



Surface forces in lignocellulosic systems

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ARTICLE INFO

Available online 25 September 2016

Keywords:

Surface forces
Cellulose
Lignocellulosics
Hemicellulose
Cellulose surfaces
Interactions
Friction forces

ABSTRACT

Lignocellulosics, i.e., cellulose, lignin and hemicelluloses, are natural renewable polymers of high technological interest. The properties of products based on these polymers are largely determined by the forces at their interfaces. This review summarizes the main findings related to surface interactions relevant for papermaking and describes how the interest in novel, high performance renewable materials has changed the focus of the research to nanocellulosic materials. Areas of interest that need further work are also outlined.

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1. Introduction

Lignocellulosics is a term that generally describes the main components of most plants, i.e. cellulose, hemicelluloses and lignin. Cellulose is the most abundant of these polymers. Cellulose fibres are widely used for the fabrication of paper, paper board, textiles, and composites. Hemicelluloses are important due to their role in the cell wall and the fact that they are not completely removed from the pulp fibres before their use. Hemicelluloses have also been investigated for the production of renewable composites. Lignin has traditionally been burned for energy, but there is a growing interest to find new applications for this abundant aromatic polymer. With the need to decrease our use of fossil resources, lignocellulosics are gaining a renewed interest and the research focus is shifting from traditional papermaking to e.g. development of renewable packaging materials, light weight strong composites, and materials for biomedical applications [1–3]. The properties of those materials are governed by the surface forces between their components. Understanding the forces in more detail is essential not only for a proper characterization of the materials, but also for the design of new functional materials and for the optimization of technological processes.

Some of the first direct surface force measurements between cellulose surfaces were performed using the interferometric surface force apparatus (SFA) developed by Israelachvili and coworkers [4,5]. The SFA allows the measurement of forces between surfaces mounted in crossed-cylinder geometry as a function of their separation. The absolute value of separation is precisely determined, but transparent and smooth surfaces are required, which in practice limits the experiments to mica or modified mica substrates. The atomic force microscope

(AFM) has also been extensively used to study surface forces in lignocellulosic systems. Initially developed to obtain high resolution images of substrates [6], soon the potential of the AFM for force measurements was recognized and exploited, especially after the introduction of the colloidal probe technique [7]. Typically, the interaction forces between a spherical microparticle and a flat substrate or between two spherical microparticles are measured in AFM force experiments.

In this review we summarize the main findings obtained from direct surface force measurements of lignocellulosics and describe how the research field has changed focus from papermaking to composites, biomedical and new materials. We also give an outlook into what we envision will be future interests.

2. Direct measurement of surface forces relevant for paper technology

2.1. Forces between model cellulose surfaces: effect of pH, ionic strength, surface charge and cellulose crystallinity

The interest in fundamental understanding of the phenomena taking place in paper technology (papermaking, paper coating, paper recycling) has fostered many studies of surface forces in lignocellulosic systems. The first attempt to measure the interaction forces between cellulose surfaces was made by Neuman et al. in 1993 using the SFA [8]. This was a pioneering work that included an impressive amount of systems relevant for papermaking, like cellulose in air and water, xylan in aqueous media, and sodium polyacrylate in the presence of Ca^{2+} ions, and was a great inspiration for future research. In their experiments, Neuman et al. used cellulose films prepared by spin-coating cellulose dissolved in trifluoroacetic acid onto mica substrates. Those films were, however, rather rough and unstable, and that affected some of their conclusions. Neuman et al. observed a very long-ranged repulsion, typical for polyelectrolyte brushes, between the cellulose

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surfaces in water, and they proposed a model for the cellulose surface as consisting of “molecular fibrils”, or dangling tails, protruding into the solution. This model was not fully supported by later research using more stable and well defined cellulose substrates.

Due to the drawbacks of the cellulose substrates used by Neuman et al. [8], two different approaches were concurrently applied to gain further understanding of the interactions in cellulosic systems. Holmberg et al. prepared model surfaces of pure, regenerated cellulose by Langmuir–Blodgett (LB) deposition of trimethylsilyl cellulose on hydrophobized mica followed by desilylation in a humid HCl atmosphere [9]. They extensively characterized the cellulose films with respect to wetting, topography, roughness, thickness, refractive index and chemical composition using the Wilhelmy plate method, AFM, ellipsometry and XPS. Holmberg et al. also estimated the Hamaker constant for cellulose across air or water, and those values were later confirmed by more thorough ellipsometry measurements [10]. The films were very stable and smooth, and reproducible results were obtained. In contrast to Neuman et al. the range of repulsion in aqueous media was only tens, not hundreds of nanometres. Since the range of repulsion was shorter than expected for electrostatic double layer forces at the electrolyte concentration used, they concluded that the cellulose was uncharged at the conditions of the experiments (pH about 6). Simultaneously, Rutland et al. measured the surface forces between two cellulose spheres, applying for the first time the AFM colloidal probe technique to study the interaction between cellulose surfaces [11]. They found that the forces were well described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [12,13], with some additional steric repulsion observed at short separations, and they concluded that the cellulose surfaces were weakly charged.

The effect of the pH and the ionic strength on the surface forces between cellulose substrates was also studied using both SFA and AFM [14,15]. The larger number of surface charged groups (deprotonated carboxyl groups) upon an increase in pH provoked a stronger and longer range repulsion between the surfaces. An increase in ionic strength, in contrast, reduced the double layer repulsion, in agreement with DLVO theory, and screened the electrostatic interaction between the outermost cellulose chains, causing the collapse of the external dangling tails and, consequently, a reduction in the electrosteric repulsion –note that the term “electrosteric” indicates a combination of steric and double layer repulsions when charged chains from the surfaces come into contact– (Fig. 1) [15]. Similar trends were observed with cellulose LB films using SFA, but steric forces dominated the interaction in that case [14]. Zauscher and Klingenberg studied the surface forces between regenerated cellulose surfaces using the colloidal probe technique and observed a similar effect of the ionic strength [16]. However, no evidence of cellulose dangling tails was observed in their experiments. On the other hand, Notley et al. were able to detect for the first time van der Waals attraction between cellulose surfaces at pH 3.5, when the protonation of the carboxyl groups prevented double layer repulsion and probably decreased the swelling of the cellulose surfaces [17].

The cellulose samples used in those early experiments were weakly anionic and mainly amorphous, with the exception of LB cellulose layers and cellulose films spin-coated from N-methylmorpholine oxide (NMMO) solution, which had a degree of crystallinity (cellulose II) around 60% [18]. The charge was due to deprotonation of carboxylic acid groups and thus pH dependent. Qualitatively, similar forces were observed. The smaller contact area provides better detection of weak double layer forces in AFM experiments, while steric forces seem to dominate the SFA measurements.

The force measurements set strict requirements on the cellulose substrates that can be used, while real pulp fibres have a very complex surface chemistry and morphology. Thus, much attention has been centred on developing more relevant cellulose model films as described in previous reviews [19,20]. The charge of pulp fibres is known to have a significant effect on dewatering and interactions with additives during papermaking. Using the AFM colloidal probe technique, Notley

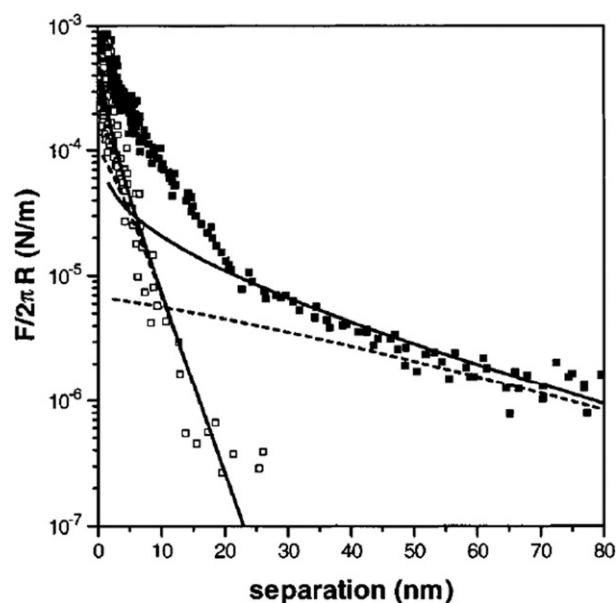


Fig. 1. Normalized force curves between two cellulose spheres in solutions of 0.1 mM (■) and 10 mM KBr (□). The solid and dashed lines correspond to DLVO fits for double layer interaction at constant surface charge and constant surface potential, respectively. [Reprinted with permission from Carambassis and Rutland, Langmuir 1999;15:5584–90, Copyright 1999 American Chemical Society.]

addressed the effect of the surface charge on the interaction between an amorphous cellulose microsphere and carboxymethylated cellulose films with different degrees of substitution of carboxyl groups on the cellulose fibres [21]. Electrical double layer forces arose at pH 8.5 which were higher in magnitude and longer in range as the surface charge of the cellulose films increased and the ionic strength of the solution decreased, as expected from DLVO theory. Van der Waals attraction was observed when the carboxyl groups were protonated at pH 3.5. Using the same technique, Ahola et al. measured the surface forces between cellulose microspheres and films of cellulose nanofibrils (CNF) with low and high surface charge [22]. The CNF films were prepared by spin-coating aqueous CNF dispersions on silica substrates using a cationic polyelectrolyte as an anchoring layer. Both steric and electrical double layer forces were observed in the interaction force curves, which were affected by the pH, the ionic strength and the surface charge of CNF. The double layer repulsion was stronger for highly charged CNF at high pH and low salt concentration, in agreement with DLVO predictions. Changes in pH and salt concentration induced changes in the swelling of the film and, consequently, in steric repulsion. These were the first force measurements using CNF films.

It is well known that crystalline and amorphous cellulose behave very differently in nature. For example, amorphous cellulose swells considerably in water, but water cannot penetrate into crystalline regions [23]. Furthermore, dissolution and regeneration of cellulose changes the crystal form from native cellulose I to the thermodynamically more stable cellulose II. Thus the scientific community has been interested in probing the effect of crystallinity on the direct forces in cellulosic systems. However, to date changes in crystallinity have been coupled with differences in charge or roughness, which has prevented drawing unambiguous conclusions about the effect of crystallinity. Notley et al. measured the surface forces between an amorphous cellulose microsphere and spin-coated cellulose films of different crystallinity: cellulose I (nanocrystals), cellulose II (regenerated cellulose from NMMO solution), and amorphous cellulose (regenerated cellulose from lithium chloride/dimethylacetamide, LiCl/DMAc, solution) [24]. Clear differences in the force curves for the different cellulose films were observed. An electrical double layer repulsion was detected for crystalline cellulose surfaces whose dependence on pH and salt concentration

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