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Structural characterization and tribological evaluation of quince seed mucilage

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ABSTRACT

The mucilage, originating from the seeds of quince fruit was characterized as a potential bio-inspired water-based lubricant. The mucilage consists mainly of fine cellulose nanofibrils and charged hemicelluloses whose structure and properties were characterized here by atomic force microscopy (AFM) and tribological Pin-On-Disc (POD) experiments. The hemicellulose-decorated nanocellulose fibrils were 3.0 ± 0.7 nm in thickness, had a very large aspect ratio and also had a tendency to self-align when dried on mica surface. Macroscale tribological tests showed that the mucilage was able to reduce the coefficient of friction of polyethylene/stainless steel contact to values below 0.03. Thus, we show that quince mucilage is a native nanocellulose material with a notable ability to lower friction.

1. Introduction

Sustainability is a major driving force for development of better processes and more efficient utilization of the existing resources. Many processes and systems developed in Nature have been optimized to meet very specialized needs and their detailed study may also help in finding new solutions for present technological problems. For instance, impressive mechanical properties of mother of pearl, wood and bone have inspired many scientists in development of tough and light-weight materials using the same principles [1–3]. The natural material which inspired this work, is carbohydrate-containing mucilage extracted from the seeds of a quince fruit. We present the characterization of this strongly hydrating and self-aligned material that consists mainly of water, cellulose nanofibrils [1,4] and hemicelluloses such as glucoronoxylans [5–7]. The mucilage shows several beneficial properties such as strong swelling and slippery appearance, probably due to hydration of carbohydrate structures that has been observed to enhance lubrication of some other water-based systems [8,9]. The structure of the mucilage in its native state is fascinating; the cellulose nanofibrils stored on the epidermal layer of the seeds are readily dispersible in water, have a very narrow size distribution, and have a tendency to self-assemble into helicoidal organization, a true cholesteric liquid crystal state [10,11]. The reasons why these fibrils are packed into such strongly chiral assemblies into the cell walls remains yet unclear, but chirality of hemicellulose has been proposed as the cause for the assembly [12].

Quince fruit and especially the mucilage from its seeds, has raised interest among engineers and plant scientists. Since the late 19th century, there have been several suggestions for innovative uses of quince mucilage in applications varying all the way from hair tonic to metal polish [13–15]. Most of the recent interest in quince mucilage is however concentrated on the water-soluble polysaccharides it contains. There are several reports on separation and purification of the special glucuronoxylan from the quince seed mucilage [6,7]. The origin of the self-alignment of the fibrils and the interplay of cellulose and the glucuronoxylans has thus far been one of the most topical research areas related to quince mucilage. However, for cellulose research society, fruits have shown their potential also as a source of high quality nanofibrillar cellulosic materials [16] that combine exceptionally good mechanical properties and all the benefits of cellulose [17]. Materials based on nanofibrillated cellulose (NFC, also known as microfibrillated cellulose MFC) show especially great potential when the alignment of the nanofibrils can be controlled [18]. As a renewable material, NFC is extremely attractive as a building component for new materials and has been employed in many studies aiming at better composite structures [1,19].

Here, physicochemical and tribological characterization of quince mucilage is presented. The results from AFM studies show that the fibrils are very monodisperse and able to self-align in

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native state (as-extracted), but also after mild purification. Slippery appearance being one of the natural properties of the mucilage, its lubrication abilities were studied by using macroscopic tribology measurements. The mucilage was able to reduce the friction of the polyethylene/stainless steel contact to a much lower level than pure water. Thus, quince seed mucilage and other nanomaterials like it, may provide a solution for efficient water-based lubrication in technologically relevant environment, which has thus far, been an unsolved problem. Many attempts to resolve the issue of water-based lubricants are based on characterization and mimicking of the synovial lubrication, which is one of the most long-lasting and versatile system for low friction found in Nature [20–22]. As a carbohydrate-based fibrillar material, quince mucilage may have similarities to the cartilage and other species found in the synovial joints, such as the water-absorbing proteoglycans and the hydrogel structure supported by the collagen fibrils. The lubrication of the synovial joint is a combination of mixed lubrication mechanisms involving several immobilized and soluble active species combined with self-healing abilities. Studies on certain individual species extracted from the synovial system or synthetic molecules mimicking their essential features including hyaluronan [23] and bottle-brush polymers [24] have shown promising results but the overall performance of the natural system has not been obtained. All of these features may appear impossible to capture in a synthetic system, but understanding the most essential ones that are responsible for the high performance may help us to solve technological problems and to replace oil-based lubrication systems.

2. Materials and methods

2.1. Lubricants

Quince seeds (*Cydonia oblonga*) were separated from fresh fruit, dried in ambient and stored in dry before use. Mucilage was extracted from quince seeds by immersing seeds into fresh water. A certain amount of seeds were weighed and kept in ~40 mg mL^{-1} concentration in deionized water (Milli-Q Plus Pf/Milli RO 30 Plus, US) overnight. The solution was decanted and extraction was repeated once more. The extract contained some solid impurities originating from the seeds, which were removed by a gentle centrifugation and filtration through three layers of cotton gauze. The mucilage was stored in +4 °C. The dry mass of the mucilage, 0.55 m%, was determined by lyophilization. The mucilage could also be lyophilized and redispersed in deionized water to gain a higher concentration.

Washing of the mucilage was carried out by ethanol as described earlier [7]. Concentrated mucilage was dispersed in three volumes of ethanol and centrifuged. The excess ethanol was removed and the mucilage was dialyzed and freeze-dried. A part of the mucilage was freeze-dried without dialysis and used in the lubrication studies.

Reference measurements were carried out using deionized water (Merck Millipore, US) and 1 M sodium chloride (Sigma-Aldrich, US) solution as the lubricant.

2.2. Total enzymatic hydrolysis of quince seed mucilage and the analysis of sugar content

Hydrolysis of ethanol-washed and freeze-dried mucilage suspension was performed to determine its sugar contents [25]. A mixture of four different commercial enzyme was used (Econase (cellulase, Roehm Enzyme Finland) 20 mL, Ecopulp X-200 (xylanase, Roehm Enzyme Finland) 50 mL, Gamanase (mannanase, Novo, Denmark) 100 mL and Novozyme 188 (β-glucosidase, Novo, Denmark) 50 mL). Before use, the mixture was diluted with 200 mL of 50 mM sodium acetate buffer pH 5 and desalted using a Biogel P-6 gel (Bio-Rad, UK) column using the same buffer. The total activity of the mixture was 29.8 FPU (filter paper units) mL^{-1}. The load of enzyme used for total hydrolysis of 50 mg dried mucilage was 50 FPU g^{-1} and the reaction was allowed to proceed for 48 h at 40 °C (stirring 250 rpm), after which an additional 10 FPU g^{-1} amount of enzyme cocktail was added and the reaction continued for another 18 h to ensure total hydrolysis of the sample. The mixture was cleared by centrifugation (4000 rpm, 10 min, Eppendorf, Germany) and boiled for 5 min to inactivate enzymes. Monosaccharides were determined by chromatography (DIONEX ISC-5000, CarboPac PA20, Thermo Scientific, US). The dry weight of the first pellet from the total hydrolysis reaction was also determined.

2.3. Atomic force microscopy

Morphology of quince mucilage was studied by atomic force microscopy. A NanoScope IIIa Multimode (E-scanner, J-scanner, Bruker, Germany) AFM instrument was used with an NSCI5/AlBS cantilever with less than 10 nm tip radius (μMASCH, US). All images were recorded in tapping mode in air with scan rates of 0.5–1 Hz. The damping ratio was around 0.7–0.85. All images were flattened to remove possible tilts in the image data. Some images were further flattened by filtering out non-directional noise.

The samples were prepared by placing a droplet of diluted (<1 g L^{-1}) quince mucilage on a mica substrate (Electron Microscopy Sciences, US), which was then let dry in ambient conditions. Mica was cleaved just before sample preparation.

2.4. Epifluorescence microscopy

Surface of the quince seed was studied by an epifluorescence microscope (Olympus BX-50, Japan). Fluorescence imaging was carried out either based on samples autofluorescence or a fluorescent dye, Calcofluor (Scandinavian Brewery Laboratory Ltd., Denmark), which is specific towards cellulose.

2.5. Circular translation pin-on-disc tests

Tribological properties of quince mucilage in polyethylene (PE)/stainless steel contact were characterized in a flat-on-flat configuration by a high load friction circular translation pin-on-disc (CTPOD) device designed and constructed at TKK/Aalto University and described in detail elsewhere [26]. Briefly, in the HL-Friction CTPOD device the pin translates along a circular track of 10 mm diameter relative to the disc. The sliding speed is constant, 31.4 mm/s. Such a low speed ensures that a boundary lubrication mechanism prevails. In the CTPOD device, the pin translates along a circular track of 10 mm diameter relative to the disk. Neither the pin nor the disk rotates. In this way, the direction of sliding relative to the pin changes continually, and uniaxial grooving by wear can be avoided. The disc holder is supported by low-friction ball bearings. The rotation of the disc is prevented by a load cell and a lever arm. From the load signal, the frictional torque and coefficient of friction (COF) are calculated. In the present study, the pin was a flat-ended cylinder with a diameter of 9 mm and length of 12 mm. It was made from ultra-high molecular weight polyethylene (UHMWPE), type GUR 1050, which is a tough and chemically inert material. The disc was made from austenitic stainless steel 316 (ASTM F 138), polished to a surface roughness R_a of 0.01 μm. Its hardness is 200 HB. The contact was flat-on-flat and the nominal contact pressure was 4.4 MPa. The load was constant 277 N. The test duration varied from 5–24 h, and the tests were run at room temperature. The specimens were surrounded