactions on polypropylene in the solid state. *Prog. Polym. Sci.* **2002**, *27*, 1195−1282.

(26) Borsig, E.; van Duin, M.; Gotsis, A. D.; Picchioni, F. Long chain branching on linear polypropylene by solid state reactions. *Eur. Polym. J.* **2008**, *44*, 200−212.

(27) Huang, Z.; Lu, J.; Li, X.; Tong, Z. Effect of mechanical activation on physico-chemical properties and structure of cassava starch. *Carbohydr. Polym.* **2007**, *68*, 128−135.

(28) Huang, Z.; Xie, X.; Chen, Y.; Lu, J.; Tong, Z. Ball-milling treatment effect on physicochemical properties and features for cassava and maize starches. *C. R. Chimie* **2008**, *11*, 73−79.

(29) Huang, Z.; Liang, X.; Hu, H.; Gao, L.; Chen, Y.; Tong, Z. Influence of mechanical activation on the graft copolymerization of sugarcane bagasse and acrylic acid. *Polym. Degrad. Stab.* **2009**, *94*, 1737−1745.

(30) Liao, Z.; Huang, Z.; Hu, H.; Zhang, Y.; Tan, Y. Microscopic structure and properties changes of cassava stillage residue pretreated by mechanical activation. *Bioresour. Technol.* **2011**, *102*, 7953−7958.

(31) Sasikumar, C.; Rao, D. S.; Srikanth, S.; Mukhopadhyay, N. K.; Mehrotra, S. P. Dissolution studies of mechanically activated Manavalakurichi ilmenite with HCl and H$_2$SO$_4$. *Hydrometallurgy* **2007**, *88*, 154−169.

(32) Baláž, P.; Dutková, E. Fine milling in applied mechanochemistry. *Miner. Eng.* **2009**, *22*, 681−694.

(33) Geng, F.; Chang, P. R.; Yu, J.; Ma, X. The fabrication and the properties of pretreated corn starch laurate. *Carbohydr. Polym.* **2010**, *80*, 360−365.

(34) Huang, Z.; Tan, Y.; Zhang, Y.; Liu, X.; Hu, H.; Qin, Y.; Huang, H. Direct production of cellulose laurate by mechanical activation-strengthened solid phase synthesis. *Bioresour. Technol.* **2012**, *118*, 624−627.

(35) Winkler, H.; Vorwerg, W.; Wetzel, H. Synthesis and properties of fatty acid starch esters. *Carbohydr. Polym.* **2013**, *98*, 208−216.

(36) He, J.; Ma, W.; Tan, S.; Zhao, J. Study on surface modification of ultrafine inorganic antibacterial particles. *Appl. Surf. Sci.* **2005**, *241*, 279−286.

(37) Horchani, H.; Chaâbouni, M.; Gargouri, Y.; Sayari, A. Solvent-free lipase-catalyzed synthesis of long-chain starch esters using microwave heating: Optimization by response surface methodology. *Carbohydr. Polym.* **2010**, *79*, 466−474.

(38) Luengwilai, K.; Beckles, D. M. Structural investigations and morphology of tomato fruit starch. *J. Agric. Food Chem.* **2009**, *57*, 282−291.

(39) Zhang, Y.; Huang, Z.; Yang, C.; Huang, A.; Hu, H.; Gong, Z.; Sun, G.; Huang, K. Material properties of partially pregelatinized cassava starch prepared by mechanical activation. *Starch/Stärke* **2013**, *65*, 461−468.

(40) Martínez-Bustos, F.; López-Soto, M.; Martín-Martínez, E. S.; Zazueta-Morales, J. J.; Velez-Medina, J. J. Effects of high energy milling on some functional properties of jicama starch (*Pachyrrhizus erosus L.* Urban) and cassava starch (*Manihot esculenta* Crantz). *J. Food Eng.* **2007**, *78*, 1212−1220.

(41) Winkler, H.; Vorwerg, W.; Rihm, R. Thermal and mechanical properties of fatty acid starch esters. *Carbohydr. Polym.* **2013**. DOI: 10.1016/j.carbpol.2013.10.040.

(42) Crépy, L.; Miri, V.; Joly, N.; Martin, P.; Lefebvre, J. Effect of side chain length on structure and thermomechanical properties of fully substituted cellulose fatty esters. *Carbohydr. Polym.* **2011**, *83*, 1812−1820.

(43) Liu, T. Y.; Ma, Y.; Yu, S. F.; Shi, J.; Xue, S. The effect of ball milling treatment on structure and porosity of maize starch granule. *Innov. Food Sci. Emerg.* **2011**, *12*, 586−593.

(44) Tran, T. T. B.; Shelat, K. J.; Tang, D.; Li, E.; Gilbert, R. G.; Hasjim, J. Milling of rice grains. The degradation on three structural levels of starch in rice flour can be independently controlled during grinding. *J. Agric. Food Chem.* **2011**, *59*, 3964−3973.

(45) Kapusniak, J.; Siemion, P. Thermal reactions of starch with long-chain unsaturated fatty acids. Part 2. Linoleic acid. *J. Food Eng.* **2007**, *78*, 323−332.

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