Food Chemistry 174 (2015) 97–103

Contents lists available at ScienceDirect

Food Chemistry

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

Isolation of micro- and nano-crystalline cellulose particles and fabrication of crystalline particles-loaded whey protein cold-set gel

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ARTICLE INFO

Article history:
Received 12 August 2014
Received in revised form 6 October 2014
Accepted 6 November 2014
Available online 15 November 2014

Keywords:
Cellulose
Nanocrystalline cellulose
Microcrystalline cellulose
Whey protein
Gel

ABSTRACT

Micro- and nano-crystalline cellulose (MCC and NCC, respectively) particles isolated from cellulose filter papers via acid digestion were characterised and loaded into a heat-denatured whey protein isolate (WPI) solution which was subsequently cold-set-gelled. Both the MCC and NCC particles were rod-shaped and had higher crystallinity degrees than had the cellulose source they were isolated from. The hydrodynamic diameter of NCC particles was ≈15 nm. Fourier transform infrared (FTIR) spectroscopy suggested more surface hydroxyl groups on the NCC than the MCC particles and complete digestion of hemicellulose on the cellulosic substrate by acid. MCC- and NCC-loaded WPI gel matrices were topographically less uniform and contained many more undulations in comparison to the crystal-free counterpart. It was found, using dynamic rheometry and penetration tests, that the crystal loading into WPI gels weakened the texture. Non-covalent interactions between the cellulose crystals and whey protein strands were proposed in the gel structure according to FTIR results.

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1. Introduction

Gelation is one the most important functional properties of whey proteins and is mainly attributed to β-lactoglobulin (Gezimati, Creamer, & Singh, 1997). Amongst the several methods known to induce whey protein gelation, the cold-set procedure is regarded with great enthusiasm as it provides a route for the formation of fine-stranded gels at ambient temperatures (Alting, Hamer, de Kruif, & Visschers, 2003). Cold-set gelation encompasses two distinctly separate steps. Initially, whey protein solutions are heated at pH values far from the proteins isoelectric point (pI ~ 5.1), and at low ionic strengths. This causes protein denaturation and the formation of tiny soluble aggregates. This causes the electrostatic repulsion amongst the proteins to be decreased (through pH manipulation and/or ionic strength elaboration), which results in protein aggregation. Finally a gel is formed (Ako, Nicolai, & Durand, 2010).

Cellulose, an abundant organic homopolymer, has a hierarchical architecture arising from the inter- and intra-molecular hydrogen bonding of glucan residues (Khandelwal & Windle, 2014). The glucan sub-units in cellulose assemble and merge into nanofibrils, with a highly ordered structure (Abdul Khalil, Bhat, & Ireana Yusra, 2012). Cellulose fibres, however, are not fully crystalline and have amorphous regions of a less ordered structure (Klemm, Heublein, Fink, & Bohn, 2005). Preferential hydrolysis of the amorphous domains in cellulose fibres with mineral acids, enzymes and microorganisms (and occasion accompaniment of mechanical disintegration), causes crystalline residues with various shapes, crystallinities and dimensions (Beck-Candanedo, Roman, & Gray, 2005). The most common method is acidic hydrolysis, as it is relatively inexpensive and provides highly crystalline products (Hanna, Biby, & Miladinov, 2001). Sulphuric acid-hydrolysed cellulose suspensions are highly stable colloids, owing to the sulphate-bearing hydroxyl groups that establish considerable electrostatic repulsion amongst cellulose-derived objects (Bondeson, Kvien, & Oksman, 2006). Nano-crystalline cellulose (NCC) particles are rod-like particles with a highly crystalline structure, high aspect ratio, large surface area, unique tensile strength (0.8–10 GPa), low density and high Young's modulus (100–170 GPa) (Habibi, Lucia, & Rojas, 2010). It can be used for the reinforcement of polymer composites and enhancement of their thermal stability and mechanical properties. Another cellulose-derived product, microcrystalline cellulose (MCC) is a white, tasteless, odourless

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http://dx.doi.org/10.1016/j.foodchem.2014.11.038
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and crystalline powder. It is used as a suspension-stabilizer, thickener, a filler or binder in tablets and a flow characteristics-modifier in various formulations (Adel, Abd El-Wahab, Ibrahim, & Al-Shemy, 2011; Wang, Shang, Song, & Lee, 2010).

Incorporation of carbohydrate polymers into the composition of cold-set whey protein gels results in mixed gels that exhibit different structural, mechanical and sensorial characteristics compared with the gels made solely of proteins (Bertrand & Turgeon, 2007). There is no report in the literature on the characteristics of cellulose crystalline particles-loaded whey protein gels. We anticipated that loading of cellulose crystals into a heat-denatured whey protein solution would impact the textural and functional characteristics of the subsequently prepared cold-set gel. Therefore, microcrystalline and nanocrystalline cellulose particles were produced, characterised and incorporated into the gel matrix, followed by examination of the gel characteristics.

2. Materials and methods

2.1. Materials

Whey protein isolate (WPI), with at least an 88% protein content, was a kind gift from Arla Food Ingredients (Vibyi, Denmark). Whatman® filter paper number 1 (98% alpha cellulose) was supplied by Whatman International Ltd. (Maidstone, England). Sulphuric acid, sodium hydroxide, calcium chloride, glucono-δ-lactone and sodium azide were purchased from Merck (Darmstadt, Germany).

2.2. Preparation of MCC and NCC particles

Micro- and nano-crystalline cellulose particles were prepared through the acid hydrolysis procedure. For preparation of NCC particles, filter papers cut into small pieces (2 g) were hydrolysed with 50 ml of sulphuric acid (64%) at 45 °C for 75 min under continuous stirring at 200 rpm. The cellulose hydrolysate was centrifuged (D-37520 osterode am Harz, Germany) at 9400×*g* for 10 min, and the precipitate was washed with 2 M NaOH. This was followed by repeated centrifugation and washing with distilled water, several times, until the supernatant became turbid (Bondeson et al., 2006). The supernatant, which contained NCC, was either vacuum-dried at 60 °C and 180 mmHg or stored at 4 °C for the same-day analysis.

For preparation of MCC, filter paper pieces (2 g) were hydrolysed with 50 ml of sulphuric acid (64%) at 45 °C for 5 min while being stirred at 200 rpm. Subsequently, large amounts of water were added into the reaction beaker to stop the hydrolysis. Then the suspension was neutralized with 15 M NaOH and agitated harshly (T 18 digital ULTRA-TURRAX, IKA, Staufen, Germany) at 24,000 rpm for 5 min. The ground suspension was centrifuged (D-78532, Hettich, Tuttlingen, Germany) at 1520×*g* for 10 min, and the precipitate was washed with distilled water. The centrifugation and washing steps were repeated several times to eliminate any residues of chemical substances (Ilindra & Dhake, 2008). The sediment, which contained MCC particles, was vacuum-dried at 60 °C and 180 mmHg.

2.3. Gel preparation

WPI powder was dissolved in distilled water (80 mg ml^{-1}) containing sodium azide (0.1 mg ml^{-1}) under continuous stirring at 500 rpm for 60 min. The solution was kept at 4 °C for 12 h to allow for complete hydration and then heated at 80 °C for 15 min, followed by rapid cooling with tap water. The solution was then injected with $CaCl_2$ (4 mM) and glucono-δ-lactone (6.7 mg ml^{-1}) and stored at 4 °C for 16 h (Britten & Giroux, 2001). In preparation of MCC- and NCC-loaded gels, the heat-treated and cooled WPI solution was enriched with either MCC or NCC particles (10 mg ml^{-1}) before gelation induction.

2.4. Hydrodynamic size measurement of NCC and MCC particles

The length and diameter of NCC and MCC particles in suspension were measured with photon correlation spectroscopy method using a dynamic light scattering particle size analyser (ZetaPALS, Brookhaven Instruments Co., NY, USA). The suspensions were diluted with distilled water to 0.5 mg ml^{-1}, and subjected to duplicate size measurements with 5 readings for each.

2.5. Fourier transform infrared (FTIR) spectroscopy

The cellulose filter paper, MCC particles, NCC particles, and gel powders were vacuum-dried at 50 °C and 180 mmHg. The dry samples were mixed with potassium bromide, pressed into disks and scanned with a Perkin Elmer FTIR spectrometer (Perkin Elmer Co., MA, USA). The IR spectroscopic analysis was performed from 450 to 4500 cm^{-1} with resolution of 4 cm^{-1}.

2.6. Morphological and topographical features of MCC particles, NCC particles and gels

Atomic force microscopy (AFM) was used to characterise the topography of the gels, as well as, that of NCC particles. The AFM imaging was carried out by a Nanowizard II microscope (JPK, Germany) in the intermittent contact mode. NCC samples were diluted with distilled water to 100 μg ml^{-1} and then dripped onto a plastic lamella and air-dried before microscopic imaging. Gel specimens were cut from the interior of the samples, using a razor blade, and then fixed within glutaraldehyde (2.5%) for 1 h. Subsequently, the specimens were dehydrated by immersing in a series of aqueous ethanol solutions with increasing alcohol concentration (40%, 60%, 70%, 90% and 100%) and finally were placed on the lamella and air-dried before microscopic imaging.

Scanning electron microscopy (SEM) (KYKY-EM3200, china), with an accelerating voltage of 26 kV, was employed to capture the morphological features of MCC particles. MCC powders were coated with gold to submit them electrically conductive.

2.7. X-ray diffraction (XRD)

The crystallinity degree of cellulose filter papers, NCC and MCC was measured through X-ray diffraction (XRD) analysis, carried out by using a PW3040/60 X'Pert diffractometer (Philips, Netherlands) with Cu Kα radiation (λ = 0.154056 nm). Operating voltage and filament current were 40 kV and 30 mA, respectively. The samples were scanned in the interval $5^\circ \leqslant 2\theta \leqslant 30^\circ$ using a step size of 0.02°.

The crystallinity index (CrI) of samples was calculated, using the following equation (Eq. (1)) (Segal, Creely, Martin, & Conrad, 1959):

$$\mathrm{CrI} = \left(\frac{I - I'}{I}\right) \times 100\% \quad (1)$$

where I is the height of the peak at 2θ = 22.6°, corresponding to the crystalline and amorphous fraction and I' is the height measured at 2θ = 18°, corresponding to the amorphous fraction.

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