

Surface morphology of cellulose films prepared by spin coating on silicon oxide substrates pretreated with cationic polyelectrolyte

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Abstract

Flat cellulose films were prepared and morphologically modified by spin coating a cellulose/*N*-methylmorpholine-*N*-oxide/ H_2O solution onto silicon oxide substrates pre-coated with a cationic polyelectrolyte. Spin-coated cellulose films were allowed to stably form on the silicon oxide substrates by pretreatment with either polydiallyldimethylammonium chloride (PDADMAC) or polyvinylamine (PVAm). The film surfaces obtained were analyzed by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). AFM topographical images of the cellulose film surfaces showed a different morphology depending on the underlying polymer, where PVAm pretreatment brought about an anisotropic surface topology. These results suggest that the specific attraction acting at the cellulose/polymer interface influences both the film formation and surface morphology of the cellulose layer. Differences in the solvent used to precipitate cellulose caused variations in the surface roughness by affecting the cellulose separation behavior. The morphological features of spin-coated cellulose film surfaces could be altered to some extent by these film preparation techniques.

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1. Introduction

Cellulose, a linear (1,4)- β -D-glucan, is the major structural polysaccharide that makes up the cell walls of higher plants, and the most abundant, renewable, biodegradable and derivatizable biopolymer [1–3]. Cellulose and its derivatives have been widely used in a diverse array of applications, such as fibers, films, plastics, composites, paper and wood-based products [2,3]. Cellulose-related materials have recently been applied as membranes for hemodialysis, chiral isomer separation and calorie-free fat substitutes [3]. There is an increasing interest in the use of cellulosic materials, and in particular, cellulose surfaces. These surfaces have attracted much attention from the point of the physicochemical aspects involved in the phenomena at the interfaces of cellulose/cellulose, cellulose/various media and cellulose/chemicals in

the papermaking chemistry [4,5], pharmaceutical industry [6], among others. However, a detailed investigation with regard to such interfacial phenomena is very difficult to achieve using native celluloses (e.g. wood, pulp, cotton fiber), because of certain complicated and uncontrollable properties, such as their generally bulky and fibrous shape, the presence of co-existing materials (hemicellulose and lignin), their rough and porous morphology, and the various crystalline states in which they exist. Consequently, a smooth cellulose film with controlled structure and characteristics is eagerly anticipated as a model substance for elucidating cellulosic-related matters.

The preparation of model cellulose films on flat substrates has been carried out in a variety of ways: e.g. cellulose film formation and vapor-phase regeneration resulting from spin coating trimethylsilylcellulose (TMSC) [7], Langmuir–Blodgett deposition [8,9], and film precipitation through the removal of coordinated amines from a spin-coated cellulose film prepared from a cellulose/amine oxide solution [10,11]. New types of smooth cellulose surfaces also have been reported: cellulose I model surface prepared from colloidal dispersions of

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cellulose I nanocrystals [12] and ultra-thin film consisting of nano-sized cellulose patches by spin-coating a diluted TMSC solution [13]. These film preparation methods all provided smooth cellulose surfaces; however, the surface morphology of the film surfaces was not sufficiently discussed. The surface morphology (e.g. roughness over a micrometer-scale area) of both cellulose-based products, and several polymers, was correlated with the fundamental and practical characteristics of these materials [14]. We have previously reported that the partial modification of hydrophilic cellulose surface with hydrophobic dots covering ca. 20% of the surface resulted in nearly as high contact angle (ca. 103°) as the surface fully covered (ca. 113°) [15]. The surface morphology involved in the chemical composition, roughness, electrical charges and other physicochemical properties is of great important factors affecting wettability, swellability, chemical sensitivity and bio-affinity [10,11,15–19]. Hence, the morphological control of the cellulose model surfaces would contribute greatly to the cellulose material design aimed at understanding cellulosic interfaces.

In this study, the surface morphology of spin-coated cellulose films was modified by controlling the film formation and separation processes. The pretreatment of silicon oxide substrates with cationic polyelectrolytes, and the subsequent deposition of cellulose films using various solvents in the cellulose/amine oxide direct solvent system were investigated. The cellulose films obtained were characterized by X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Factors influencing the surface morphology of cellulose films are discussed.

2. Experimental

2.1. Materials

Commercial fibrous cellulose powder (CF1; Whatman International Ltd.) and single crystal silicon wafers (NIRACO Co. Ltd.) were used as the starting cellulose sample and flat substrates, respectively. Polydiallyldimethylammonium chloride (PDADMAC, molecular weight (Mw): ca. 3×10^5 ; Mw/Mn: ca. 2.3; charge density (CD): 5.5 meq./g; Aldrich Co. Ltd.) was obtained as a commercial product and used as received. Polyvinylamine (PVAm, Mw: ca. 1×10^6 ; Mw/Mn: ca. 2.4; CD: 3.8 meq./g) was prepared by the partial hydrolysis of synthesized polyvinylformamide [20]. The chemical structures of the cationic polymers used are illustrated in Fig. 1.

2.2. Dissolution of cellulose

N-Methylmorpholine-*N*-oxide (NMMO)/H₂O with a 4:1 ratio by weight was melted above 80°C in a silicone oil bath. CF1 cellulose powder was poured into the NMMO/H₂O solvent and stirred at 105°C for 30 min (cellulose concentration: 2.0%). The obtained homogenous cellulose/NMMO/H₂O solution was diluted with dimethylsulfoxide (DMSO) in order to lower the viscosity of the cellulose solution (DMSO concentration: ca. 18%) [10].

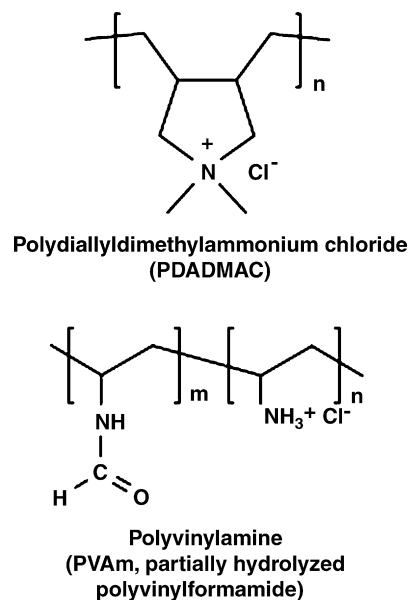


Fig. 1. Chemical structures of the cationic polymers used for the surface pretreatment of silicon oxide substrates.

2.3. Preparation of cellulose films

A silicon wafer was cut into small pieces (ca. 10 mm × 10 mm) and pre-rinsed with acetone and deionized water. Clean wafer pieces were then oxidized in an electric furnace at 1000°C for 30 min, affording an upper layer of silicon oxide of ca. 60 nm thickness. The silicon oxide surface is regarded as being negatively charged [10]. The silicon oxide wafer was soaked in the cationic polymer solution (0.1% PDADMAC or 0.1% PVAm) at room temperature for 30 min, followed by rinsing with deionized water and dried under inert nitrogen conditions.

A piece of cationic polymer-pretreated wafer was secured on a spin coater (ABLE Co. Ltd.) under vacuum, and a designated volume of cellulose solution was deposited on the wafer, which was immediately spin-coated at 2500 rpm for 10 s. The cellulose film was precipitated in various poor solvents for cellulose deposition; deionized water, ethanol, ethanol/deionized water (1/1 ratio v/v), DMSO or DMSO/deionized water (1/1), at room temperature for 1 h. The cellulose film obtained was washed with deionized water for 3 h, and dried at room temperature. Cast-coated film as a control was prepared on the PVAm-pretreated substrate by simply casting a designated volume of cellulose solution and then by immersion into deionized water (1 h), followed by rinsing with deionized water (3 h) and dried at room temperature.

2.4. Analyses

The degrees of polymerization (DP) of the cellulose samples were determined by viscometry [21]. A cellulose fraction was obtained by precipitation with deionized water. The intrinsic viscosity [η] of the cellulose molecules dissolved in 0.5 M cupri-ethylenediamine solution was measured using an Ostwald-type viscometer at 25°C , and the DP values were

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