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Effects of heat moisture treatment on the physicochemical properties of starch nanoparticles

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ABSTRACT

In this study, the effect of heat moisture treatment (HMT) on the properties of waxy maize starch nanoparticles (SNPs) was investigated. The SNPs were adjusted to 20% and 30% moisture levels and heated at 90 °C and 110 °C for 4 h. Transmission electron microscopy, X-ray diffractometry, differential scanning calorimetry, and Fourier transform infrared spectroscopy were used to characterize the morphology and crystal structure of the SNPs after HMT. The research found that the morphology of SNPs did not change significantly, keeping nanoscale size. When the SNPs were subjected to HMT at 110 °C and 30% moisture content, the crystalline structures changed from B-type to A-type, and the crystallinity of the SNPs increased significantly. HMT significantly increased the onset temperature, peak temperature, final temperature, and enthalpy value of the SNPs. As the HMT temperature and SNP moisture content increased, the hydrogen bonds between the starch molecular chains in the SNPs became stronger.

1. Introduction

Starch nanoparticles (SNPs), a novel product derived from starch, are nano-sized in at least one dimension. In recent years, many publications have reported the preparation, structure analysis, and functional performance of SNPs (Chin, Pang, & Tay, 2011; Ma, Jian, Chang, & Yu, 2008; Santander-Ortega et al., 2010; Singh, Dartois, & Kaur, 2010; Singh, Singh, Pandey, & Sanghi, 2010). SNPs are usually obtained by one of three ways: physical methods, acid hydrolysis, and enzymatic hydrolysis. Physical methods such as precipitation (Ma et al., 2008) and microfluidization (Liu, Wu, Chen, & Chang, 2009) can produce SNPs 10–20 nm in size under a pressure of 207 MPa. With hydrolysis using H_2SO_4, the amorphous domains of semicrystalline starch granules are disrupted, leaving platelet-like starch nanocrystals (LeCorre, Bras, & Dufresne, 2011). The obtained starch nanocrystals have a lamellar morphology with a thickness of 4–8 nm and a diameter of 50–120 nm. Using selective enzymatic hydrolysis, nanoscale starch particles with an average diameter of 500 nm have been prepared from waxy rice starch (Kim, Park, & Lim, 2008). A new method using enzymolysis and retrogradation has also been used to prepare SNPs. Waxy maize starch with high amylopectin content (98% amylopectin) was usually debranched with pullulanase and the ensuing branched short linear glucans could form nano-scale starch particles during the retrogradation process. This method has the advantage of being quite rapid and presenting a higher yield. The particle sizes of SNPs prepared from proso millet starch and waxy maize starch are 20–100 nm and 60–120 nm, respectively (Sun, Gong, Li, & Xiong, 2014; Sun, Li, Dai, Ji, & Xiong, 2014). In recent years, SNPs have been widely used in food packaging (Chang, Jian, Yu, & Ma, 2010; Rhim, Park, & Ha, 2013), drug delivery (Simi & Emilia, 2007; Wim & Paul, 2008), and paper fabrication, due to their high mechanical properties and renewable nature (Simi & Emilia, 2007; Yoon & Deng, 2006). However, the SNPs do not always have the physical or chemical properties appropriate for certain types of processing; thus, some modifications are commonly used to produce SNPs with special properties. There are three strategies for modifying SNPs – chemical, enzymatic, and physical methods – which could promote specific functional properties. Angellier, Molina-Boisseau, Belgacem, and Dufresne (2005) chemically modified the surfaces of starch nanocrystals using alkenyl succinic anhydride and phenylisocyanate. Chakraborty, Sahoo, Teraoka, Miller, and Gross, (2005) investigated the chemical modification of starch-derived nanocrystals with ethylene glycol methyl ether and stearic acid chloride. Namazi and Dadkhah (2008) also observed the surface modification of starch nanocrystals through the ring-opening polymerization of ε-caprolactone. Heat moisture treatment (HMT) is one of the important physical methods used to modify starch using simple and environmentally safe processes at low cost and without chemical reagent byproducts

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(Adebowale, Afolabi, & Olu-Owolabi, 2005; Sun, Wang, Xiong, & Zhao, 2013). Consumers tend to be more receptive to such physical modifications, as they avoid traditional chemical means to modify starch. To the best of our knowledge, there are no reports regarding the modification of SNPs by HMT. Therefore, in this study, SNPs were treated with moisture content (20% and 30%) at 90 °C and 110 °C for four hours, and the effect of this HMT on the physicochemical and morphological properties of the SNPs were studied by using transmission electron microscopy (TEM), X-ray diffractometry (XRD), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR). The main objective was to study the influence of HMT on the property and structure of the SNPs.

2. Materials and methods

2.1. Materials

Waxy maize starch (98% amylopectin) was obtained from National Starch & Chemical Co., Ltd. (Guangdong, China). Pullulanase (E.C.3.2.1.41, 6000 ASPU/g, 1.15 g/mL), where ASPU is defined as the amount of enzyme that liberates 1.0 mg glucose from starch in 1 min at pH 4.4 and 60 °C) was supplied by Novozymes Investment Co. Ltd. (Beijing, China). All reagents used were analytical grade.

2.2. Preparation of SNPs

The SNPs were prepared using the method described by Sun, Li, et al. (2014). Waxy maize starch (15 g, db) was dispersed in 100 mL of disodium hydrogen phosphate and citric acid buffer solution (pH 5.0), and the starch slurry was cooked in boiling water, with vigorous stirring, for 30 min to fully gelatinize the starch. The temperature of the cooked waxy maize starch was adjusted to 58 °C and pullulanase (30 ASPU/g of dry starch) was added. After an 8 h incubation period at 58 °C, the reaction was stopped by heating the starch at 100 °C for 30 min to inactivate the pullulanase, followed by cooling to room temperature. Then, the solutions were stored at 4 °C for 8 h. The suspensions were washed several times with distilled water until neutrality and then freeze dried to obtain SNPs.

2.3. Heat moisture treatment (HMT)

HMT of the SNPs was performed according to the method described by Hormdok and Noomhorm (2007), with some modifications. The moisture content of the SNPs was adjusted to 20% and 30%, after which the samples were placed in sealed glass tubes and heated at 90 °C and 110 °C for 4.0 h.

2.4. Transmission electron microscopy (TEM)

Transmission electron micrographs of the SNP samples were taken with a Hitachi 7650 (Tokyo, Japan) transmission electron microscope with an acceleration voltage of 80 kV. The samples were deposited on a carbon-coated grid and freeze dried.

2.5. X-ray diffraction (XRD)

The crystalline structures of the SNP samples were studied using an X-ray diffractometer (AXS D8 ADVANCE; Bruker, Karlsruhe, Germany). The samples were stored in a sealed container in a saturated solution (1000 mL) of NaCl to standardize moisture content, with Cu Kα radiation (λ = 1.543). Signals of the reflection angle of 2θ from 4° to 40° were recorded. Samples crystallinity was determined by plotting the peaks baseline on the diffractogram and calculating the area using the software spectrum viewer (Version 2.6) according to the method described by Jivan, Madadlou, and Yarmand (2013). The area above and under the curve corresponded to crystalline domains and amorphous regions, respectively. The ratio of upper area to total area was taken as the crystallinity degree:

$$\text{Crystallinity percentage} = \text{Area under the peaks/Total curve area} \times 100 \quad (1)$$

2.6. Differential scanning calorimetry (DSC)

Gelatinization parameters of the SNP samples were measured using a differential scanning calorimeter (DSC1; Mettler Toledo, Schwerzenbach, Switzerland) equipped with a thermal analysis data station and data recording software (STAR@ SW 9.20), as described by Chanvrier et al. (2007), with some modifications. Using a microsyringe, deionized water (20 μl) was added to the SNPs (10.0 mg db) in an aluminum pan. The pan was hermetically sealed before DSC analysis. The scanning temperature range and the heating rates were 25–120 °C and 10 °C/min, respectively. In all measurements, the thermogram was recorded with an empty aluminum pan as a reference. During the scans, the space surrounding the sample chamber was flushed with dry nitrogen to avoid condensation. The transition temperatures reported are the onset (T_o), peak (T_p), and conclusion (T_c). The enthalpy of gelatinization (ΔH), estimated by integrating the area between the thermogram and a baseline under the peak, was expressed in Joules per gram of dry starch; three replicates per sample were analyzed.

2.7. Fourier transform infrared spectroscopy analysis (FTIR)

The infrared spectra of the SNP samples were recorded on an FTIR spectrophotometer (NEXUS-870; Thermo Nicolet Corporation, Madison, WI, USA) as described by Kunal, Banthia, and Majumdar (2008). All of the samples were mixed with KBr and pressed into pellets, which were then subjected to attenuated total reflectance spectroscopy in a 4000–400 cm^{-1} range. Intensity measurements were performed on the spectra by recording the height of the absorbance bands from the baseline.

2.8. Statistical analysis

Each measurement was carried out using at least three fresh, independently prepared samples. The results were reported as the mean value and standard deviation. The data were subjected to analysis of variance (ANOVA) using the SPSS V.12 statistical software package (SPSS Inc., Chicago, IL). Duncan's multiple range test was also used to determine the difference of the means from the ANOVA, using a significance test level of 5% ($p < 0.05$).

3. Results and discussion

3.1. Morphology of SNPs

The morphologies of unmodified and HMT SNPs under different heat treatment conditions were examined by TEM (Fig. 1). As shown in Fig. 1, the shapes of the SNPs before and after modification were nearly spherical or elliptical and the particle sizes of the SNPs were 50–100 nm wide and 80–120 nm long. It appeared that the HMT did not change the sizes or shapes of the SNPs to any obvious extent. Watcharatewinkul, Puttanlek, Rungsardthong, and Uttapap (2009) reported that HMT did not alter the shape or size of canna starch, and similar observations were reported for heat-moisture-treated finger millet (Adebowale et al., 2005), rice (Khunae, Tran,

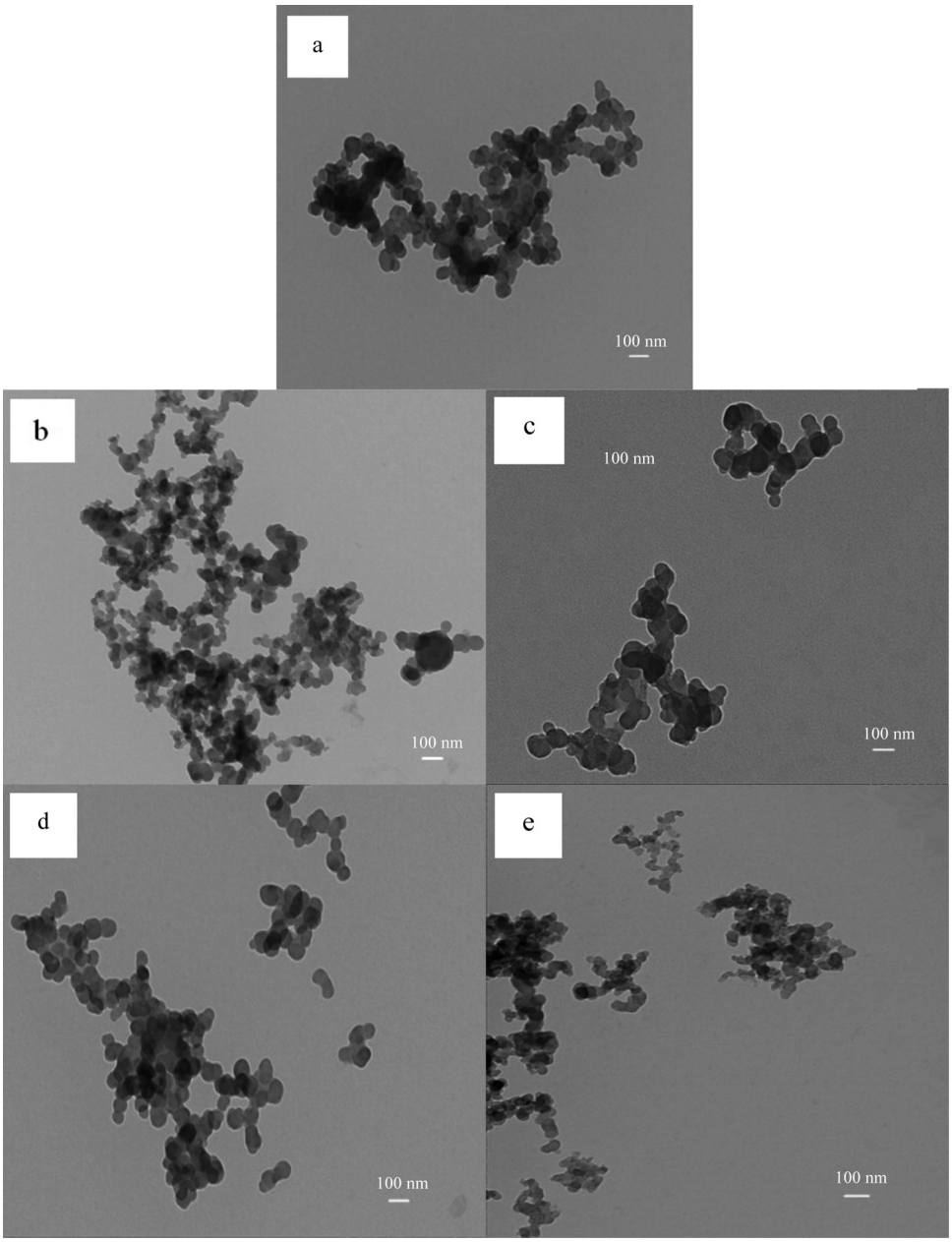

Fig. 1. The morphology of (a) untreated SNPs, SNPs treated with (b) 20% moisture at 90 °C, (c) 30% moisture at 90 °C, (d) 20% moisture at 110 °C, (e) 30% moisture at 110 °C.

& Sirivongpaisal, 2007), new cocoyam (Lawal, 2005), potato, taro, true yam, and cassava (Gunaratne & Hoover, 2002) starches.

3.2. X-ray diffraction pattern (XRD)

The XRD patterns of SNPs with and without modification are shown in Fig. 2. The untreated SNPs showed a typical "B" X-ray pattern, with peaks at $2\theta = 5.6^\circ$, 17.1°, 22.5°, and 24.3°. When the SNPs (with 20% moisture) were heated at 90 °C for 4 h, the characteristic B-type diffraction peak disappeared slightly at $2\theta = 5.6^\circ$. There was no obvious characteristic diffraction peak at 2θ=5.6° upon HMT (110 °C at 30% moisture), and there were increases in the peaks at intensities of 2θ=15.6° and 17.1° for all modified SNPs after HMT.

The XRD results showed that the crystalline structures were changed from B- to A-type with an increase in the HMT temperature and moisture content of the SNPs. Gunaratne and Hoover (2002) observed a change in the X-ray patterns of "B" type starches to "A+B" after HMT. According to Vermeylen, Goderis, and Delcour (2006), the double helices in B-type starches present both a lateral and a hexagonal movement when subjected to HMT, losing the initial diffraction peak at $2\theta = 5.6^\circ$, thus changing its pattern from B-type to A-type. The HMT-induced changes in the diffraction patterns of starches can be attributed to dehydration as well as to movement of a pair of double helices into the central channel. This movement during HMT could disrupt starch crystallites and/or change the crystalline orientation (Gunaratne & Hoover, 2002). In this study, crystallinity increased from 55.4% to 69.7% as the temperature of the HMT increased. Similar results were reported for heat-moisture-treated sweet potato starches (Vieira & Sarmento, 2008).

3.3. Thermal properties

The gelatinization transition temperatures T_o, T_p, and T_c, and ΔH of untreated and HMT SNPs are presented in Table 1 and Fig. 3. HMT increased the T_o, T_p, and T_c and ΔH in all SNP samples. The DSC

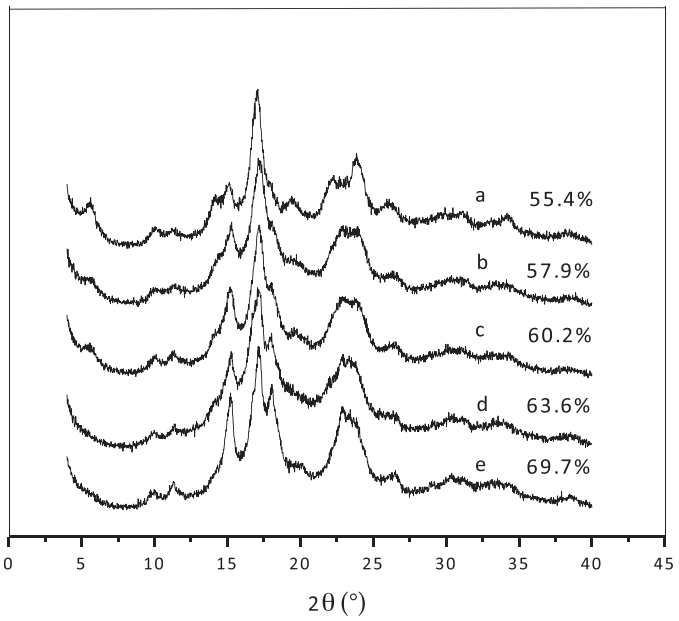

Fig. 2. X-ray diffraction of (a) untreated SNPs, SNPs with (b) 20% moisture at 90 °C, (c) 30% moisture at 90 °C, (d) 20% moisture at 110 °C, (e) 30% moisture at 110 °C.

Table 1
Thermal properties of untreated and treated SNPs with HMT.

Samples	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
SNPs	62.4 ± 1.6^a	78.3 ± 1.5^a	93.2 ± 1.6^a	10.1 ± 1.6^a
HMT20-90	66.8 ± 1.2^b	83.3 ± 1.2^b	96.2 ± 1.2^b	16.0 ± 1.2^b
HMT30-90	78.7 ± 1.3^c	90.5 ± 1.3^d	98.8 ± 1.3^b	15.8 ± 1.2^b
HMT20-110	76.8 ± 1.3^c	87.0 ± 1.3^c	103.2 ± 1.3^c	15.7 ± 1.2^b
HMT30-110	75.9 ± 1.1^c	95.6 ± 1.4^e	110.0 ± 1.4^d	15.2 ± 1.3^b

All data represent the mean of three determinations.
Mean ± standard deviation.
Means with the same letter in each column are not significantly different ($p < 0.05$).
To, onset temperature; Tp, peak temperature; Tc, conclusion temperature.
ΔH, enthalpy of gelatinization.
SNPs, waxy maize starch nanoparticles.
HMTxx-yy is heat-moisture treated SNPs: xx = % moisture content and yy = heating temperature (°C). (e.g. HMT20-90 is HMT flour using 20% moisture content and at 90 °C).

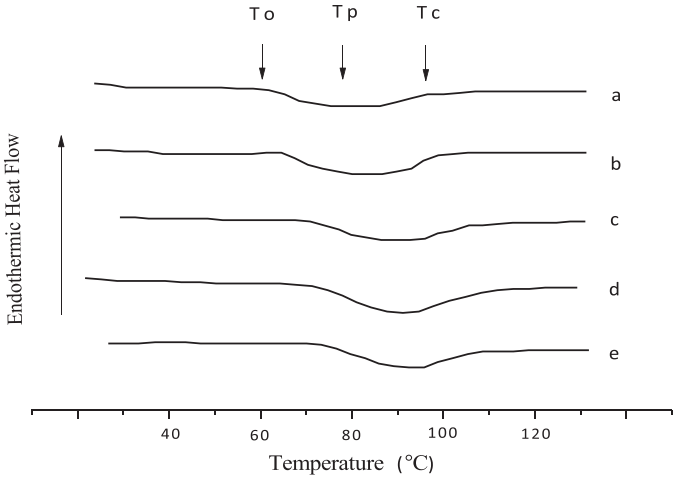

Fig. 3. DSC gelatinization curves of (a) untreated SNPs, SNPs treated with (b) 20% moisture at 90 °C, (c) 30% moisture at 90 °C, (d) 20% moisture at 110 °C, (e) 30% moisture at 110 °C.

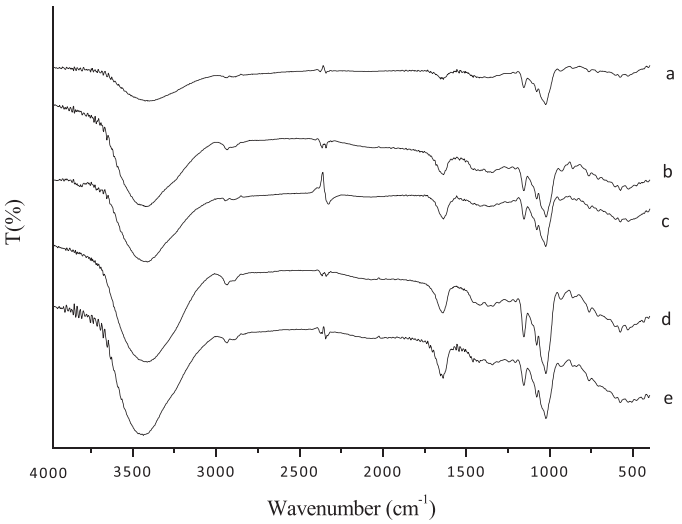

Fig. 4. FTIR spectra of (a) untreated SNPs, SNPs with (b) 20% moisture at 90 °C, (c) 30% moisture at 90 °C, (d) 20% moisture at 110 °C, (e) 30% moisture at 110 °C.

pattern of untreated SNPs showed an endotherm near 62 °C, which was the onset gelatinization temperature. The endotherm peaks of HMT SNPs were observed at 66 °C, 78 °C, 76 °C, and 75 °C. The T_ps of HMT SNPs were much higher than those of the controls. The higher temperature required for gelatinization was due to the formation of an intermolecular hydrogen bond. T_o, T_p, T_c, and gelatinization temperatures rose as the heat and moisture intensity increased. During HMT, there was probably a higher number of short amylose chains that formed a double-helix structure. Increased T_o, T_p, and T_c have been attributed to the formation of a stable configuration, which was formed as a result of the reorientation of the starch molecules and crystalline reorganization (Sun et al., 2013). The increase of T_o, T_p, T_c and ΔH by the HMT was due to the formation of a better packaged and ordered crystalline array, leading to a high energy requirement for the dissociation of the new crystals. The ΔH increased with the increase of the HMT temperature and time which was in accordance with the relative crystallinity measured by X-ray diffraction analysis (Fig. 2). Li et al. (2013) reported that the increase of crystallinity in the starch granule would be account for the increase in ΔH. Adebowale, Henle, Schwarzenbolz, and Doert (2009) observed higher T_o, T_p and T_c in African bean starch subjected to HMT at different moisture levels. Vermeylen et al. (2006) reported that HMT of potato starch increased DSC gelatinization temperatures. There was a significant increase in the ΔH value of HMT SNPs compared with untreated SNPs (10.1 J/g). The increase in enthalpy might be attributed to the reassembling of the double helix structure during HMT.

3.4. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of unmodified and modified SNPs under different heat treatment conditions are shown in Fig. 4. The absorbance spectra of the SNPs were quite similar between 4000 and 2000 cm^{-1} before and after HMT treatment. The stretching modes of the hydrogen bonded hydroxyl groups (O—H) of the SNPs were observed in the region of 3700–3100 cm^{-1}, due to the complex vibrational stretches associated with free, inter-, and intra-molecular hydroxyl groups. When heat treated at 90 °C or 110 °C, the modified SNPs had an increased peak in the region of 3700–3100 cm^{-1} as the moisture level increased. When the same moisture content was applied, there was an incremental peak at 3700–3100 cm^{-1} as the temperature level increased. The results showed that short amylose

molecules were able to form additional hydrogen bonds through high temperature or high moisture content.

The characteristic band at 2926 cm^{-1} of the C—H stretching vibration was found. The intensity at about 2077 cm^{-1} was attributed to the interactional force between C—H and C—C bonds. The band at 1640 cm^{-1} was due to bound water in the inner structure of the starch (Fang, Fowler, Tomkinson, & Hill, 2002). As shown in Fig. 4, more differences were found at wavelengths of 1300–900 cm^{-1}. The peaks at 900–1200 cm^{-1} were characteristic of coupled C—O and C—O—H vibrational modes in starch (Julious, 2008). The peak at 1155 cm^{-1} for original nanocrystals was due to C—O bond stretching (Jivan et al., 2013). The peaks at 1083 and 1023 cm^{-1} were characteristic of the anhydroglucose ring O—C stretch (Fang et al., 2002). The C—O—H bending modes observed at 1047 and 1022 cm^{-1} have already been assigned to ordered and amorphous starch samples, respectively (Liu, Charlet, Yelle, & Arul, 2002; Sevenou, Hill, Farhat, & Mitchell, 2002). The intensity at about 940 cm^{-1} was attributed to skeletal mode vibrations of α-1, 4 glycosidic linkage (C—O—C). The absorption bands that occurred at 1020 cm^{-1}, 1081 cm^{-1}, and 1156 cm^{-1} were characteristic of the C—O stretching vibration. After HMT, the modified SNPs showed an increase in the peak intensity in the region of 1020 cm^{-1}, 1081 cm^{-1}, and 1156 cm^{-1}, which indicated that the hydrogen bonds between starch molecular chains were stronger than untreated SNPs.

4. Conclusions

In this study, SNPs modified with HMT exhibited marked property and structure changes. The intact SNPs had a B-type crystal pattern, while the modified SNPs showed an A-type crystal pattern and higher crystallinity. The T_o, T_p, T_c, and ΔH of the SNPs that underwent HMT were significantly higher than those of unmodified SNPs. However, the sizes and shapes of the SNPs did not change. The results of this study can help food processors tailor the properties of SNPs modified by different moisture and temperature levels; thus, SNPs subjected to single HMT could be widely used in both the food and non-food sectors.

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