Food Chemistry 141 (2013) 1661–1666

Contents lists available at SciVerse ScienceDirect

Food Chemistry

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

# An attempt to cast light into starch nanocrystals preparation and cross-linking

Mehdi Jalali Jivan, Ashkan Madadlou *, Mohamadsaeed Yarmand

*Department of Food Science and Technology, University College of Agriculture & Natural Resources, University of Tehran, Karadj, Iran*

ARTICLE INFO

*Article history:*
Received 28 November 2012
Received in revised form 25 March 2013
Accepted 23 April 2013
Available online 3 May 2013

*Keywords:*
Acid hydrolysis
Cross-linking
Potato starch
Starch nanocrystals

ABSTRACT

Potato starch was hydrolyzed with 2.2 or 3.7 M hydrochloric acid in order to obtain the nanocrystals which afterwards were chemically cross-linked with sodium hexametaphosphate. The stronger acidity resulted in smaller nanocrystals with mean size of 48 nm in a shorter time. X-ray diffraction confirmed the dominant crystalline nature of particles and Fourier transform infrared spectroscopy suggested the presence of lower number of free hydroxyl groups in nanocrystals after cross-linking. Starch nanocrystals showed two distinctive differential scaning colorimetry endotherms at 26 and 125 °C, attributed to destruction of nanocrystals lattice and moblizing of each nanocrystal's structure, respectively. Cross-linking resulted in a tenacious spatial arrangement of nanocrystals, strengthening the crystals lattice against phase transitions induced by heating. Scanning electron microscopy images confirmed the particle size measured for nanocrystals by light scattering. Atomic force microscopy topographic images suggested that starch nanocrystals were originated from small amylopectin blocklets in granular assembly of starch.


## 1. Introduction

Native starch granules are composed of amorphous regions and crystalline blocklets having different diameters which depend on the botanical origin of starch and their location in the granule (Gallant, Bouche, & Baldwin, 1997). Starch hydrolysis by hydrochloric or sulphuric acid at sub-gelatinization temperatures causes preferential attack of acid molecules on the amorphous regions of the granule. This results in an acid-resistant crystals residue (Wang, Truong, & Wang, 2003) organized from platelet crystallites with 20–40 nm length and 15–30 nm width (Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). Because of the unique properties such as nanoscalar platelet morphology, the intrinsic rigidity, high crystallinity and low permeability, starch nanocrystals are considered convenient ingredients for the preparation of bioparticles. These particles may be used in widespread biomedical, biochemical and technological applications, as well as vehicles for carrying bioactive substances and nutraceuticals. Starch nanocrystals however tend to aggregate and settle down in aqueous solutions which limits their application in most biological and food systems. The hydroxyl groups at the reactive surface of nanocrystals become oxygen onions under alkaline conditions enabling them to cross-link the crystals with sodium hexametaphosphate through intra- and interester linkages. This results in water-dispersive starch nanocrystals (Ren, Jiang, Wang, Zhou, & Tong, 2012).

The literature on the structure of starch nanocrystals lacks information on the thermal behaviour and the topography of these crystals. In addition, information on the crystal changes that occur due to cross linking is missing. The objective of the present study was therefore to prepare and characterise the starch nanocrystals followed by lightening some features of water-dispersive cross-linked crystals.

## 2. Materials and methods

### 2.1. Materials

Native potato starch, 37% hydrochloric acid, sodium hexametaphosphate, sodium hydroxide and sodium hydrochloride were purchased from Merck (Darmstadt, Germany). All other chemicals were of analytical grade and used without further purification. Double distilled water was used throughout this work.

### 2.2. Starch nanocrystals preparation and modification

Starch nanocrystals were prepared following the method of Angellier, Choisnard, Molina-Boisseau, Ozil, and Dufresne (2004) with slight modification. Starch was dispersed (5% wt/wt) either in 2.2 or 3.7 M hydrochloric acid and incubated at 35 °C for up to 50 days while shaken at 120 rpm. At various time intervals, the solution was allowed to rest for 15 min and supernatant was centrifuged (Refrigerated Centrifuge 2 K 15, SIGMA Laborzentrifugen GmbH, Osterode am Harz, Germany) at 15,600g for 6 min.

* Corresponding author. Tel./fax: +98 26 32248804.
*E-mail address:* Ashkan.madadlou@gmail.com (A. Madadlou).

0308-8146/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodchem.2013.04.071

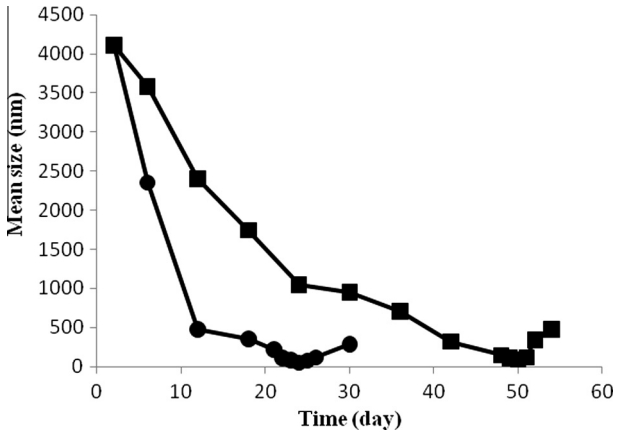


**Fig. 1.** Mean size of particles hydrolyzed with 2.2 M (■) or 3.7 M (●) hydrochloric acid as function of hydrolysis time.

The sediment was washed with double distilled water for several times and re-precipitated through centrifugation at 18,000*g* for 5 min. The neutralised starch nanocrystals were lyophilized as powder for further processing.

The method of Ren et al. (2012) with slight modifications was used to prepare the water-dispersive cross-linked starch nanocrystals. At first, nanocrystals suspension (30 mg/mL water) was ultrasonicated (D-78224 ultrasonic cleaner, Elma, Germany) at nominal power of 550 W for 2 min, followed by continuous stirring for 30 min to obtain a monophasic suspension. Then, 30 mg NaCl and 2.5 mg sodium hexametaphosphate (8 wt.% of starch nanocrystals) were added and pH of suspension was adjusted on 10.0. The cross-linking reaction was allowed to continue overnight at 35 °C while shaking at 1000 rpm. Subsequently, pH of dispersion was adjusted on 7.0. The water-dispersive nanocrystals when required were precipitated with centrifugation at 6000*g*, washed several times with water and oven dried at 50 °C.

### 2.3. Particle size measurement

The mean size of nanocrystals during hydrolysis was measured with a dynamic light scattering (Nano ZS, Brookhaven Instruments, Zeta Plus Particle Sizing, New York, NY, USA) photon correlation spectrometer. Samples were prepared by suspending 2 mg dry nanocrystal in 600 μL water followed by shaking at 1000 rpm for 2 min. Samples were read five times per measurement.

### 2.4. X-ray diffraction (XRD) pattern

The XRD patterns for starch and starch nanocrystals were obtained using an X-ray powder diffractometer (Xpert MPD, Philips, Amsterdam, The Netherlands) with Cu anode at 40 kV and 25 mA. The diffraction angle ranged from 6° to 50° with step-scan of 0.02° and count time of 2 s per step. Samples crystallinity was determined by plotting the peaks baseline on the diffractogram and calculating the area using the software spectrum viewer (Version 2.6). 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:

$$\text{Crystallinity percentage} = \left(\frac{\text{Area under the peaks}}{\text{Total curve area}}\right) \times 100 \qquad (1)$$

### 2.5. Fourier transform infrared spectroscopy (FTIR)

Starch, starch nanocrystals, and cross-linked nanocrystals were grinded together with potassium bromide (weight ratio 2:500) and pressed into disks for scanning with a FTIR spectrometer (PerkinElmer Spectrum one, Waltham, MA, USA). Samples were scanned at 4000–450 $cm^{-1}$ with resolution of 4 $cm^{-1}$.

### 2.6. Thermal analysis

Temperature-dependent behaviour of samples was analysed with a differential scanning calorimeter (DSC 6 MV1, PerkinElmer,

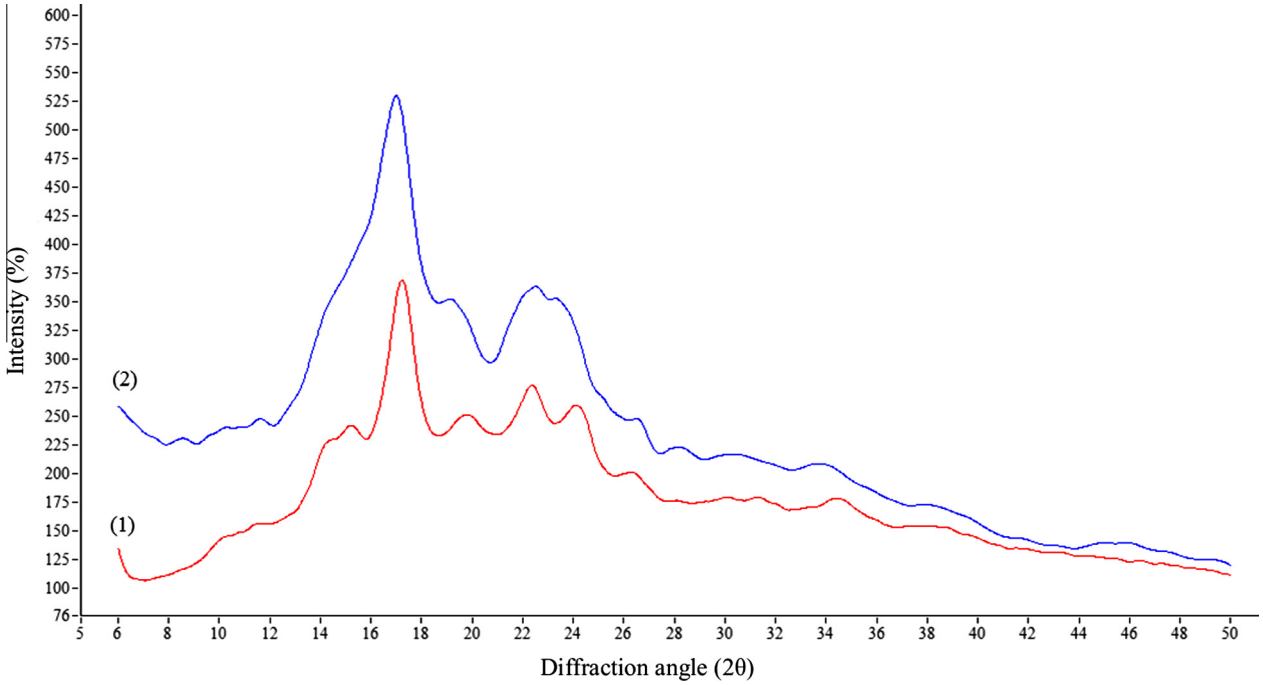


**Fig. 2.** X-ray diffraction patterns of potato native starch (1), and starch nanocrystals (2).