Journal of Colloid and Interface Science 364 (2011) 351–358

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Surface and friction forces between grafted polysaccharide layers in the absence and presence of surfactant

Cathy E. McNamee[a,*], Shinpei Yamamoto[b], Michael Kappl[c], Hans-Jürgen Butt[c], Ko Higashitani[d], Andra Dėdinaitė[e,f], Per M. Claesson[e,f]

[a] Shinshu University, Tokida 3-15-1, Ueda-shi, Nagano-ken 386-8567, Japan
[b] Institute for Integrated Cell-Material Sciences, Kyoto University, Yoshida-Ushinomiyacho, Sakyo-ku, Kyoto 606-8501, Japan
[c] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[d] Department of Chemical Engineering, Kyoto University – Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[e] Department of Chemistry, Surface and Corrosion Science, Royal Institute of Technology, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden
[f] Institute for Surface Chemistry, YKI, P.O. Box 5607, SE-114 86 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 1 July 2011
Accepted 25 August 2011
Available online 1 September 2011

Keywords:
Dextran
Silane coupling agent
Polymer layer
Silica
Friction
Surface forces
Adhesion
Tethered polysaccharide
AFM
Ellipsometry

ABSTRACT

We analyzed the interaction between chemically grafted polysaccharide layers in aqueous solutions. To fabricate such layers, an end-terminated dextran silane coupling agent was synthesized and the polydextran was grafted to oxidized silicon wafers and to silica particles. This resulted in the formation of a 28 nm thick layer (in air) and a grafted amount of 40 mg/m^2 as determined by ellipsometry. The physical properties of the grafted layer were investigated in aqueous solutions by atomic force microscope imaging and colloidal probe force measurements. Surface and friction forces were measured between one bare and one polydextran coated silica surface. A notable feature was a bridging attraction due to affinity between dextran and the silica surface. Surface interactions and friction forces were also investigated between two surfaces coated with grafted polydextran. Repulsive forces were predominant, but nevertheless a high friction force was observed. The repulsive forces were enhanced by addition of sodium dodecyl sulfate (SDS) that associates with the tethered polydextran layers. SDS also decreased the friction force. Our data suggests that energy dissipation due to shear-induced structural changes within the grafted layer is of prime importance for the high friction forces observed, in particular deformation of protrusions in the surface layer.

1. Introduction

Knowledge and understanding of physico-chemical and mechanical properties of surfaces are needed for designing materials for optimum performance, e.g. for uses as biomaterials. An implant surface should be non-toxic, display biocompatibility to neighboring cells, and possess pseudo-physiological mechanical properties [1]. For example, materials to be used in orthopaedic/periodontal applications as hard tissue substitutes should be tough but flexible [2]. Depending on the intended use, other requirements also need to be fulfilled. Biomaterials to be used in tissue engineering applications, such as the scaffolds used in regenerative medicine to promote cell growth on implants, only serve as a temporary matrix and should therefore be biodegradable [1,6]. The coating of a material that is to be used in a joint area must be resistant enough that it will not be eroded by the combined action of shear and load [3,4]. It should also display enough lubricity to allow the two surfaces to move against one another without a large friction [5,4], which would otherwise impair the relative motion of the constituents in the joint. Thus, in this case important material properties are hardness, elasticity, low wear and lubricity.

Polysaccharides are becoming increasingly popular as biomaterials for use in the body. This is due to their low toxicity, low cost, and large-scale availability [1,6–8]. Physically adsorbed layers of polysaccharides have been shown to provide a low friction coefficient when two such modified surfaces are sheared against each other [9–11]. This suggests that polysaccharides can be used for producing films with favorable lubricating properties. However, physically adsorbed polymers most often have a limited load bearing capacity since they are relatively easily removed under the combined action of load and shear.

This limitation may be overcome by chemically attaching the polysaccharide, which has the potential to achieve high lubrication ability and high load bearing capacity even though wear of the film can be a problem during prolonged sliding.

A film consisting of chemically attached polysaccharides would allow the thickness and density of the film to be controlled by choosing the polysaccharide type, molecular weight, and reactant

---

* Corresponding author.
E-mail address: mcnamee@shinshu-u.ac.jp (C.E. McNamee).

0021-9797/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2011.08.065

concentration. The lubricating ability of a film is affected by the presence of other species in the surrounding fluid. For instance, the addition of a surfactant, sodium dodecyl sulfate, between two surfaces coated with a mucin layer has been shown to decrease the friction significantly [9]. Therefore, naturally occurring compounds, such as phospholipids and proteins, may affect the lubrication of a grafted polysaccharide layer and enhance the lubrication ability of the manufactured biomaterial. For other applications, this may also be achieved by adding man-made surfactants.

We have synthesized an end-terminated dextran silane coupling agent (*DEX-si*) and chemically attached it to silica surfaces. The physical properties of *DEX-si* modified silica surfaces were studied with an atomic force microscope (AFM) in order to obtain information on layer morphology, and surface and friction forces. The effect of introducing a surfactant into the surrounding aqueous solution on the physico-chemical properties of the surface bound polymer layer was studied by using different concentrations of sodium dodecyl sulfate (SDS).

2. Experimental

2.1. Materials

Dextran (*DEX*, molecular weight (M_w = 20 kg/mol), GR grade, Nacalai Tesque, Japan) was used without further purification. The polydispersity (M_w/M_n) of the dextran sample was determined to be 1.42 by employing poly(ethyleneglycol)-calibrated GPC (Shodex GPC-101, SHOWA DENKO, Japan) using water as the eluent. The radius of gyration (R_g) of a typical polymer in our *DEX* sample in water was estimated to be about 5 nm, using literature data on R_g versus M_w [12]. The contour length of a typical dextran chain can be estimated to be 32 nm from the M_w and the length of one maltose unit, 0.52 ± 0.03 nm [13].

Potassium hydroxide (GR grade, Nacalai Tesque, Japan), ethanol (GR grade, Nacalai Tesque, Japan), dimethylsulfoxide (DMSO, GR grade, Nacalai Tesque, Japan), 3-aminopropyltriethoxysilane (GR grade, Nacalai Tesque, Japan), iodine (99.9% purity, Wako Pure Chemical, Japan), and sodium dodecyl sulfate (SDS, 95% purity, Wako, Japan) were used without further purification. Naturally oxidized silicon wafers (Silicon Quest INT., USA) were used as the substrates. The water used was distilled and de-ionized to give a resistivity of 18.2 MΩ cm and a total organic content of <5 ppm. The non-modified and *DEX-si* modified silica particles had a radius of 3.4 μm (Bangs Laboratory, USA) and 3 μm (micromer, micromod Partikeltechnologie GmbH, Rostock, Germany), respectively.

Dextran having a lactonized end (Dextran-Lactone) was prepared according to reported methods (Fig. 1) [14,15]. Briefly, 0.1 M iodine in water and 0.8 M potassium hydroxide in water were added slowly to a 0.01 M dextran aqueous solution. The reaction mixture was stirred at ambient temperature for 24 h. It was then placed in a cellulose dialyzer tubing (M_w cut-off, 14 000 g/mol) and purified by dialysis. The solution was subsequently passed through a column packed with a cation-exchange resin (Amberlite IR-120), lyophilized, and a white powder of Dextran-Lactone was obtained. Next, 3-aminopropyltriethoxysilane (0.2 g) was added to a solution of Dextran-Lactone (1.5 g) in DMSO (15 mL) and ethanol (7.5 mL), corresponding to concentrations of 0.9 mM and 0.075 mM for 3-aminopropyltriethoxysilane and Dextran-Lactone, respectively. The mixture was then stirred for 20 h at 60 °C. As the reaction solution was concentrated, a large amount of acetone was subsequently added. Finally, the white precipitate was collected and dried in vacuo to give the dextran-silane-coupling agent (*DEX-si*). The structure of the compound is shown in Fig. 1.

The silica wafers, cleaned by solvents washing (acetone, ethanol, and then water) and then by plasma treatment (PDC-002, Harrick Plama, Ithaka, NY)), and silica particles were rendered fully hydroxylated [16] by placing them in a glass container and adding 3 mL of a solution containing 17.5 mL methanol (high purity, Wako, Japan) and 1.39 g of 28% ammonium hydroxide solution (Wako, Japan) for 2 h, after which a freshly prepared solution of 0.1 g *DEX-si* in 1 mL water was added drop-wise to the wafer/particle containing solution. This solution was then left for 16 h, after which the substrate/particles were washed with copious amounts of water and ethanol to remove non-chemically adsorbed material. The presence of the silane coupling agent facilitates chemical grafting to the surface and also results in chemical binding between the *Dex-si* molecules. The end result is a firmly attached and partly cross-linked dextran layer on the surface. The grafted layer on flat silica surfaces was characterized by ellipsometry (M-2000U, J.A. Woolam, USA) measurements in air.

The colloid probes for the force and friction measurements were prepared by evaporating the solvent from a small volume of the particle dispersion, and then attaching a single particle to a cantilever by using an XYZ micromanipulator and an epoxy resin (rapid araldite, Vantico, Showa polymer company, Tokyo, Japan). Tipless V-shaped gold-plated Si_3N_4 cantilevers (normal spring constant 0.12 N m^{-1} and 0.58 N m^{-1}, NP-S, Veeco NanoProbe™ Tips, USA) and rectangular cantilevers (tip-less, non-Al coated, nominal spring constant 0.08 N m^{-1}, CSC12/tipless/noAl, MikroMasch, USA) were used for the force and friction measurements, respectively.

2.2. Methods

2.2.1. Atomic force microscopy

The substrates were imaged in aqueous solutions with an AFM (Digital Instruments NanoScope III Multimode, Santa Barbara, USA) in tapping mode by using a tapping mode fluid cell and Si_3N_4 cantilevers (NP-S, Veeco NanoProbe™ Tips, USA) with reflective gold coating. The V-shaped cantilevers were 196 μm long and 23 μm wide, and had a nominal spring constant of 0.06 m^{-1}, a resonant frequency of 31 kHz (in air), and square pyramidal tips with an end-tip radius of curvature in the range 10–40 nm. The imaging scan rate was 2 Hz, and the scan size was 1 × 1 μm^2. Both the resolution of data points per line and the number of lines were 512. All images are unmodified (i.e., no filtering was applied), except for a 1st order flattening along the scan lines. The images shown for each condition are representative of the images made from at

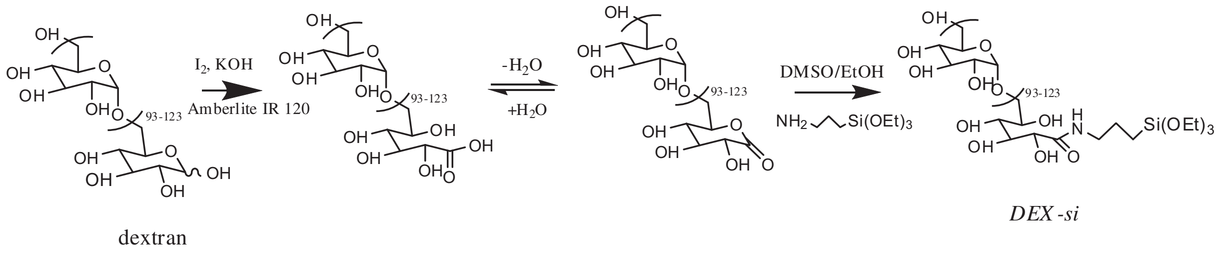

Fig. 1. Schematic diagram showing the synthesis of dextran-triethoxy silane (*DEX-si*).