Journal of Food Engineering 128 (2014) 96–102

Contents lists available at ScienceDirect

Journal of Food Engineering

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

High resolution imaging of native wheat and potato starch granules based on local mechanical contrast

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ARTICLE INFO

Article history:
Received 21 October 2013
Received in revised form 6 December 2013
Accepted 20 December 2013
Available online 28 December 2013

Keywords:
Starch granules
Atomic force microscopy
Growth rings
Morphology
Stiffness
Friction

ABSTRACT

We studied the nano-scale properties of dry native starch granules of wheat and potato by atomic force microscopy. Whereas at the macroscale the mechanical behavior of starch powders is known, its origin at sub-granule level has still to be understood. We observed fine morphological structures, such as the growth rings and blocklet domains, with minor differences between the two starches. The granules, embedded in resins with known stiffness, were analyzed with lateral-force, force-distance and force-modulation microscopy. Integer granules exhibited a similar friction coefficient to the tip, decreased with respect to the embedding resin, without occurrence of stick-slip. The compressive modulus measured was also similar for both starch types (~1.4 GPa in indentation and ~2.0 GPa in dynamic mode), with slightly higher values for potato starch. On sectioned granules, the effect of aging in air likely due to moisture produced in both starches a strong reduction in apparent modulus (~0.2 GPa).

1. Introduction

Starch contributes to the textural properties of many native (e.g. potatoes, rice, maize) and processed foods (e.g. wheat-paste and sugars), and has notable industrial applications as a thickener, colloidal stabilizer, gelling and water retention agent and adhesive (e.g. in paper industry and biodegradable bag fabrication) (BeMiller and Whistler, 2009; Wawro and Kazimierczak, 2008; Ha and Broecker, 2002; Lim and Jane 1992). Starches from various botanical sources have received attention, in relation to their different structural and physico-chemical properties (Singh et al., 2003; Molenda et al., 2006). These properties affect the quality of starch as a raw material, determining its performance in the respective application both directly and indirectly, via the effects of processing, handling and storage subsequent to its extraction. It is therefore a primary goal to reach a better understanding of the correlation between the morphology and structure of starch powders, and the associated properties (Stasiak et al., 2011; Schroeter and Hobelsberger, 1992; Desse et al., 2010; Cornuéjols and Pérez, 2010; Szymońska et al., 2009; Seetharaman and Bertoft, 2012; Landillon et al., 2008). At the same time, the locally different properties inside starch granules, for example their mechanical response to external stress, can be used to image granule substructures at high resolution, down to the nanoscale, by means of appropriate imaging techniques. Atomic force microscopy (AFM) is actually one imaging device based on probe-sample force interaction, and thus appears to be the most appropriate technique for pursuing both goals (Juszczak et al., 2003; Ohtani et al., 2000; An et al., 2008; Baldwin et al., 1997, 1998; Park et al., 2011; Ridout et al., 2002, 2003; Szymońska and Krok, 2003; Tang and Copeland 2007; Ayoub et al., 2006; Sujka and Jerzy, 2009). Since AFM does not require invasive or time-consuming sample treatment, this technique can be used to monitor and control the starch granules quality and stability before and possibly during their use, if exposed to the surface of films or other objects including them.

In this work we focused on native wheat and potato starches (supposed moisture content, m.c. ~20%), which were considered both at powder level, i.e. collective scale of a large quantities of particles, and at micro/nano-scale level of single particles (i.e. individual granules). In this respect, we addressed both (i) granule morphology, which was characterized by measuring the particle shape and size distribution, and the sub-particle domain features; and (ii) granule mechanical properties, which were determined by AFM indentation/compression and friction force measurements.

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0260-8774/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jfoodeng.2013.12.023

2. Materials and methods

2.1. Materials

Native starch powders were from Cargill (USA) for wheat starch, and from Melvit (Poland) for potato starch. On the shelf aging time of the both powders at the moment of use was in the order of few months.

For optical microscope imaging, the specimens were prepared by simply spreading the powder on glass microscope slides. For AFM operation, in order to provide the specimen with the stability required for physical probe contact, the granules were embedded in a polymer according to different recipes depending on the needs for the specific operating mode. For low-resolution indentation measurements, a faster and simpler procedure was adopted, consisting in dispersing the granules (50 mg/mL) in a 40 wt.% Toluene solution of <Mw>=950 kDpolymethyl methacrylate (PMMA, Sigma-Aldrich, Italy), and the suspension was spin-coated at 3000 or 500 rpm on glass slides. After drying, the granules were laterally trapped in a solid PMMA film of approximately 300 nm or 1.8 μm thickness, respectively, as measured by AFM across scratches manually made on the glass substrate with wooden tooth-stick. For high-resolution imaging, a high-end procedure was adopted, in which the granules were dispersed into a pure high-quality dual-component resin of common use in electron microscopy, namely Epon 812 (Taab, England).

2.2. Methods

2.2.1. Microscopic imaging

Granule imaging was carried out using optical microscopy in transmission at the powder level, and by AFM in tapping mode at the individual granule level. Optical images were acquired on an Eclipse 80i microscope (Nikon, Japan) at 400× magnification in ambient air, saved in digital format (1600 × 1200 pixels) with NIL software (Nikon, Japan), and subsequently examined for grain analysis in Igor Pro 6.22 (Wavemetrics, USA) to determine the granule size. Several images (at least 6) from different regions of each sample were acquired and analyzed to obtain sufficient statistics.

AFM (MFP-3D, Asylum Research, USA) allowed to detect granule feature details. For standard imaging the instrument was used in tapping mode in air, typically with gold coated silicon cantilevers of type NSG10 (NT-MDT, Russia). For all the other measurements we worked in contact mode, either with CSG10 probes (NT-MDT) for lateral force measurement, or with probes NSG01, NSG10 or even NSG20 (all NT-MDT) for nano-indentation, and with NCHR (nanoWorld, Switzerland) for force modulation. All probes had standard tip size (i.e. no super-sharp tips), with typical nominal diameter of 10–20 nm.

2.2.2. Micro/nano-mechanical tests

At the macro-scale, the stress–strain parameters of the powders have been determined previously in the literature, typically by uniaxial compression and shear testing, exhibiting a good degree of repeatability and thus shown to be reliable (Molenda et al., 2006; Stasiak et al., 2011). At the micro/nano scale, AFM in air was used to detect and quantify locally the stiffness contrast of granule sections after cutting with a diamond blade microtome. AFM measurements were carried out in lateral-force microscopy (LFM) of Contact mode, to measure the friction force on the samples; in force–volume (FV) mode, to measure arrays of force–distance curves on the surface and be able to quantitatively map local adhesion and elastic modulus; and in force-modulation (FM), to detect stiffness contrast at high resolution.

3. Results and discussion

3.1. Macroscale morphology

As it can be seen in Fig. 1, it appears that potato starch granules are larger than wheat starch ones. We opted for standard optical imaging rather than the often used scanning electron microscopy (SEM) since the granules are large enough not to require ultra-high resolution. Also, optical microscopy allows for native operating conditions, without the use of high vacuum chamber, which could alter the granule size or require sample dehydration (Sujka and Jerzy 2009).

Both types of granules in our images presented a widespread distribution, mainly bimodal, with quite differently sized particles. The results of grain analysis on several optical images like in Fig. 1 ($N \geqslant 6$) resulted in granule size (mean ± one standard deviation) of 35 ± 20 and 17 ± 13 μm for potato and wheat powder, respectively, when modeling the systems with single normal distributions. Even

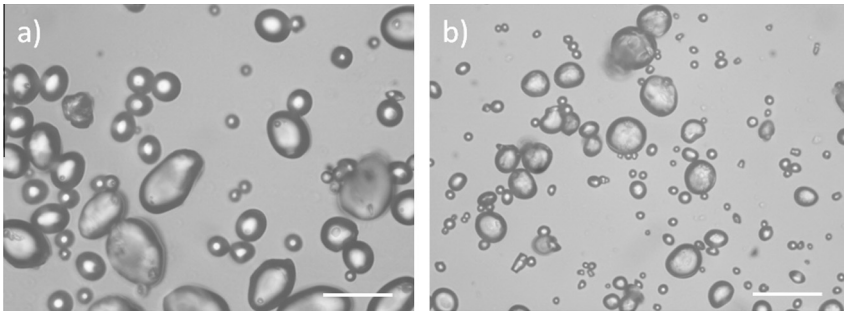

Fig. 1. Optical images in transmission of starch granules spread on a glass slide (scale bar 50 μm): (a) potato and (b) wheat.

Table 1
Size and surface area of granules of potato and wheat starch powders.

Starch type	Size values from optical images		Size distribution from SEM (Molenda et al., 2006)		Specific surface area (m^2/g) (Molenda et al., 2006)
	Mean (μm)	Standard deviation (μm)	d(0.5) (μm)	Span [d(0.9)-d(0.1)]/d(0.5)	
Potato	35	20	41.5	1.22	0.56
Wheat	17	13	20.2	1.10	0.32