Carbohydrate Polymers 112 (2014) 520–524

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Polyoxometalates acid treatment for preparing starch nanoparticles

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ARTICLE INFO

Article history:
Received 28 February 2014
Received in revised form 14 June 2014
Accepted 16 June 2014
Available online 23 June 2014

Keywords:
Starch
Polyoxometalates acid
Nanoparticles

ABSTRACT

In this article, a new way of preparing starch-based nanoparticles (SNPs) with high yields by a polyoxometalates acid treatment is presented. The particle morphology, mean size and size distribution of the obtained SNPs are characterized using a dynamic light scattering (DLS) and scanning electron microscope (SEM). By changing parameters such as temperature, concentration of polyoxometalates and treating time the size of SNPs can be controlled. In addition, there are no changes in the structures of the starch granules as confirmed by IR or ^{1}H NMR. Freeze-dried SNPs are amorphous as characterized by wide-angle X-ray diffraction (WXRD).

1. Introduction

Currently, extensive efforts have been focused on replacing petroleum-based plastics with sustainable bio-based plastics to solve the increasing environmental problems (Mecking, 2004; Tan et al., 2009). However, up to now the bio-based plastics cannot be used for wide applications because of their high cost and limited performance. Processing polymeric composite materials filled with nanoparticles is a practical method to enhance the properties of biopolymers (Darder, Aranda, & Ruiz-Hitzky, 2007). Due to the nanometric size effect (Angellier, Molina-Boisseau, Belgacem, & Dufresne, 2005a), these bionanocomposites display some special and excellent properties with respect to their conventional micro-counterparts. The availability and homogeneous dispersion in the continuous matrix are necessary for nanoparticles and corresponding nanocomposite materials, which is the basic requisites for excellent mechanical performances.

With sustainable development, there has been considerable interest in the use of the biodegradable renewable starch nanoparticles (SNPs) (Daniels & Donald, 2004; LeCorre, Vahanian, Dufresne, & Bras, 2011; Ma, Jian, Chang, & Yu, 2008). SNPs have been successfully explored to enhance the property of various natural and synthetic materials, such as natural rubber (Angellier, Molina-Boisseau, & Dufresne, 2005b), poly (styrene-co-butyl acrylate) (Dufresne, Cavaille, & Helbert, 1996), poly (lactic acid) (Lee & Hanna, 2008), polycaprolactone (Perez, Alvarez, Mondragon, & Vazquez, 2007) and so on. Usually, starch-based nanocrystals or nanoparticles can be prepared by some ways such as acid or enzymatic hydrolysis (Angellier, Choisnard, Molina-Boisseau, Ozil, & Dufresne, 2004; Ma, Chang, Yu, & Stumborg, 2009; Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003), regeneration (Ma et al., 2008; Tan et al., 2009), alkali-freezing treatment (Zhang et al., 2013) and mechanical treatment (Gao et al., 2011; Song, Thio, & Deng, 2011). Traditionally, acid hydrolysis is the most popular method for preparing starch nanocrystals (SNCs) (Le Corre, Bras, & Dufresne, 2010). But there are several drawbacks to this method such as the long duration (at least 5 days), low yield (below 15%), high cost due to low production yields, and environmental concerns and cost relating to the disposal of spent acids, these factors have hindered the practical application of SNCs. So it is necessary to explore a new method to shorten the hydrolysis time and enhance the productivity.

"Polyoxometalates (POMs) are a subset of metal oxide clusters that represent a diverse range of molecular clusters with an almost unmatched range of physical properties and the ability to form dynamic structures that different size particular can be formed from nano- to micrometer scale" (Long, Tsunashima, & Cronin, 2010). Heteropoly acids (HPAs), as a kind of POMs, is a strong BrØnsted acid. BrØnsted acid is another definitions of acid independently proposed by Danish chemist Johannes Nicolaus Brønsted and English chemist Martin Lowry in 1923. HPAs with strong acidity have been considered as efficient acid catalysts for certain reactions, such as esterification, hydrolysis and Friedel-Crafts alkylation (Kozhevnikov, 1998).

Herein, phosphotungstic acid ($H_3PW_{12}O_{40}$) as a simple type of HPAs was chosen as a substitute of sulfuric acid to produce starch-based nanoparticles (SNPs). It was reported that phosphotungstic acid can reduce by about 20% the energy demand for the hydrolysis

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http://dx.doi.org/10.1016/j.carbpol.2014.06.040
0144-8617/

(Tsubaki et al., 2013). The aim of this study is to use phosphotungstic acid as a new kind of acid to produce SNPs quickly (usually in several hours) and in high yields (the productivities of all the obtained samples were above 50% in 8 h, which were much higher than that of sulfuric acid). In order to optimize the operative conditions, the hydrolysis experiments of starch were conducted at 40 °C and the concentration of starch was constant (0.2 g mL^{-1}). The influence of the concentrations of $H_3PW_{12}O_{40}$ and the hydrolysis time on the size of the particles was investigated. Yield calculations, dynamic light scattering (DLS) and scanning electron microscope (SEM) were used to characterize the insoluble nanoparicles. The structures of SNPs were characterized by IR, ^1H NMR and XRD. We hope to provide a facile way to prepare SNPs quickly and in high yields for use in practical application.

2. Experimental

2.1. Materials

Corn starch and waxy maize starch were provided by Da Cheng Starch Development Company (Changchun, Jilin, China).

2.2. Characterizations

Proton nuclear magnetic resonance (^1H NMR) spectra were collected on a Bruker 300 MHz spectrometer. FT-IR spectra were performed on a Bruker Vertex 70 Fourier Transform Infrared spectrometer by using the KBr disk method. The X-ray diffraction measurement was carried out on a Bruker D8 Advance X-ray diffractometer by using Cu Kα radiation in the scattering angle range of $2\theta = 10–30°$ at a scan speed of 4°/min. Scanning electron microscopy (SEM) was performed on a XL 30 ESEM FEG Scanning Electron Microscope (Micrion FEI PHILIPS). Thermo-gravimetric analysis (TGA) of approximately 5 mg freeze-dried samples was performed on Perkin-Elmer TGA7 at a heating rate of 10 °C/min from room temperature to 800 °C under a nitrogen atmosphere.

2.3. Preparation of corn starch nanoparticles (C-SNPs)

Corn starch (2 g) and $H_3PW_{12}O_{40}$ (0.5 g, 1 g, 2 g, 3 g, respectively) were dissolved in water (10 mL) in air. The concentrations of $H_3PW_{12}O_{40}$ were 0.05 mg mL^{-1}, 0.1 mg mL^{-1}, 0.2 mg mL^{-1} and 0.3 mg mL^{-1}, respectively. After being vigorously stirred at 40 °C, 1 mL of the above solution was taken out at specified times and precipitated in 10-fold ethanol to remove $H_3PW_{12}O_{40}$. C-SNPs were obtained by centrifuge, dialysis and lyophilization. The products were weighted by an electronic balance, and the corresponding productivities were calculated.

2.4. UV-absorption of SNPs combined with iodine

Firstly, I_2/KI (1:3) solutions with 5% (w/v) total iodine were prepared. Then, 5.0 mg samples were dissolved in 4.0 mol L^{-1} NaOH solution, and the pH value was adjusted to 7.0. After that, 0.25 mL I_2/KI (1:3) solution was added into the samples solution and the solutions were sent to scan (800–400 nm) after 30 min by Shimadzu UV-2401PC UV–vis spectroscopy.

3. Results and discussion

In this article, corn starch was chosen as a representative. The influence of the $H_3PW_{12}O_{40}$ concentrations and the hydrolysis time on the size distributions of C-SNPs were characterized by DLS listed in Fig. 1 and Table 1. At the higher concentration of $H_3PW_{12}O_{40}$ corn starch was obviously hydrolyzed only in several hours. As shown in Fig. 1, with the concentration of $H_3PW_{12}O_{40}$ increasing the size distribution of C-SNPs decreased obviously (Fig. 1A). When the concentration of $H_3PW_{12}O_{40}$ was 0.3 g mL^{-1}, the size distribution of C-SNPs also decreased with the hydrolysis time increasing (Fig. 1B). These results showed that SNPs with predictable size could be obtained by choosing adaptive $H_3PW_{12}O_{40}$ concentration and hydrolysis time. As compared, starch hydrolysis was also performed at 20 °C. However, there were no obviously changes in the size of starch during several hours with different $H_3PW_{12}O_{40}$ concentrations which exhibited that temperature played an important role on the hydrolysis process. Similarly, no obvious changes of the size were observed when the concentration of $H_3PW_{12}O_{40}$ was 0.05 g mL^{-1} or 0.1 g mL^{-1}, which indicated that the concentration of $H_3PW_{12}O_{40}$ was another vital parameter.

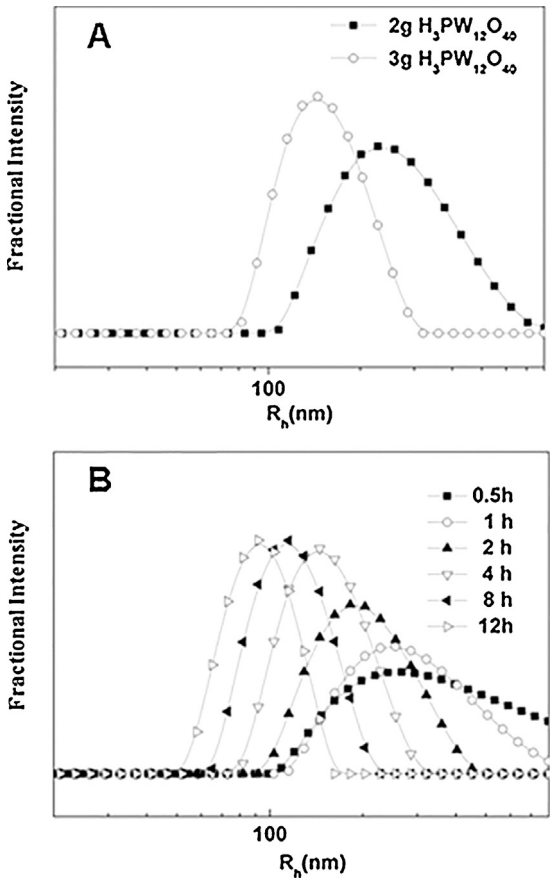

Fig. 1. Size distribution of C-SNPs measured by DLS with different concentration of $H_3PW_{12}O_{40}$ at 4 h (A) and at different times (B) ($H_3PW_{12}O_{40}$ 0.3 g mL^{-1}).

Table 1
The effect of preparation conditions on the size of C-SNPs.

Sample	Concentration of $H_3PW_{12}O_{40}$ (g mL^{-1})	Time (h)	Size of C-SNPs (nm)[a]	Productivity (%)
1	0.2	4	227.4 ± 103.2	68.43
2	0.2	8	151.2 ± 71.3	61.45
3	0.2	12	105.7 ± 37.8	55.64
4	0.3	0.5	255.1 ± 131.4	74.23
5	0.3	1	233.6 ± 98.7	69.83
6	0.3	2	184.4 ± 51.1	70.23
7	0.3	4	131.9 ± 37.2	62.47
8	0.3	5	116.1 ± 25.5	63.12
9	0.3	8	107.4 ± 18.9	53.14
10	0.3	12	91.0 ± 16.3	50.47

[a] Determined by DLS.

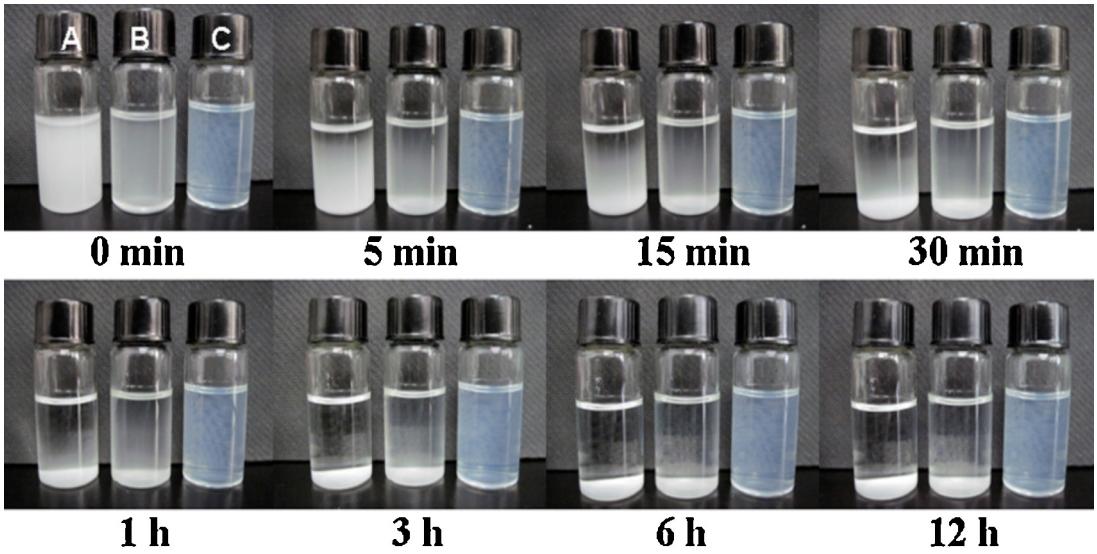

Fig. 2. Photos of the solutions of corn starch (A), C-SNPs hydrolyzed for 0.5 h (B) and C-SNPs hydrolyzed for 4 h (C) ($H_3PW_{12}O_{40}$ 0.3 g mL^{-1}) stand at different time at room temperature.

Furthermore, in order to study the stability of SNPs the native corn starch (A), C-SNPs hydrolyzed for 0.5 h (B) and C-SNPs hydrolyzed for 4 h (C) were dispersed in water to prepare homogeneous suspension, respectively. Fig. 2 showed the appearance of above samples after standing for different intervals in room temperature. In about 15 min, native corn starch without any treatment wholly precipitated due to the large size. While the stabilization of SNPs suspension solution hydrolyzed using $H_3PW_{12}O_{40}$ for 0.5 h was slightly enhanced. Just as what we expected, SNPs suspension hydrolyzed using $H_3PW_{12}O_{40}$ for 4 h kept the stable state in several weeks which was attributed to a size reduction of the starch granules.

The size and morphology of SNPs were also confirmed by TEM photographs as shown in Fig. 3. The diameters of SNPs were about 300 nm with an even size distribution, which was corresponding to the results from DLS. From the observations of TEM, it could be seen clearly that the insoluble residue obtained by hydrolysis with $H_3PW_{12}O_{40}$ (0.3 g mL^{-1}) after 4 h had a nanosphere shape, which was quite different from the parallelepiped nanoplatelets shape of SNCs prepared by sulfuric acid (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006). So we infer that the hydrolysis mechanism of polyoxometalates acid treatment is quite different from that of sulfuric acid hydrolysis.

To further testify the above deduction, the structural properties of corn starch and C-SNPs with different treatment times were analyzed by X-ray diffraction. As shown in Fig. 4, native corn starch presents a strong intensity peak at 15.3°, a double peak at 17.1° and 18.2°, and a last strong intensity peak at 23.5°, which is the typical A-type crystalline structure (Imberty, Chanzy, Perez, Buleon, & Tran, 1987). While as the hydrolysis continued, the intensity of peaks weakened gradually and the crystalline structure of starch granules disappeared, which was different from that of sulfuric acid hydrolysis with observably crystalline structure. This result revealed that there were different mechanisms to explain the hydrolysis process between the sulfuric acid treatment and $H_3PW_{12}O_{40}$ treatment. It is reported that the sulfuric acid hydrolysis process includes two stages: Firstly, the amorphous regions of starch hydrolyze (main chain), which is influenced by the granule size, pores on the surface, amylase content and the amount of lipid-complexed amylase chain; Secondly, the crystalline regions hydrolyze, which is influenced by the amylopectin content, modes of distribution of R(1–6) branches between the amorphous and the crystalline regions, and degree of packing of the double helices within the crystallites (Daniels & Donald, 2004). But for $H_3PW_{12}O_{40}$, all molecular chains either amorphous or crystalline might be irregularly cut down and the hydrolysis reaction proceeded quickly, which resulted that the molecular weight of starch decreased accordingly. And with the molecular weight decreasing, the crystalline structure disappeared gradually (Leroy et al., 2012). As the further demonstration, waxy maize starch and corn starch hydrolyzed by sulfuric acid were hydrolyzed again by $H_3PW_{12}O_{40}$. The size distributions and structure properties were also characterized by DLS and X-ray diffraction (shown in Fig. S1-S3). Fig. S1 shows the size distributions of the obtained waxy starch

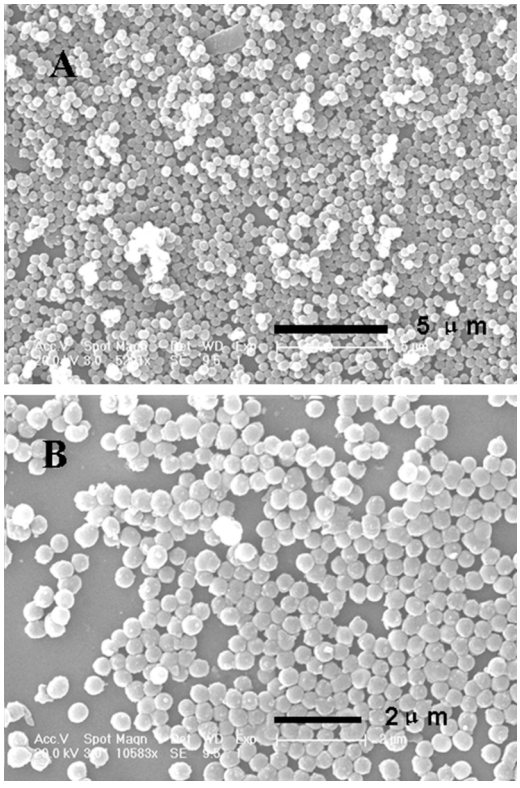

Fig. 3. SEM images of C-SNPs hydrolyzed by $H_3PW_{12}O_{40}$ (0.3 g mL^{-1}) for 4 h under different magnifications.

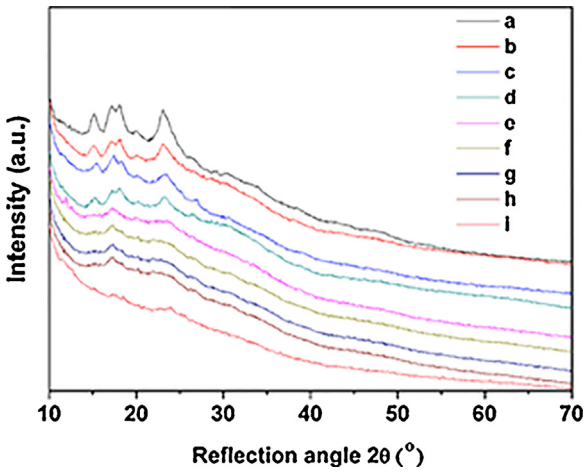

Fig. 4. X-ray diffraction pattern of C-SNPs prepared at different times. Pure corn starch (a), time of hydrolysis 0 min (b), 10 min (c), 30 min (d), 60 min (e), 120 min (f), 180 min (g), 240 min (h) and 300 min (i). ($H_3PW_{12}O_{40}$ 0.3 g mL^{-1}).

nanoparticles (W-SNPs) at different time characterized by DLS. It could be concluded that waxy starch was also obviously hydrolyzed under higher concentration of $H_3PW_{12}O_{40}$ in several hours. Just as Fig. S2 shown, waxy maize starch had strong intensity peaks attributed to the typical A-type crystalline structure before hydrolysis, while the intensity of peaks obviously weaken and the crystalline structure of starch granules disappeared after hydrolysis. C-SNPs hydrolyzed by sulfuric acid exhibited the typical A-type crystalline structure as shown in Fig. S3. The crystalline structure of C-SNPs (hydrolyzed by sulfuric acid) disappeared after hydrolysis by $H_3PW_{12}O_{40}$ for 4 h, which further indicated that the hydrolysis mechanisms of SNPs by sulfuric acid and $H_3PW_{12}O_{40}$ were quite different. In addition, to characterize the changing ratio between amorphous and crystalline regions the UV-absorption of the SNPs combined with iodine was performed as previous literature (Lian, Zhang, Luo, Wang, & Liu, 2012). As depicted in Fig. 5, there was a slight red shift as the hydrolysis time increasing, which indicated that the ratio of crystalline regions gradually decreased because the molecular chains either amorphous or crystalline region were cut down randomly during the hydrolysis process.

The chemical structure of SNPs was also investigated by ^{1}H NMR spectra and FT-IR spectra shown in Fig. 6. It was worth noting that there were no substantive changes in ^{1}H NMR and FT-IR spectra of starch before and after hydrolysis, which further indicated that the

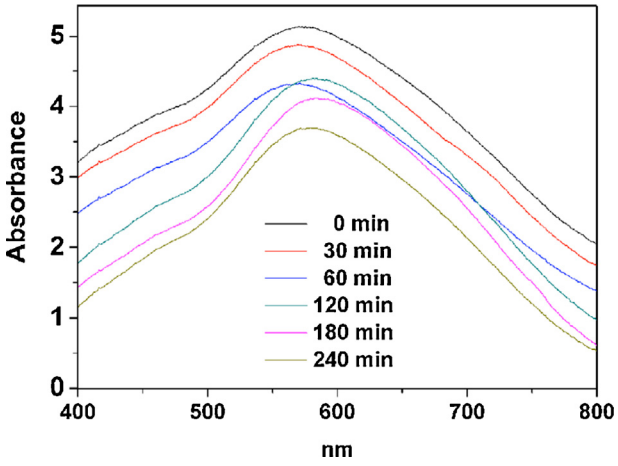

Fig. 5. The UV spectra (binding with iodine) of I_2/KI solutions for C-SNPs hydrolyzed by $H_3PW_{12}O_{40}$ at different time.

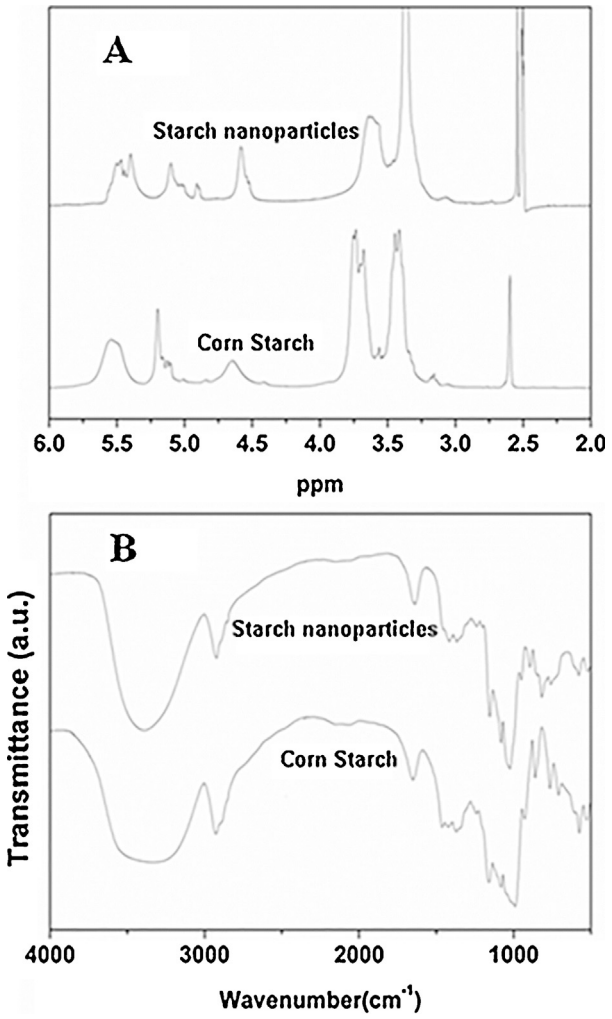

Fig. 6. ^{1}H NMR spectra (A) and FT-IR (B) spectra of corn starch and corn starch-based SNP.

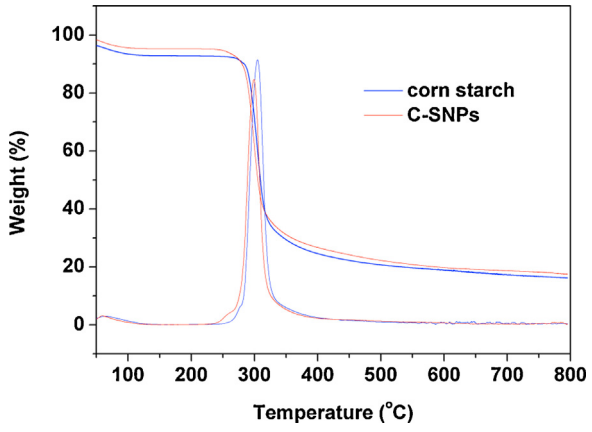

Fig. 7. TGA/DTG profiles of corn starch and corn starch-based SNPs (C-SNPs) hydrolyzed by $H_3PW_{12}O_{40}$.

structure of glucose units was stable during the whole hydrolysis process.

Fig. 7 shows the thermo-gravimetric analysis (TGA) and differential thermal gravity (DTG) curves for starch samples, which demonstrates the changes of thermal stability. For corn starch without hydrolysis, the main weight loss stage occurred in the range of 280–330 °C, and the maximum thermal degradation temperature

from DTG is approximately 291 °C. While, for SNPs, the main weight loss stage converted to the ranges of 270–320 °C and the maximum thermal degradation temperature from DTG decreased to 255 °C correspondingly. These results implied that not only the size of the particles but also the molecular weight of starch decreased during the hydrolysis process. A similar convert was also observed between waxy maize starch and waxy maize starch nanoparticles (W-SNPs) prepared by $H_3PW_{12}O_{40}$ treatment in Fig. S4, indicating the randomly break of either amorphous or crystalline region during the hydrolysis process.

4. Conclusions

In summary, this paper provides a facile way to prepare starch nanoparticles by polyoxometalates acid treatment. This method can efficiently reduce the hydrolysis time and enhance the productivity compared to the classical hydrolysis methods. There are no changes in the chemical structure of SNPs after hydrolysis procedure. Moreover, the crystallinity pattern is changed from A-type to amorphous. This special method can be used for all types of starch and exhibits extensively potential industrial applications for SNPs produce.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (Projects 50903012 and 51273037), Jilin Environmental Protection Bureau (201127), Jilin Science and Technology Bureau (International Cooperation Project 20120729, 20130206074GX), Jilin Human Resources and Social Security Bureau (201125020).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.06.040.

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