

Cellulose—model films and the fundamental approach

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This *critical review* describes the recent arrival of ultrathin films of cellulose. The methodology of preparation as well as the applications of the films for fundamental research is fully covered. The review places cellulose in a wider scientific context where cellulose research is no longer a field of interest for specialised scientists only. Cellulose and cellulosic materials should interest communities such as biochemists, physical chemists, surface chemists, organic chemists, polymer chemists and also physicists working close the disciplines mentioned. (149 references.)

1. Introduction

As the most abundant biomacromolecule, cellulose has been extensively exploited throughout human culture. It is the principal ingredient of woody plants, which makes the diversity of its applications range from housing to papermaking and textiles. Perhaps it is precisely this natural ubiquity and industrial importance that has belittled the scientific impetus of cellulose with more fundamental aspects. The challenges raised by, for example, papermaking are commonly generalised to engineering problems, not scientific dilemmas. With this critical review, we want to give an account of a more scientific approach to the physical chemistry of cellulose. We will give an overview of recent breakthroughs in cellulose chemistry and we want to demonstrate how the relatively new field of cellulose model surfaces uses methods generally applied in surface science to illuminate fundamentals behind the phenomena of industrial or natural kind. Furthermore, we want to speculate on the novel, unexplored possibilities that are offered by the omnipresence of cellulose and the recently popular fundamental approach.

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In surface science, model surfaces consist of a small amount of chemically defined compound or compounds which are deposited on a flat substrate. In colloid science, a model surface can also be a dispersion of particles of defined composition and dimensions in a solution. Whatever the case,



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Eero Kontturi received his Master's degree from Helsinki University of Technology in 2001, majoring in wood chemistry. During the years 2001–2005 he lived in Eindhoven, the Netherlands, where he performed his PhD research in the Laboratory of Inorganic Chemistry and Catalysis under the supervision of Professor J. W. Niemantsverdriet. From early 2005 onwards he has been involved in postdoctoral research back in Helsinki in the Laboratory of Forest Products Chemistry. His research



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interests include surface chemistry of cellulose and cellulose related materials as well as properties of natural fibres.

Tekla Tammelin obtained an MSc in forest products chemistry from Helsinki University of Technology, Finland, in 2004. Her PhD studies are dealing with surface and colloid chemistry in papermaking applications. Her research has focused on adsorption studies of polyelectrolytes present in the wet-end of the papermachine.

the seminal idea is that not only the chemical nature of the system is well defined but also the morphology—as opposed to model substances which only use the chemical composition as the modelling parameter. This review is focused on the surface science approach to model surfaces, *i.e.* model films.

The reasoning behind model surfaces is multifold. The most straightforward one is the modelling approach: complex materials provided by nature and further refined by industry are a difficult subject of research and interpretation of their behaviour can often be ambiguous. On the other hand, the analytical methods also provide limitations. Of the techniques in surface science, for instance, X-ray Photoelectron Spectroscopy (XPS), Surface Force Apparatus (SFA), or Atomic Force Microscopy (AFM) are cumbersome to exploit with naturally rough surfaces, such as wood or paper. A need for defined, smooth model surfaces is evident.

Model surfaces are already a well-established field of research in, for example, polymer chemistry,^{1–4} physical organic chemistry⁵ or catalysis.⁶ Ultra-high vacuum technology has made it possible to develop highly surface-sensitive methods, such as the XPS⁷ or Secondary Ion Mass Spectroscopy (SIMS)⁸ in the 1960s and 1970s. From the 1980s onwards, the advent of scanning probe techniques, AFM in particular,⁹ has provided a means for unprecedented interpretation in supramolecular chemistry and surface force studies. The most recent addition to high profile surface analysis has been the quartz crystal microbalance with dissipation monitoring (QCM-D) in the 1990s, enabling the detection of adsorbates on thin films down to nanogram precision as well as the characterisation of the adsorbed layer's viscoelastic properties.¹⁰ The progress in analytics has triggered a huge interest in 2D chemistry which is inextricably linked to model films.^{1,2,11} In this context, the research on model surfaces of cellulose is still in its infancy. Fundamental issues in cellulose chemistry have, nevertheless, considerably advanced within the past 10 years, and it is the function of this review to place model surfaces on the background of modern cellulose research. Besides the unquestionable advantages of the model surface approach, we will highlight the fundamental challenges in the methodology of the preparation of cellulose model surfaces, as well as the interpretational difficulties arising from the differences of model surfaces and the native state of cellulose. In consequence, this review consists of this introduction (1), a basic section on supramolecular chemistry (2), methodology of model surface preparation (3), and the applications of model surfaces (4) before the concluding outlook (5).

2. Cellulose—aspects of supramolecular chemistry and native state

Anselme Payen suggested in 1838 that the cell walls of almost any plant are constructed of the same substance.¹² It was not until the 20th century, however, that the molecular structure of cellulose was resolved, after numerous efforts, by Sponsler and Dore¹³ and Haworth¹⁴ in the 1920s. Depicted in Fig. 1, cellulose is a linear homopolymer composed of (1→4)- β -glucopyranose. The dimer cellobiose is actually the repeating unit of cellulose, but the degree of polymerization is dictated by the number of chair-conformed, single anhydroglucose units. Furthermore, the cellulose chain has a direction since the terminal groups on the chain ends are different: non-reducing end with closed ring structure and reducing end with aliphatic structure and a carbonyl group in equilibrium with cyclic hemiacetals.

As with any polymer and its monomer, cellulose differs a great deal from water-soluble glucose. Already cellohexaose, consisting of six anhydroglucose monomers, does not dissolve in water and the ¹³C NMR spectrum is close to that of cellulose. Thirty anhydroglucose units are enough to represent the polymer 'cellulose' in its structure and properties.¹⁵

The supramolecular chemistry of cellulose, on the other hand, is a far more complex issue. Four different polymorphs of cellulose are known, named cellulose I, II, III, and IV. Cellulose I is the form found in nature and it occurs in two allomorphs I_{α} and I_{β} . Cellulose II is the crystalline form that emerges after re-crystallization or mercerisation with aqueous sodium hydroxide, and it is thermodynamically the most stable crystalline form.¹⁶ Cellulose III_I and III_{II} are obtained by a liquid ammonia treatment of cellulose I and II, respectively. Cellulose IV is a result from heating cellulose III, the transformation being usually partial. In addition, cellulose is found abundantly in amorphous form, usually incorporated with cellulose I.^{16,17}

The hunt for the supramolecular structure of native cellulose (cellulose I) lasted for most of the 20th century. The developments in understanding the crystalline alignment give a good overview of how the analytical methods have developed, from X-ray diffraction^{18–20} to electron diffraction²¹ and infrared spectroscopy,²² further on to computer handling of results,²³ solid state NMR,²⁴ molecular dynamics calculations,²⁵ electron microscopy,²⁶ and AFM.²⁷ In the early 21st century, the supramolecular structure was finally resolved in 1 Å resolution by synchrotron X-ray and neutron diffraction for cellulose II,²⁸ cellulose I_{β} ,²⁹ cellulose I_{α} ,³⁰ and cellulose

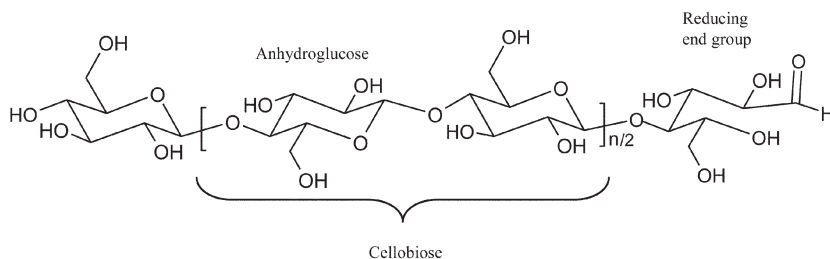


Fig. 1 The structure of cellulose. Anhydroglucose unit is the monomer of cellulose, cellobiose is the dimer. Cellulose chain has a direction, one end being a closed ring structure and the other being an aliphatic reducing end in equilibrium with cyclic hemiacetals.

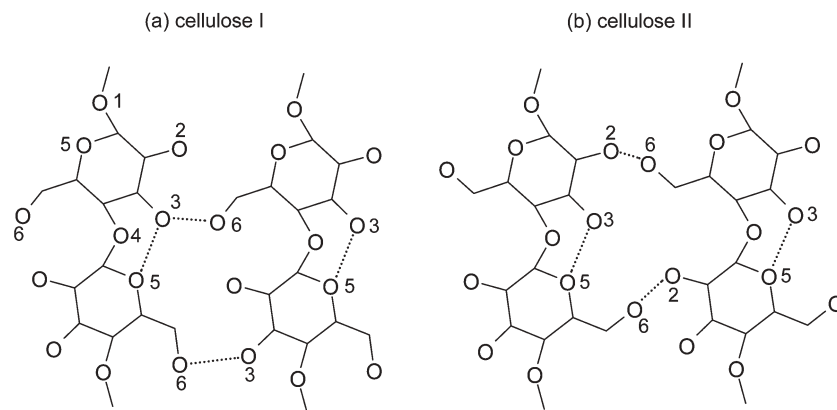


Fig. 2 The major supramolecular distinction of (a) cellulose I and (b) cellulose II (re-crystallized cellulose). The hydrogen atoms are not indicated to emphasize the fact that “free” hydroxyl groups do not really exist in cellulose as all of them are more or less hydrogen bonded.³⁴ The main intrachain hydrogen bond is that of O3–H···O5 for both polymorphs. Cellulose I has an O6–H···O3 inter-chain bond whereas cellulose II has it at O6–H···O2 position.

III.³¹ The results for cellulose I concur with the latest data from refined solid state NMR.³² For supplementary information about the history of cellulose research, the reader is referred to a thorough review by Hon.³³

The distinction between cellulose I and cellulose II is highlighted in Fig. 2. The dominant intra-chain hydrogen bond in both polymorphs is O3–H···O5 which gives cellulose chain its rigid, linear shape. The inter-chain bonding is different: in cellulose I O6–H···O3 dominates, whereas in cellulose II it is O6–H···O2. Furthermore, cellulose II has an antiparallel packing whereas the chains in cellulose I run in parallel direction.^{28–30}

Molecular dynamics and electron microscopy have confirmed that the most probable packing for cellulose I is “parallel-up”, *i.e.* that the bridging oxygen in the glucopyranose ring (O5) has a higher *z* coordinate than that of its nearest carbon (C5).^{25,26} The native allomorphs I_α and I_β can be distinguished with solid state ¹³C NMR,²⁴ IR spectroscopy,³⁵ or electron diffraction.³⁵ In I_β, there are two conformationally distinct chains in a monoclinic unit cell. Each chain lies on a *P2*₁ symmetry axis that requires adjacent glycosyl residues in the same chain to be identical.²⁹ In I_α, there is one chain in a triclinic unit cell.³⁰ Cellulose I_α undergoes conversion to I_β during heating.³⁶ The appearance of the two allomorphs is dependent on the source of cellulose: cellulose I_β is overall the more common form which dominates the cotton, wood and ramie fibres, and cellulose I_α is enriched in some algae and bacterial cellulose.³⁷

The crystallinity of cellulose is important when cellulosic matter is in contact with water. Cellulose is hydrophilic because of the abundance of the hydroxyl groups in the glucopyranose ring (Fig. 1) but it does not actually dissolve in water. Amorphous cellulose, however, swells in water since water can penetrate inside the amorphous matrix by disrupting the inter-molecular hydrogen bonds.³⁸ Crystalline cellulose is largely impenetrable by water,³⁸ but complete deuteration has been achieved for both cellulose I³⁹ and cellulose II⁴⁰ in a NaOD/D₂O system.

The peculiar supramolecular features of a cellulose network account for the difficulties in dissolving the substance, and

cellulose is, indeed, insoluble in the common organic or inorganic solvents. In modern context, the non-derivatizing solvents for cellulose can roughly be divided into two categories: aqueous and non-aqueous. The aqueous category often utilises transition metal complexes, including the traditional cellulose solvents cupric hydroxide with aqueous ammonia (Cuam),⁴¹ cupriethylenediamine hydroxide (Cuen),⁴¹ and tri(ethylenediamine) cadmium hydroxide (Cadoxen).⁴² Ni-tren and Cd-tren (tren = tris(2-aminoethyl)amine) are among the more recently discovered aqueous solvents for cellulose.⁴³ Furthermore, microcrystalline cellulose has successfully been dissolved in 10% aqueous NaOH solution.⁴⁴ There is also a continuing interest to exploit suitable inorganic molten salts as cellulose solvents.⁴⁵ The non-aqueous solvents, on the other hand, are the most important substances in today’s industry and laboratory work. This group contains unicomponent solvents, like *N*-methylmorpholine-*N*-oxide (NMMO),⁴⁶ bicomponent solvents, such as dimethylacetamide with lithium chloride (DMAc–LiCl)⁴⁷ or dimethyl sulfoxide with tetrabutylammoniumfluoride trihydrate (DMSO–TBAF),⁴⁸ and tri-component systems, like dimethyl sulfoxide with sulfur dioxide and diethylamine (DMSO–SO₂–DEA).⁴⁹ There are, moreover, some novel, more eccentric solvents like ionic liquids which have only recently been applied to cellulose chemistry.⁵⁰ Nevertheless, the solvents for cellulose are rather exotic and often suffer from high toxicity and high reactivity. Of the listed solvents, DMAc–LiCl is probably the most popular solvent in laboratory synthetic work and NMMO is the most important industrially, being used in the industrial fibre making Lyocell process. A comprehensive, up-to-date review on cellulose solvents is hard to find. A sizeable review of the non-aqueous solvents exists,⁵¹ and some textbooks and reviews on synthetics give a decent overview of the solvents.^{52,53}

It is important to understand that cellulose rarely exists in nature in pure single-compound entities. For instance, in wood cells cellulose is integrally embedded with other materials, such as lignin (a polyphenol) and hemicellulose (various polysaccharides).^{54,55} This chemical versatility of the native appearance further justifies the use of model surfaces.

3. Methodology of cellulose model surface preparation

As mentioned in the previous section, the complex supramolecular features of cellulose provide obstacles for the model surface preparation. Therefore, the methodology of preparation is not a straightforward issue and, recently, several quite different methods have been presented as interest towards cellulose model surfaces has gathered momentum. Concerning instrumentation, there are two established methods, with which successful, smooth cellulose model surfaces have been prepared: Langmuir–Blodgett (LB) deposition⁵⁶ and spin coating.⁵⁷

3.1 Deposition methods

Be it LB-deposition or spin coating, both techniques involve dissolving the coating material before its deposition on the substrate. This requirement exposes the seminal difficulty in preparation of cellulose model surfaces: its immiscibility with common solvents. The solvents for cellulose are somewhat exotic and it is not straightforward to use them for deposition. Nonetheless, some of the solvents have been successfully exploited for model surfaces. A means to circumvent the cumbersome solvents is to synthesise an easily dissolving derivative of cellulose which can later be transformed back to cellulose after the film deposition. Both methods require a separate treatise. An additional section is devoted to the so-called open films—an important emerging subject in polymer science but poorly explored with cellulose surfaces.

3.1.1 Direct deposition of cellulose. Cadoxen (tri(ethylene-diamine) cadmium hydroxide) was successfully applied to create monolayers of cellulose on water in the first paper on cellulose model surfaces in 1967.⁵⁸ The concept of the liquid substrate is intriguing and it is probably something modern scientists should consider when generating yet another preparation method of cellulose films. Model surfaces cast directly from a substrate surfaced again in 1993 in a paper by Neuman *et al.*⁵⁹ who used trifluoroacetic acid (TFA) as a solvent to prepare spin-coated films on mica. TFA, however,

has the problem of reacting with cellulose, whence the purity of the model substance is mutilated.⁶⁰ If efforts of casting thick films by evaporation from NMMO⁶¹ or by coagulation from NaOH–urea solution⁶² are omitted, the first model film to be directly cast from dissolved cellulose and properly characterised was published by Wågberg and co-workers in 2002.⁶³ With a sequel publication⁶⁴ they established the preparation of 20–270 nm thick films, spin coated from NMMO with traces of dimethyl sulfoxide (DMSO) on SiO₂ wafers with glyoxalated polyacrylamide as an anchoring polymer to improve the adhesion between the substrate and cellulose (Fig. 3a). AFM, XPS, and size exclusion chromatography (SEC) neatly expose the physical and chemical characteristics of these films. However, the determination of the crystallinity of the films is dubious: the authors' conclusion is that the cellulose has a similar crystallinity to Lyocell fibres since Lyocell is prepared by re-crystallisation from NMMO under high shear. This indirect evidence is doubtful in the presence of the substrate and geometrical constraints which might well affect the crystallinity of cellulose during spin coating. Recent analysis with AFM phase imaging supports that the Lyocell-like crystallinity is plausible with these films⁶⁵ but the hard evidence is nonetheless missing. Of the spin coating parameters, concentration of the coating solution predominantly determined the thickness of the films.⁶⁴ Thickness is also the factor for a minor deficiency in reproducibility with these films: the constraints are rather large, such as 20–40 nm or 50–60 nm, but this is probably due to the rather high roughness of the films.

An “anchor” is often used in spin coating to facilitate the physisorption of the coating to the carrier surface (as in references 63 and 64). In contrast, Freudenberg *et al.*⁶⁶ suggested covalent bonding of cellulose to the substrate to attach the film more firmly on the substrate. They eventually came up with 20–300 nm layers of cellulose with a thin covalently bonded layer between the film and the substrate. The initial deposition was done by spin coating. These films have potential if the model surfaces are applied in harsher conditions, such as the elevated pressure and temperature ranges of pulping and bleaching.

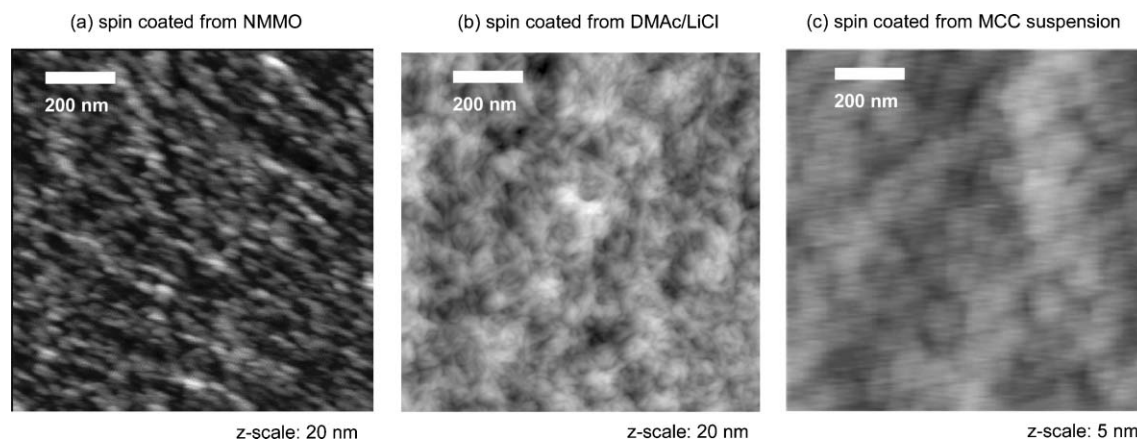


Fig. 3 $1 \times 1 \mu\text{m}^2$ AFM images of model cellulose films: (a) the film is spin coated from NMMO according to references 63–65, *Courtesy of Shannon Notley*; (b) the film is spin coated from DMAc/LiCl solution according to reference 67, *Courtesy of Jonny Eriksson*; (c) the film is spin coated from a microcrystalline cellulose suspension according to references 68,69, *Courtesy of Derek Gray*.

Dimethylacetamide with lithium chloride (DMAc–LiCl) has also been exploited as a spin coating solvent for cellulose films.⁶⁷ The high boiling point of DMAc required increased temperature (100 °C) during spin coating and lithium chloride had to be removed by rinsing with water afterwards. The resulting films were relatively pure according to the XPS data, but morphologically rather rough with an RMS roughness of almost 5 nm for 28 nm thick films (z -scale variation of *ca.* 20 nm), *i.e.* similar to the films from NMMO (Fig. 3b).

Spin coating is also applicable to colloidal suspensions. This fact was utilised by Gray and co-workers who spin coated colloidal (or “nanocrystal”) water suspensions of microcrystalline cellulose (MCC) on mica (Fig. 3c).^{68,69} MCC is achieved by controlled acid hydrolysis of native cellulose, resulting in a stable suspension of “nanorods”.⁷⁰ Although the films were characterised with XPS, X-ray diffraction (XRD), and AFM, they unfortunately lack thickness analysis. On the other hand, the determination of crystallinity is more reliable in the case of MCC than with the alleged films of cellulose II:⁶⁴ XRD is performed on the film itself.⁶⁸ In summary, the method elaborated in references 68 and 69 is one of the most effortless to create ultrathin cellulose films and it has the advantage of exposing cellulose in its native crystalline state.

Ordinary dialysis membranes of regenerated cellulose have also been used as model surfaces for surface force studies.^{71,72} Their problem is a relatively high roughness throughout the film.

3.1.2 Deposition of cellulose *via* a dissolving derivative. Partial substitution of the hydroxyl groups of cellulose leads to cellulose derivatives that often dissolve in common solvents. To generalise, a charged substituent, such as a carboxymethyl group, yields water-soluble derivatives whereas an organo-soluble derivative is achieved with a hydrophobic substituent, for instance a silyl ether. Cellulose derivatization has received extensive reviews, *e.g.* in references 53 and 73.

If a model surface is cast using a cellulose derivative, the reversibility of the initial reaction is important, *i.e.* regenerating the derivative back to cellulose must be relatively effortless. An early paper explains the use of cellulose xanthogenate (viscose) and cellulose acetate to cast thick films on glass plates.⁷⁴ The films were regenerated to cellulose by sulfuric acid and methanol, respectively. Unfortunately, the characterisation was poor and the authors lacked modern morphological tools like AFM.

The early 1990s brought the use of trimethylsilyl cellulose (TMSC) as a model surface medium. TMSC is a hydrophobic derivative, well-soluble in the common non-polar solvents, such as chloroform or toluene.^{75,76} Schaub *et al.* used TMSC to prepare well characterised cellulose films in what might be called a seminal publication in the field of cellulose model surfaces.⁷⁷ Their method introduced ultrathin cellulose films of <10 nm thickness on silicon wafers, glass slides and gold surfaces. The elegance of the technique lies in the vapour phase transition of TMSC to cellulose after LB deposition of TMSC (Fig. 4). An exposure to liquid is detrimental to the smooth morphology created by LB-deposition. Therefore, the easy acid hydrolysis of TMS groups, complete in vapour phase, is ideal. The films were credibly characterised with IR

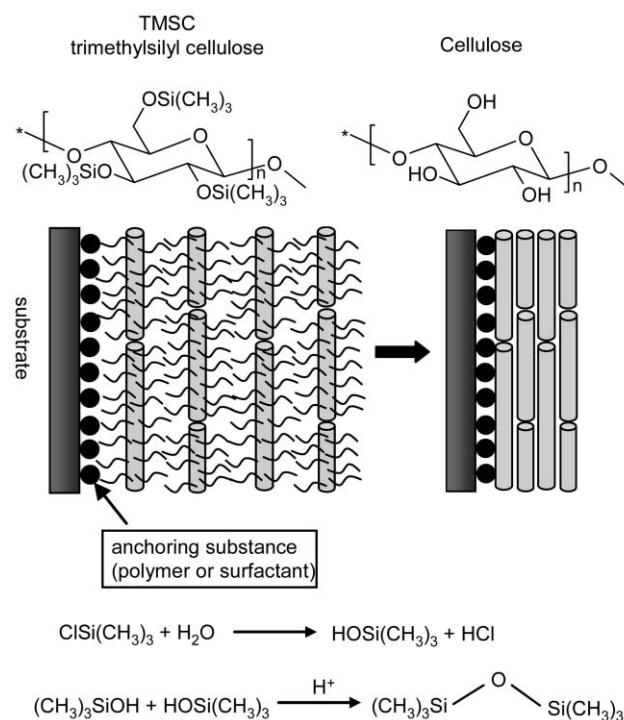


Fig. 4 Schematic representation of the hydrolysis of TMSC to cellulose. The bulky, “hairy-rod” type of TMSC structure is compressed to a compact, tightly hydrogen bonded structure of a cellulose network by the removal of the TMS groups. The reactions underneath present the reactions of the by-products: trimethylsilylchloride is immediately hydrolysed to trimethylsilanol which condenses into hexamethyldisiloxane.⁷⁵ The volatile hexamethyldisiloxane can easily diffuse through the film.

spectroscopy and X-ray reflectance.⁷⁷ A follow-up publication covered more elaborate characterisation (surface plasmon resonance) and explored the influence of varying LB parameters on the film thickness.⁷⁸

The LB-deposition of TMSC and the film’s subsequent hydrolysis to cellulose were further refined by Holmberg *et al.*⁷⁹ The TMSC was cast on a mica substrate, hydrophobised by a surfactant mixture, and the hydrolysis to cellulose took place in 10% HCl for 1 minute. The characterisation of these films is impressive: XPS, ellipsometry, surface force measurements, contact angle measurements, and AFM are applied. This lengthy paper marks actually the first AFM imaging of a modern cellulose model surface. It is also the first one to establish a completely reproducible preparation method and to confirm the stability of these films in aqueous solutions. Furthermore, some fundamental issues are investigated, such as the swelling of the films in humid atmosphere, and the layer thickness of cellulose was determined as 0.5 nm in dry air. Fig. 5a shows an AFM image of LB-deposited TMSC and the same film converted to cellulose in Fig. 5b. The transition from a bulky, rough TMSC structure into smooth cellulose, akin to the scheme in Fig. 4, is clearly visible.

The aforementioned publications^{77–79} established LB-deposition of TMSC as a viable and reproducible method for preparing smooth, ultra-thin films of cellulose by hydrolysing the TMSC. The thickness of the films could be varied

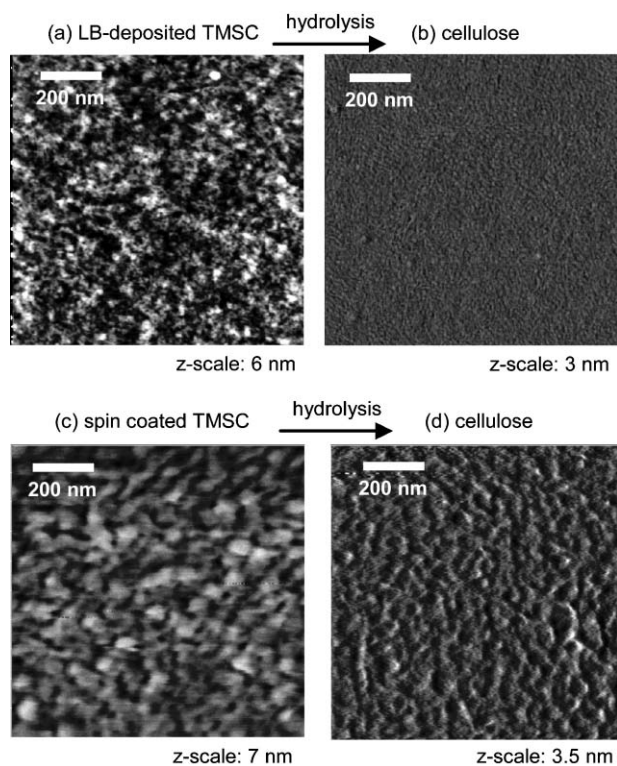


Fig. 5 $1 \times 1 \mu\text{m}^2$ AFM images of TMSC and cellulose films: (a) LB-deposited TMSC film according to references 77–79; (b) same film, subsequently hydrolysed to cellulose as described in references 77–79; (c) spin coated TMSC film according to references 82,83; (d) same film, subsequently hydrolysed to cellulose as described in references 82,83.

between *ca.* 5–50 nm. The pivotal issues were that the hydrolysis of TMSC to cellulose is complete and that the morphology remains smooth after the hydrolysis. (Actually, the roughness variation is smaller in the subsequent cellulose films than in the corresponding TMSC films because of the bulkiness of the TMSC groups and the tightly bound hydrogen bonding network of cellulose (Fig. 4).)

Despite the fundamental work,^{77–79} model surfaces of cellulose started to attract more interest only during the present decade. Geffroy *et al.* were the first to apply spin coating with TMSC and succeeding hydrolysis, but the characterisation of the films was minimal.⁸⁰ In 2003, Rehfeldt and Tanaka published a study comparing LB-deposition and spin coating of TMSC and its hydrolysis.⁸¹ However, the work focused on examining hydration forces (swelling) of the films in water atmosphere and, in consequence, it was not methodology oriented. Spin coating received more attention in a broad survey by Kontturi *et al.*^{82,83} of spin coating TMSC on untreated silicon and gold substrates. The research included characterisation by XPS, IR, ellipsometry and AFM, confirming the purity of the coated cellulose and smoothness of the morphology. AFM images of spin coated TMSC and a subsequent cellulose film are depicted in Fig. 5c and 5d, respectively. The advantages of this method are fast preparation and high degree of reproducibility. On the other hand, the smooth films (<10% roughness/thickness) are only produced with 20 nm film thickness, whereas in LB-deposition the smoothness is independent on the number of

monolayers—as long as the film has full coverage over the substrate.⁷⁸ In any case, the influence of spin coating parameters—solution concentration, spinning speed, choice of solvent—on the eventual cellulose film is covered extensively.^{82,83} The study on the hydrolysis of TMSC to cellulose was shown to proceed from the surface to the substrate interface by a comparison of IR and XPS data.⁸³ Furthermore, both Rehfeldt⁸¹ and Kontturi⁸³ denote that the transformation of the TMSC film to a cellulose film results in a *ca.* 60% contraction in thickness with <20 nm thick films. The LB-films of the same thickness, in contrast, contract 50% or less.^{78,81} Thus, in the ultra-thin region, LB-deposition appears to be a technique which can cast more compact layers of TMSC.

3.1.3 Open films. All cellulose surfaces covered in this review so far have been so-called closed films, *i.e.* the coating substance (cellulose) uniformly and completely covers the substrate. If the concentration of the solution, from which the films are cast, is decreased substantially, there is not enough matter to cover the substrate totally. In this case, an open film occurs. Open films may consist of aggregates (“islands”) on a flat substrate⁸⁴ or—as is often the case with polymer chemistry—open films are used to study evenly spread single molecules with AFM (Fig. 6).¹ Applications of the open films from single polymer molecules and AFM include determining the molecular weight distribution,⁸⁵ visualizing conformation and structural diversity,⁸⁶ measuring elasticity,⁸⁷ and visualizing conformational transitions.⁸⁸ Open films are also an indispensable tool in modern supramolecular chemistry.¹¹

By refining the well-characterised spin coating method⁸³ with a simple decrease in concentration, open films of cellulose on silicon were achieved.⁸⁹ These open films consisted of nanosized cellulose domains that were *ca.* 50–200 nm long, 20 nm wide and only 1 nm high (Fig. 7a). The reproducibility of the open films was confirmed by quantifying the volume of the cellulose domains in AFM images. The size of these domains suggests that they are conglomerates of a few tens of individual cellulose chains and clearly not individual molecules. As the cellulose domains are conspicuous, yet very small, they provide a novel medium for interpreting supramolecular changes in cellulose network on the nanoscale. These open films of nanosized cellulose may prove to be a valuable tool in exploring the supramolecular chemistry of cellulose during various treatments, for instance, aqueous wetting and drying.

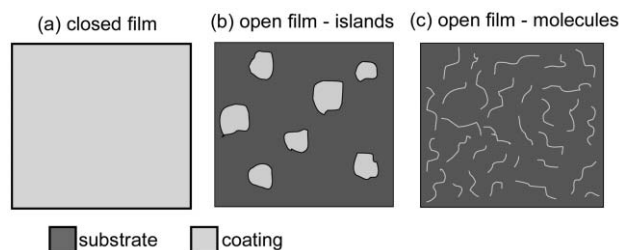


Fig. 6 Schematic representation of the concept of open films. If the concentration of a coating solution is decreased enough, the film-forming substance will either agglomerate into islands or spread evenly as single molecules on the substrate.

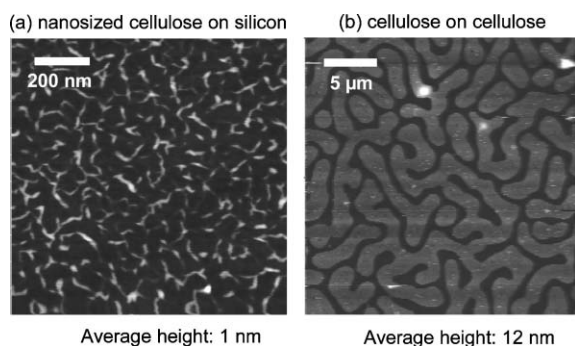


Fig. 7 AFM images of open films of cellulose: (a) $1 \times 1 \mu\text{m}^2$ height image of a nanosized open film of cellulose on untreated silicon, prepared as described in reference 89; the height of the cellulose domains is 1 nm on average; (b) $25 \times 25 \mu\text{m}^2$ height image of cellulose islands on cellulose, prepared by spin coating TMSC–polystyrene mixture on silicon, hydrolysing the TMSC to cellulose and selectively dissolving the polystyrene as described in reference 91.

The already discussed paper by Rehfeldt and Tanaka also briefly introduces a method of preparing open cellulose films by micropatterning with UV photolithography.⁸¹ A grid was placed on the closed cellulose film, regenerated from TMSC, and the film was subsequently illuminated with a mercury lamp, ablating the exposed cellulose but leaving the cellulose underneath the grid intact. The result is a 40 nm wide grid of cellulose with 60 nm rectangles of silica in between. These films are revisited in a follow-up paper which introduces an additional method to prepare open films of cellulose: stamping protein barriers of bovine serum albumin (BSA) labelled with fluorescein isothiocyanate (FITC) onto closed cellulose films.⁹⁰

Another recent paper on open films of cellulose describes the preparation of micrometer sized cellulose islands of *ca.* 10–15 nm height on top of a thin layer (3–5 nm) of cellulose (Fig. 7b).⁹¹ The films were achieved by exploiting the phase separation of blends of incompatible polymers in thin films,^{92,93} in this case polystyrene and TMSC. Hydrolysis transformed TMSC to completely hydrophilic cellulose, after which the polystyrene could be washed away with a hydrophobic solvent. These surfaces overcome a certain limitation of organic model surfaces on inorganic substrates: that the model substance is physically and chemically seriously different from the substrate. For instance, large differences in Young's modulus and thermal expansion coefficient can lead to rupture and delamination upon harsh treatments.⁹⁴

A curious offshoot within cellulose films is the method by Kasai *et al.* to prepare honeycomb-patterned cellulose films.⁹⁵ The application uses the recently discovered self-organization of hexagonal array of micropores by casting a polymer emulsion of water in oil on a substrate.⁹⁶ The authors cast the films from cellulose triacetate, dissolved in chloroform in a water suspension and regenerate the acetate to cellulose with aqueous NH_4OH after deposition. The resulting film is honeycomb-shaped cellulose on a layer of cellulose. The pore size of the honeycombs can be altered between 1–100 μm . The width of the features was around 10 μm and the height *ca.* 1–3 μm , which makes traditional AFM imaging difficult. The IR data illustrate convincingly that the deacetylation is complete and the films are thus pure cellulose.

3.2 Summary of methodology

The modern methodology of preparing cellulose model surfaces was initiated by Schaub *et al.* in their paper about LB-deposition of TMSC and its subsequent complete hydrolysis to cellulose in vapour phase acidic conditions.⁷⁷ The method was further refined by Buchholz *et al.*⁷⁸ and Holmberg *et al.*⁷⁹ The extensive characterisation of the LB-films in various conditions established the LB-deposition *via* TMSC a reliable and adjustable technique already in the 1990s.

The other route to cellulose films has been developed during the present decade with the use of spin coating. Gunnars *et al.* demonstrated how ultrathin cellulose films may be spin coated directly from an NMMO solvent.^{63,64} Kontturi *et al.* explored the possibilities of spin coating TMSC and hydrolysing it to cellulose,^{82,83} precisely as with the LB-films^{77–79} but in a simplified procedure. Meanwhile, Gray and co-workers focused on spin coating a nanocrystal suspension of microcrystalline cellulose, resulting in a smooth film of crystalline cellulose I.^{68,69}

Spin coating is the technique which has been applied to both deposition methods (direct deposition and deposition *via* TMSC). The results published so far indicate that spin coating *via* TMSC offers a way to prepare smoother films than spin coating directly from solution of NMMO or DMAc–LiCl (Fig. 5 *vs.* Fig. 3). It might be, however, that the direct deposition has not been fully optimised. As shown with TMSC, the spin coating conditions—concentration, substrate and choice of solvent in particular—have a profound impact on the smoothness of the film.⁸³ Smooth films from the nanocrystalline suspensions^{68,69} (Fig. 3c) are encouraging examples that direct deposition is as viable an option as spin coating when maximum smoothness is desired. Besides, both the rougher and the smoother films have their peculiar advantages as will be later revealed in the section on applications.

The advantage of LB-technique over spin coating is its controlled adjustability. Thickness of the films may be controlled by a deposition of one monolayer at a time while the roughness of the films remains constant. Spin coating, on the other hand, provides a faster method. The reproducibility of the films is also reliable with spin coating but there is certain robustness within the control parameters. For instance, a 20 nm thick film may be reproduced with as high a degree of smoothness with spin coating as with LB-deposition, but the case is not necessarily the same for 50 nm film.⁸³

The newly introduced open films of cellulose have a potential for a more morphologically oriented interpretation.^{81,89,91} Films consisting of conspicuous cellulose domains of defined size and shape are set to be important tools for tracking the behaviour of cellulose in diverse conditions which resemble natural or industrial conditions. The hitherto dominant smooth films are excellent for adsorption or surface force studies since they simplify the porous morphology of cellulosic fibres to the extreme. In fact, when totally smooth, the model surfaces reduce the morphology parameter to non-existence. The deliberately “rough” films, however, with defined cellulose shapes may prove to be important in interpreting the supramolecular and chemical changes in

cellulosic material during different reaction conditions, such as pulp bleaching, or even in simple wetting and drying (swelling/shrinking) of cellulosic material as will be explained further on with the Applications section.

4. Applications of cellulose model surfaces

Since the modern methodology of cellulose model surface preparation is fairly new—most methods have been presented only during the past few years—the field of applications is somewhat nebulous. Fundamental aspects of adsorption and surface interactions are the most prominent areas of applications. Another popular subject of research has been to examine the swelling of cellulose in aqueous media. These three topics will each receive a separate treatise in this section.

Although the research on cellulose model surfaces is mainly fundamental, it has a genuine link to mundane industrial problems and phenomena. These applications include polyelectrolyte adsorption to natural fibres (papermaking), fibre-dye adsorption (printing, textiles), interaction between two fibre surfaces (papermaking), and swelling/shrinking of fibres during wetting/drying (papermaking, paper recycling in particular).

4.1 Adsorption

4.1.1 Polyelectrolytes. The adsorption of added polyelectrolytes in the wet end of a paper machine enhances the filler and fines retention in the end product. Due to this vast industrial importance, adsorption studies on cellulosic materials have focused largely on polyelectrolytes.⁹⁷ Contrary to the natural fibres, model surfaces allow, for instance, the *in situ* quantification by reflectometry or quartz crystal microbalance (QCM). Furthermore, comparison with theoretical predictions in polyelectrolyte adsorption, such as the self consistent field theory⁹⁸ or the Monte Carlo approach,⁹⁹ is a far less complex affair with the model surfaces.

In an early communication, Buchholz *et al.*⁷⁸ investigated the adsorption of weakly charged poly(acrylamidopropyl) trimethylammonium chloride (APTAC C) onto LB deposited cellulose films. Analysis by surface plasmon resonance yielded good isotherms but the results numbered only a few. A more detailed investigation was performed by Geffroy *et al.* who applied weakly charged polyvinylamine on spin coated cellulose, regenerated from TMS. The adsorption kinetics, studied by reflectometry, were examined as a function of pH and electrolyte concentration. The authors found that the experimental data differed from the self consistent field theory because it failed to take the competition of the ions for the surface sites into account. The kinetic equilibrium was successfully compared with the metastable state of two particles in the DLVO theory of colloidal stability.¹⁰⁰

An important contribution to adsorption studies was provided by Rojas *et al.*¹⁰¹ who revised a previously established method¹⁰² to study polyelectrolyte addition on mica with X-ray photoelectron spectroscopy (XPS). The polyelectrolytes applied were [3-(2-methylpropionamido)propyl] trimethylammonium chloride (MAPTAC) and a random copolymer of acrylamide and MAPTAC (AM-MAPTAC) which represented a weakly

charged species. The adsorption on LB-deposited cellulose was quantified from the element specific XPS spectrum by plotting the growing nitrogen band intensity as a function of growing amount of the adsorbed polyelectrolyte. The results showed that the adsorption of AM-MAPTAC on cellulose decreased as the charge density increased (Fig. 8a). It was found, moreover, that the number density of charged segments adsorbed in AM-MAPTAC increased as the polyelectrolyte charge density grew (Fig. 8b). The authors concluded that this kind of behaviour indicates that also the nonelectrostatic factors have to be considered for adsorption on cellulose substrates. Thus, with cellulose films, the electrostatic driving force on adsorption seems to be important below the charge neutralisation point.

Paananen *et al.* utilised QCM-D to study the adsorption of xylan on LB-deposited cellulose surfaces.¹⁰³ Xylan is one of the common hemicelluloses, coexisting with cellulose in wood cells. The continuous decrease in frequency in the QCM data implied positive mass accumulation, thus indicating that xylan does, indeed, adsorb on pure cellulose. The moderate concomitant increase in dissipation implied viscoelastic properties of the adsorbed layer, indicating that the quantification of the

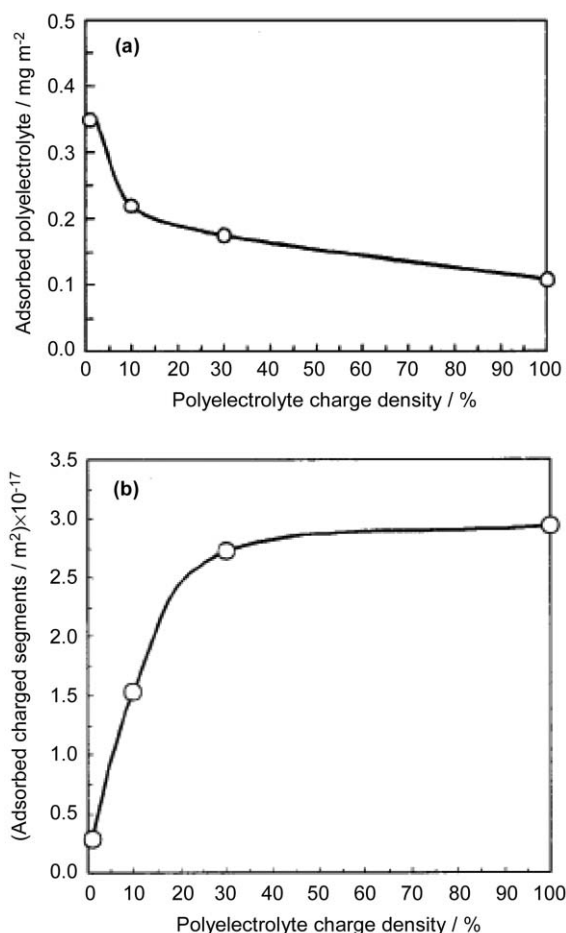


Fig. 8 (a) Plateau-adsorbed amount for copolymers of AM-MAPTAC of different charge densities on cellulose; (b) charged segment number density of AM-MAPTAC copolymers adsorbed on cellulose. (Reproduced with permission after reference 101. Copyright American Chemical Society 2000.)

adsorbed layer from the frequency values (3 mg m^{-2}) is somewhat underestimated.

QCM-D was applied again in a study on LB-deposited cellulose by Tammelin *et al.*¹⁰⁴ who found out that, at low electrolyte concentration, the highly charged poly(diallyldimethylammonium chloride) (PDADMAC) adsorbed less on cellulose than the low charge cationic polyacrylamide (C-PAM). This correlates well with the results by Rojas *et al.*¹⁰¹ who also found that the adsorption decreased as a function of increasing charge density. Furthermore, the adsorbed amount of PDADMAC increased with increasing ionic strength, which is expected since higher electrolyte concentration reduces the radius of the polyelectrolyte by lowering the osmotic pressure between its charged segments,¹⁰⁵ thus allowing more polymer to fit on the surface. With weakly charged C-PAM, the effect of electrolyte was not as pronounced.

4.1.2 Surfactants. Surfactants are used in papermaking as hydrophobing agents and to facilitate the de-inking process in paper recycling and, indeed, surfactant adsorption on cellulose fibres has already received substantial attention.¹⁰⁶ Recently, a detailed study on the adsorption of nonionic surfactants to cellulose model surfaces was published by Torn *et al.*¹⁰⁷ They utilised three different poly(ethylene oxide) alkyl ethers: $C_{12}E_5$, $C_{12}E_7$, and $C_{14}E_7$, thus investigating the effect of different hydrophobic tails (C_n) and hydrophilic headgroups (E_m) on adsorption to a cellulose surface, hydrolysed from spin coated TMSC. Fig. 9a shows the adsorption isotherms on a semi-logarithmic scale. Roughly three regimes can be distinguished from the isotherms: at low surfactant concentrations the adsorption is meagre (i), after which there is a strong increase in adsorption (ii), and eventually a (pseudo)plateau is reached (iii). An important inflection within the isotherms is at the bulk critical micelle concentration (CMC) of the surfactants after which the curve starts reaching a plateau (between regimes (ii) and (iii)). CMCs are indicated with arrows in Fig. 9a. Moreover, the borderline between strong increase in adsorption (regime (ii)) and the low adsorption levels (regime (i)) takes place at *ca.* 0.1 CMC. A comparison reveals that the surfactants have a higher affinity for a cellulose surface than for other typical hydrophilic surfaces: with silica surface, for instance, the stronger adsorption only starts at (0.7–0.9) CMC.^{108,109} Furthermore, the plateau values of the isotherms in Fig. 9a are rather high, around $7\text{--}8 \mu\text{mol m}^{-2}$. The corresponding levels for hydrophilic surfaces in the literature are $4\text{--}6 \mu\text{mol m}^{-2}$ for hydrophilic surfaces^{108,109} and $2\text{--}4 \mu\text{mol m}^{-2}$ for hydrophobic ones.^{110,111} The authors¹⁰⁷ attribute the relatively large adsorbed amount on cellulose to the “soft” nature of the cellulose film: the films swell while exposed to water during adsorption and the surfactants are able to partially penetrate inside the film. Also the shortcomings of the optical model in reflectometry due to the surface roughness of the adsorption-induced further swelling are mentioned.

Furthermore, an extensive kinetic survey featured in the paper by Torn *et al.*¹⁰⁷ A curious “hesitation” showed up in the initial stages of adsorption with concentrations higher than CMC (Fig. 9b). The tentative explanation for the hesitation is offered in the form of rearrangements of adsorbed molecules:

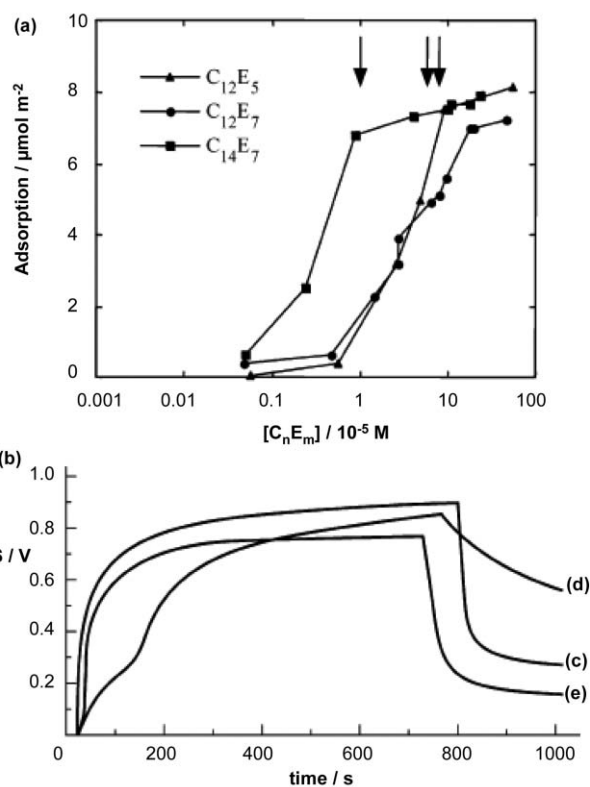


Fig. 9 (a) Adsorption isotherms of three non-ionic surfactants on a cellulose surface; the arrows indicate the CMCs; (b) adsorption-desorption curves of non-ionic surfactants onto flat cellulose surfaces at concentrations above CMC: (c) $C_{12}E_7$: $4.6 \times 10^{-4} \text{ mol dm}^{-3}$, (d) $C_{14}E_7$: $4.0 \times 10^{-5} \text{ mol dm}^{-3}$, (e) $C_{12}E_5$: $5.6 \times 10^{-4} \text{ mol dm}^{-3}$. pH = 5.0, $I = 10^{-2} \text{ mol dm}^{-3} \text{ NaCl}$, $T = 22 \text{ }^\circ\text{C}$. (Reproduced with permission from reference 107. Copyright 2005 American Chemical Society.)

energetically more favourable, denser aggregates are formed on the surface, fresh surface area is exposed and molecules arriving near the surface experience a weaker energetic adsorption barrier. The explanation is in correlation with the fact that the hesitation is the most pronounced with the longest aliphatic chain which promotes the hydrophobic surfactant-surfactant interaction. Moreover, the authors speculate that rearrangements in the soft cellulose layer in aqueous environment may have an effect on the surfactant rearrangements.

Koopal and Avena¹¹² have proposed a simple model for adsorption kinetics at solid-liquid interfaces, describing a two-step adsorption process: (1) transport from a bulk phase over a stagnant layer to the “subsurface”, immediately adjacent to the surface, and (2) transfer from the subsurface to the surface. Similar phases, only *vice versa*, apply to desorption. The experimental results in reference 107 are reliably linked to this theory. The relative desorption rates are found to correspond to the ratios of CMCs of the surfactants, which has also been noted for a silica substrate, although the absolute values are a factor 5 lower for silica.¹⁰⁹ This is attributed to the stronger binding of surfactants to cellulose. The correlation of desorption rates with the CMC strongly suggests that similar aggregates are formed on the cellulose surface as within the bulk solution.

4.1.3 Dyes. Despite the obvious pragmatic significance of dye adsorption to textiles and to a paper surface (printing technology), there is only one extensive study of dye adsorption on cellulose model surfaces. Agnihotri *et al.* used the cellulose monolayers on aqueous substrate to investigate the adsorption of dyes, studied by film expansion, compressibility, viscosity measurements, and refractometry.¹¹³ They found weak association of cationic dyes with the cellulose monolayer, increasing the compressibility. Refractometry, on the other hand, revealed weak complexing between cellulose and amino-groups in dyes, probably of acid–base type. Anionic dyes were suggested to orient face-to-face with the cellulose layer since a larger molecule expanded the film more than a smaller one. Dye adsorption on cellulose films was briefly revisited by Buchholz *et al.* in their deepening study of the cellulose films regenerated from TMSC.⁷⁸ The adsorption of three different dyes was followed as a function of time by surface plasmon resonance. As a consequence, indicative kinetic data is extracted and the adsorbed amounts are compared with theoretical values in good correlation. However, the results are rather examples of how to apply the cellulose model surfaces, not systematic studies on dye adsorption.

4.1.4 Enzymes. Industrial use of enzymes is commonplace nowadays and, concerning fibrous material, cellulases have recently received attention because of their applicability in, for instance, paper and textile chemistry.¹¹⁴ Cellulose model surfaces offer a good research medium for fundamental studies because of the controlled adsorption of the enzymes in contrast to the morphologically and chemically ambiguous fibre. There are two recent applications of cellulose model surfaces with enzymatic adsorption and degradation.^{67,115}

The cellulose films spun from dimethylacetamide–lithium chloride solution are relatively rough (see Methodology 3.1.1) but their suitability for adsorption experiments is demonstrated in an ellipsometry study of enzymatic adsorption and degradation.⁶⁷ The general tendency was that an initial increase of mass was observed because of the enzyme adsorption, after which a decrease of mass signified the cellulose degradation by the enzymes. The initial adsorption strongly depended on the enzyme concentration but also a weak influence of pH, temperature and ionic strength was evident. During the degradation, film mass and thickness exhibited a linear decrease but the film density remained constant, based on the stability of the refractive index. Since the degradation also increased as a function of concentration, the degradation was concluded to depend on the initial adsorption. However, degradation reached a plateau value during a growing adsorption, *i.e.* the cellulose degradation rate remained the same even though the adsorption still increased. The authors attributed this behaviour to the accessibility of the cellulose surface being the rate-limiting factor in degradation.

A subsequent paper on enzymes applied to cellulose films links the results with the recent progress in the understanding of protein adsorption.¹¹⁵ In addition to the native enzyme, two other variants were used: one having an inactive catalytic domain and one containing only the catalytic domain without the carbohydrate-binding module. For the native enzyme, the

results correlated well with the authors' previous work,⁶⁷ *i.e.* the degradation depended on adsorption up to a certain level. The inactive enzyme showed only adsorption without degradation whereas the catalytic core without the binding module exhibited degradation without adsorption. Compared with the native enzyme, the lower absolute values of the catalytic core without the binding module demonstrated the importance of the adsorption to the efficiency of enzymatic degradation.

4.1.5 Biomembranes. The application of cellulose film as a support for biomembranes is not strictly speaking research on adsorption since the cellulose films are used merely as supports. However, the usage is described here since we want to exemplify the versatility of cellulose films as tools for viable fundamental research.

Planar membranes can be applied to immobilize glycolipids, membrane receptors, and proteins to generate models of cell and tissue surfaces.¹¹⁶ One advantage of these flat model membranes is the possibility to study structural and dynamical properties by numerous surface sensitive techniques. However, there are problems involved: for example, direct deposition of lipid bilayers on solids leads to rather high defect densities which are probably caused by surface roughness. The defects are then prone to introduce nonspecific binding sites for proteins. A soft polymer layer in between the lipid and the solid substrate provides a lubricating surface, enabling the self-healing of defects in the supported membrane. Polymer/lipid films, however, are likely to destabilise due to their strong tendency for de-wetting. In 1997, Sigl *et al.* presented a study of numerous hydrophobic cellulose derivatives as polymer cushions for lipid layers, including the LB-films of TMSC, hydrolysed to cellulose.¹¹⁷ The cellulose films of *ca.* 5–10 nm thickness proved to be ideal substrates for continuous phospholipid bilayers. In a later study, cellulose was deposited on indium–tin oxide (ITO) electrodes and an artificial lipid bilayer was further implanted on the system, increasing the electric resistance of the membrane up to 0.5 M Ω cm².¹¹⁸ This value was larger by a factor of 5 than that obtained for the lipid bilayer directly deposited on ITO.¹¹⁹

The advantage of cellulose films in membrane immobilization was broadened with a survey on human erythrocyte membranes.¹²⁰ The right-side-out (RSO) human erythrocyte ghosts not only spread homogeneously on an LB film of cellulose on glass—the membrane also demonstrated an orientation-selective immobilization which was identified with fluorescent labelling. The homogeneous spreading behaviour was compared with two other substrates to their disadvantage: plain glass and cationic polylysine showed a poor, disoriented surface coverage. The superior qualities of a cellulose surface as a binding site were attributed to the modulated, relatively weak, carbohydrate–carbohydrate interactions which also allowed for the lateral diffusion of the erythrocyte membranes.

Further research on human erythrocyte membranes was performed for the open cellulose films, already described in the methodology section (3.1.3). Tanaka *et al.* utilized two different patterned microtemplates of cellulose: the first one a grid of cellulose with 40 μ m feature size, glass substrate in between (60 μ m spacing between the grids) and the second one a continuous cellulose surface which has been “stamped” with

bovine serum albumin (BSA) labelled with fluorescein isothiocyanate (FITC) (feature size: 5 μm , spacing between the grids: 25 μm).⁹⁰ After incubation, the erythrocyte membrane spreads on the open cellulose grid, exposing the cytoplasmic domain uniformly. As for the continuous cellulose layers stamped with FITC-BSA, the erythrocyte membrane adsorbs only on the cellulose, not on the FITC-BSA stamps. Fluorescence imaging reveals an “inside-out” orientation for the spread cell membranes. In consequence, the two novel microtemplates demonstrate their capabilities for local immobilization of native biomembranes on planar supports without losing membrane asymmetry.

Biomembranes on ultrathin cellulose films have also been exploited for fundamental studies on cell adhesion. Goennenwein *et al.* used lipid vesicles bearing reconstituted blood platelet integrin receptors called $\alpha_{\text{IIb}}\beta_3$ forming a biomembrane on a cellulose film.¹²¹ The supported membranes exhibited a homogeneous coating over large areas (18 \times 18 mm^2), enabling partially long-range lateral diffusion of reconstituted receptors pointing in their extracellular domains into the aqueous phase. No such diffusion was observed for membranes directly deposited on glass slides. The functionality of the membranes was tested quantitatively by measuring the adhesion strength to giant vesicles containing liquid coupled hexapeptides which are specifically recognized by integrin $\alpha_{\text{IIb}}\beta_3$. With the micro-interferometric technique, the estimated receptor–ligand binding energy was determined to be 10 $\text{k}_\text{B}\text{T}$ under bioanalogue conditions.

4.1.6 Summary on adsorption studies. So far, only a few extensive and scientifically unambiguous studies on adsorption to cellulose model surfaces have been made. These include polyelectrolytes,^{80,101,103,104} non-ionic surfactants,¹⁰⁷ and enzymes.^{67,115} As for the modern analytical methods, the use of XPS was explored by Rojas *et al.*,¹⁰¹ reflectometry by Geffroy *et al.*⁸⁰ and Torn *et al.*,¹⁰⁷ and ellipsometry by Eriksson *et al.*^{67,115} Astonishingly, QCM-D has been applied to study adsorption on model films of cellulose only tentatively,^{103,104} although there is ongoing research on the subject in, for instance, our group.¹²² Extensive exploitation of the highly sensitive QCM-D would be absolutely vital to illuminate many adsorption processes whose fundamental aspects have remained vague and which therefore have not been exploited in practice due to, for instance, problems in reproducibility. An example of this kind of adsorption phenomenon is the adsorption of carboxymethylcellulose onto cellulosic fibres in order to improve paper strength.¹²³ There are numerous problems in this clearly advantageous treatment and the only way to fully understand the problems is by fundamental research. Furthermore, the introduction of diverse cellulose films would shed light on the role of the supramolecular state of cellulose in adsorption. For instance, the comparison between amorphous^{77,90} and crystalline^{78,80} films would already solve the speculation by Torn *et al.*¹⁰⁷ about the impact of the “softness” of the cellulose films, since crystalline cellulose does not possess the said “softness”. Also the open films, in particular those of cellulose on cellulose,⁹¹ would demonstrate the importance of surface area on adsorption: the open films have a different surface area to

the closed films and the area can be calculated from the AFM height images.

In other words, the recent advent of cellulose model surfaces has opened an exceptionally large field of possibilities for fundamental physicochemical research on adsorption phenomena to cellulose. This research is complementary with the already established area of applied research to cellulosic fibres. The recent paper on surfactant adsorption¹⁰⁷ is a sound example how the basic research, initiated by pragmatic phenomena in cellulose research, may be linked to theoretical considerations to reach more profound understanding.

4.2 Direct measurements of surface forces

In contrast to the rather scattered nature of adsorption studies, the surface force measurements applied to cellulose model surfaces are a far more uniform body of work, with plenty of cross-referencing to each other's works. The pragmatic approach has usually been the driving force for the research: the formation of the all important fibre–fibre bond in papermaking, for instance, is largely a question of interaction between two cellulose surfaces. Only the roughness and chemical ambiguity of ligno-cellulosic fibres prevents fundamental studies, which is why the model surfaces with their smooth morphology and chemical uniformity provide a perfect subject to study.

4.2.1 Interaction between pure cellulose surfaces. The first attempt to directly measure the forces between cellulose surfaces on a molecular level was made in 1993 by Neuman *et al.*⁵⁹ using the interferometric surface force apparatus (SFA). Unfortunately there were numerous problems involved as the methodology of cellulose model surface preparation had not been properly established (see section 3.1.1) and direct surface force measurements have strict requirements for the uniform chemistry and overall smoothness of the films. TFA has a tendency of chemically modifying the cellulose and the cellulose surface was not perfectly smooth with a roughness of 2–5 nm. Furthermore, the force measurements were complicated because the cellulose film was not firmly attached to the mica. Sometimes it delaminated and even when it did not delaminate the structure of the film was irreversibly altered when the surfaces were brought together with a compressive load more than about 0.5–1 mN m^{-1} . Neuman *et al.* described the water swollen cellulose film as a cellulose layer which has long and weakly charged cellulose chains, so called dangling tails, extending out about 100 nm from the surface.

Another preliminary paper about surface forces was published by Kräuter *et al.* who measured the bond strength between silicon wafers covered with LB-cellulose films.¹²⁴ The bond strength was determined by inserting a blade between the two wafers and imaging the crack geometry using transmission IR as described by Maszara.¹²⁵ This time the cellulose films were prepared with the well described method of Schaub *et al.*⁷⁷ In our view, however, the bond strength determination does not strictly qualify as a surface force technique since force is not followed as a function of distance. An adhesion measurement would be a more appropriate categorisation.

In a pioneering surface force study between two cellulose surfaces, Holmberg *et al.* found that the LB-cellulose film could also be used in direct surface force measurements using the SFA.⁷⁹ The films were smooth enough for the SFA and no delamination upon exposure to water was observed (see Methodology, section 3.1.2). However, the small scale roughness still introduced a rather large variation in measured pull-off forces, since the true contact area varied between measurements. Across a dilute electrolyte solution short-ranged steric repulsion was observed between two LB-cellulose coated mica surfaces. The dangling-tail model suggested by Neuman *et al.*⁵⁹ did not apply to these surfaces and here the cellulose film was described as a water-swollen gel with only a few protruding chains. These chains give rise to the steric repulsion. The act of measuring surface forces flattens the cellulose film and the steric force measured on the first approach is stronger than the forces measured on separation and consecutive approaches to the same position as illustrated by the force curves in Fig. 10.

The LB-cellulose film was later used to measure forces as a function of surface separation at different pH's and different electrolyte concentrations.¹²⁶ It was found that the film was slightly negatively charged although the steric forces dominated over the electrostatic forces and the force curves could not be fitted successfully to the DLVO theory.¹⁰⁰

Zauscher *et al.* used commercial regenerated cellulose films (Spectra/Por 4) and regenerated cellulose beads to study forces between cellulose surfaces using AFM and the colloidal probe (CP) technique.¹²⁷ The forces in electrolyte solutions were governed by double-layer forces at large separations and the fitted surface potentials were low, in agreement with earlier AFM CP findings using two cellulose spheres.¹²⁸ At small separations both speed dependent forces and steric forces were observed, but the author did not observe the hysteresis between the first and consecutive approaches reported by Holmberg *et al.*⁷⁹ They interpreted this to be due to the rate of measuring the forces, but it might as well be due to the

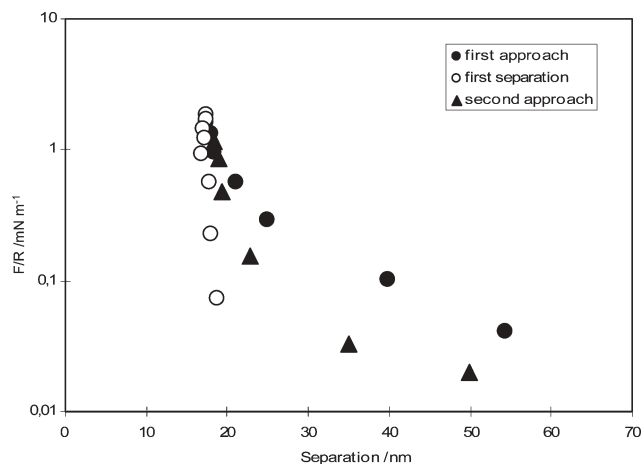


Fig. 10 Forces (F) normalized by the local radius of curvature (R) as a function of surface separation between two LB-cellulose surfaces across an aqueous 0.1 mM KBr solution. The decrease in steric repulsion on separation and the second approach as compared to the first approach shows that the act of measuring forces flattens the cellulose film.

difficulty to measure the first contact between probe and surface using the AFM. Since the forces were not normalized with the radius of curvature they cannot be directly compared with other studies and besides, the range of forces was rather long, which probably is due to the roughness of the cellulose films and beads used. The RMS roughness of the cellulose film was 3–4 nm determined from a $1 \mu\text{m}^2$ area and for the bead it was 35 nm for a $5 \times 5 \mu\text{m}$ area.

At this point, some fundamental differences between the SFA and AFM CP measurements should be pointed out. When measuring surface forces using the colloidal probe technique one is not restricted to transparent films, as is the case when using the SFA. Weaker forces can also be detected in comparison to SFA. An illustrative example of this is that double-layer forces have been reported between cellulose surfaces using the colloidal probe technique,^{127,128} while the cellulose surfaces were often described as uncharged in the SFA studies.⁷⁹ The low surface potentials (10–20 mV) obtained for the cellulose surfaces are below or close to the detection limit of the SFA. The advantage of the SFA is again that surface deformation can be detected and the absolute distance between the surfaces can be measured. Hence, swelling of the layers and thicknesses of adsorbed polymer layers can easily be determined. Actually, if the studied surfaces are too soft it is difficult to determine the constant compliance region and that may interfere with the interpretation of the results. For a more detailed comparison of the methods see reference.¹²⁹

In a recent publication Notley *et al.* were able to measure attractive van der Waals forces between cellulose surfaces.¹³⁰ They used a cellulose sphere prepared from LiCl–dimethylacetamide solution and a spin coated cellulose film from NMMO, prepared as described by Gunnars *et al.*⁶³ The measurements were performed at low pH (3.5) to ensure that all carboxylic groups present remain undissociated, which ensured that no repulsive double-layer forces were observed. Although the surfaces were rather rough—RMS roughness for $1 \mu\text{m}^2$ images of 1.4 nm and 5.9 nm for the spin-coated flat film and the sphere, respectively—they observed no steric repulsion between the surfaces in contrast to all previous reported observations.^{79,127,128} This rather surprising result may occur because also the steric forces are pH dependent. Österberg and Claesson reported an increase in the swelling of LB-cellulose films, which was seen as an increase in range and magnitude of the mainly steric repulsion.¹²⁶ This was interpreted to be due to the dissociation of carboxylic groups present in the film. Unfortunately, they did not investigate the effect of lowering the pH on swelling.

4.2.2 Interaction between cellulose and other materials. The forces between a cellulose film and a mineral surface are dominated by electrostatic repulsion at larger separations and steric repulsion at smaller separations.^{131–134} Surface potential for the cellulose films and mineral surface were obtained by fitting the data to DLVO theory and the values varied depending on the cellulose films and mineral surfaces applied in the study: mica,¹³² silica,¹³⁴ or glass.¹³³ Pull-off forces stronger than those between two cellulose surfaces were reported for the interaction between cellulose and a mineral surface but the forces on separation were not studied in

detail.^{132,133} Radtchenko *et al.*, however, performed an exceptionally thorough investigation on the attractive force present between cellulose and silica surfaces.¹³⁴ They utilised two different spin coated cellulose films: a rough film spun directly from DMAc–LiCl solution and a smooth film, hydrolysed from spin coated TMSC. A strong attraction due to bridging of cellulose chains to the bare silica was observed upon separating cellulose and silica. This effect was the most pronounced for the smoother and softer cellulose film, regenerated from TMSC, than for the rougher and more rigid film from DMAc–LiCl. The comparison between the two distinct cellulose films sheds light also on the differences between a cellulose surface deposited directly from a solution and a film cast *via* a dissolving derivative (see Methodology section 3.1). The more rigid nature of the cellulose films from DMAc–LiCl supports the assumption by Notley and Wågberg⁶⁵ that the films cast directly from a cellulose are at least partially crystalline. Unfortunately, the authors did not explore the behaviour of LB-cellulose films, which would have been interesting given that the LB technique initially deposits a far more ordered structure than spin coating.

An important question, both fundamentally and pragmatically, is the effect of adsorbed polyelectrolytes on the forces between cellulose surfaces.⁹⁷ Österberg studied a highly charged cationic polyelectrolyte poly[[2-propionyloxy]ethyl]-trimethylammonium chloride] PCMA,¹³² Poptoshev *et al.* studied polyvinylamine (PVA),¹³³ and Leporatti *et al.* compared a standard wet strength agent poly(amideamine) epichlorohydrin resin (commercially Servamine) with copolymers from poly(diallyldimethylammonium chloride) PDADMAC and vinylalcohol (VA).¹³⁵ One main finding of Österberg¹³² was that when the polyelectrolyte fully covered the surface, the forces at large separations were dominated by the properties of the polyelectrolyte, but close to contact the underlying substrate affected the forces and, for example, the adhesion between the cellulose surfaces covered with polyelectrolyte differed totally from the adhesion between mica surfaces covered with the same polyelectrolyte.¹³⁶ Leporatti *et al.* found that the commercial wet strength agent improved the adhesion between cellulose surfaces in electrolyte solutions substantially more than copolymers of DADMAC and VA.¹³⁵

An interesting observation with LB films was that the attraction between cellulose and cationic polyelectrolyte was sometimes stronger than the mutual attraction between the cellulose chains in the layered cellulose film. The phenomenon was observed when the forces between cellulose covered with PVA and bare silica¹³³ and between two cellulose surfaces, only partially covered with PCMA, were studied.¹³² In these cases a very long ranged attractive force was observed due to stretching of the LB film.

Lefebvre and Gray studied multilayers of carboxymethyl cellulose (CMC) and PDADMAC.⁶⁹ Cationic (PDADMAC) and anionic (CMC) polyelectrolytes were consequently adsorbed to a surface of cellulose I nanocrystals to give single bilayers. Force–distance curves were then recorded with a Si₃N₄ AFM tip from 1, 3 and 5 bilayer samples in different ionic strengths. They found an interesting difference between single and multiple polyelectrolyte bilayers, which would be worthwhile to study in a more quantitative way.

Nigmatullin *et al.* have studied the interaction between cellulose surfaces modified by CBDs (cellulose binding domains), *i.e.* peptides specifically binding to cellulose.¹³⁷ They used thick cellulose films prepared by casting a cellulose acetate solution on a porous polypropylene support followed by alkaline saponification and colloidal probes of 3–6 µm cellulose beads. They observed less repulsive forces after adsorption of CBD despite an increase in surface charge owing to the irregularity of the topography of protein surface and the non-uniform distribution of surface charges. Binding double CBD hybrid protein to cellulose causes adhesion, probably due to cross-links between the cellulose surfaces.

4.2.3 Friction forces. The friction between cellulose surfaces and between cellulose and other materials is important in papermaking and the end-uses of paper products. Hence, model cellulose films have also been used to study the friction forces in cellulose systems. Zauscher *et al.*^{72,127} found that the friction exhibits irregular stick-slip behaviour related to surface roughness. Adsorption of small amounts of high molecular weight polyelectrolytes decreases significantly the sliding friction between cellulose surfaces.

4.2.4 Adhesion measurements. A completely different method was applied by Rundlöf *et al.* who used the JKR method to measure the adhesion between LB deposited cellulose films from TMSC and poly(dimethylsiloxane) (PDMS) caps.¹³⁸ The JKR method utilizes the deformation under zero or applied load to accurately determine the adhesion between two bodies.¹³⁹ Although not a method to measure forces as a function of separation, the JKR technique is recognized as an effortless way to determine adhesion forces. It is far less time consuming than SFA or AFM CP. Rundlöf *et al.* conclude rather tentatively that the hysteresis between loading and unloading cycles depends on a multitude of factors, such as viscoelastic deformation, interpenetration of the surface layers and surface roughness among others.¹³⁸ As a feasibility study, the paper is nevertheless an important contribution to the surface force studies with cellulose films; only more systematic experiments are needed.

4.2.5 Summary on surface force studies. Since surface force studies are probably the most obvious application to smooth, ultrathin model surfaces of cellulose, the body of research is also more extensive than with adsorption or swelling studies. Pioneering experiments on cellulose–cellulose interactions were performed by Österberg and co-workers with SFA.^{79,126} Recently, an important result was achieved by Notley *et al.* who pointed out that steric repulsion forces between cellulose surfaces may be pH dependent, based on AFM CP measurements.¹³⁰

As for the forces between cellulose surfaces and other materials, fits to the Poisson–Boltzmann theory have been made, based on measurements between cellulose and silica,¹³⁴ mica,¹³² and glass.¹³³ Furthermore, surface forces have been investigated in the presence of various polyelectrolytes.^{132,133,135}

The problem with surface force studies is that, although the most established application to cellulose model surfaces, the

research does not form a uniform body but rather a scattered domain of publications. Much more research is necessary to explore properly the fundamentals behind the interactions of cellulose with itself and other materials. Already a simple comparative, pH-controlled study between amorphous^{79,83} and crystalline^{68,69} cellulose surfaces would provide much more insight in the steric repulsion between two cellulose surfaces. Moreover, the open films of cellulose on silica^{81,89} could provide an important intermediate between a pure cellulose and pure silica surface, especially as the amount of the cellulose on silica in the open films is adjustable.

It must be emphasized that, although an important field of research, the surface force measurements between two cellulose spheres are not included here since this review is about model films of cellulose. A motivated reader is referred to reference 128 and the references therein concerning the interactions between two cellulose spheres.

In conclusion, surface force studies on cellulose films already contain sound work linking theory to experiments prompted by pragmatic phenomena.^{79,130,132–134} More exploitation of the recent literature on the methodology of the preparation of films is needed to push the research forward.

4.3 Swelling

4.3.1 Swelling of natural fibres vs. model surfaces. The swelling properties of an ionic network in aqueous solution are controlled by the charge density of the polymer, the degree of crosslinking, the ionic strength and the nature of the counter ions.¹⁴⁰ Cellulosic fibres can be considered a polyelectrolyte gel which swells upon exposure to water because water molecules penetrate between hydrogen bonded fibrils in the fibre cell wall.¹⁴¹ The availability of the OH-groups affects absorption; in amorphous regions of cellulose and in amorphous hemicelluloses the internal bonding is weak, and OH-groups are readily available for water. In crystalline cellulose, bonding is stronger and the availability of OH-groups is lower. Grignon and Scallan applied the theories by Donnan¹⁴² as well as Proctor and Wilson¹⁴³ on the swelling of gels, to the swelling of wood pulps and carboxymethylated cotton.¹⁴⁴ Experimental evidence on the swelling of the fibre wall and its dependence on the chemical environment (pH, ionic strength) has been extensively documented.^{145,146}

One key question when using cellulose model surfaces is whether they are representative and reliable models for the cellulose fibres: the model films should show the similar kind of swelling behaviour when compared to the pulp fibres. The swelling behaviour of cellulose model surfaces was first reported in the work conducted by Neuman *et al.*⁵⁹ The deficiencies with these model surfaces have already been discussed (see section 3.1.1) but, nevertheless, the results clearly indicated that the model cellulose film did swell in aqueous solutions.

The more stable and well characterised films by Holmberg *et al.*, deposited with the LB-technique, demonstrated considerable swelling when exposed to water.⁷⁹ In aqueous solution, the film thickness increased by about 40% measured with SFA and ellipsometry. In humid air (RH 100%), the SFA measurements gave a thickness increase of *ca.* 12%. AFM

imaging conducted by the same authors confirmed the LB-cellulose layer swelling.¹²⁶ In water the swollen cellulose film gave rise to an increase in surface roughness, which was determined from AFM topography images.

The effect of solution pH on swelling behaviour of these LB-cellulose films was also investigated by Österberg and Claesson.¹²⁶ In dilute electrolyte solutions, the cellulose film was uncharged and rather compact at pH 6.0. No electrostatic double-layer repulsion was observed between the cellulose surfaces at pH 6. When pH was raised above 7 the long-range steric repulsive forces increased. The authors concluded that the pronounced swelling effect was due to the increased charge density of the cellulose film (carboxylic acid groups, originating from the oxidation of the cellulose surface, are dissociated). The increase in charge density favours intra-chain repulsion which results in longer tails extending outwards from the surface, causing the increased range of the steric force.

Rehfeldt and Tanaka investigated film thickness variations with respect to relative atmospheric humidity using the desilylated Langmuir–Blodgett and spin coated cellulose films.⁸¹ Films with different dry thicknesses were compared and the effect of film structure on hydration properties was discussed. Thickness values of dry and hydrated cellulose films, swelling ratios (thickness when equilibrated in humid air/dry thickness) and hydration forces of the films were analysed by ellipsometry. It was found that when the films were allowed to equilibrate at the relative humidity below 80% there were no considerable changes in film thickness. In higher humidity conditions, the film thickness sharply increased, giving a maximum swelling ratio of 1.7 for LB-cellulose film. Maximum swelling ratios varied between 1.4–1.7 regardless of the preparation techniques used or the dry film thickness. The authors concluded that although spin-coated films are more isotropic than LB-deposited cellulose films, the hydration properties are similar and independent from the initial film thickness.

The paper also reports the dynamic swelling (non-equilibrium state of the film) and the swelling kinetics of the cellulose films.⁸¹ Hydration of the films was investigated under osmotic shocks by rapidly changing the relative humidity of the system. The cellulose film was shown to be able to uptake water very fast seen as a sharp increase in film thickness. The characteristic time constants for swelling and draining of the cellulose films were calculated but the dynamic swelling studies were not profound enough for further discussion. Therefore, the authors pointed out the need of more detailed analyses for kinetic processes upon swelling.

The water uptake ability of the cellulose model films with different charge densities was investigated using quartz crystal microbalance with dissipation (QCM-D) by Fält *et al.*¹⁴⁷ Charge density of the cellulose films was adjusted by carboxymethylation of the dissolving pulp fibres to a desired degree. The cellulose model films were deposited on quartz crystals by spin coating as described in an earlier paper by the authors.⁶³

The advantage of QCM-D is the possibility to follow the changes in the layers' physical properties during the swelling process. Thus, swelling kinetics and viscous changes of the film when exposed to water and aqueous solutions of electrolytes was measured. Fält *et al.* extensively studied the swelling and

de-swelling ability of the cellulose films, not only as a function of charge density of the cellulose but also as a function of different electrolytes, electrolyte concentration and pH.¹⁴⁷ Results showed swelling at low electrolyte concentrations and de-swelling when the electrolyte concentration was increased. These observations were explained with pH changes inside the cellulose film (Donnan effect) which strengthen the swelling forces at low ionic strength and reduced osmotic pressure. High ionic strength, in turn, leads to a decrease in water uptake. Increasing charge density of the cellulose films results in more pronounced swelling effects. These conclusions were well in accordance with the theories of the polyelectrolyte gel behaviour.¹⁴⁴ Furthermore, the swelling in the presence of NaCl, CaCl₂ and Na₂SO₄ were compared. The behaviour of the film when increasing the electrolyte concentration was mainly the same but some dissimilarities were also observed. The effect of pH on swelling was well in accordance with the earlier reported studies of the fibre swelling:¹⁴⁵ the higher the pH, the more the model films swelled. Softening and stiffening of the film were observed concomitantly with the swelling/de-swelling effects, respectively. Moreover, the authors quantified the cellulose layer swelling using AFM.

Comparison of the swelling behaviour of the cellulose model surfaces with the swelling behaviour of carboxymethylated dissolving fibres gives the added value to the research by Fält *et al.*¹⁴⁷ AFM and water retention values, measured from the real fibres, supported the effects observed with QCM-D.

Tammelin *et al.* conducted a similar kind of work relating to the cellulose model film swelling by using QCM-D.¹⁰⁴ In this case the film was analogous to the films by Holmberg *et al.*, *i.e.* an LB film with very low charge density.⁷⁹ The swelling results correlate well with those obtained by Fält *et al.* for cellulose films with low charge.¹⁴⁷ Both studies conclude that cellulose films with low charge do not show considerable swelling/de-swelling ability, but slight water coupling ability and layer softening is observed. Fig. 11 gives an account of swelling as investigated by QCM-D in both publications.^{104,147} The observed trends are also in accordance with the study of Holmberg *et al.*⁷⁹ but the estimated thickness values differ to some extent. The reason for the differences in the amounts of water imbibed after swelling analyzed by SFA, ellipsometry and QCM-D was stated to be unclear. It was speculated that the differences might result from the diverse techniques which may give very different values for polymer film thickness.¹⁰⁴ Moreover, values achieved from ellipsometry and QCM-D are not absolute thickness values, they are only estimated or calculated from models using other quantities such as refractive index or frequency change.

4.3.2. Wetting and drying of the cellulose film—hornification.

The term hornification defines the irreversible changes in the structure of natural fibres upon removal of water, resulting in inferior strength properties of fibres.¹⁴⁵ Its fundamental reasons are still under debate.^{148,149}

Despite its practical importance, there are only two recent studies focusing on hornification with model surfaces. Notley and Wågberg saw irreversible supramolecular transformations taking place in amorphous cellulose during heat treatment.⁶⁵ Meanwhile, Kontturi *et al.* also managed to image

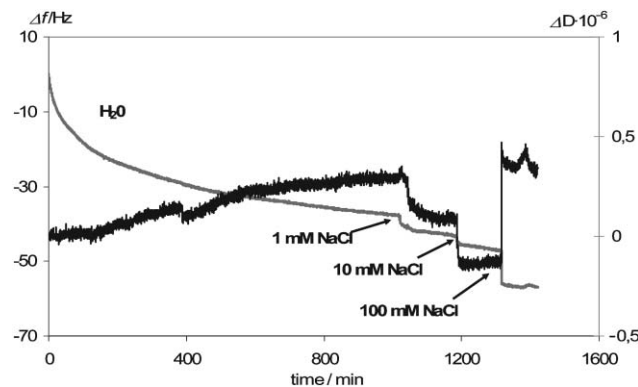


Fig. 11 Change in frequency and dissipation as a function of time during swelling and stabilization of LB-cellulose film in aqueous solutions of increasing ionic strength. The frequency decreases when the electrolyte solution is added on the cellulose, indicating that mass increases on the crystal, *i.e.* water penetrates into the cellulose structure. After the addition of pure water on the cellulose surface, the slight increase in dissipation indicates that some swelling of the film occurs. Reduced dissipation at higher electrolyte concentrations indicates de-swelling of the film, which can be explained with the Donnan effect of pH changes within the film. ($f_0 = 5$ MHz, $n = 3$).

supramolecular rearrangements upon wetting and drying of open films of nanosized cellulose.⁸⁹ However, both studies were descriptive in nature, lacking fundamental explanations. Hornification is, nevertheless, a phenomenon which will undoubtedly be explored in the future with the morphologically straightforward model surfaces.

4.3.3 Summary on swelling studies. The hydration force study by Rehfeldt and Tanaka⁸¹ is arguably the seminal study within the swelling investigations concerning model surfaces of cellulose. It is not only due to the viability of swelling research but also to the fact that the authors compare the behaviours of two distinct surfaces: cellulose hydrolysed from both LB-deposited and spin-coated TMSC—a rare case in the literature on cellulose films. The fact that the swelling is independent of the preparation methods has intriguing implications. After all, LB deposition is a highly controlled technique as opposed to the rather violent solvent ablation of spin coating. In addition, the initial TMSC films from LB deposition and spin coating appear quite different as their contraction upon hydrolysis to cellulose varies significantly (see Methodology in section 3.1.2). Also the results from the kinetics of swelling, followed by a means of osmotic shocks by Rehfeldt and Tanaka,⁸¹ show that the swelling happens very fast in the supposedly amorphous films.

Another landmark publication in swelling research to the cellulose films is the QCM-D study by Fält *et al.*¹⁴⁷ Qualitatively the results are self-evident, following the trends of the Donnan theory, but importantly the authors demonstrate the applicability of QCM-D to quantitatively examine the swelling of cellulose model surfaces. This aspect is enhanced in the study by Tammelin *et al.*¹⁰⁴

One of the straightforward pragmatic applications in swelling studies would be to apply the model films in tracking down the origin of the hornification phenomenon. There are

already two preliminary studies on the issue^{65,89} and the subject will certainly receive more attention in the future.

5. Conclusion and future perspectives

Since the introduction of a modern preparation method for smooth, ultrathin films of cellulose by Schaub *et al.* in 1993,⁷⁷ the research on cellulose model surfaces has gradually begun to gain more interest. First, during the latter half of the 1990s, the publications were scarce,^{78,79,118,124,128,131} but the current decade has seen a sharp increase in the literature on ultrathin cellulose films.^{63–66,67–69,80–83,89–91,95,101,103,104,107,115,120,121,126,130–135,138,147}

However, the model surfaces of cellulose are by no means an intensive area of research, yet. Cellulose research is still largely executed by specialists—“cellulose chemists”, “textile chemists” or “wood chemists”—who might occasionally miss a broader picture in scientific development. These people traditionally—though not always—exhibit the contempt of a technical researcher towards fundamental aspects. Similarly, cellulose chemistry is often seen by the general scientific community as an eccentric offshoot of polymer chemistry which requires profound specialisation. We feel that this review appears at a watershed: more and more scientists without the status of a “cellulose chemist” are starting to see cellulose as an extremely viable subject to research. The substance is no longer just an ingredient in cardboards or textiles: it is the most abundant biopolymer, the principal ingredient in biomass; perhaps, in a properly managed form, an ecologically sustainable source of energy. Similarly, more and more chemists dealing primarily with cellulose are beginning to recognise the importance of the fundamental aspects which have so far been scrutinised by a very small group of researchers. The development is aided by the recent progress in understanding the supramolecular chemistry of cellulose^{28–30,38,39} and, for instance, the applications of the model films of cellulose elaborated in this review. It is the task of the present decade to bring the cellulose experts and the general scientists together.

In conclusion, the model surfaces of cellulose present a fundamental aspect to the physical chemistry of cellulose which has largely been unexplored so far. The fundamental research helps the understanding of various phenomena which have hitherto remained unexplained in the molecular level. Likewise, the development in the preparation techniques of cellulose model surfaces may lead to emergence of unprecedented surfaces with novel properties. This review intends to advocate this progress.

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