

Interaction forces between cellulose microspheres and ultrathin cellulose films monitored by colloidal probe microscopy—effect of wet strength agents

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Abstract

Colloidal probe microscopy was employed to study forces between cellulose surfaces upon addition of a series of cationic copolymers in aqueous solution, as model compounds for wet strength agents. The content of quaternary ammonium groups and primary amines was systematically varied in the cationic polymers, to distinguish between the importance of electrostatic and H-bonding effects. Cellulose microspheres were glued at the apex of tipless microfabricated cantilevers and used as colloidal probes. Ultra thin cellulose films and cellulose fibres were employed as model surfaces. The cellulose films of a thickness of about 5 nm were spin-coated from cellulose solution onto silicon substrates. The root-mean-square-roughness (RMS) was 0.3–0.8 nm. The cationic model polymers were compared to Servamine, a polymer employed as standard wet strength resin in papermaking industries. Force versus separation measurements showed a detailed picture of adhesion and contact breaking. Relatively strong adhesion of the order of 0.3 mJ/m² was observed with Servamine within a range of approximately 10 nm. At larger distances weak bond breaking and elastic chain pulling were identified. When approaching the surface one to two small jump-in's possibly related to strong binding of Servamine and subsequent attraction could be found in the case of Servamine. In contrast, all the model copolymers showed only a weak adhesion of 8–30 μJ/m², i.e., an order of magnitude less than that of Servamine and subsequent elastic rupture domains. The contour length, persistence length and characteristic rupture distances were calculated by means of applying the WLC model. Measurements against cellulose fibres obtained from the production process proved the relevance of the model systems.

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1. Introduction

Different kinds of chemicals are added to improve specific properties of the paper. Most importantly, fillers are added to the paper to enhance the optical properties and the printability of the paper, but typically, they decrease paper strength. Therefore strength-increasing additives are needed.

Starch is one of the most frequently used dry strength additives, but synthetic polymers are used, too. They improve the paper strength by taking part in the H-bonding between the fibres, and by forming gels. The latter consists of polyelectrolyte complexes [1]. When paper is exposed to water, the fibres start to swell and the water penetrates into the pores. In the presence of water, a fibre–water H-bond may replace the fibre–fibre bond. To counteract the resulting loss of stability at least partially, so-called wet strength agents are employed. Paper is said to have a good wet strength when it holds for 15% of the strength of dry paper. Wet strength ad-

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ditives are most commonly composed of cationic polymers containing reactive groups, or resins, that can react in different ways when adsorbing onto the fibres. The resins can react with themselves and create a network around the fibres, they can react covalently with the fibres or they can penetrate into the pores of the cellulose. The real mechanism is often assumed to be a combination of these three effects ((c) of Ref. [1]). Traditionally, paper strength is improved by adsorbing cationic polymers on the anionic cellulose fibres.

Most of the current understanding concerning the interaction of polymers with fibres and their effect on suspension rheology is inferred empirically. Macroscopic rheological techniques [2–5] are applied to probe interaction between fibres and wet strength additives ((a) and (b) of Ref. [1]).

Forces acting between two slowly approaching cellulose surfaces were first measured by Neuman et al. [6] on regenerated, spin-casted cellulose films and recently by Holmberg et al. [7] on Langmuir–Blodgett (LB) cellulose films, using the surface force apparatus (SFA) [8]. For the spin-casted films strong steric repulsion was observed and interpreted as the interaction of molecularly fibrillated cellulose surfaces. A weak steric repulsion was found for LB cellulose films. In a study of cellulose–cellulose interactions using colloidal probe microscopy (CPM) [9,10] Rutland et al. [11] found no evidence for steric repulsion. Recently, Carambassis and Rutland [12] measured steric forces whose extent depended on the electrolyte type and concentration.

Despite the importance of polymer-mediated interactions in papermaking, there are only a few studies in which these interactions were measured directly. Holmberg et al. [13] studied the interaction of a silica particle and a LB cellulose surface in the presence of poly[2-(propionyloxy)ethyl]trimethylammonium chloride (PCMA). An attractive bridging force appeared but the adhesive force was less than that of pure cellulose interacting with silica. In a study of cellulose–chitosan interactions using the SFA, Holmberg et al. [7] found a strong attractive force that was attributed to polymer bridging.

More recently, S. Zauscher et al. [14] examined normal forces between model cellulose surfaces in aqueous electrolyte solutions in the presence of polyelectrolytes by CPM. Forces between surfaces in absence of soluble polymer are dominated by electrostatic repulsion, and at large probe speeds by hydrodynamic forces. In presence of soluble sodium carboxymethyl celluloses or cationic polyacrylamide, repulsive interactions appear at large surface separations. Noticeable adhesion has not been recorded.

Studies of interactions between cellulose surfaces on the molecular level in the presence of soluble polymer are still lacking. A better understanding of the interaction between cellulose fibres on a molecular–mechanical level may help to design novel wet strength compounds with improved properties regarding paper and tissue functionality. The purpose of the present study is to investigate and compare a series of cationic, water soluble polymers and co-polymers with a variable content of quaternary ammonium groups and pri-

mary amines, with standard wet strengthening agents for paper from fibres. This comparison shall improve the understanding of the interaction of paper wet strengthening agents, and evaluate the relative importance of different binding effects, such as electrostatic, H-bonding or covalent binding. Colloidal probe microscopy measurements provide also details of the mechanical properties of individual polymers under an applied external load. This may help to bridge the gap between macroscopic paper and tissue properties, such as strength, softness on one hand and molecular mechanics on the other hand. Colloidal probe microscopy measurements were therefore performed using polycation-coated microspheres of cellulose and ultrathin spin-coated cellulose films as model surfaces.

2. Materials and methods

2.1. Materials

Native dried cellulose microparticles (pearls) [15] of 20–30 μm diameter were provided by the FhG-IAP and used as colloidal probes without further modification. Poly(amide amine) epichlorohydrin resin (PAE) termed as Servamine KCZ 14 with a viscosity of 10–50 mPa s and a pH of 3–4 was purchased from Servo Delden BV, Delden, Netherlands, and cellulose fibres were obtained from SCA. Both were used without further purification and in the same concentration as usually used in papermaking industry for direct comparison. The cationic polymers (see Table 1) were synthesized by free radical copolymerization of the appropriate amounts of diallyldimethylammonium chloride with vinylformamide [16], and subsequent hydrolysis of the amide to the primary amine group by refluxing the precursor polymer in 2 M HCl, in analogy to an established literature procedure ((c) of Ref. [16]).

Ultrathin cellulose films were obtained by spin coating of dissolved cellulose from solution (0.1%) onto Si wafer [17]. The wafers were cleaned by the RCA method [18]. Single cellulose fibres, Avicel derived from Sigma–Aldrich, are adsorbed from solution onto glass microscope slides.

2.2. Methods

2.2.1. Attachment and characterization of cellulose microspheres to microfabricated cantilevers

Cellulose microspheres were attached with epoxy glue (UHU Plus Endfest 300, Germany) to the free end of the microfabricated V-shaped tipless silicon nitride cantilever (Digital Instruments, length = 200 μm , nominal spring constant $k = 0.12$ N/m) or rectangular shaped cantilever (ULTRASHARP, non contact silicon cantilever CSC12 from Silicon-MDT, Ltd.) using a micromanipulator (Transferman NK2 from Eppendorf). Fig. 1 shows typical scanning electron microscope (SEM, EM 900 electron microscope, Zeiss, Germany) images of microspheres attached at the end of the

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