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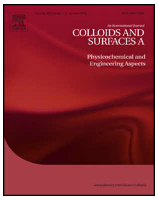

Surface forces and friction between non-polar surfaces coated by temperature-responsive methylcellulose

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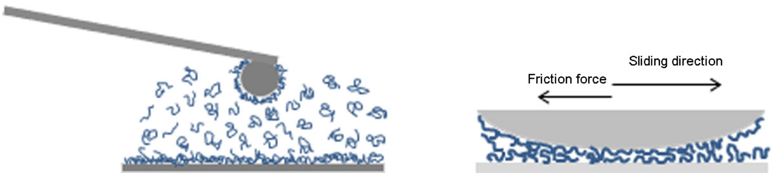
HIGHLIGHTS

- Studies of modified cellulose adsorbed at hydrophobic surfaces.
- Normal and frictional forces between adsorbed layers.
- Weak hydrophobic anchor and shear-induced wear.
- Self-healing properties with free polymers in solution.

GRAPHICAL ABSTRACT



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ABSTRACT

Methylcellulose is a heterogeneous polymer that exposes both methyl groups and –OH-groups to the solution, and the solvent quality of water for methylcellulose deceases with increasing temperature. In bulk solution this leads to aggregation into fibrils at high temperatures. In this report we address how temperature affects adsorbed layers of methylcellulose on hydrophobized silica surfaces in contact with an aqueous methylcellulose solution. The layers were imaged using PeakForce tapping mode atomic force microscopy, in order to determine how the additional adsorption that occurs with increasing temperature affects the layer structure. Surface force and friction measurements were carried out using the AFM colloidal probe method. The data demonstrate that the normal surface forces were rather insensitive to temperature, whereas the friction forces changed significantly with increasing temperature. At low loads the friction increases with increasing temperature, whereas at high loads the reverse is observed. These findings are discussed in terms of how the worsening of the solvent condition affects the aggregation state in the adsorbed layer, and the polymer-surface affinity.

1. Introduction

The colloidal stability of dispersions can be controlled by electrostatic forces or due to steric interactions between adsorbed polymer layers, where the latter is preferred in high ionic strength solutions. Of particular interest is to be able to control the dispersion stability by using polymers that are responsive to the environmental conditions, such as temperature [1,2].

For many types of polymer, water becomes a less good solvent with increasing temperature. This is the case, for instance, for polymers like poly(*N*-isopropylacrylamide) (PNIPAAm) [3–5], poly(2-isopropyl-2-oxazoline) [6,7], poly(2-(dimethylamino)ethyl methacrylate [1], poly(ethylene oxide) (PEO) [8,9], poly(propylene oxide) (PPO) [10–13], ethyl(hydroxyethyl)cellulose (EHEC) [14], methylcellulose (MC) [15] and hydroxypropylmethylcellulose (HPMC) [16]. The responsive properties of these types of polymers have inspired attempts to use them in controlled delivery applications. For instance, the cellulose ethers have received interest from this perspective [16,17], even though their main application may be as temperature-responsive viscosity modifiers in e.g. paints.

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Surfaces are present in all of the above application areas, and it is thus of high interest to understand adsorption properties as well as interactions between surfaces coated with cellulose ethers, as they approach each other and as they slide past each other. Only a few reports can be found on this topic. The surface forces acting between hydrophilic [18] and hydrophobic surfaces [19,20] coated with EHEC has been described in a few studies, but to our knowledge no investigation on interactions between surfaces coated with methylcellulose has been reported. Likewise, no report of the nanotribological properties of surfaces coated with cellulose ethers exists.

This study has been initiated to gain better understanding of interactions within and between methylcellulose layers adsorbed to non-polar surfaces. To this end we have used the AFM colloidal probe technique to investigate surface forces and friction forces. Here we aimed at determining if attractive surface forces were observed at the aggregation temperature observed in solution, or if enhanced steric stabilization was facilitated due to preferential orientations of hydrophobic and hydrophilic groups within the layer. A further aim was to elucidate the lubricating ability of the methylcellulose for non-polar surfaces in water, with particular emphasis on temperature effects on the friction force and the load bearing capacity. We have further used AFM PeakForce imaging to elucidate if aggregation occurs within adsorbed methylcellulose layers with increasing temperature.

2. Materials and methods

Freeze-dried samples of methylcellulose were obtained from Akzo Nobel, Stenungsund, Sweden. It will be referred to as $M_{1.6}C$ in this report in order to highlight that the methoxy degree of substitution per anhydroglucose unit is 1.6. The structure of methylcellulose is illustrated in Fig. 1. The polymer was purified from eventual by-products by first dissolving it in water to a concentration of around 1 wt%. The solution was subsequently centrifuged at ca. 7000 × *g* for 60 min to remove water insoluble material. Water soluble impurities such as salt and glycols were removed through dialysis of the supernatants against excess of Millipore water for 7 days. A Spectra/Por® membrane tubing with M_w cut-off of 6–8000 g/mole was used for the dialysis. The Millipore water in the water tank was exchanged once a day. After the dialysis the polymers were freeze-dried. The molecular weight, 530 kDa, was obtained from size exclusion chromatography at 30 °C with a mobile phase of 0.04 M sodium acetate and 0.02% sodium azide at pH 6. Refractive index, light scattering (at 7° and 90°) and viscosity measurements were employed in the analysis.

Solutions were prepared by dispersing the freeze-dried polymers in water at high temperature (80–90 °C) under stirring, and then cooling to room temperature under continued stirring. Finally, the solutions were stirred in an ice bath for at least 30 min.

2.1. Substrates

A silicon substrate with a 100-nm thick thermally grown silica layer (WaferNet GmbH, Eching, Germany) with a typical rms roughness below 1 nm was used as the flat surface in AFM colloidal probe force measurements. The colloidal probe was a spherical silica bead (SS06N, Bangs Laboratories Inc.) with a diameter of 7 μm. All surfaces, except for the colloidal probe, were cleaned for 5 min in 80 °C 5:1:1 (w/w/w) H_2O:NH_3:H_2O_2, rinsed extensively with Milli-Q water, then cleaned for 5 min in 80 °C 5:1:1 (w/w/w) H_2O:HCl:H_2O_2, and rinsed with Milli-Q water again.

Hydrophobic substrates were obtained by silanization by exposing the surfaces to the vapour of (3,3-dimethylbutyl)dimethylchlorosilane (DDS) in a desiccator overnight. The hydrophobized surfaces were then rinsed with water and stored in ethanol. The contact angle of water was approximately 100°.

2.2. Atomic force microscopy—Peak force imaging

Topographical images of hydrophobized surfaces with an adsorbed polymer layer and polymers present in solution were recorded using an atomic force microscope (AFM) Nanoscope Multimode V (Bruker) operating in PeakForce mode [21–24] using ScanAsyst, silicon nitride cantilevers (ScanAsyst Air, Bruker probes) and a fluid cell with in- and outlets allowing for solvent exchange. The temperature was set by use of a thermal application controller attached to a Bioheater element (Bruker) mounted under the sample. The temperature on the sample surface was calibrated by an external thermocouple and controlled with an accuracy of ±1 °C. Hydrophobic substrates were prepared as described above and the experiments were conducted as follows: The cell was filled with 40 ppm aqueous $M_{1.6}C$ solution and the system was left for 30 min to allow adsorption at 25 °C before the surface was imaged. Next, the temperature was increased to first 40 °C and then 50 °C. At both temperatures images were acquired 30 min after the temperature had stabilized to allow the system to equilibrate. The imaging was carried out using a peak force setpoint of 1 nN.

2.3. Atomic force microscope—Colloidal probe measurements

Friction and normal force measurements were performed in a fused silica liquid cell using an atomic force microscope, Multimode Nanoscope III Pico Force (Bruker) and the colloidal probe technique [25,26]. A silica particle with diameter of approximately 7 μm were attached to the end of a tipless cantilever (CSC12, F-lever, Mikromasch, Estonia) with the aid of an Ependorf Micromanipulator 5171, a Nikon Optiphot 100S reflection microscope, and a small amount of high-temperature melting epoxy glue (Shell Epikote 1009). The size of the particles was determined using a Nikon Optiphot 100S reflection microscope, employing image analysis with National Instrument Vision Assistant 8.0. Before particle attachment, the values of the normal and torsional spring constants were determined by the Sader method [27,28]. The type of cantilever was chosen such that the maximum force of interest was not leading to a cantilever deflection outside the linear region of the detector [29]. The lateral photodetector sensitivity was calibrated using the method of tilting the AFM head as suggested by Pettersson et al. [30].

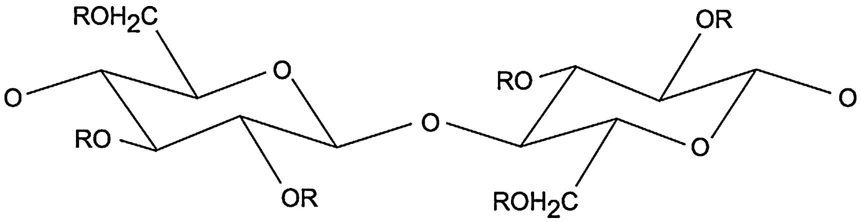

Fig. 1. Structure of methylcellulose, where R=H or R=CH_3.