Errata
(Updated 13th of January 2020)

Composites from nanocellulose and water-soluble polysaccharides – interfacial tailoring from nanoscopic to macroscopic level

Jessica Lucenius PhD thesis

Section 3.2, page 41. missing subsection "Colloidal probe microscopy" and two references related to it.

Colloidal probe microscopy (CPM)
CPM was used to determine the surface interactions both between CNF and the polysaccharide as well as between cellulose surfaces after adsorption of the modified polysaccharides. In CPM a colloidal sphere (in this case cellulose) is glued to a tipless AFM cantilever and the forces between the probe and a flat surface as a function of relative separation are measured upon approach and retraction (Ducker, Senden et al. 1991).

AFM force and friction measurements were done in contact mode in liquid utilizing the colloidal probe technique (CPM). The samples were prepared by spin coating the crystal with CNF solution and then adsorbing the polysaccharide using QCM-D as explained above or, alternatively, the polysaccharide was adsorbed *in situ* in the AFM liquid cell and waiting for 50 min to stabilize. In samples adsorbed *in situ* in AFM the surface forces were measured three times: 1) in buffer before polysaccharide adsorption on cellulose surfaces; 2) in polysaccharide solutions after letting the polysaccharides adsorb on the cellulose surfaces; and 3) after rinsing with only buffer.

Lateral and vertical spring constants of CSC12 and CSC38 cantilevers (MikroMasch, Estonia) were determined from the thermal vibrations measured in air using Nanoscope 8.15 software and calculated with Sader equations (Green, Lioe et al. 2004). The values for vertical and lateral spring constants were 0.032-0.104 N/m and 1.0×10^{-9}-2.45×10^{-9} Nm/rad, respectively.

After the calibration of cantilevers, colloidal probes were prepared by gluing cellulose spheres with a radius of 14-19 ± 0.1 µm to the tipless cantilever using a micro manipulator (Narishinge, Japan). The optical adhesive (Norland Products Inc., Cranbury, USA) was hardened using UV-light. The dimensions of probe and glued cellulose sphere were measured with a Leica DM400 optical microscope (Leica Microsystems, GMbH, Germany).

During measurements the samples were in liquid sample holder (AFM picoforce scanner holder, Bruker Corporation, MA, USA). The measurement procedure is described in detail by (Ralston, Larson et al. 2005)

The cellulose surfaces with or without adsorbed polysaccharides were approached at 2 µm/s speed and separated in 12 mM sodium phosphate buffer. The surface forces were related to the vertical deflection of the cantilever. The force was calculated from the deflection of the cantilever and the vertical spring constant and it was normalized by the radius of the probe

The friction forces were obtained from the lateral twist of the cantilever and the lateral spring constant. When measuring friction force, the cellulose colloidal probe slid over the flat substrate at 10 µm/s speed with different applied loads. The friction was measured from at least three places of the sample in 12 mM sodium phosphate buffer. Sequentially different loads were applied (11 different loads, loading and unloading) and each friction datum was the average of 10 friction loops.

AFM normal force measurements were performed before and after friction measurement. At least eleven force curves were registered from each position to gain good statistics. Representative curves are presented. The force and friction data were analyzed using ForceIT-, FrictionIT- and Matlab R1014b software's.

GREEN, C.P., LIOE, H., CLEVELAND, J.P., PROKSCH, R., MULVANEY, P. and SADER, J.E., 2004. Normal and torsional spring constants of atomic force microscope cantilevers. *Review of Scientific Instruments,* **75**(6), pp. 1988-1996.

RALSTON, J., LARSON, I., RUTLAND, M.W., FEILER, A.A. and KLEIJN, M., 2005. Atomic force microscopy and direct surface force measurements (IUPAC technical report). *Pure and applied chemistry,* **77**(12), pp. 2149-2170.

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