INTERFACIAL INTERACTIONS AND FOULING IN PAPER MACHINES

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Interfacial interactions and fouling in paper machines

Abstract

The aim was to understand the role of surface forces in paper machine fouling. Also possibilities to develop antifouling paper machine surface materials were studied. Experiments were focused on adsorption kinetics, adhesion and wetting kinetics of substances causing fouling in paper making. In addition, antifouling properties of photocatalytic titanium dioxide were investigated. Adsorption kinetics were studied with a quartz crystal microbalance with dissipation monitoring (QCM-D). The experiments were made with wood resin, AKD, latex and several other model deposits. Rates of adsorption were found to be diffusion controlled in the beginning of adsorption. Blocking by already adsorbed particles hindered the adsorption at later stages. It was concluded that changes in surface roughness affect the detected dissipation and frequency shifts. Hence, QCM-D can be used to study the spreading kinetics of soft colloids which was demonstrated experimentally with styrene-butadiene latex and wood resin emulsions. Contact angles adhesion and wetting kinetics of lipophilic wood extractives were studied on surfaces present in a paper machine. The adhesion of oleic acid and other lipophilic wood extractives is large to a hydrophobic fluoropolymer and small to hydrophilic surfaces in solution. Therefore, extractives tend to accumulate on hydrophobic paper machine parts and hydrophobic spots on paper web in the wet end. Van der Waals forces determined the adhesion of oleic acid in air on most surfaces studied. A water film is formed between the drop of extractives and the interface prior to spreading in solution. The removal of this water film may take several seconds, which prevents the spreading of aggregated drops of extractives. An increase in surface roughness shortens the pre-wetting period significantly and enhances the contact of extractives. The photocatalytic decomposition kinetics of wood extractives under UV illumination was studied with QCM-D. In the beginning of the degradation measurements, a 0-3 minute long initation period, with hindered or prevented degradation was often detected. After the initiation period, the degradation continued with a relatively constant rate until it decelerated again near the end of experiment. The primary mechanism of removal of the films was photocatalytic degradation, but it was shown that the penetration or formation of water at the TiO2/film interface and the flow of oxygen to the interface are also of importance. Correlation of the flow of oxygen to the rate of photocatalytic degradation was observed.

The results can be utilized, when antifouling paper machine surface materials and paper chemicals for deposit control are developed.

Tekijä   Timo Kallio

Väitöskirjan nimi
Pintavoimat ja niiden vaikutus paperikoneen likaantumiseen

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Tiivistelmä

Tavoitteena oli ymmärtää pintavoimien vaikutusta paperikoneen likaantumiseen. Tutkittiin paperikonetta likaavien aineiden adsorptionopeutta, adheesiota ja leviämisnopeutta. Lisäksi tutkittiin mahdollisuuksia kehittää likaantumattomia paperikonepintoja. Kokeissa käytettin AKD:ta, uuteaineita, lateksia sekä useita muita mallilikoja. Kuten oletettua likapartikkelien diffuusio pintaan määräsi likapartikkelien adsorptinopeuden. Adsorption myöhemmässä vaiheessa jo adsorboituneet partikkelit hidastivat adsorptiota. Polyuretaanipinnalle adsorptio oli DLVO -voimien aikaansaamaa. Todettiin, pinnan karheuden muutosten vaikuttavan QCM-D:llä mitattuihin taajuus, ja dissipaatiosiirtymiin. QCM-D:tä voi täten käyttää kolloidien leviämiskinetiikan seurantaan. Puun uuteaineita käytettiin mallilikana kontaktikulma- ja adheesiomittauksissa. Vedessä uuteaineiden adheesio oli korkeaa hydrofobiselle fluoropolymeeripinnalle, ja pientä hydrofiilisille pinnoille. Ilmassa mitatut adheesiot olivat pienimmät fluoropolymeerille. Uuteaineilla on täten taipumus kerääntyä hydrofobisille paperikonepinnoille ja hydrofobisiin kohtiin paperirainaa paperikoneen märkäosalla. Voimakkaasti hydrofobiset fluoropolymeerit vähentävär uuteaineiden aihettamaa likaantumista paperikoneen kuivalla osalla. Heikosti hydrofobiset pinnat taas eivät estä likaantumista tehokkaasti. Van der Waals voimat pääosin määräsivät oleiinihapon ja uuteaineiden adheesiota. Kun uuteainepisarat leviävät vedessä, jää leviämisen alkuvaiheessa pisaran ja pinnan väliin jää ohut vesikerros, jonka tyhjenemisaika on hyvin hidas. Tämän vuoksi uuteaine-emulsion ja pinnan välille ei muodostu heti kontaktia, mikä vähentää aggregoituneiden uuteainepisaroiden taipumusta liata. Pinnan karheuksien todettiin nopeuttavan leviämistä sen alkuaiheessa, koska karheuspiikit rikkovat vesikalvon rakennetta. Uuteaineet hajosivat titaanidioksidipinnalla UV-valossa, mikäli kerrospaksuus oli riittävän alhainen. Fotokatalyyttinen hajoaminen ei alkanut useinkaan heti UV-valon sytyttyä, vaan usein havaittiin 0-3 minuutin mittainen hidastuneen hajoamisen aika, jonka jälkeen hajoaminen nopeutui. Tämän pääteltiin liittyvän hapen ja veden tunkeutumiseen likakerroksen läpi. Veteen liuenneen hapen diffuusio määräsi useissa tapauksissa fotokatalyyttisen hajoamisnopeuden. Lisäksi pääteltiin, että veden tunkeutuminen TiO2-pinnan ja uuteainekerroksen väliin edistää fotokatalyyttistä puhdistusta.

Tuloksia voidaan hyödyntää mm. likaantumattomien paperikonepintojen ja likaamattomien paperikemikaalien kehittelyssä.

Asiasanat   Paperikoneen likaantuminen, pintavoimat, adsorptiokinetiikka, adheesio, kontaktikulmat, QCM-D

Alkusanat

Perheelle

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1. List of Publications

Paper I Timo Kallio and Juha Kekkonen, Fouling in the paper machine wet end, *Tappi Journal* **2005,** 40, 20-24.

Paper II Timo Kallio, Juha Kekkonen and Per Stenius, The formation of deposits on polymer surfaces in paper machine wet end, *Journal of Adhesion* **2006**, 80, 933-969.

Paper III Timo Kallio, Janne Laine and Per Stenius, Intermolecular interactions and the adhesion of oleic acid, accepted to *Journal of Dispersion Science and Technology.*

Paper IV Timo Kallio, Juha Lindfors, Janne Laine and Per Stenius, Spreading and adhesion of lipophilic wood extractives on surfaces in paper machines, accepted to *Nordic Pulp and Paper Research Journal.*

Paper V Timo Kallio, Sanna Alajoki, Viljami Pore, Mikko Ritala, Janne Laine, Markku Leskelä and Per Stenius, Antifouling properties of TiO_2: Photocatalytic decomposition and adhesion of fatty and rosin acids, sterols and lipophilic wood extractives, *Colloids and surfaces A: Physicochemical and engineering aspects* **2006,** 291, 162 -176.

1.1. Contributions of the author

Paper I Timo Kallio wrote the manuscript and made the literature review

Papers II-IV Timo Kallio was responsible for the experimental design, performed the experimental work related to surface preparations, QCM-D and contact angle measurements, analysed the corresponding results and wrote the manuscripts.

Paper V Timo Kallio defined the research plan, performed the experimental work together with Sanna Alajoki, analysed the experimental work, and wrote the manuscript.

He has also published three additional papers related to this thesis and has presented the results at several international conferences.

1.2. Related publications

Juha Lindfors, Susanna Ylisuvanto, Timo Kallio, Janne Laine and Per Stenius, Spreading and adhesion of ASA on hydrophilic and hydrophobic SiO_2. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2005**, 256, 217-224.

Juha Lindfors, Susanna Ahola, Timo Kallio, Janne Laine, Per Stenius and Mikael Danielsson, Spreading and adhesion of ASA on different surfaces present in paper machines, *Nordic Pulp and Paper Research Journal* **2005**, 20, 453-458.

Timo Kallio, Juha Kekkonen and Per Stenius, Acid-Base Properties and Adsorption of an azo dye on coating pigments, *Journal of Dispersion Science and Technology* **2006**, 27**,** 825-834.

2. Introduction

Surfaces are never fully clean. Foreign atoms, molecules and dust are always presented on every surface. Vapor molecules (water, hydrocarbons) and dust are collected on surfaces from air and they largely determine the surface properties of surfaces. For example, when mica is cleaved in high vacuum its surface energy is 4500 mJ/m^{-2}, but cleaved in laboratory air it falls below 300 mJ/m^2 (Bailey et al. 1970).

Impacts of fouling are significant in most industrial processes: Deposits act as catalyst poisoners in chemical processes, microbial deposits are a problem in food processing and micro-circuits are manufactured at clean room environment in order to avoid fouling.

The technical and economic impacts of fouling are significant in paper making (see chapter 3). The basic mechanisms of fouling in paper machines are, however, not well investigated. In particular, the role of surface forces on fouling is poorly understood, which limits the possibilities to reduce fouling problems in paper mills. This has motivated me to publish this thesis, where the aim was to understand the role of surface interactions in paper machine fouling and cleaning.

2.1. Outline

Surfaces forces and fouling mechanisms in paper machine are summarized in chapters 2-8 and in Paper I. Also common methods to control fouling and cleaning are briefly reviewed (chapters 6-7 and Paper I). Experimental research papers are summarized in chapters 9-12. They are focused on the adsorption of fouling substances (Paper II and chapter 10), on the adhesion extractive-based deposits (Papers III, IV and chapter 11) and on the removal of deposits by photocatalytic cleaning with TiO_2 (Paper V and chapter 12). Complementary studies with hemicelluloses and microbe adsorption are summarized in chapter 10.

3. Fouling in papermaking

Formation of deposits during papermaking is very complex, because of the following:
1) Many kind of substances cause fouling. Substances can be hydrophilic or hydrophobic, soft or hard. They can be particles, polymers liquids or gases. Their size varies from salt ions with atomic size range up to fibres, which may be several millimeters long. 2) There are many fouling mechanisms whose nature is very complicated (chapter 6): A deposit can be formed by different substances due to aggregation, coagulation, adsorption or reactions or microbiological activity. Several surface forces have an influence on the formation of deposits (chapter 4). 3) The process chemistry is very variable, pH, concentration and quality of ions, the content of different gases and temperature in the processes fluctuate and the quality of raw materials, pulp and broke varies; These variations are different on each machine and the formation of deposits depends strongly on the particular conditions in each process. 4) The influence of hydrodynamic and mechanical forces on the process surface or on deposits varies and depends on the surface morphology and the mechanical softness or hardness (viscoelasticity) of deposits. Process surfaces are showered, cleaned with chemicals and subjected to forces from mechanical cleaning. 5) The amount of water on the process surface alternates; Equipment operates in wet, half-dry or very dry conditions. The presence and amount of water has very strong influence on fouling mechanisms and surfaces forces related to fouling.

Often one main component is enriched into the macroscopic layer deposits. For example deposits composed of pure hydrophobing agents or calcium carbonate are often found from equipment surfaces. It is, however, also very common that the deposits are composed many substances without enrichment of any particular component. Although the reason of fouling is not obvious in these cases, the problem is often connected to only one or two substances that "release" the deposit formation.

Substances a tendency to form macroscopic deposits include:

- **Wood extractives** (also often denoted pitch) are particularly common in mills using thermomechanical pulps. Extractives occur as independent molecules, micelles, colloidal or macroscopic droplets in process water. The composition of wood extractives varies depending on wood species. Fatty and resin acids, sitosterols, steryl esters and triglycerides are among the most common extractive components in Nordic wood species (Back and Ekman 2000).

- "**White pitch**" originates from coated broke. White pitch is composed of latex and other pigment materials (von Seyerl and Beck 1993; Vähäsalo 2005).

- **Hydrophobizing agents** such as alkenyl succinic anhydride (ASA), alkyl ketene dimer (AKD) and resin can cause fouling. The ASA reaction with calcium which forms a sticky ASA calcium soap is often the main reason for ASA-based deposits (Lindfors 2005).

- **Recycled fibers** contain a wide variety of fouling substances. These include styrene-butadiene rubber, polyvinyl latex, calcium carbonate (Wang et al. 2003), calcium stearate etc.

- **Microbes** in the papermaking process consist of numerous species of bacteria, yeast and mould. Most species of bacteria in paper machine originate from thermal springs. (Kolari 2003).

- **Inorganic salts** and pigment particles cause deposits especially in processes where calcium concentrations are elevated (neutral processes). Calcium carbonate, calcium sulphate and calcium oxalate are among the most common ones.

- Fouling substances are often present as **complexes**. Pitch droplets may be covered by microbes (Lindberg et al. 2004). Wood resin may increase the deposition tendency of white pitch (Vähäsalo 2005).

Besides macroscopic precipitates, thin layers of deposits are common on process equipment. It is seldom recognized that they may have a large impact on paper machine operation. Thin deposited layers have influence on e.g., web releasing, wetting, hydrodynamic and wearing properties of the process surfaces. A monomolecular film of polyelectrolytes can alter the corrosion potentials of steel surfaces (Tammelin 2006a).

Equipment that are especially sensitive to fouling include press felts, transfer belts and center rolls in the press section and drying cylinders in the early part of the drying section, the base and process water/air interface in tanks, places with slow flow or stagnant point places in pipes (e.g. pipe bends), suction boxes and several others (listed by Lindfors (2004)[1]). A special problem is the fouling of on-line measurement instruments, which affects the measured on-line process parameters.

3.1. Impacts of fouling

Deposits cause breaks in paper production (Palonen, 1999) decrease dewatering of the web (Kilpeläinen et al. 2000), cause wearing of paper machine parts and decrease paper quality (Palonen 1999 p. 243, Vappula et al. 1999, p. 181, Zhang et al. 1999). Deposits in pipes affect the flow properties influencing on the energy losses caused by pumping. In heat exchangers deposits inhibit heat flow.

Deposits may also be beneficial. They may seal the surface from wearing. A thin adsorbed film can prevent the further collection of deposits, so that they do not reach harmful thicknesses.

Breaks in paper production, decrease in paper quality and other consequences of fouling cause significant direct costs. The indirect economic losses are, however, even higher. Several kinds of chemicals are added continuously to the process waters in order to control fouling. Process water cleaning with filters, centrifuges and other methods

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[1] http://tinyurl.com/272ypw

increase energy consumption. Cleaning devices require costly investments. Fouling problems often prevent papermakers operating with optimal process parameters.

4. Surface forces

Surface forces and diffusion have dominating importance for the adhesion, adsorption and colloidal stability of dissolved or colloidal substances (size is less than 1 μm). When the size of substances increases, also inertial and gravity forces become important (Israelachvili 1992). Although paper machine process water also contains large particles with sizes up to several millimetres, most of the substances are small enough to be controlled by surface forces. The adhesion and wetting properties of substances are always controlled by surface forces regardless of the particle size.

Over a dozen different surface forces are thought to be of importance in an aqueous environment and in air. Although many of them remain poorly studied in the field of papermaking and fouling, one may estimate that they all have influence on fouling.

4.1. Van Der Waals forces

Van der Waals forces occur between all molecules and surfaces. They have an influence both on adhesion and adsorption. Van der Waals interactions can further be divided into those involving permanent dipole moments (Debye and Keesom interactions) and those due only to fluctuations in electron densities (dispersion or London interactions). Of these dispersion interaction is usually dominant when condensed phases (i.e. liquids or solids) are interacting. The van der Waals force depends above all on the geometry and distance of the interacting interfaces and Hamaker constant of the material.

The van der Waals interaction energy between two spheres with similar radius can be expressed as:

$$\Delta G_{vdW} = -\frac{AR}{12D} \tag{4.1}$$

where D is the distance between the sphere and the surface, R is a radius of the spheres and A is the material dependent Hamaker constant. The non-retarded Hamaker constant of phase 1 interacting with phase 2 a across medium can be approximately calculated as (4.2):

$$A \approx \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3hv_e(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{8\sqrt{2}(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2}\{(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2}\}}$$

where k is the Boltzmann constant, T is the temperature, n_i is the refractive index, ε_i is the dielectric constant, v_e is the main electronic absorption frequency in the UV region and h is the Planck's constant. Equation 4.2 is based on the theory developed by Lifschitz (Lifshitz 1956), where the atomic structure of molecules is ignored and the forces between large bodies are treated as continuous media. Equation 4.2 is valid at distances < ~10-20 nm. At longer distances, retardation effects become dominant and the interaction becomes negligible, when D is over 100 nm (Israelachvili 1992).

If the surfaces are immersed in aqueous solution, the magnitude of the van der Waals interaction is reduced. The effective Hamaker constant (A) of surfaces of materials b and c immersed in a solution a is approximately

$$A = (\sqrt{A_{bb}} - \sqrt{A_{aa}})(\sqrt{A_{cc}} - \sqrt{A_{aa}}) \tag{4.3}$$

Or for the surfaces of the same material (b)

$$A = (\sqrt{A_{bb}} - \sqrt{A_{aa}})^2 \tag{4.4}$$

The interaction between two similar particles is therefore always attractive. For dissimilar particles in a solution van der Waals interactions can sometimes be repulsive.

Israelachvili et al. (1972) have studied the effect of a thin adsorbed layer on van der Waals forces between surfaces (Fig. 1).
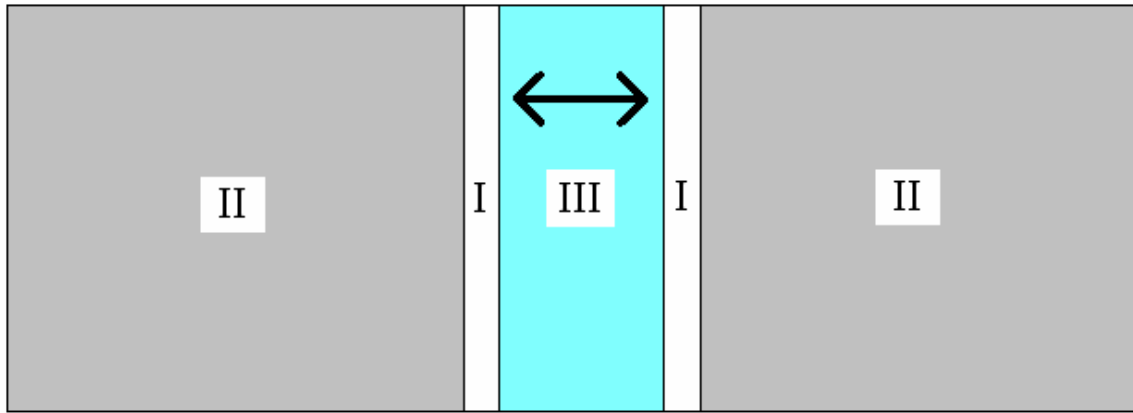
Figure 1. A thin adsorbed film (I) between symmetric surfaces (II) in solution (III).

The study is relevant in the context of paper machine fouling, because fouling layers can be often very thin. Based on the study it can be concluded that a thin (monomolecular) and even layer of deposits (I) determines the adhesive properties of the surface. However, both the original surface (II) and the thin adsorbed film (I) determine the van der Waals forces that affect adsorption. When the fouling film grows to a ≈ 100 nm thick layer with full surface coverage, the fouling layer fully screens the effects of van der Waals forces due to the original surface.

4.2. Electro-osmotic forces and DLVO theory

Electro-osmotic forces are long-range and have an influence mainly on adsorption and aggregation in aqueous solutions. It is due to the electric double layer formed by mobile ions near charged surfaces. The electric double layer can be divided into three sub-layers:

1) A surface layer with surface charge density σ_0 created by charged groups at the surface.

2) A layer immediately outside the surface layer (with charge density σ_s), where the motions of the ions are restricted. This layer is denoted the *Stern* layer.

3) A layer outside the Stern layer, denoted the *diffuse double layer* (with charge density σ_s). In the diffuse double layer the ions are freely mobile but still electrostatically attracted or repelled by the surface.

The electric double layer as a whole is neutral:

$$\sigma_0 + \sigma_s + \sigma_d = 0 \tag{4.5}$$

When two charged surfaces approach each other in solution the diffuse double layers overlap, which results in an osmotic pressure, and, hence, give rise to the electro-osmotic force.

The interaction is usually repulsive between two surfaces carrying charges of the same sign, but becomes attractive if their charges are opposite.

The thickness of the diffuse double layer is usually characterized by the Debye length κ^{-1}.

$$\kappa^{-1} = \sqrt{\frac{RT\varepsilon_r\varepsilon_0}{2F^2I}} \tag{4.6}$$

where R is the molar gas volume, T is the temperature, ε_r is the permittivity of the solvent and ε_o is permittivity of vacuum F is the Faraday constant, $I = 1/2\Sigma z_i^2 c_{0,i}$ is the ionic strength, where z is the valency of the ion and c its concentration. κ increases, when electrolyte concentration becomes higher. Hence both the repulsive interaction between surfaces of the same sign and the attractive interaction between surfaces of different signs decrease when salt is added. Also, if the valency of ions increases the thickness of the double layer decreases and the electro-osmotic interaction is screened. If only

monovalent ions (e.g. Na^+, Cl^-) are present in the solution, electro-osmotic interactions become negligible when the salt concentration increases above 200-300 mmol/l. Multivalent ions can, however, screen electro-osmotic interactions at much lower concentrations (divalent ions such as Ca^{2+}, SO_4^{2-} 4-5 mmol/l, trivalent ions such as Al^{3+}: 0.2-1 mmol/l). While paper machines often operate in conditions, where electro-osmotic interactions are relevant, there are many paper mills in which salt concentrations are so high that electro-osmotic interactions are fully screened.

The classic DLVO theory of colloidal stability (Verwey and Overbeek 1955) in many cases is able to predict the adsorption and aggregation behaviour of colloids in paper machine environments. According to the theory colloids due to attractive van der Waals forces tend to aggregate or adsorb rather than stay dispersed. However, repulsive electro-osmotic forces and hydrodynamics may render the kinetics of these processes extremely slow so that colloids can stay dispersed for very long times.

At constant potential, the total DLVO interaction potential for two spheres of radius R is

$$\Delta G_R^{tot} = \Delta G_R^{el} + \Delta G_R^{vdW} \approx 2\pi\varepsilon_0\varepsilon R\Phi_0^2 e^{-\kappa H} - \frac{AR}{12H} \qquad (4.7)$$

where Φ_0 is the surface potential. Often noticeable adsorption, aggregation or fouling starts when the salt concentration exceeds some critical limit (critical adsorption or coagulation concentration). In particular, this is the case if the surface and the colloid are similarly charged. Critical coagulation concentration for similar spherical particles can be calculated from

$$c_c \approx K_c \frac{1}{A^2 z^6} \qquad (4.8)$$

when the surface potential Φ_0 is large (> 100 mV)

At low potentials ($\Phi_0 < 25$ mV)

$$c_c \approx K_c \frac{\Phi_0^4}{A^2 z^2} \qquad (4.9)$$

Equations 4.8 and 4.9 hold only, if the surface potential (Φ_0) remains constant. However, the surface potential decreases when salt is added. Counter-ions with high valency also often adsorb in the Stern layer. Hence, it is rather common that colloids behave according to eq. 4.8 also, when the surface potential is low. If coagulation occurs at 0.2 mol/l with 1:1 electrolyte, it will occur at ~ 0.2/64= 0.0031 mol/l with a 2:2 electrolyte. Therefore, the behavior of charged fouling substances is very sensitive to the valency of ions present in process water.

4.3. Lewis acid-base interactions

Lewis acid-base interaction is a short-range force operating at distances < 3 Å. In a Lewis acid-base reaction a base donates electron density to an acid. The bonds formed are strongly directional. The energy of most Lewis acid-base bonds is 5-40 kJ/mol, which implies that they are stronger than the typical van der Waals "bond" (~1 kJ/mol).

During the acid-base -reaction the electronic orbitals are mixed in a way which has to be described using quantum chemical concepts. In general, this mixing process is not very well understood. For this reason the formation and strength of Lewis acid/base reactions can often be predicted only qualitatively.

Brönsted acids or bases (i.e., substances capable to donate or accept protons) and the several forms of hydrogen bonds (e.g. HOH/aromatic, $C=CH_2/C=C$ and O=C-OH/O=C-OH bonds) can be regarded as special cases of the Lewis acid-base concept (Jensen 1991; Steiner 2002).

The acid-base interaction is too short-range to be of importance as attractive forces that enhance the rate of collision between particles and surfaces. However, they are of great importance as factors that determine the strength of adhesion of particles.

Water molecules have both donor and acceptor properties. Therefore, it can be argued that they are often able to strongly compete with acid-base interactions between dissolved and colloidal substances and surfaces (Kallio 2006). Although the significance of acid-base interactions between surfaces immersed in water is often rather low, they may be of importance to adhesion in the drier part of the paper-making process.

4.4. Steric forces

When surfaces covered by layers of soluble polymers approach each other a repulsive steric force usually arises. One reason for this is that two polymer chains in two interpenetrating polymer layers have to adopt a more dense conformation and loose some of their conformational freedom. For this reason the interpenetration process is entropically unfavorable and there is an increase in Gibbs' energy (Israelachvili 1992). The other important contribution is the change in enthalpy which is associated with replacing polymer-solvent interactions with polymer-polymer and solvent-solvent interactions. This contribution can be either attractive or repulsive and depends on polymer solubility. Thus, the Gibbs energy of interaction is a sum of entropic and enthalpic contributions:

$$\Delta G^{st} = \Delta H^{st} - T\Delta S^{st} \tag{4.10}$$

Surfaces and colloidal particles can be sterically stabilized by polymers. Steric stabilization is an especially important mechanism for colloidal wood resin (Sundberg 1995), and hydrophobing agents (ASA, AKD, resin size).

4.5. Bridging

Polymers may form bridges between surfaces or colloids, which enhances aggregation and adsorption. Situations favouring a strong bridging attraction are those where the polymer is attracted to the surfaces, but where the coverage is not too high nor too low. If the coverage is too high there will be too few free binding sites for bridges to form, whereas if it is too low the density of bridges will also be low. Attractive bridges can be strong and long range (several hundreds of nanometers), if the polymer is long-chained.

It has been suggested that bridging is of strong importance in the operation of retention polymers that bind the fouling particles to the web (Salmi et al. 2007). Also, hydrophobizing agents are often covered with long-chain polymers. Hence the bridging interactions influence their fouling behaviour.

4.6. Other

Attractive *capillary force* has an influence on surfaces that are covered by a thin wetting film of water or other liquid. The maximum capillary force (F_{max}) between a sphere and surface composed of same material is

$$F_{max} = 4\pi R\gamma cos\theta \tag{4.11}$$

where R is the radius of sphere θ is the contact angle of the material and γ is surface tension of liquid. Capillary forces become significant when the relative humidity increases. This can be seen from well known Kelvin equation (4.12) (Adamson 1990).

$$r_k = \frac{V\gamma}{RT \log(\frac{p}{p_0})} \tag{4.12}$$

where r_k is the Kelvin radius, V is molar volume, T is temperature, p/ p_0 is the relative vapour pressure, γ is the surface tension and R is the molar gas constant. r_k is – 10 nm at 90 % relative humidity, but only - 0.1 nm at 10 % relative humidity (20˚C). Therefore, capillary attraction is long-ranged in high humidities and has therefore significant effect on adhesion of deposits. Capillary force weakens when the liquid wets the surface completely as a thick layer (Israelachvili 1992). The influence of capillary force on fouling can be recognised e.g. during a walk on a beach after rain. Sand particles are easily collected on soles due to capillary force.

Water molecules tend to reorient near hydrophobic surfaces, because they are unable to form hydrogen bonds near surfaces of this kind. This results in a rather short range attractive interaction force, the so-called *"hydrophobic interaction"* (Israelachvili 1992).

Phase-separation of polymers may occur inside a capillary (e.g. between two colloidal particles in solution) in solutions close to the solubility limit of the polymer. This may lead to aggregation of particles (Olsson et al 2005) and is called *"capillary induced phase separation"*. This interaction may have influence on the interactions of poorly soluble polymers (e.g. galactoglucomannan) and fouling particles (e.g. colloidal wood resin) presented in process water.

Undulation, peristaltic and protrusion forces are present between liquid interfaces. They are repulsive and short-range (< 2-3 nm). They may have significance e.g. in the coalescence of liquid fouling emulsions (e.g. hydrophobing agents and wood resin).

4.7. Effects of flow on surface forces

The role of surface forces is largest and the role of the flow is smallest in stagnant point regions. "Valleys" on rough surfaces, wire pit and tanks can be mentioned as examples of places, where the influence of flow on fouling is diminished. Laminar flow usually reduces the effect of surface forces on colloids, because the flow tends to carry particles past each other or past macroscopic surfaces so that collisions due to diffusion and

attractive interactions are reduced (Van de Ven and Mason 1981). The strength of these effects depends on the relative size of the colloids and the shear rate. If the size of particles increases over colloidal range (> 1 μm), hydrodynamic forces may be less effective in preventing the formation of deposits. Wood resin droplets with sizes in the colloidal range do not attach to steel surfaces, but in aggregated form they may collide quite effectively and cause deposits when turbulence is presented (Blanco et al. 2000).

The "ion cloud" around a charged particle is often stretched when particles flow. Flow also deforms soft particles. These have influence on the adsorption and coagulation of fouling substances.

5. The viscoelasticity of deposits

Fouling is largely related to viscoelasticity or "stickiness" of substances. The sticky deposit are also much harder to remove, since a significant part of the mechanical energy is dissipated during the cleaning process. This energy goes to the deformations of viscoelastic particle and is eventually released as thermal energy (Barnes 1989). Also the contact area on the surface compared to hard particles. The viscoelastic properties are determined by surface forces (e.g. van der Waals forces and Lewis acid-base interaction).

Viscoelasticity is time-dependent. A useful characteristic that describes conditions under which viscoleastic properties are important is the Deborah number:

$$
\text{De} = \frac{\text{relaxation time of a material}}{\text{observation time}} \tag{5.1}
$$

For a viscoelastic material De~1, for a solid material De << 1 and for a liquid >> 1 (Hunter 1989). The phenomena related to fouling have very variable contact times. They are very small (on the order of microseconds), when the fouling colloidal particles collide and form aggregates. Viscoelastic colloids behave more like solid during the rapid

aggregation. Deposits may also stand for weeks or even months on paper machine surfaces, which emphasizes their liquid character.

An example about the time-dependent rheology of fouling substances is the so called "Pitch drop experiment" established at the University of Queensland, Australia, in 1927. A solid-like pitch sample that was breakable with a hammer was used. The sample was spilled into a sealed funnel and was allowed to settle for three years. In 1930, the seal at the neck of the funnel was broken and the pitch was allowed to flow. Ever since large droplets have been formed and have fallen over every 8-12 years [2, 3].

6. Fouling mechanisms in paper machine

A wide variety of fouling mechanisms occur during papermaking. The mechanisms presented below give a simplified insight into fouling phenomena. One must note that in reality the fouling mechanisms are usually much more complex and the mechanisms presented are often related to each other. Surface forces are of importance in all of them.

6.1. Impurities from air

Paper machine surfaces are fouled already in the presence of air. Moisture, hydrocarbons and other impurities are collected on them. These impurities significantly alter e.g. the wetting properties of paper machine surface materials (as shown in paper IV).

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[2] http://en.wikipedia.org/wiki/Pitch_drop_experiment#The_pitch_drop_experiment_at_the _University_Of_Queensland

[3] http://www.physics.uq.edu.au/pitchdrop/pitchdrop.shtml

6.2. Adsorption of dissolved and colloidal substances

Deposits may form directly on the surface as dissolved or colloidally dispersed substances diffuse towards it. Adsorbed layers are often so thin that they are not visible, but they nevertheless significantly change the surface properties of the surface. Different kinds of films can also adsorb sequentially, resulting in the build-up of thicker deposits. Multilayer adsorption of deposits may occur e.g., if the substances in process water are not stable, but oscillate between anionic and cationic net charge (Paper I; Kekkonen 2001). Adsorption is controlled by surface forces and in many cases diffusional flow towards the surface. (Kekkonen 2001; Paper II)

6.3. Formation and adsorption of insoluble salts, gels and emulsions

As a result of changes in concentrations, pH, temperature and process conditions, dissolved compounds (such as polyelectrolytes, surfactants or ions) may form insoluble salts or complexes. They can occur as stable colloids or as macroscopic phases (e.g. gels (Merta 2001)) that form particles that are larger than colloidal size, depending on pH, temperature, gas content, concentration of substances, ionic strength etc. For example, soluble surfactants form insoluble salts (soaps) with di- of multivalent metal ions (Holmberg 1999; Allen 1988). The formation of inorganic salts from ions (e.g. $Ca^{2+}, C_2O_4^{2-}, CO_3^{2-}$) is a relatively common fouling mechanism, since the process waters are very often saturated with ions (e.g. calcium ions in neutral papermaking). Hydrophilic interfaces are commonly assumed to be the best sites for nucleation for inorganic salts (Brekevic, L. and Kralj 2000). Most of the substances in process water and surfaces are to some extent hydrophilic offering good nucleation sites for inorganic salt formation.

6.4. Formation of microbiological deposits

Process conditions (temperature, pH etc.) control the amount and type of microbes present. The proper supply of nutrients is also especially important.

The size of bacteria varies from around 200 nm up to tens of micrometers. Therefore their interactions with surfaces are partly colloidal, and their adhesion to surfaces is certainly controlled by intermolecular interactions.

At pH > 4, the net charge of almost all bacteria is negative (Van der Val et al. 1997). The surface of bacteria is, however, multiform and contains different kinds of structures and charged groups (Camesano et al. 2002). The wetting properties of bacteria vary remarkably. Contact angles from 15° up to 117° with water have been reported (Rijnaarts et al. 1995a). The slime secreted by bacteria has an influence on their surface properties. DLVO interactions (see chapter 2.1.) partly control bacterial adsorption (Jucker et al. 1998). Generally it is assumed that a bacterium can attach on a surface with the aid of cell surface appendages or extracellular polymeric substances (Kolari 2003). This kind of binding with polymeric "threads" makes it possible for a negatively charged bacteria to also adsorb on negatively charged surface. Bacterial adsorption is affected also by steric forces (e.g. due to threads) (Rijnaarts et al. 1995b; Vadillo et al. 2003).

Only a small part of the microbe flora can directly adsorb on paper machine surfaces. Most species are unable to adsorb unless the surface has already been colonized by the so called "primary biofilm formers" (Kolari 2003). For the further development of biofilm other microbes, hydrodynamics and cell-to-cell communication (Stoodley et al. 2002) with signalling molecules (Davies 1998) are important.

Bacterial surfaces are to large extent fouled in paper machine process water, because the adsorption or aggregation of process water components on the surface of bacteria cannot be avoided. One example is the bacterial complexes with wood resin presented in Figure 2.
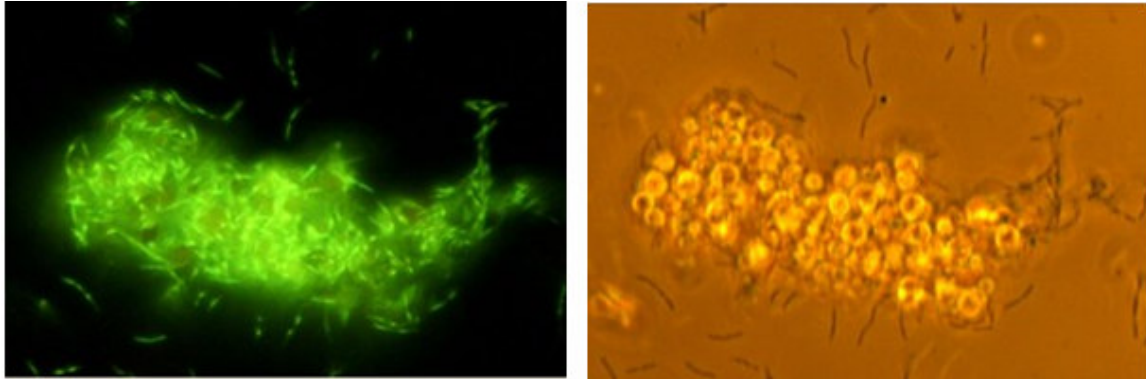
Figure 2. Complexes of aggregated wood resin and Pseudoxanthomonas taiwanensis – bacteria. The bacteria can be seen in fluoresense figure (up) as green. The bacteria seem to be enriched on the surface of aggregated pitch droplets. Complexes were created in 45˚C with continuous stirring overnight at pH 6, 10 mM CaCl$_2$ 0,5 g/l wood resin particles and 1 g/l bacteria. Wood resin emulsion was prepared as described by Sundberg 1996. Figure by Mari Raulio, University of Helsinki, Laboratory of Applied Chemistry and Microbiology, 2006.

6.5. Fouling due to large particles

Process waters contain many substances larger than the colloidal range (> 1 μm). Latex aggregates (size range 2-1000 μm, Berg 2002) and pitch aggregates are among the most common ones. Colloidal substances may join together to form larger aggregates. These may be build up when colloids became unstable due to changes in process conditions. Another common reason is charged polymers (flocculants etc.) which adsorb on oppositely charged particles that then bind together with the aid of bridging force (Stenius 2000). In stagnant point conditions the rates of aggregation are often controlled by diffusional flow. For non-interacting, spherical particles the time required of the number of particles to be reduced to half of its initial value is approximately:

$$t_{1/2} = \frac{3\eta}{4kTN_0} \qquad\qquad (6.1)$$

where η is viscosity of solution, N_0 is the initial particle concentration. Thus for 0.1 g/l dispersion in temperature 60°C with particle size 0,5 μm the $t_{1/2}$ is ~ 5-10 minutes. This is relatively long but still significant time in the context of paper machine fouling. Note that according the $t_{1/2}$ is independent of particle size. As discussed in chapter 4.7. particles may also collide with each other due to shear. Whether shearing will actually lead to aggregation will depend on the relative sizes of colliding particles, diffusion and the nature of attractive interactions. In some cases the collision frequencies caused by shear are high and lead to rapid aggregation. One example is the fast aggregation of fibers in turbulent flow in the presence of long-chain polymers (Wågberg and Lindstöm 1987). Hydrodynamic shearing forces may also increase the rate of adsorption by transporting aggregates to points where the flow is stagnant (see chapter 4.7.).

Also sedimentation due to gravity can enhance their adsorption. Aggregates less dense than water (such as wood resin) do not sediment but cream on the water surface. Air bubbles assist often creaming. This may result in effective deposition of aggregates at the solid/liquid contact line (Davies et al. 1998). A relatively stable and thin film of water is often present between the large particles and the surface (Manev and Nguyen 2005), which clearly inhibits the contact between large particles and surfaces (Paper IV; chapter 11.2).

6.6. Foam and air bubble induced deposits

Also air and other gases in process water can be classified as an "impurity". Gas may have negative impacts on the process stability in many ways. Foam and gas bubbles collect hydrophobic substances from circulation water at the solid/liquid /air contact line. The particles are then carried by the bubbles to the surfaces of solutions (compare the formation of rims of dirt on the sides of wash basins), which is an important fouling mechanism in storage tanks (Allen 1980).

6.7. Fouling mechanisms related to the paper web

In the press section one common fouling mechanism is related to the releasing of the web from roll or transfer belt. Fibers are sometimes detached from the web to the equipment surface. Capillary forces are very important to web release (Silanterä 1996). Changes in the wet web structure or the roll surface alter capillary forces between the roll and the web, which may lead into impaired web release or web breaks.

Fouling of the process surface due to e.g. adsorption of wood resin is a common reason for impaired web releasing. Other reasons are related to the properties of the paper web and to the roughness of the process surface. A wet web is more difficult to release than a dry one. Substances (e.g. wood resin or hydrophobing agents such as AKD) may also transfer from the paper web to the surface (Allen 1980).

6.8. Other

Places subjected to splash water are commonly fouled. The obvious mechanism is the drying of the splash, in which case the deposits inside the splash are transferred to the process surface. Some species of bacteria that often cause fouling problems have adapted to living in the splash water environment (Kolari 2003).

Relative humidities are near 100 % in splash water places and in paper machine press section and early part of dry section. In these places capillary forces can "glue" dirt particles and thereby enhance fouling。

Hydrophobing agents may evaporate and condense on process surfaces. This mechanism is common in the dry section of paper machines, where the temperatures are elevated. Also evaporated water condenses on process surfaces. The condensed water may dribble onto the paper web causing spots and thereby decreasing paper quality.

7. Control of fouling

7.1. Removal of the fouling substances

Wood and pulps used in papermaking can be pre-treated in order to reduce fouling. Wood chips are often let to stand several days or weeks before use. Chip aging enhances the hydrolysis of the triglyserides and thereby can reduce the problems related to wood extractives. Conditions of screening and other operations during the de-inking and pulping of recycled fibre are optimized in order to remove tacky materials (Hubbe et al 2006). Wood extractives are removed from pulp by pressing.

Polymers with high molecular weight, nano- or microparticles and aluminium-containing species (e.g. aluminium sulphate) enhance the aggregation and retention of fouling substances in the web in paper machine. (Norell et al. 1999). Process chemicals added seldom affect only one specific parameter or surface force. The use of long-chain polymers is based e.g. on bridging interactions, charge neutralization and the formation of charged patches on colloids (Stenius 2000; Moudgil et al. 1987). Aluminium-containing species has high ionic valences, for which reason they efficiently screen electrostatic interactions. Some aluminum species may also adsorb on negatively charged surfaces and thereby render them neutral or cationic (Matijevic and Stryker 1966).

Flotation, centrifugal cleaning and sedimentation are applied to remove fouling substances (Weise et al. 2000). All these methods are based on gravity. Also process water de-aeration decreases fouling, and particularly foaming. Other methods that remove fouling substances include filtration and screening.

7.2. Control of process chemistry

Salt concentrations and pH of process water are under active control in many paper mills. Buffering agents such as $NaHCO_3$ are added to process water to reduce harmful pH pulses (Leino and Holmberg 1998; Weaver 2003). Stable salt and pH conditions assist the colloidal stability of fouling substances.

Inorganic and organic dispersants are used to increase the colloidal stability of potential deposits. Dispersants often introduce a high negative surface charge to surfaces they adsorb and may therefore stabilise fouling substances electrostatically. Polyelectrolytes and surfactants are used to stabilize the potential contaminants sterically or electrostatically. Polyelectrolytes may also adsorb on the equipment surface and alter it antifouling (as shown in Paper IV).

Process chemical interactions with potential deposits often affect the viscoelastic properties of fouling substances. This may reduce fouling. Especially effective detackifiers include talc, bentonite and lipase enzymes. Lipase enzyme degrades triglycerides into free fatty acids in wood resin (Mustranta and Buchert 2001). Also aluminium sulfate may detackify extractive particles (Dreisbach and Michalopoulos 1989).

Biocides, surface-active agents, non-toxic biodispersants, hydrolytic enzymes and chelating agents are applied for controlling slime produced by microbes (Jucker 1998).

The removal and control of fouling substances sometimes introduces new problems: Filters are fouled (Kyllönen et al. 2005). The use of aluminium-containing species may lead to the deposition of aluminium soaps (Ohtani and Shigemoto 1991).

It is noteworthy that the development of paper chemicals has mainly been focused on the modification and control of electro-osmotic, steric and bridging forces. The active

modification of van der Waals forces has drawn much less attention despite of its large importance in DLVO and other interactions.

7.3. Cleaning of paper machine equipments

Mechanical cleaning methods include the use of doctor blades, high-pressure showers and ultrasonics. Doctor blades continuously remove deposits from rolling surfaces in press section. Ultrasound is applied in cleaning filters (Kyllönen et al. 2005) and high-pressure showers e.g. for transfer belts.

Some cleaning methods are based on oxidation of fouling substances. Pulsed electric fields and ultrasound produce oxygen radicals and other active oxygen species that clean the surfaces. The use of cleaning chemicals (e.g. KOH or H_2O_2) is often based on these same oxygen species.

Hot water and organic solvents (e.g. limonene) and surfactants are used to clean the papermaking equipment (Hubbe et al. 2006; Paper I).

Mist showers are applied to maintain cleanliness in press section. Deposits are, after all, easier to clean up in wet (showered) environment than in dry one. In wet environment water molecules penetrate between deposited substances and surfaces and prevent bond formation between them. Showering has also a large influence on capillary forces that often cause fouling in press section.

7.4. Antifouling process equipment

Fouling can be reduced by developing surfaces that do not collect deposits (Paper I). Both strongly hydrophilic or hydrophobic surfaces have been applied. Strongly hydrophobic fluoropolymers are used in the dry part of the paper machine (drying

cylinders). Also the use of very smooth surfaces decreases fouling. Hence, electrochemical polishing is used for steel surfaces in head boxes[4].

Recent research activities have focused on developing strongly hydrophobic lotus surfaces. They could be useful in splash water places and the paper machine dry section (Paper I), because the contact time of water splashes decreases, when the drops roll. Possibilities to develop antifouling surfaces are further discussed in Papers I, III and V.

A proper process design assists process cleanliness. One way is to avoid stagnant points (e.g. in pipes), where the deposits often collect due to the presence of surface forces and sedimentation (Holmberg 1999). The topography of equipment surface can be such that it enhances the flow of water. For example, stripe-like surfaces are used in press section.

7.5. Titanium dioxide as an antifouling material

The antifouling properties of titanium dioxide are based on its strongly hydrophilic character and ability to catalyze the degradation of organic substances, which are induced by UV –illumination. The photocatalytic effect is mainly due to the formation of radicals (such as O_2^-, •OOH, •OH), and other active species (H_2O_2). Therefore titanium dioxide – based cleaning contains similarities with ultrasonic or electric pulsing methods or the use oxidating cleaning chemicals. The strong hydrophilicity of TiO_2 is utilized in self-cleaning glasses and antifogging mirrors or eyeglasses. The water drops moving on the TiO_2 window glass are able to penetrate between fouling substances and the glass surface removing contaminants collected on the window (Hashimoto et al. 2005). The antifogging property of TiO_2 is based on the hindered droplet formation of water on strongly hydrophilic surface. Titanium dioxide with UV illumination is of potential interest for antifouling material in pulp and paper machine parts. It has been investigated in water purification in pulp and paper mills (Balcioglu and Cecen 1999; Perez et al. 1997). TiO_2 with UV illumination prevents microbiological fouling caused by bacteria present in paper machines (Raulio et al. 2006).

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[4] http://tinyurl.com/272ypw

8. Control of fouling in nature

The antifouling properties of strongly hydrophobic Lotus leaves have been widely investigated topic (Reichel 1997; Barthlott and Neinhus 1997; Marmur 2006). However, it is seldom recognized that from natural structures not only Lotus leaves are antifouling. Evidently, *surfaces and other structures in living organisms are all antifouling.* After all, the inhibition of fouling is of crucial importance on the subsistence of living organisms. The antifouling character of living organisms is not very well understood and there are a lot to learn about the way that nature avoids fouling.

Similarities occur between the fouling in paper machine wet end and blood circulation of vertebrates. Fouling problems have decreased and process stabilities have been improved when the process pH has been stabilized using buffering agents. Solutions in living organisms are buffered (Stryer 1999). It has been suggested that the collection of colloidal cholesterol begins from a stagnant point (e.g. a place of bifurcation in blood vessels) (Wada et al. 2002). The mechanism is similar to that in a paper machine, where the colloidal substances tend to collect on stagnant points (Kekkonen 2000). As in process water a complicated mixture of substances (colloidal, semi-colloidal, polyelectrolytes, polyelectrolyte complexes) are circulating in blood, whose stabilization mechanisms resemble those used in papermaking. Enzymes are used to control fouling both in papermaking and in living organisms.

9. Experimental background

9.1. Experimental objectives

The purpose was to understand mechanisms how the deposits reach the contact with the surface by adsorption, how they adhere on the surface and how they could be removed with photocatalytic cleaning. The aim was to utilize the achieved results in developing

deposition control in paper making. Antifouling process equipments and process chemicals are examples of potential applications.

The main experimental methods were Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) and the contact angle goniometer. QCM-D was used in adsorption studies and photocatalytic degradation experiments. Contact angle goniometer was used in the studies with adhesion and interfacial tensions. Also several other methods such as MAMA (micro adhesion measurement apparatus), atomic force microscopy (AFM) and the Langmuir-Blodgett technique were utilized. Theoretical background related to the adsorption measurements with QCM-D and the adhesion measurements with contact angle method is given in the following.

9.2. Experimental techniques: theoretical background

9.2.1. Adsorption kinetics

Long-range surface forces mainly determine whether adsorption occurs or not. These include DLVO –forces (electro-osmotic and van der Waals forces), steric and bridging forces that were discussed in chapter 3.

The rate of adsorption is often controlled by diffusion at stagnant point conditions. If each individual particle adheres to the surface upon collision with the surface independently of other adsorbed particles, the amount adsorbed is (Crank 1956)

$$M_t = 2C_0\sqrt{\frac{Dt}{\pi}}$$
(9.1)

where M_t is the concentration of diffusing substance that has left the dispersion at time t, C_0 is the bulk concentration (assumed to remain constant) and D is the diffusion coefficient. Since diffusion coefficients of small particles are larger, they migrate faster to

the surface than large particles. This affects the structure of the adsorbed layer (see e.g. Tammelin et al. 2004). Equation 9.1 holds in the beginning of adsorption. Already adsorbed particles affect the kinetics of further adsorption. This can be called "blocking effect". Boluk and and van de Ven (1990) suggested that the effect of blocking on adsorption can be calculated from

$$\Gamma = \left(\frac{d\Gamma}{dt}\right)_o \tau_{bl}(1 - e^{-t/\tau_{bl}})$$
(9.2)

where Γ is the amount adsorbed, $(d\Gamma/dt)_0$ is the initial rate of deposition, τ_{bl} is the blocking time and t is the time from the beginning of the experiment.

9.2.2. Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

The Quartz crystal microbalance (QCM) was developed in 1950's. QCM with dissipation monitoring (QCM-D) is somewhat newer method invented in 1995 (Höök 1997). QCM-D has been used e.g. in adsorption studies with wood resin, lignin and cellulose (Tammelin 2006b).

In QCM an external electronic oscillator drives a piezoelectric quartz crystal that resonates at its resonance frequency. When the mass of the crystal is increased by adsorption on the crystal surfaces, its resonance frequency is shifted towards lower values. The frequency shift is related to the adsorbed mass, which thus can be determined with very high sensitivity. If the adsorbed layer is rigid, even and and small compared to the mass of the crystal, the Sauerbrey equation may be used to estimate the mass adsorbed (Sauerbrey 1959)

$$\Delta m = -\frac{C\Delta f}{n}$$
(9.3)

where C is a constant (for crystals in this study 17.7 ng/cm^2), Δf is the change in frequency and n is the overtone number. If the crystal with the adsorbed mass is not fully elastic, some of the energy driving the crystal oscillation is dissipated. With the QCM-D-technique it is also possible to record dissipation of energy:

$$D = \frac{E_{diss}}{2\pi E_{stor}} \qquad\qquad (9.4)$$

where E_{diss} is the total dissipated energy during one oscillation cycle and E_{stor} is the total energy stored in the oscillation. The dissipation measurement is used to determine the viscoelastic properties of the adsorbed layers and changes of conformation during the adsorption process (Höök 1997). A useful quantity is the change in dissipation versus change in frequency *(ΔD/Δf)*. If *ΔD/Δf* is large, the adsorbed substances can be viscoelastic. Small *ΔD/Δf* indicates a relatively rigid adsorbed layer. Further interpretation of frequency and dissipation shifts can, however, be rather complicated. The following factors need to be taken into account in the interpretation:

1) *Roughness;* Frequency shifts are to some extent sensitive to surface roughness. It is usually assumed that a surface roughness under 15 nm does not affect frequency or dissipation (Höök 1997). This assumption has not, however been fully verified experimentally. In this study, significant shifts in dissipations and frequencies were detected. The main cause was the change of surface roughness in the scale of tens or hundreds of nanometers (see Paper II).

2) *Slipping;* The adsorbed layer may slip, which affects the shifts in frequency (Urbakh et al 2007) and dissipation. The effect of slipping may become important if the adhesion of the adsorbent is poor on the substrate. It is shown in Paper II that the adherence of adsorbed rigid particles can be very poor in aqueous solution. Therefore, the slipping

effect can be important in aqueous systems. Its relative influence on the frequency and dissipation shifts is, however, difficult to estimate.

3) *Swelled substrate;* The appearance of an adsorbed layer alters the equilibrium between a swelled substrate and solution. Hence the amount of water inside the swelled layer alters, which affects the detected values of dissipation and frequency. Polyurethane and adsorbed polyelectrolyte layers are examples of swelling substrates used in this study.

9.2.3. Contact angles and adhesion

Contact angle measurement is the oldest and still the most popular method in adhesion research. Some of its basic theories date back to the 19th century.

The thermodynamic work of adhesion of a liquid to the solid surface can be calculated from equilibrium contact angle and surface tension data using the Dupré equation (1869)

$$W_A = \gamma_l \left(1 + cos\,\theta\right), \tag{9.5}$$

where γ_l is the surface (interfacial) tension and θ is the contact angle measured.

For macroscopic droplets Young's equation is applicable only if the surface is smooth enough. Surface roughness alters the measured contact angles. The detailed influence of roughness on contact angles is still somewhat unclear and the topic has been studied intensively.

Besides Dupré equation, adhesion in aqueous solution can also be calculated from equations 9.6 and 9.7 (Israelachvili 1992):

$$W_{swl} = W_{sl} + W_{ww} - W_{sw} - W_{lw} \tag{9.6}$$

where the term W means the adhesion energy of different interfaces (s = solid l = liquid and w = water). W_{ww} is the cohesion of water. W_{lw} is

$$W_{lw} = \gamma_l + \gamma_w - \gamma_{lw} \tag{9.7}$$

where γ represents the corresponding surface or interfacial tensions.

Molecules in close contact (i.e. at distances around 0.1-0.5 nm) with the surface determine the work of adhesion. At these dimensions, Van der Waals forces and Lewis acid-base interactions are often the strongest forces interacting (Vrbanac and Berg, 1991).

The commonly used Good-van Oss-Chaudhury (GvOC) approach can be used to determine the Lifshitz-van der Waals (γ^{LW}), acid (γ^+) and base (γ^-) components of adhesion and surface tensions (Della Volpe and Siboni 2000; van Oss 2006). Thus, adhesion between a liquid (l) and a solid (s) is assumed to be

$$W_A = \gamma_l (1 + \cos\Theta) = W_A^{LW} + W_A^{LB} = 2\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + 2(\sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_s^+\gamma_l^-}) \tag{9.8}$$

where W_A^{LW} and W_A^{AB} are the van der Waals and acid-base (AB) components of adhesion. For a probe liquid for which $W_A^{AB} = 0$, $\gamma_l^{LW} = \gamma_l \equiv \gamma_{probe}$. Then

$$\gamma_s^{LW} = \frac{\gamma_{probe}}{4}(1 + \cos\Theta_{probe})^2 \tag{9.9}$$

Acidic, basic and neutral probe liquids (in this study diiodomethane, water and ethylene glycol) are used to determine the acid-base and Lifshitz-Van der Waals components.

9.3. Instruments

Two different set-ups of the QCM-D instruments were used, QSense D300 and QSense E4. The instruments have slight differences further described by Tammelin (2006b). The QWic 301 chamber with a window on the QCM-D crystal was used for the measurements with photocatalytic degradation with UV illumination (Paper V). Unless otherwise stated, the QCM-D measurements were performed at $25 \pm 0.2 ˚C$.

A contact angle goniometer (KSV Instruments, Finland) was used for contact angle measurements. The experimental set-up is described in Paper III and by Lindfors et al. (2005). The Axisymmetric Drop Shape Analysis (ADSA) method, based on the principle described by Jennings and Pallas (Jennings and Pallas 1988), was applied for calculations. The software needed was delivered with the instrument.

Other techniques utilized were Micro adhesion measurement apparatus (adhesion studies, Papers III and IV), X-ray photoelectron spectroscopy (determination of the model surfaces Papers II and IV), Coulter N4 and N5 (determination of particle size and diffusion coefficient of model deposits) and the Coulter Delsa 440 (electrophoretic mobilities). Atomic Force Microscopy (AFM) was used to determine the topography of model surfaces and the settling of model deposits on the surfaces (Paper II).

9.4. Materials

Model deposits for QCM-D experiments

Colloidal particles (cationic alkyl ketene dimer (AKD) –wax anionic styrene-butadiene latex, polystyrene latex, kaolin, talc) and anionic emulsions of TMP wood resin were studied. Cationic starch was used to render AKD cationic. The properties of the adsorbed model deposits are presented in Paper II. Galactoglucomannan, pectin and other

hemicelluloses were prepared as described in Tammelin et al. (2007). The wood resin surface was prepared as in Tammelin et al. (2006 c). Two species of bacteria were studied: Pseudoxanthomonas Taiwanensis and Deinococcus Geothermalis. The bacteria were prepared by Mari Raulio from the Laboratory of Applied Chemistry and Microbiology, University of Helsinki.

Model deposits for contact angle experiments

Oleic acid, model TMP wood resin and calcium linoleate were investigated. Their composition and properties are given in Papers III and IV. TMP model extractive solution contained 40 % triolein, 22 % steryl esters, 20 % linoleic acid, 6 % sitosterol, 6 % dehydroabietic acid and 6 % abietic acid.

Surfaces

Most adsorption studies with QCM-D were performed with aromatic polyester polyurethane that was received from industry. It was negatively charged in aqueous solutions in the pH range studied. The model surface was prepared with spin-coating. The properties and preparation method of the polyurethane substrate are described in Paper II.

The titanium dioxide surface for photocatalytic decomposition measurements was prepared with atomic layer deposition. Langmuir-Blodgett and spin-coating techniques were used to coat the titanium dioxide surfaces with extractives (Paper V).

Several surfaces were studied with contact angle measurements. Surfaces representing those of paper machine surface materials wood components or chemicals that control the behavior of wood resin in paper process. The properties and the use of the surfaces are further presented in paper IV. The preparing was:

Poly-(diallyldimethylammonium)chloride (PDADMAC) was purchased from Ciba Specialty Chemicals (Salcare SC30 100000 - 300 000 g/mol and charge density 6.10

meq/g. PDADMAC was adsorbed on SiO_2 QCM-D crystals or on silicon wafers from in 10 mM acetate buffer (pH 4.6). The SiO_2 substrates were purified in UV ozonator.

Polyethylene oxide (PEO) surfaces were prepared in two ways. In the first method, a 1 g/l solution of PEO (from Kemira Chemicals, molecular weight ~ $6 \cdot 10^6$) in methyl ethyl ketone (1 g/l) was spin-coated on a piece of silicon wafer at 4000 rpm. The second method was to adsorb PEO on silicon wafers from a 10 ppm PEO solution pH 4.6. Same experimental results were achieved regardless of the preparation method.

For *Poly(sodium 4-styrenesulfonate)* (NaPSS), a 30 % aqueous solution with molecular weight ca. 70000 was purchased from Sigma-Aldrich. The NaPSS was thereafter ultrafiltrated to give a fraction with M_w < 30000. NaPSS was adsorbed on glass plates covered by TiO_2 or on TiO_2 QCM-D crystals from a 0.85 g/l solution (pH 4.6). The TiO_2 substrate was purified by keeping it under UV illumination at least half an hour.

Hemicelluloses from bleached spruce TMP were prepared by the method described in (Thornton et al. 1994). They were adsorbed on preadsorbed PDADMAC and on preadsorbed PSS. Preadsorbed PSS and PDADMAC layers were prepared as described above.

The lignin surface was prepared on a polystyrene-coated QCM-D crystal as described by Tammelin et al. 2006a.

The cellulose surface was prepared by spin-coating an untreated silicon oxide wafer as described by Kontturi 2003.

Fluoropolymer (Teflon AF 2400) was purchased from Du Pont. According to the manufacturer the fluoropolymer was composed of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (87 %) and tetrafluoroethylene (13 %). A 1 % solution was spin-coated on silanated SiO_2 at 4000 rpm. The SiO_2 substrates were silanated by keeping them in 1 mmol dicholorodimethylsilane in xylene over night at ambient temperature.

Polyethylene was spin-coated on SiO_2 from hot decaline solution as described in Paper III.

Polystyrene –coated QCM-D crystals were used.

Titanium dioxide (TiO_2) was spin-coated from 0.1 M titanium (IV) bis(ammoniumlactato)dihydroxide on a silicon wafer at 2800 rpm. The spin-coated sample was kept in an oven at 600˚C for 2 h. of TiO_2.

Silicon dioxide (SiO_2) was manufactured by Okmetic Oy. They were purified by a 10 min treatment in an UV –ozonator.

Polyamide (Nylon 6 from Aldrich) was spin-coated on untreated silicon wafers from a 0.5 % solution of formic acid at 1500 rpm. The sample was freeze-dried for several hours in order to remove the excess formic acid.

Stainless Steel samples (AISI 316 L) were purchased from Outokumpu Stainless Oy. The samples were purified by a 5 minute ultrasound cleaning in ethanol and a 10 minutes UV-ozone treatment.

Mica (Ruby Red Mica Sheets) was purchased from Electron Microscopy Sciences, USA from Electron Spectroscopy Sciences (U.S.A.). The surface layer of the mica sheets was removed, just before the measurement. No further purification was made.

The adsorbed PDADMAC, PSS and PEO and hemicellulose samples were transferred in wet state for the contact angle measurements in solution.

10. Adsorption and spreading studies with QCM-D (Papers II, IV and unpublished)

Adsorption of colloids, of emulsions, of hemicelluloses and other polymers and of bacteria present in paper machines was investigated. The nature of studied substances was diversified, because the purpose was to have a "broad view" related to the fouling caused by adsorption. Polyurethane was mainly used as a substrate in the adsorption experiments. Polyurethane is used e.g. in shoe press felts (Paper II) and deposits collected on polyurethane cause runnability problems. Hemicelluloses were adsorbed on surfaces present in TMP process waters. Adsorption measurements were made at stagnant point conditions, since the role of adsorption in fouling is often largest with low flow rates. QCM-D was also used to determine the spreading kinetics of soft colloids (chapter 10.1.), which was a new way to interpret QCM-D results.

10.1. Adsorption of colloids on polyurethane

AKD, wood resin, kaolin, talc, polystyrene latex beads and styrene butadiene -latex were used as colloidal model deposits. All of them (except polystyrene latex) are a common source of macroscopic deposits causing runnability problems in paper machine wet end. Particles and emulsions studied were negatively charged except cationic AKD and their size varied between 150-700 nm (see Table 1).

Observations indicated that DLVO forces mainly drive the adsorption of cationic AKD on polyurethane. AKD particles adsorbed on polyurethane when the salt concentrations were low (Paper II, Table 5). Raising the salt concentration screened the electrostatic interaction which is why the adsorption of AKD was hindered at higher salt concentrations, i.e. other attractive forces are too weak to bind the AKD. Polyurethane surface swelled particularly at high salt concentrations (< 100 mM) which affected its surface properties (Hamaker constant, electrostatic properties) and had influence on adsorption. Adsorbed AKD particles on polyurethane are seen in AFM Figure 3.
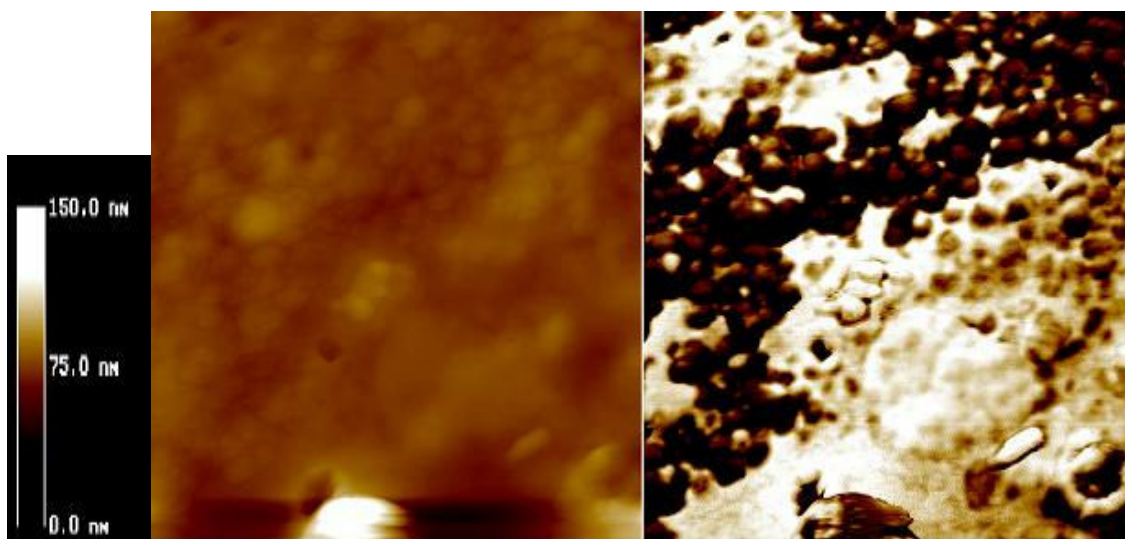
Figure 3. Representative AFM images (1x1 µm) of adsorbed AKD-particles (0,5 g/l, pH 7, 10 mM NaCl). The topography image is to the left and the phase contract image is to the right. Images are taken in air. In the phase contrast image the color is the lighter, the softer is the material. Thus, the soft AKD is colored white and the harder polyurethane dark brown (Paper II).

Also the adsorption of anionic particles on polyurethane is mainly governed by DLVO-forces. Electrostatic repulsion between anionic substances and anionic polyurethane surface prevents the adsorption, when the salt concentration is too low. Examples are the very small adsorption of wood resin in 0.1 mM NaCl and the adsorption of polystyrene latex that only started after the salt concentration was increased to 1-1.5 mM NaCl (see Paper II Table 5). As predicted by the DLVO-theory, the concentration of calcium ions needed to induce adsorption was much smaller than the amount of sodium ions.

Anionic and cationic colloidal particles or polymers formed multilayers when adsorbed sequentially on polyurethane at low salt concentrations (Paper II, pages 954-958). The driving force was again electro-osmotic force. DLVO –driven deposition of colloids and polymers to form multilayers is among the mechanisms in which thick deposits are formed.

The adsorbed amounts of particles were calculated using equation (9.1) for the first 60 seconds of adsorption. Dynamic light scattering was used to determine the diffusion coefficient.

The calculated adsorbed amounts are compared with results from the QCM-D experiments in Table 1. The measured values are too high because the Sauerbrey equation (9.3) overestimates adsorbed amounts of large particles. With polystyrene latex the adsorbed amount estimated with the Sauerbrey equation (9.3) are around 4 times larger than the adsorbed amounts estimated with AFM (Paper II). This is due to increased roughness and possible slipping of adsorbed colloids. Nevertheless, the differences observed between values calculated from eq. (9.1) and eq. (9.3) are in most cases so large that they must be considered significant.

Table 1. Calculated and observed amounts (by QCM-D) of adsorbed particles at pH 7.

C_0/salt conditions	Particle size	D cm^2/s	Amount adsorbed after 1 min ng/cm^2	
			Calculated from eq. 9.1	Observed (calculated from eq. 9.3)
AKD	350-360 nm	$1 \cdot 10^{-8}$		
0.1 g/l/0.1 mM NaCl			43.6	619.5
0.5 g/l 10 mM NaCl			217.9	1416
0.1 g/l/ 10 mM NaCl			43.6	395.3
Kaolin	400-500 nm	$8.7 \cdot 10^{-9}$		
0.1 g/l/ 20 mM NaCl			81	8.85
Polystyrene latex	225-260 nm	$2.1 \cdot 10^{-8}$		
0.1 g/l/ 10 mM NaCl			63.3	5.9
0.1 g/l/100 mM NaCl			63.3	236
0.1 g/l/0.1-0.3 mM NaCl, 0.1mM CaCl$_2$			63.3	419
Talc	600-700 nm	$6.2 \cdot 10^{-9}$		
0.1 g/l/ 10 mM NaCl			67.5	112
Wood resin droplets	135-265 nm	$1.4\text{-}2.7 \cdot 10^{-8 \text{ 1)}}$		
0.1 g/l/ 10 mM NaCl		$2.42 \cdot 10^{-8}$	69.9	318.6
0.1 g/l/ 1 mM CaCl$_2$		$2 \cdot 10^{-8}$	61.7	224
0.1 g/l/ 300 mM NaCl	several µm	Much smaller than above	-	Near 0

1) From Kekkonen et al. 2001

Only very little adsorption of aggregated wood resin could be detected at 300 mM NaCl. This indicates that the kinetics of adsorption kinetics was limited by diffusion. Colloidal resin droplets adsorbed faster, because they diffuse more rapidly to the surface. Aggregated droplets did not adsorb due to their larger size that lowers the rate of diffusion. Hence, colloidal wood resin may cause more fouling than the aggregated resin at stagnant point conditions, which is in accordance with earlier observations by Kekkonen (2001).

The adsorption of polystyrene latex is retarded at low salt concentration (Table 1). Electrostatic repulsion is the probable reason. The adsorption of AKD-wax seems to be faster than predicted by equation (9.1). In addition to the bridging mechanism presented in Paper II, it seems likely that the fast adsorption of AKD in the beginning of the experiment was due to adsorption of excess cationic starch from solution.

The model suggested by Boluk and Van de Ven (1990) was used to determine the effects of blocking on adsorption (equation 9.2). Satisfactory fits could be made of experimental data to equation (9.2), when the amount adsorbed was relatively low and depletion had only a moderate influence on adsorption and the $\Delta D/\Delta f$ – plots did not radically change during adsorption (as with talc or AKD). These requirements were fulfilled in the case for the adsorption of wood resin droplets in 10 mM NaCl, polystyrene latex in 10 mM NaCl and kaolin in 20 mM NaCl. Calculated blocking times (τ_{bl}) from these experiments are listed on Table 2.

Table 2. Blocking times (τ_{bl}) interpreted from results and used in fittings.

Adsorbed substance and salt condition	Blocking time (min)
Kaolin in 20 mM NaCl, pH 7	170
Polystyrene latex in 10 mM NaCl, pH 7	580
Wood resin droplets in 10 mM NaCl, pH 7	3.4

The blocking times are much longer in case where the rate of adsorption is slower than predicted by the diffusion controlled model (kaolin and latex) and the salt concentration is relatively low. Electrostatic repulsion between negatively charged polyurethane and negatively charged kaolin or latex particles is the likely reason for prolonged blocking times. Blocking effects evidently enhance paper machine cleanliness. They retard the adsorption of deposits in those machines operating in relatively low salt concentrations and in press section, where the use of fresh water for showering lowers salt concentrations locally.

Spreading kinetics of soft particles

During the studies with colloidal adsorption it was realized that QCM-D can be used to study the spreading kinetics of soft colloids and emulsions. Shifts in dissipation and

frequency are sensitive to surface roughness and $\Delta D/\Delta f$ –values alter when the colloids spread on surfaces.

One example is the spreading behavior of styrene-butadiene latex (Figures 4-6). The latex particles (particle size 125 nm) were adsorbed on polyurethane in 100 mM NaCl. The glass transition temperature of the latex was 28-33ºC. Below the glass transition temperature (25ºC), the dissipation shift was significantly different compared to the experiment that was carried out around the glass transition temperature at 30°C (see Figs. 5 and 6). It is suggested that the decrease in the dissipation after 40 minutes (Fig. 5) is due to the flattening of the adsorbed layer. It took over 3 hours at 25°C before the adsorbed layer had spread on the surface. At 30°C the flattening of the adsorbed layer was much faster due to the softness of the latex layer. No decrease in dissipation could be detected.
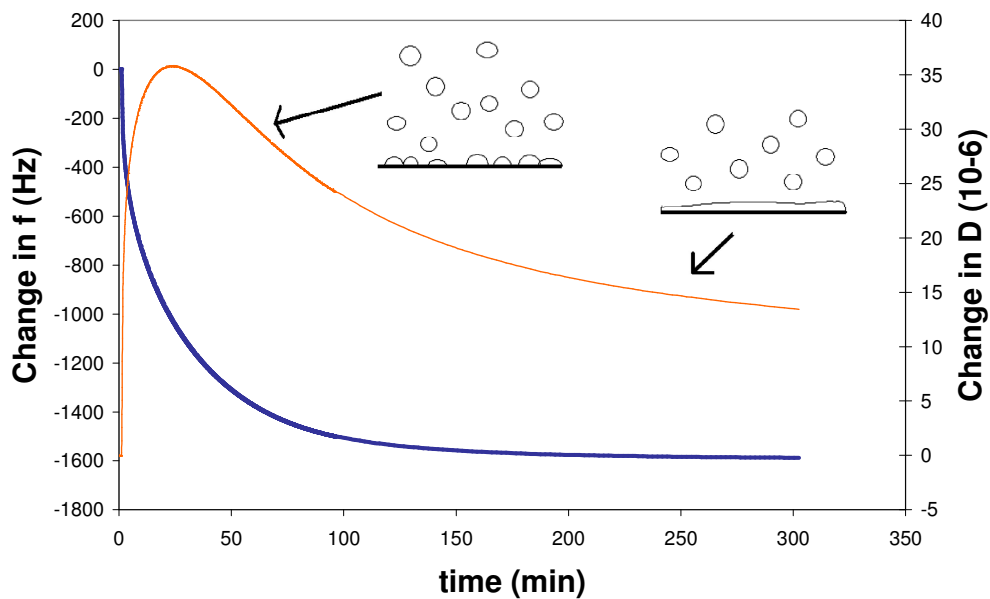
Figure 4. Adsorption of styrene-butadiene latex (0.25 g/l) in 100 mM NaCl, pH 7 at 25°C (below the glass transition temperature) on polyurethane. D is dissipation (thin curve) and f frequency (bold, black curve), f_0= 5 MHz, n=3. The suggested adsorption mechanism is presented inside the Figure (Kallio 2004).
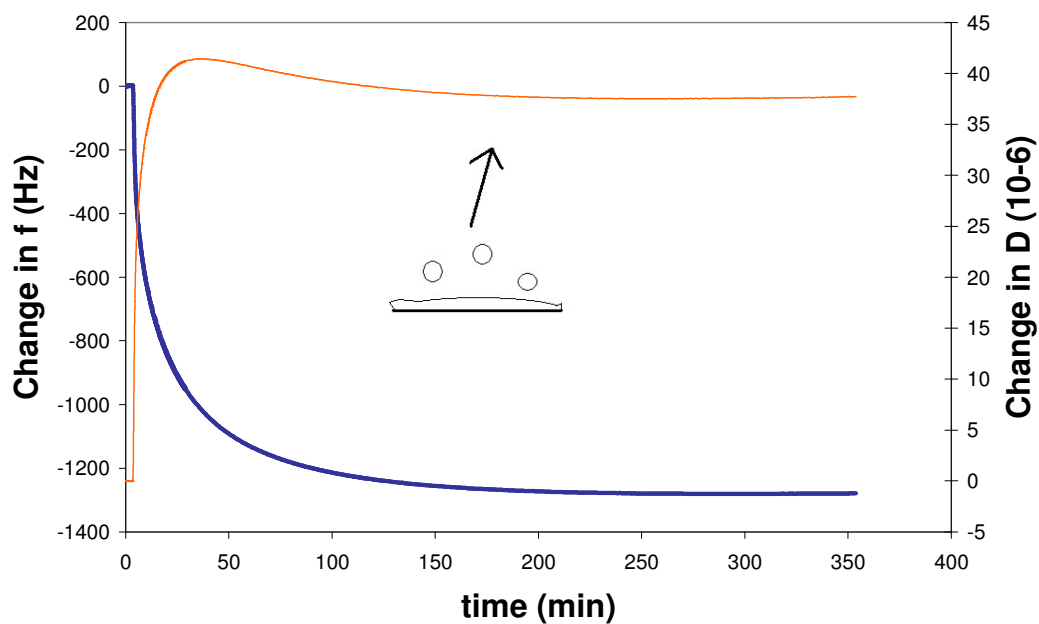
Figure 5. Adsorption of styrene-butadiene latex (0.25 g/l) in 100 mM NaCl, pH 7 at 30°C (around the glass transition temperature) on polyurethane. D is dissipation (thin curve) and f frequency (bold, black curve), f_0= 5 MHz, n=3. The suggested adsorption mechanism is presented inside the figure (Kallio 2004).
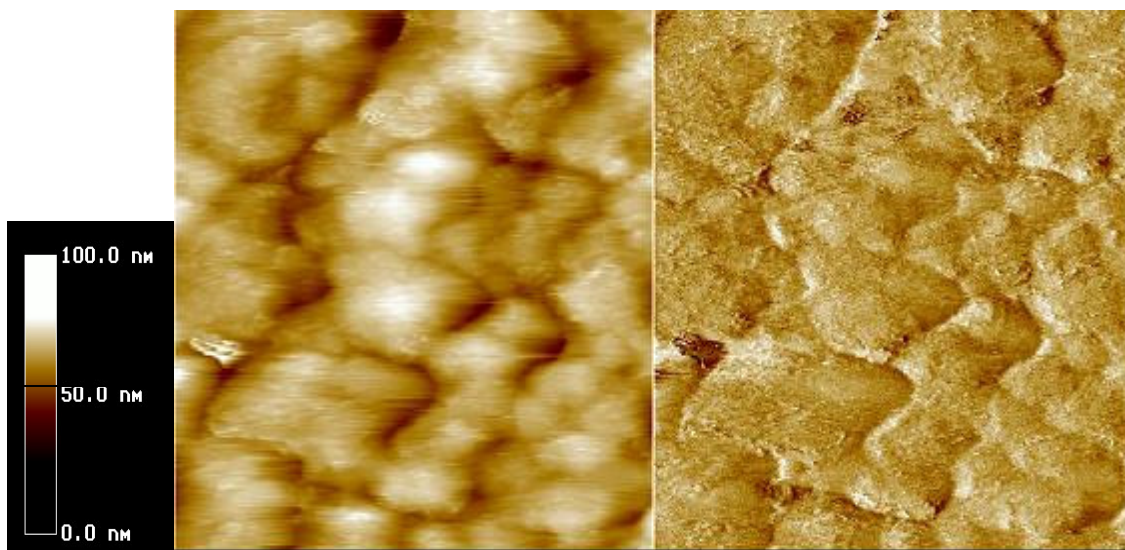
Figure 6. Structure of the adsorbed layer of styrene-butadiene latex as measured with AFM in UHQ water at 25°C (2x2 µm). Spread styrene-butadiene latex particles can be seen shapes with size 100-300 nm (Kallio 2004).

10.2. Adsorption of microbes

QCM-D has previously been used for studies with bacterial adsorption by Otto et al. 1999. The microbes studied (Pseudoxanthomonas Taiwanensis and Deinococcus Geothermalis) form often biofilms in paper machines.

QCM-D studies indicated that the effect of roughness on frequency and dissipation shifts is pronounced with microbes (Figure 7). The size of the bacteria was 1-2 μm.
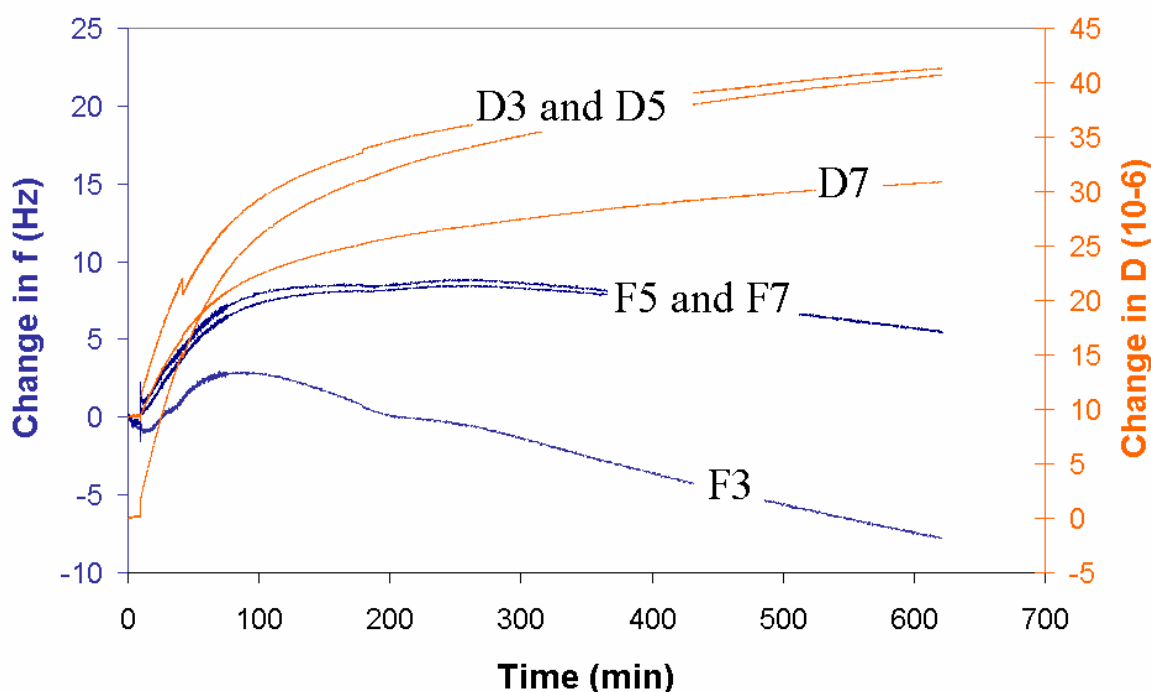
Figure 7. The adsorption of Pseudoxanthomonas Taiwanensis on TiO_2 (pH 7, 10 g/l, 5 mM Na_2SO_4 and 1 mM $NaHCO_3$). F3, F5 and F7 are the 3rd, 5th and 7th overtone numbers. D3, D5 and D7 are the corresponding dissipations (unpublished).

The frequency change remains low despite the rather large adsorption of bacteria. The large amount adsorbed was confirmed with an optical microscope and fast electron scanning microscope (FESEM) by Mari Raulio, University of Helsinki. Also, the dissipation values indicate very large adsorption. Similar results were obtained with Deinococcus Geothermalis. The heavy roughness and the apparent viscoelasticity of microbes causes the very large shifts in dissipation.

QCM is used for on-line measurements to detect fouling in paper mills[5]. The result presented in Fig. 7 suggests that QCM based on pure frequency measurement is not always suitable for on-line monitoring of microbiological deposits. Although significant amounts of bacterial deposits are adsorbed, the frequency values may increase and no deposition is detected. Dissipation monitoring clearly improves the applicability of QCM for on-line measurements with microbiological fouling.

10.3. Adsorption and desorption of dissolved polymers

Adsorbed polymer layers are a common source of deposits. They do not necessarily form macroscopic precipitates, but thin adsorbed films, whose influence can be significant in paper machine operations (as discussed in chapter 3). Adsorption of cationic starch, PDADMAC, cationic polyacrylamide and other polymers were studied on a polyurethane surface. Also the adsorption of hemicelluloses was studied. The studies were focused on NaPSS/hemicellulose, PDADMAC/hemicellulose and wood resin/hemicellulose interactions. As mentioned earlier, NaPSS and PDADMAC are used for pitch control. Interactions between hemicelluloses, wood resin and pitch control chemicals are important in TMP processes (Sundberg 1995). Studied hemicelluloses included anionic pectin (M_w ~ 12kDa), nonionic O-acetyl-galactoglucomannan (M_w ~ 50 kDa) "galactoglucomannan" and bleached anionic hemicellulose fractions containing both anionic pectin and nonionic galactoglucomannan.

Adsorption on polyurethane

Electrostatic interactions seem to control the adsorption of cationic polyelectrolytes (cationic starch and cationic polyacrylamide) on polyurethane. The adsorption of non-ionic polymers on polyurethane (PEO, PVA, native starch) was very minor, since there is no driving force for adsorption (Paper II). An example of an adsorbed layer of cationic starch on polyurethane is seen in Figure 8.

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[5] http://www.freepatentsonline.com/20060281191.html
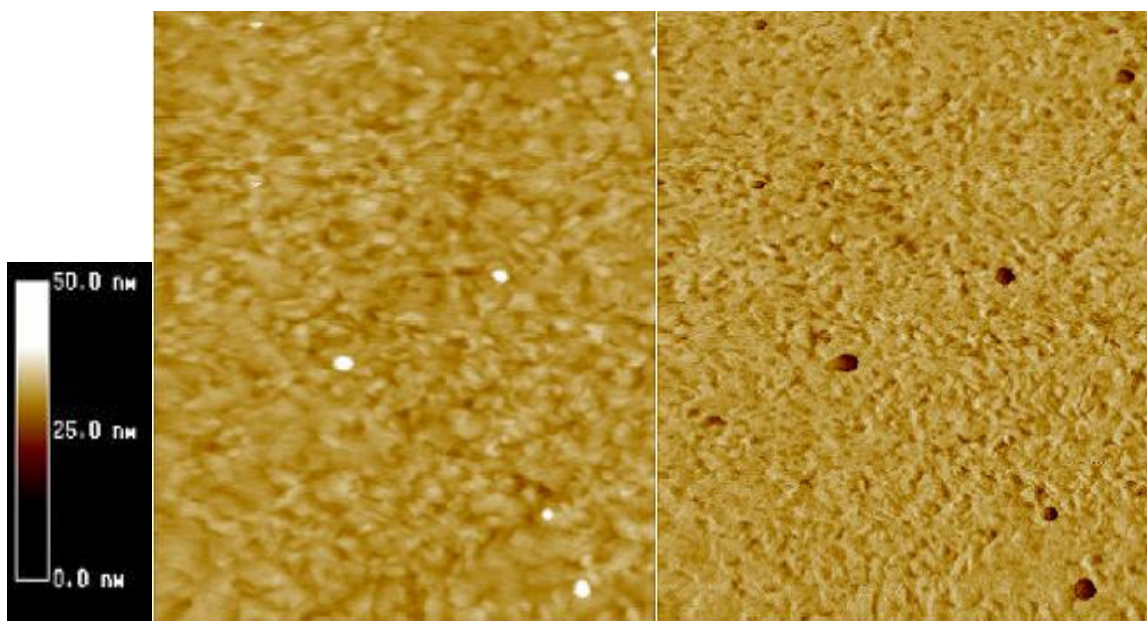
Figure 8. Representative AFM-images of an adsorbed layer of cationic starch on polyurethane. The topography image is to the left and the phase contract image is to the right. The size of both images is 3x3 μm. The measurement was made with the surface immersed in water. Note that the topography of the adsorbed layer to some extent reproduces the morphology of original polyurethane layer (see Paper II, Fig. 2).

Adsorption and desorption of hemicelluloses

Earlier studies have indicated that the adsorption of hemicelluloses and galactoglucomannan is extensive on lignin, cellulose and wood resin (Tammelin 2007). Also in this study hemicelluloses adsorbed on all of the surfaces studied (PSS, PDADMAC and wood resin). An example of galactoglucomannan adsorption is given in Figure 9.
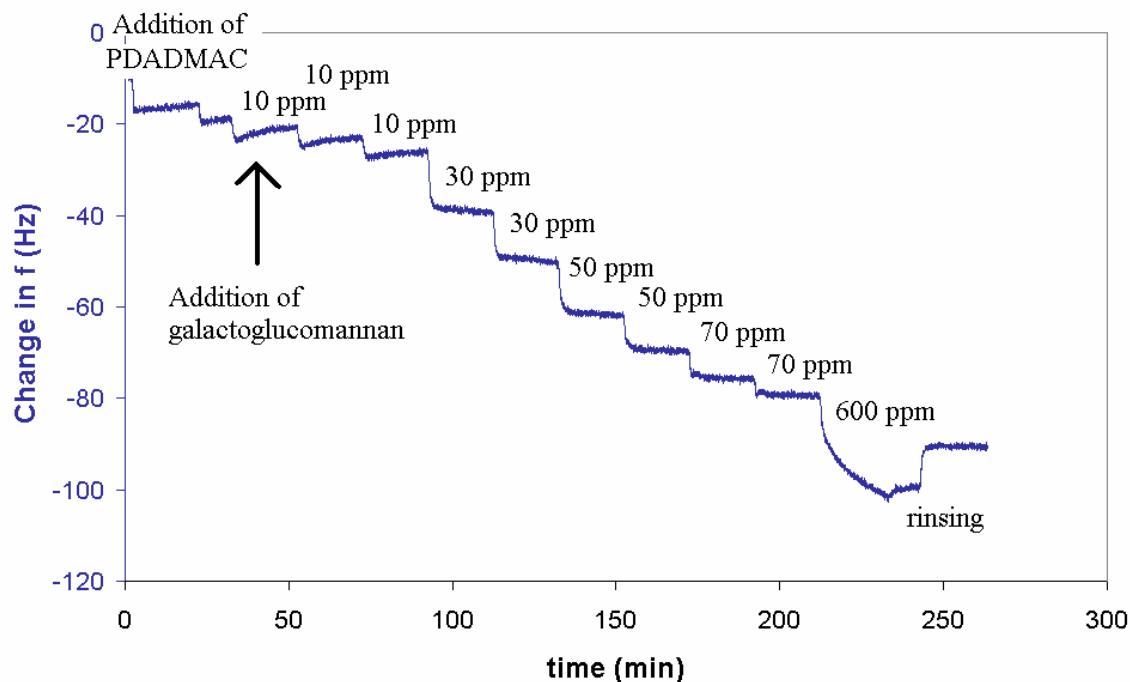
Figure 9. Adsorption of galactoglucomannan on preadsorbed PDADMAC in pH 4.7, 10 mM NaAC/HAc buffer, f_0= 5 MHz, n=3. PDADMAC adsorbed on SiO_2.

Unlike the adsorption of other substances, the adsorption of galactoglucomannan cannot be explained with DLVO theory. Because of the non-ionic nature of galactoglucomannan, there was neither attractive nor repulsive electrostatic forces present. Instead, the driving force was probably related to the attractive van der Waals forces and the relatively poor solubility of the galactoglucomannan.

Results from experiments with pectin, galactoglucomannan and hemicelluloses with a similar experimental set-up as present in Figure 9 are collected on Table 3.

Table 3. Adsorption of pectic acid and galactoglucomannan on PDADMAC /SiO$_2$ and NaPSS/TiO$_2$ surfaces (pH 4.8, 10 mM NaAC/HAc buffer). Every addition was made after 20 minutes, f$_0$= 5 MHz, n=3. Concentrations were 0.5 g/l PDADMAC, 0,8 g/l Na- PSS, 100 mg/l pectin, 100 mg/l, GGM. PDADMAC adsorption on SiO$_2$ ~ 10 Hz. PSS adsorption on TiO$_2$ ~ 14 Hz.

Addition	Pectin on PDADMAC/SiO$_2$ (Hz)	Pectin on PSS/TiO$_2$ (Hz)	GGM on PSS/TiO$_2$ (Hz)	Bleached hemicelluloses on PDADMAC/SiO$_2$ (Hz)	Bleached hemicelluloses on PSS/TiO$_2$ (Hz)
3*10 ppm	40.5	7.5	15.0	43.8	10.2
2* 30 ppm	- 10.2	2.7	12.3	13.8	4.2
2* 50 ppm	-3.3	0.9	9.0	4.8	4.2
2*70 ppm	- 1.8	1.5	1.8	2.1	4.5
600 ppm (pH 5,6)	~ 0	5.4	39	3.6	4.2
Net amount adsorbed	**25**	**18**	**77**	**68**	**27**
Rinsing	~ -3	~ -1.8	~ - 6	~ -4.8	~ -3

Anionic pectin seems to form soluble complexes with cationic PDADMAC on the surface. The dissolution of these complexes explains the detected desorption, when more pectic acid was added (Table 3 column 2). Pectin adsorbed also on PSS/TiO$_2$. However, the amount adsorbed was smaller than on PDADMAC/SiO$_2$, which probably was due to electrostatic repulsion between anionic polystyrene sulfonate and pectin (Table 3 column 3). Larger amount of hemicelluloses adsorbed on preadsorbed PDADMAC than on preadsorbed PSS. This possibly was due to electrostatic attraction between pectin and PDADMAC. Also the Hamaker constant of these two substrates is different. Hence, the

changes in van der Waals attraction can also explain the observed differences. As expected, adsorption of hemicelluloses with smaller size is relatively rapid compared to colloids.

Part of the adsorbed hemicelluloses was detached by rinsing (as can be seen from Figure 9) from preadsorbed PSS and PDADMAC layers. Especially strong desorption of the adsorbed hemicelluloses was detected from wood resin model surface when the chamber was rinsed several times with slightly acidic solution (pH 5). A typical result from adsorption and desorption experiment with TMP hemicelluloses on extractive surface is presented in Table 4.

Table 4. Adsorption and desorption of bleached TMP hemicelluloces (400mg/l) in 5 mM Na_2SO_4 pH 5.5, f_0= 5 MHz, n=3. Rinsing with water (pH 5).

Surface	Adsorbed amount (Δf) Hz	Change in dissipation during adsorption $\Delta D*10^{-6}$	Desorbed amount after rinsing(Δf) Hz	Change in dissipation during desorption $\Delta D*10^{-6}$
Wood resin	48	4.0	- 38	- 1.4

The rate of desorption and the desorbed amounts were to some extent sensitive to the strength of rinsing flow. There were cases, when the frequency shifts indicate full desorption of hemicelluloses on wood resin. The desorption phenomena needs further studies. It is, for example, unclear, why the shift in dissipation indicates much smaller desorbed amount than the shift in frequency. Nevertheless, the strong desorption indicates that the binding of hemicelluloses on the wood resin are rather weak.

Concentrations of hemicelluloses can be very high in TMP processes. Hence, process equipment is often covered by a layer of hemicelluloses at stagnant point conditions. The adsorption of hemicelluloses and other short-chain polymers is relatively rapid compared to colloids. Therefore, hemicelluloses tend to act as primary adsorbents. Larger substances (e.g. colloids) with smaller diffusion coefficients tend to adsorb on the pre-adsorbed layer of short-chain hemicelluloses and other polymers. Desorption of

hemicelluloses from wood resin during dilution may decrease the colloidal stability of wood resin particles, which may assist fouling.

11. Interfacial tensions, contact angles and adhesion of wood extractives (Papers III and IV)

Wood extractives were chosen as model deposits for the studies with interfacial tensions, contact angles and adhesion. Oleic acid, model solutions of wood extractives ("TMP wood resin") and fatty acid calcium soaps were studied. They represent the "pitch" released during thermomechanical pulping.

11.1. Surface and interfacial tensions

The purpose was to understand the interactions of extractives at the extractive/solution and extractive/air interface. Interfacial tensions of fatty acids and other extractive components have been investigated earlier (e.g. Harkins 1917; Chatterjee 2002). However, to my knowledge there are no studies related to the intermolecular origin of interfacial and surface tensions of extractives.

Interfacial and surface tensions of oleic acid, TMP model wood resin and calcium linoleate/linoleic acid are presented in Table 5.

Table 5. Interfacial tensions of wood extractives in aqueous solutions at 25.0 ± 0.7 ºC.

Substance	Conditions	Interfacial or surface tension[*] mJ/m^2
Oleic acid	Air	31.8
Model TMP wood resin	Air	31.0
Oleic acid	pH 2-8	11.8
Model TMP wood resin	pH 4.6	12.8
Model TMP wood resin	pH 5.7, 10 mM $CaCl_2$	12.2
Model TMP wood resin	pH 4.6, 100 mM NaCl	11.8
Model TMP wood resin	pH 4.6, 600 mM Na_2SO_4	13.3 ± 1
Linoleic acid/Ca-linoleate 1.5:1	pH range 3-8	7.2

* Standard deviation ± 0.4 mJ m^{-2} unless otherwise stated.

The surface and interfacial tensions of oleic acid and TMP wood resin are close to each other. Therefore, oleic acid is a good model compound that also represents other TMP extractives. In air the acid-base (AB) contribution to surface tension of oleic acid is estimated to be roughly 3 mJ/m^2 and the dispersion contribution 29 mJ/m^2 (Paper III).

In solution the situation is more complicated. If it is assumed that the interaction between oleic acid (and TMP model extractives) is purely due to van der Waals (dispersion) forces, the interfacial tension of: $72 + 31.8 - 2 \cdot \sqrt{22 \cdot 29} \sim 53$ mJ/m^2 would be expected. 22 mJ/m^2 and 29 mJ/m^2 are the dispersion contributions of water and oleic acid, respectively. Several reasons can be found for why the actual value is significantly lower (11-13 mJ/m^2). Firstly, oleic acid orients in aqueous solution with polar carboxyl groups towards the water phase. This increases the dispersion contribution of oleic acid (as discussed in Paper III). Secondly, the Lewis acid-base bonding of water molecules on COOH-groups decreases the interfacial tension between oleic acid and water. Thirdly, the carbon double bond of oleic acid may also lower the interfacial tension. Studies of aliphatic hydrocarbons with similar chain length indicate that carbon double bonds significantly lower the interfacial tension. For octadecane, the interfacial tension in water is 50 mJ/m^2 and for 1-octadecene it is 15 mJ/m^2 (Israelachvili, 1992). In addition, the

dispersion contribution of water (22 mJ/m^2) is altered at oleic acid interface due to the formation of hydrogen bonds with carboxyl groups and carbon double bond (as discussed in Paper III). Besides, the entropic contributions of oleic acid and water surface tensions are changed due to the structuring of oleic acid and water molecules at the interface.

Furthermore, I suggest that the interfacial tension between wood resin and fatty acids and water is mainly determined by the residual hydrocarbon/water contact. This interpretation explains the relative independency of the interfacial tension on salt conditions and pH. At the higher values of pH investigated here (4.6, 5.7), the carboxylic groups will be partially dissociated which have an influence on the bonding of acid-base bonding of water and dispersion interactions. The binding of salt ions on ionized carboxyl groups is also different in different salt concentrations at pH 3-6. However, as long as the contribution of the hydrocarbon chain/water contact is of dominant importance, changes in pH or salt conditions has only small influence on the interfacial tensions.

Calcium ions did not have any significant influence on the interfacial tension of fatty acids and wood resin. Apparently, calcium ions did not bind on the charged groups of TMP wood resin to form disoaps. Extensive formation of such soaps would have lowered the interfacial tension, as shown by the results for pure calcium-linoleate.

11.2. Contact angles and adhesion of wood extractives

11.2.1. Contact mechanism and wetting kinetics of extractive drops

The transfer of fouling substances from web onto the roll surface or the retention of fouling substances are examples of mechanisms, where the time-scales are very fast and wetting rates are of large importance. The influence of wetting kinetics on fouling is a poorly understood topic. Also the mechanism, how large fouling substances (e.g. aggregates) reach contact with the surface in solution is somewhat unclear. Useful

information related to the contact mechanism of wood extractive drops was achieved from images taken with contact angle goniometer.

In solution, two-stage kinetics of spreading was observed. The drop first rolled along the surface or stayed on the surface without spreading. The pre-wetting period lasted from 100 ms up to tens of seconds after which the spreading started suddenly. Typical pre-wetting times for relatively smooth surfaces (such as silicon dioxide) were on the order of 4-5 seconds. It was observed on every surface studied regardless of the surface energy. An example of pre-wetting is presented in Figure 10. The delay period is due to the presence of a slowly draining thin water film between the droplet and the surface. The draining phenomena is reviewed e.g. by Manev and Nguyen 2005.

Furthermore, I suggest that the spreading begins, when the drop meets a discontinuity that induces rupture of the draining water film. The discontinuity may be a dust particle, very rough asperity or an air bubble on the surface. This would explain why the period without significant spreading varies more or less randomly, because the number of dust particles or asperities at the interfaces or in solution varies. The pre-wetting period was also absent on macroscopically rough polystyrene surface and is shorter, when the surface was rough in micro-scale (e.g. thermally sprayed Cr_2O_3 surfaces studied in Paper IV). The beginning of the spreading process and film rupture is seen in Figure 10.

Fig 10 A. Time t= 0   B t=0.04 s   C t=0.92 s

D t=0.96 s   E t=1.00 s
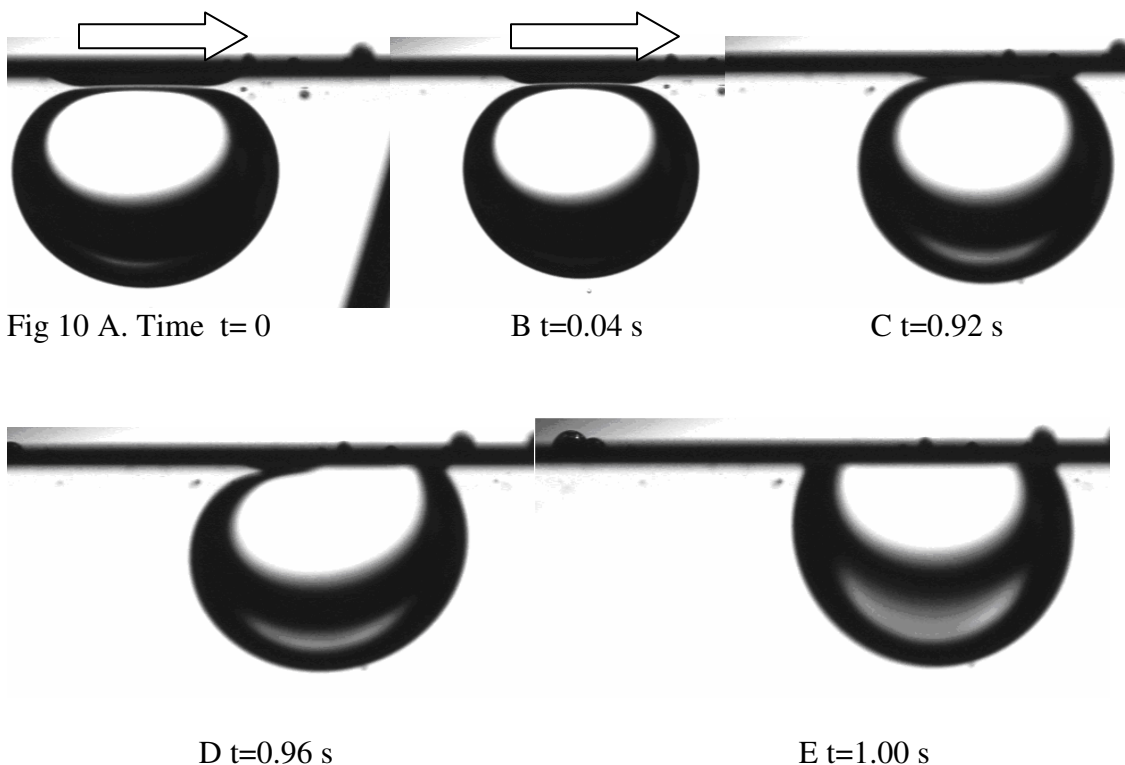
Figures 10 A-G. The beginning of spreading of oleic acid on hydrophobic SiO_2 in aqueous solution (pH 2.3).

A: The drop collides with the surface, and deforms slightly. A thin water film can be seen between the drop and the surface. B: After the collision the drop is again reshaped so that the liquid/liquid interface becomes more spherical. The drop starts to slide along the thinning water film on the slightly tilted surface (inclination < 0,3º). Due to the deformation the contact surface of the drop is somewhat parallel with the solid surface. C and D: The other side of the drop reaches contact with the surface. The formation of the contact is probably enhanced by surface aspertice (dust particle) or a small air bubble. E: Both sides of the drop reach the contact. The drop is again more symmetric in shape and the spreading begins rapidly. The asymmetry of the drop is not, however, fully removed. The value of left and right contact angle differs 1-3º from each other until the end of spreading.

After pre-wetting period the spreading continued with concomitant decrease in contact angle, as expected. Examples of spreading kinetics are presented in figure 11.
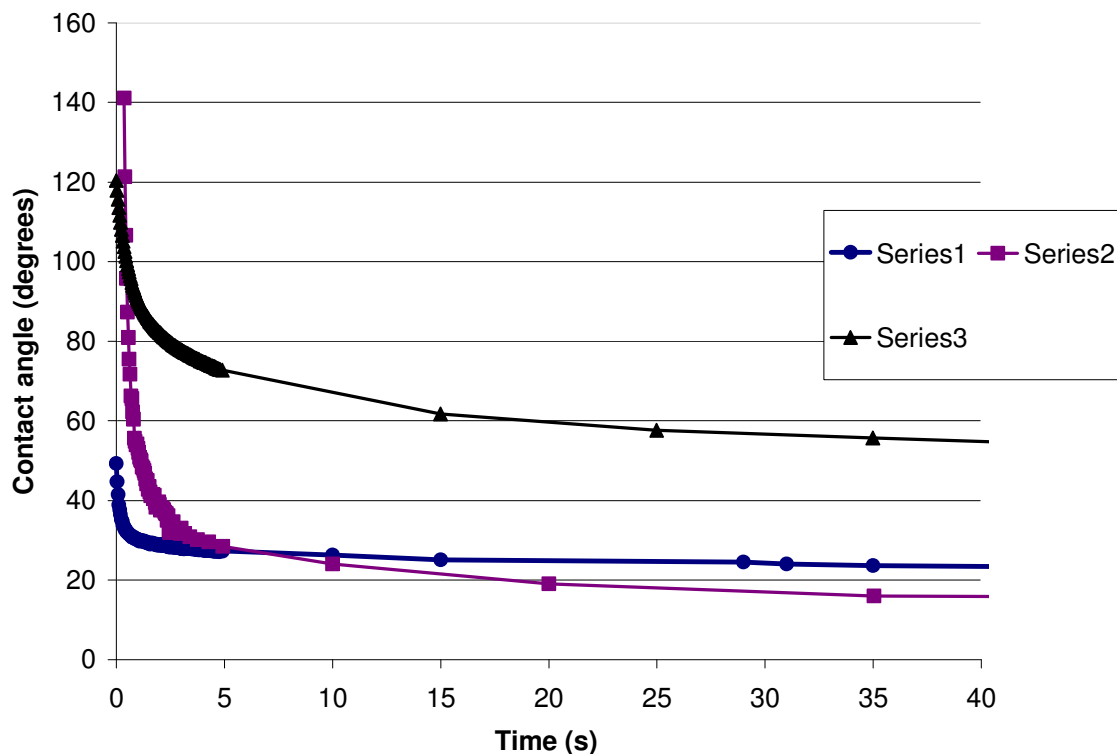
Figure 11. Spreading of oleic acid on hydrophobised SiO_2 in acidic (pH< 3) water (series 1), on SiO_2 in air (series 2). Spreading of acidic water on SiO_2 in oleic acid (series 3) (based on data presented in Paper IV).

The largest speeds of the contact line detected with extractives were on the order of 20-50 mm/s (between 60-120° contact angle). The undetected maximum wetting speeds were probably much higher. Blake et al. (1993) have measured speeds as high as 500-2000 mm/s with aqueous glycerol solutions on polyethylene terephtalate, when the contact angles were near 180°. The viscosity of these solutions was comparable to wood extractives. The contact angles reached the "near equilibrium" –state in some seconds both in air and in solution. When oleic acid was used as medium, the rate of spreading was significantly lower due to the higher viscosity of oleic acid (Fig. 11, series 3).

The spreading of extractives continued slowly on most of the surfaces after the state of "near equilibrium" was reached. A typical change in contact angle was 1-5 degrees at this stage. On SiO_2 the spreading continued for at least 10 minutes and on polystyrene for several hours in air. However, the oleic acid contact angle remained unchanged after 3-4 seconds spreading on fluoropolymer. Therefore, the "state of equilibrium" is somewhat

vague concept and strongly surface-dependent. This causes uncertainties in the comparison of contact angles between different surfaces. I note that wetting kinetics is relatively poorly understood topic (as discussed by Blake 2006). A common interpretation is that wetting speeds are diffusion controlled, when the contact angles are far from equilibrium. Near equilibrium viscous drag determines wetting speeds (de Ruijter et al. 2000).

Practical implications of wetting kinetics

It is evident that large pitch drops do not have time to form the equilibrium contact angle (= full adhesion) on the paper web or on many paper machine parts in operation. For example, the typical contact times are on the order of several milliseconds e.g. between the web and rolling paper machine equipments (Paper IV). Higher machine speeds prevent wetting by large deposits, which enhances process cleanliness. On the other hand, colloidal pitch droplets may have time to reach the equilibrium angle. This is of course dependent on the viscosity of the pitch droplet. There are also some slower fouling processes during which the large resin droplets may reach the equilibrium. These include e.g. the settling of the deposits at stagnant point conditions.

The formation of a thin water film between the surface and resin droplets will prevent the retention of aggregated pitch droplets in the web. Therefore, it is very important that the process water contain chemicals, fibres, fines and other material suitable for bridging the pitch droplets to the web by causing film rupture. The occurrence of a pre-wetting period on smooth surfaces also enhances their cleanliness. This is in accordance with practise, where very smooth surfaces (e.g. electrochemically polished steel) are used to prevent the collection of deposits on paper machine surfaces.

11.2.2. The work of adhesion near equilibrium

Besides rheological effects thermodynamic work of adhesion largely determines how deposits are detached from the surface. Thermodynamic adhesion also affects the retention of fouling substance and operation of pitch control chemicals. Adhesion of deposits should be low on an antifouling surface. Some studies exist related to the adhesion of fouling substances (e.g. Lindfors et al. 2005). However, the adhesion of extractives on different surfaces is not well understood. To my knowledge, only one scientific article has been published, where contact angles and adhesion of extractives were investigated in air (Qin et al. 2003).

In the following sections, I have compared the contact angles of oleic acid and wood resin which have been assumed to be in equilibrium after ~5 minutes of spreading. This assumption contains, as discussed in previous chapter, uncertainties. Works of adhesion are calculated from equation 9.5 using the data from surface and interfacial tension measurements (Table 5). Based on AFM measurements most of the surfaces studied were estimated to be smooth enough so that the Dupré equation (9.5) is applicable. Part of the study was focused on the intermolecular origin of extractive adhesion (Papers III and IV and chapter 11.3.).

Adhesion on paper machine surface materials

A wide range of paper machine surface materials were studied. Polyamide is used e.g. in felts. Stainless steel, titanium and silicon dioxides, polyethylene and polystyrene- and mica-like surfaces are also present in many paper machine equipments. Fluoropolymers (e.g. Teflon) are used in paper machine dry section in order to avoid the formation of deposits.

The results from contact angle measurements with wood resin and paper machine surface materials in solution are present in Tables 6 and 7.

Table 6. Contact angles and adhesion of wood resin on paper machine surface materials in solution.

Surface	Contact angle in solution (pH 4.6) degrees	Work of adhesion in solution (pH 4.6) mJ/m^2
SiO$_2$	149 ± 5	1.8 ± 0.6
TiO$_2$	114± 4	7.6±0.6
stainless steel*	> 165	-
polyamide (pH 3-5.9)	80 ± 3	15 ± 0.8
Fluoropolymer	16 ± 6	25.2 ± 0.4

* The sample is estimated to be too rough for Dupré equation to be applicable.

The basic trend in the work of adhesion was clear. In solution the adhesion of wood resin was large on hydrophobic fluoropolymer and small on hydrophilic surfaces. The observed trend can be understood from equations 9.6 and 9.7. In case of oleic acid adhesion at liquid water interface (W_{lw}) is (31.8+72-11.8)mJ/m^2 = 92 mJ/m^2. The cohesion of water is W_{ww} = 2*72 mJ/m^2 = 144 mJ/m^2. Therefore,

$$W_{slw} = W_{sl} - W_{sw} + 52 \text{ mJ/m}^2 \qquad (11.1)$$

Oleic acid and other wood extractives spread on hydrophobic surfaces in solution, because the difference in adhesion energies $W_{sl} - W_{sw}$ is much larger than ~ -52 mJ/m^2. This mainly due to the small adhesion of water on hydrophobic surface (small W_{sw}). The adhesion of extractives is low on hydrophilic surfaces, because the difference in adhesion energies $W_{sl} - W_{sw}$ is close to ~ -52 mJ/m^2. This is mainly due to extensive bonding of water with the acid-base sites of the surface (large W_{sw}).

Hence, strongly hydrophilic (hydrogen bonding) surfaces are repellent to wood extractives in the paper machine wet end. The finding is in accordance with observations with alkenyl succinic anhydride (Lindfors et al. 2005).

The results from contact angle measurements with oleic acid and paper machine surface materials in air are present in Table 7.

Table 7. Contact angles of oleic acid on paper machine surface materials in air.

Surface	Contact angle in air degrees	Work of adhesion mJ/m^2
Mica	33 ± 3	56 ± 1.2
Fluoropolymer	79 ± 2	37 ± 0.7
Polyethylene	6	> 60
Polystyrene	Near 0	> 62

In air the adhesion on fluoropolymer was very low. However, adhesion on the other hydrophobic surfaces (polyethylene and polystyrene) was higher than on some hydrophilic, polar surfaces (e.g. on mica). Therefore, the surfaces must be very strongly hydrophobic in the dry part of the paper machine before fouling due to extractives can be reduced. Mildly hydrophobic surfaces do not render the surfaces repellent against the extractives.

Adhesion on wood components

Wood components studied were lignin, hemicelluloses and cellulose. The results from contact angle measurements are presented in Table 8.

Table 8. Contact angles and adhesion of wood resin on wood components. Contact angles of PDADMAC are also given as a comparison.

Surface	Contact angle in solution (pH 4.6) degrees	Work of adhesion in solution (pH 4.6) mJ/m^2	Contact angle in air degrees	Work of adhesion in air mJ/m^2
Cellulose	>165	< 0.4	2	> 63
Lignin	129 ± 3	4.7 ± 0.5	15 ± 3	61
Hemicelluloses on PSS/TiO$_2$	163 ± 4	0.6 ± 0.3	-	-
Hemicelluloses on PDADMAC/SiO$_2$	140 ± 4	3.0 ± 0.5	-	-
PDADMAC/SiO$_2$	107 ± 3	9.0 ± 0.6	-	-

The adhesion of wood components in solution was larger on lignin than on hemicelluloses and particularly on cellulose (Table 8).

The results suggest that wood resin emulsions tend to detach from those parts of the wet web surface composed of hemicelluloses or of cellulose. They tend to accumulate on hydrophobic surface materials or on lignin rich parts of the web. Fiber hydrophilicity increases when lignin is removed so that the adhesion of extractives to the fiber decreases. For this reason they are more easily released to the process water during TMP pulping. The low adhesion of extractives to cellulose and hemicelluloses evidently prevents the retention of wood resin.

The adhesion of wood resin to different wood components clearly increases when the web dries. Their tendency to detach is, therefore, smaller in the dry part of the paper machine.

The presence of hemicelluloses decreased the adhesion of wood resin on PDADMAC. Also the hemicelluloses/PSS layer was very repellent to wood resin. Besides, the adsorbed layer of hemicelluloses on surfaces sterically inhibits adsorption of fouling substances (Kekkonen 2001; Tammelin 2007). Adsorbed layers of hemicelluloses are, therefore, antifouling. Low adhesion of wood resin on hemicelluloses means that they

may easily detach from a wood resin surface. This is in accordance with the detected desorption (chapter 10.3.).

Adhesion on pitch control chemicals

Wood resin adhesion on chemicals that control the behavior of wood resin in paper process were studied. These included Poly-(diallyldimethylammonium)chloride (PDADMAC) that is used as a fixative to bound wood resin to the web, Polyethylene oxide (PEO) that is used as a retention aid in the same purpose and Poly(sodium 4-styrenesulfonate) (NaPSS) that is used as a releasing agent in press section to prevent fouling. The results are presented in Table 9.

Table 9. Contact angles and adhesion of wood resin on pitch control chemicals.

Surface	Contact angle in solution (pH4.6) degrees	Work of adhesion in solution (pH 4.6) mJ/m^2	Contact angle in air degrees	Work of adhesion in air mJ/m^2
PDADMAC 1 mM	107 ± 3	9.0 ± 0.6	-	-
PDADMAC, 10 mM	140 ± 10	3.0 ± 2.0	-	-
PDADMAC, 100 mM	126 ± 10	5.3 ± 2.0	-	-
PEO	127 ± 3	5.1 ± 0.6	Near 0	> 62
PEO, 600 mM Na$_2$SO$_4$	126 ± 3	5.5 ± 0.6	-	-
NaPSS/TiO$_2$	162 ± 5	0.5	-	-

Considering its hydrophilic character, large adhesion on PEO was detected in solution. Apparently, the hydrophobic ethylene moieties determine the adhesion of wood resin on PEO surface in solution. The work of adhesion did not alter, although the experiment was carried out below (no salt) or above (0.6 M Na$_2$SO$_4$) its clouding point (Table 9). Apparently, the relatively high values of adhesion enhance the operation of PEO as retention aid.

The adhesion of wood resin to PDADMAC was highest at low salt concentration (Table 9). The lower adhesion at higher salt concentrations was due to the swelling of the

adsorbed PDADMAC layer. In a study of the PDADMAC surfaces with QCM-D, Saarinen *et al* found that the PDADMAC –layer became soft and water-swollen in 10-100 mmol/l NaCl ($\Delta D/\Delta f > 40 \cdot 10^{-9}$ s) , whereas in 1 mM NaCl the adsorbed layer was more rigid and apparently not much swelled ($\Delta D/\Delta f \sim 0$). The operation of PDADMAC as a fixative is enhanced at low salt concentrations due to the relatively large adhesion of extractives. On the other hand, the increase in salt concentration may negatively affect its operation due to the lower adhesion of extractives.

On the adsorbed polystyrene sulfonic acid the adhesion of wood resin is very small at low salt concentration. QCM-D experiments (Paper IV) indicate that also the adsorbed NaPSS layer was water-swollen in the conditions studied. This probably explains the low adhesion. The result suggests that equipment surfaces can be rendered pitch repellent by polyelectrolyte adsorption.

11.3. The influence of van der Waals and acid-base interactions on adhesion

Oleic acid was used as a model compound to determine the intermolecular origin of wood extractive adhesion in different model surfaces (Paper III). Table 10 compares experimentally determined values of the adhesion of oleic acid and the calculated dispersion contributions to the adhesion from equation 11.2.

$$W_A^D = 2\sqrt{\gamma_s^D \gamma_l^D} \qquad\qquad (11.2)$$

γ_s^D is the dispersive component of the surface tension of the surface, determined with diiodomethane using equation 9.9. γ_l^D is the dispersive component of the surface tension of oleic acid, taken to be 29 mJ m^{-2}. Acid-base parameters showed in the Table 10 were determined using the contact angles of diiodomethane, water and ethylene glycol and equation 9.8.

Table 10. Adhesion of oleic acid on model surfaces (25˚C, relative humidity 60 %)

Surface	Acid-base character of the surface	Determined oleic acid adhesion mJ m^{-2}	Dispersion contribution to the oleic acid adhesion mJ m^{-2}	Acid-base contribution to the oleic acid adhesion
Mica	Basic $\gamma^+ = 0.5$, $\gamma^- = 30$	59.1 ± 1.0	66.7	0
SiO$_2$	Acidic	62.7 ± 1.3	68.8	0
TiO$_2$	Amphotheric	> 63	75.2	Possibly some
Cellulose	Basic $\gamma^+ = 0.5$, $\gamma^- = 18$	> 63	70.6	Possibly some
H.fob. SiO$_2$	Neutral	55.8 ± 1.0	51.6	0
Fluoropolymer	Neutral	38.4 ± 0.7	41.9*	0
Polystyrene	(nearly) Neutral	> 63	70.9	0

*using 15.1 mJ/m^2 for fluoropolymer.

The results indicate that oleic acid forms no or very weak acid-base bonds with the surfaces. Only with cellulose and TiO$_2$, on which oleic acid was almost fully spreading (i.e. the angles were roughly 2-7º), it is possible that some AB bonding occurs, but also on these surfaces the dispersion contribution is dominant. Therefore, the estimated work of adhesion of oleic acid on cellulose and TiO$_2$ is not much above 63 mJ/m^2 and the calculated dispersion contributions are close to the actual adhesion. The dispersion contribution to adhesion calculated from the separately determined dispersive contributions to the surface tensions are usually larger than the total adhesion determined from contact angle measurements (Table 10 columns 3 and 4). This difference is possibly due to the overestimation of dispersive interactions, when diiodomethane is used as a probe liquid (see Paper III for further discussion).

In aqueous solution water compete Lewis acid-base sites (chapter 4.3) and the formation of Lewis acid-base bonds between the extractives and surfaces is of minor importance. However, adhesion of negatively charged wood resin at pH 4-6 could, in principle, be affected by the formation of Brönsted acid-base bonds on cationic surfaces.

To determine this, experiments were performed with wood resin on cationic TiO_2 and polyamide at pH:s 3, 4.6. and 5.9. The results are collected on Table 11.

Table 11. Adhesion of wood resin on TiO_2 and polyamide in different pH:s

Surface	Charge of the surface	Charge of wood resin	Contact angle Degrees	Adhesion mJ/m^2
TiO_2 pH-range 4-5*	Cationic	Anionic	114± 4	7.6±0.6
TiO_2 pH 3.0	Cationic	No charge	120± 4	6.4±0.6
Polyamide pH-range 3.5-5**	Cationic	Anionic	80 ± 3	15 ± 0.8
Polyamide pH 3.0	Cationic	No charge	80 ± 3	15 ± 0.8

* IEP of TiO_2 is 5-7 (Kosmulski 2004). Above this pH TiO_2 is anionic.

** IEP of the polyamide studied (PA 6) is 5.25 (Kekkonen 1996). Above this pH it is anionic.

Wood resin contact angles on polyamide remained constant regardless of the pH changes. The resin did change its contact angle slightly (~ 5º) on cationic TiO_2 at pH 4.6. Hence, it is probable that the formation of ionic (Brönsted) acid-base bonds have only minor influence on the adhesion of wood resin.

12. Titanium dioxide as an antifouling material (Paper V)

As discussed in chapter 7.5., fouling due to organic deposits can be reduced, if the surfaces are coated with titanium oxide and kept under UV illumination. Although photocatalytic cleaning with TiO_2 is a relatively studied topic, the details of photocatalytic decomposition mechanisms and the applicability of photocatalytic cleaning for paper making are not well understood.

Wood extractive components (e.g. stearic acid) and TMP wood resin were used as model deposits. Stearic acid is also a widely used model compound in photocatalytic decomposition studies, which allows the comparisons with earlier studies related to photocatalytic cleaning.

As expected the TiO_2 surface studied altered strongly hydrophilic after UV illumination.

12.1. Degradation of stearic acid

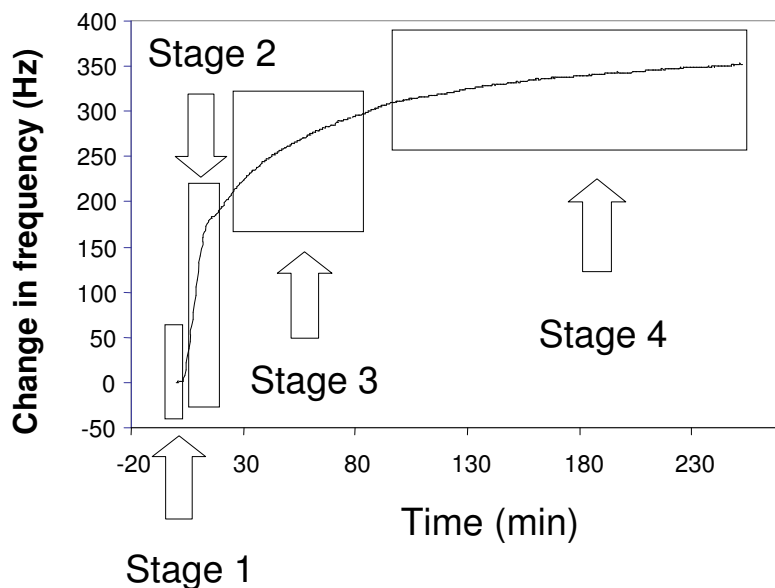An example of an observed degradation kinetics with stearic acid is given in Figure 12.

Figure 12. Degradation of stearic acid LB films deposited on a QCM-D crystal coated with TiO_2 under UV irradiation (wavelength 315-400 nm, peak at 352 nm, radiation intensity 20 W/m^2). The crystal was immersed in aqueous solution at pH 3 (HCl); $[O_2]$ = 6 mg/l. f_0= 5 MHz, n =3 (Based on data presented in Paper V).

The final frequency shifts in Figure 12 indicate that the film formed by ten layers of stearic acid degrades almost completely (amount decomposed 2044 ng/cm^2, amount deposited 2258 ng/cm^2). A closer look to Figure 12 reveals that the degradation process is complicated. The rate of decomposition was low during the first 0-3 minutes (Fig. 12,

stage 1). The effect was only qualitatively repeatable. The slow initial decomposition may be related to the penetration of water or of oxygen through the extractive layer. The penetration of oxygen or of water very likely would take place through channels and faults in the extractive layer.

The rate of decomposition increased after the hindered degradation period, after which it remained relatively constant between 3-10 min after turning on the UV light (Fig. 12, stage 2). At this stage the rate of oxygen diffusion largely determines the rate of decomposition. This can be concluded from the amounts of oxygen consumed during the experiment. The degradation pathways of fatty acids are complicated (see, e.g. Minabe et al. 2000), but assuming that the photocatalytic degradation goes to the end, the net decomposition reaction can be written in the following simplified form:

$$C_{18}H_{36}O_2 + 26\ O_2 \rightarrow 18\ CO_2 + 18\ H_2O \hspace{4cm} (12.1)$$

Calculations based on equations (12.1) and (9.1) are collected in Table 12.

Table 12. Oxygen diffusion and photocatalytic oxygen consumption during degradation of different layers of stearic acid in UHQ water and in air.

Preparation method	Oxygen conc. mg/l	Rate of degradation nmol cm^{-2} min^{-1}	Diffusion limited flux of oxygen nmol cm^{-2} min^{-1}	Estimated oxygen consumption nmol cm^{-2} min^{-1}
10 LB-layers	6	0.40*	*8.0*	*10.9*
Spin-coated	1.5	0.10	*2.0*	*2.7*
experiment in air (spin-coated)	260	0.06	$3.1 \cdot 10^8$ **	1.6

* between 4-5 minutes after UV illumination was turned on.
** $D \approx 0.2$ cm^2/s (CRC 2003-2004)

As can be seen from Table 12, the diffusion limited flux and calculated oxygen consumption correlate at low oxygen concentrations in UHQ water. This observation agrees well with earlier studies, where the degradation of octanoic acid was connected to

the combination of radicals formed from water and dissolved oxygen (Schwitzgebel 1995). Besides oxygen diffusion, other mechanisms hinder the degradation of stearic acid at high O_2 concentrations and in air.

Also the experiments with the spin-coated stearic acid layer in different oxygen concentrations indicated that the diffusion of oxygen has influence on the rate of degradation.
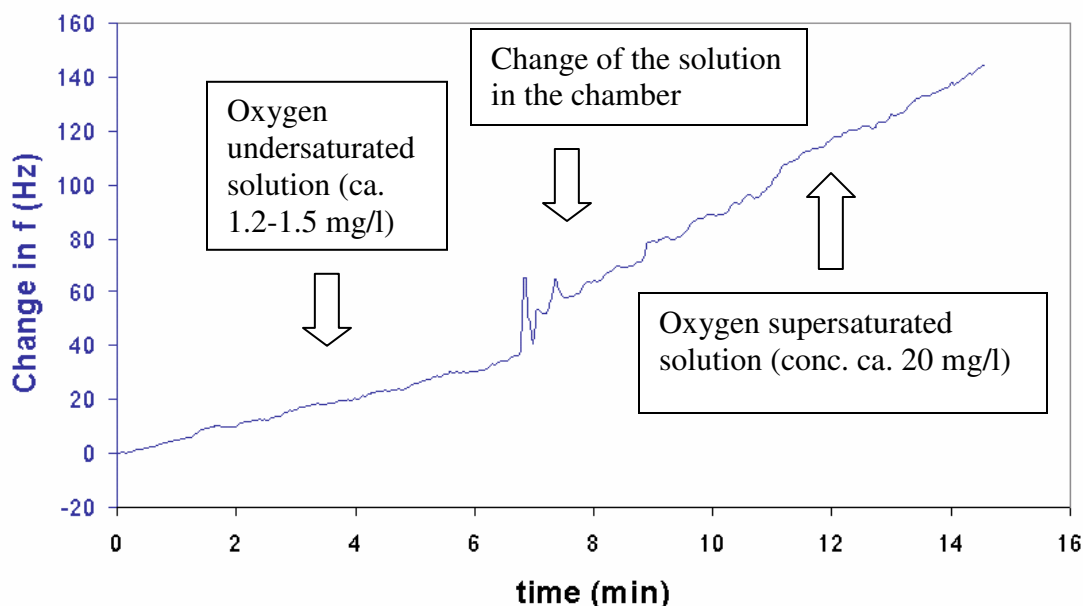

Figure 13. The influence of oxygen concentration on the degradation kinetics of a layer of stearic acid spin-coated on TiO_2 in UHQ water. The rate of change in frequency was 2.5-2.6 times higher after introducing oxygen the supersaturated solution, f_0=5 MHz, n=3 (Paper V).

The rate of degradation is slower at the later stages of experiment presented in Figure 12 (stages 3 and 4). This is due to the lower amount of stearic acid to be degraded. The residual stearic acid may also locate far from the TiO_2 defect sites where the active oxygen species are formed, which retards the decomposition reactions.

Thicker films (20 or 30 LB layers) degraded only partially (Paper V). It is possible that this is because dissolved oxygen is not able to penetrate to a sufficient degree into the TiO_2/film interface when the film is thicker than 10 LB layers.

12.2. Degradation of TMP wood resin

TMP wood resin films on TiO_2 immersed in water degraded as presented in Figure 14. The TMP extractive layer was spin-coated on the sensor surface with acetone (see Paper V for details).
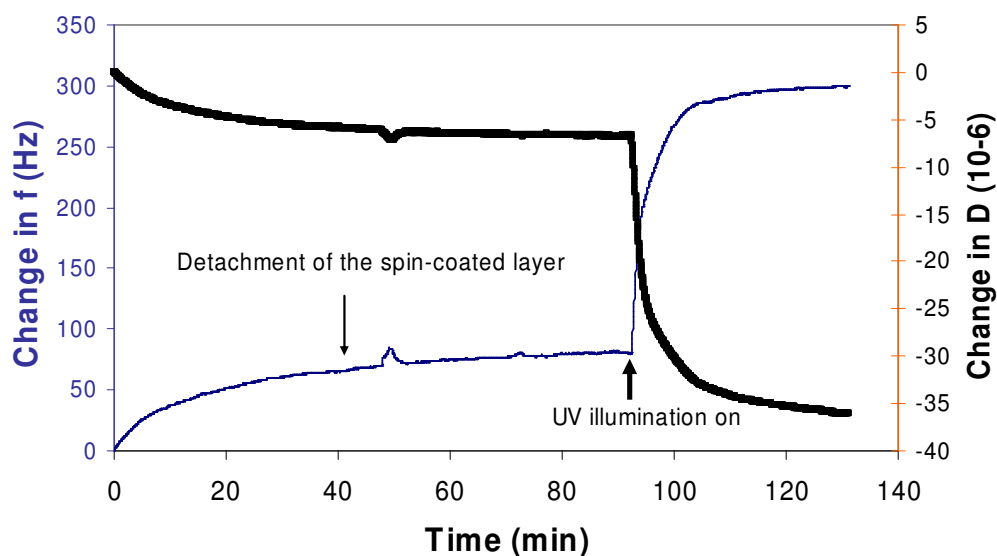

Figure 14. Detachment and photocatalytic cleaning of a spin-coated layer of wood resin in water (pH 5.6), bold line dissipation, thin line frequency, f_0=5 MHz, n=3.

Changes in frequency and dissipation started already before any illumination. Although this change may, in principle, be due to a change in wood resin topography, it is more likely that the change in frequency and dissipation are due to the detachment of wood resin from the surface after the sample was put in solution. The adhesion of wood extractives decreased due to the UV illumination (Paper V). Hence, the detachment was evidently caused by penetration of water between the resin layer and TiO_2 surface. Obviously, the uneven layer of extractives contained spots not covered by wood resin, through which water could penetrate.

Penetration of water between the TiO_2 and extractives also explains part of the detachment of wood resin during UV illumination. Photocatalytic decomposition created new holes in the layer of extractives, after which water penetrated between the wood resin and TiO_2. The transportation of water through faults and channels is the probable wetting mechanism of layers of wood resin on TiO_2. When the UV illumination was turned off during the decomposition, a clear decrease in frequency (around 19Hz) was detected. This was due to the reattachment of the detached wood resin layer or adsorption of dispersed resin particles onto the TiO_2 surface.

The spin-coated extractive layers degraded very unevenly. The observed spots of undegraded wood resin were domains where the layer was too thick for photocatalytic cleaning to be effective.

Finally I note that storage had, in some cases, crucial importance in the degradation kinetics (Paper V). The storage conditions may alter the number and quality of cracks in the extractive layer and the amount of residual water between the extractive and TiO_2 interface. For this reason it can be difficult to quantitatively compare the degradation of substances between different surfaces used in different studies.

12.3. Photocatalytic cleaning mechanisms

As a summary I suggest that the following mechanisms schematically presented in figures 15 A-C play a role in the removal of deposits from TiO_2 by UV degradation.
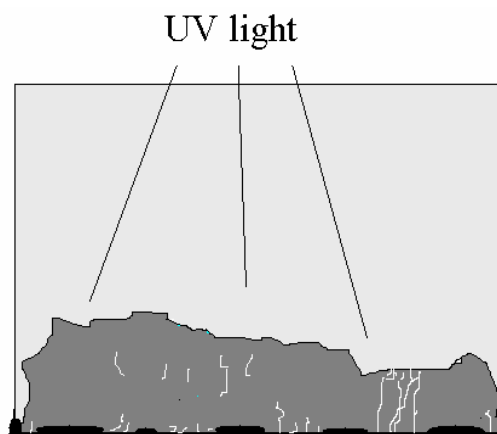
Figure 15 A. The starting point of the photocatalytic process. Oxygen and water molecules penetrate down to the TiO_2 surface at thin places with several cracks. Besides the water penetrating through the extractive layer, the water captured or bound in the extractive layer or between the TiO_2/extractive interface is important in the initiation of photocatalytic reactions (Paper V).
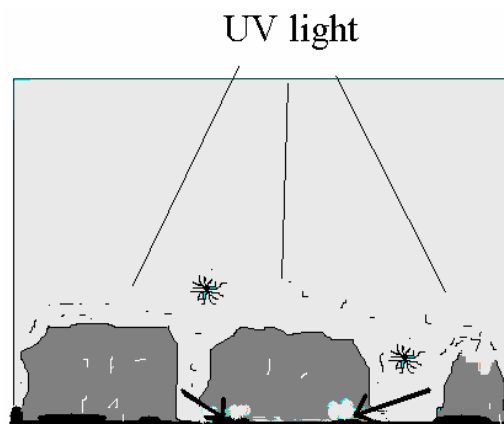

Figure 15 B. During the photocatalytic degradation some solution starts to penetrate under the layer of extractives. Also, the water released during the degradation reactions remains trapped between TiO_2 and the extractive layer. Some of the intermediate products dissolve as monomer molecules or as micelles (Paper V).
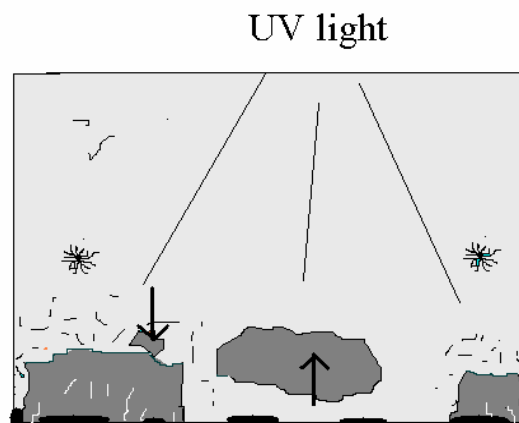
Figure 15 C. Due to the penetration of water under the layer of extractives some extractives disperse. The dispersed or dissolved species may readsorb. The layer of extractives may remain in some places where oxygen is unable to penetrate through the film, or where the extractive layer does not contain captured, bound or penetrated water that initiates the photocatalytic cleaning process (Paper V).

12.4. Applications in paper making

Utilization of photocatalytic TiO_2 could be advantageous if the accumulation of deposits on surfaces is slow enough and the layer of deposits is thin enough (tens of nanometers or less). Industrial experience has also shown that the collection of deposits is often so slow and the films deposited are so thin that decomposition achieved by photocatalytic TiO_2 could help with fouling problems. When the thin and viscoelastic layer of extractives is removed, the collection of further deposits on the surface also decreases.

The drawbacks of the method include the need for UV illumination, the inability to degrade thick layers of deposits and the strong adhesion of extractives on TiO_2 in air (Paper V). The need for UV illumination limits the utility of photocatalytic TiO_2 on pipes and on other subaquatic surfaces, since process water effectively absorbs and scatters UV light. Places accessible for UV illumination include rolls, wires, felts, belts, calenders and splash water places in tanks.

Strong hydrophilicity can be utilized in preventing the formation of condensed water drops on the paper machine surfaces. The problems caused by condensed water drops were discussed earlier in chapter 6.8.

13. Conclusions

13.1. Adsorption of fouling substances

In locations of a paper machine where there are no forces that continuously remove formed deposits, the formation of adsorbed layers are difficult to avoid. Adsorption is rapid and the adsorbed amount large in typical concentrations present in paper machine.

The adsorption of model deposits was mainly driven by van Waals and electro-osmotic forces. Indications of van der Waals force/poor solubility –driven adsorption was found with galactoglucomannan. Diffusion usually controls the rate of adsorption of fouling substances in stagnant point conditions. Hence, substances with the smallest size and the largest diffusion coefficient tend to act as the primary adsorbents. These include short-chain polymers, surfactants and releasing agents. Substances with larger size (e.g. microbes, hydrophobing agents, wood resin emulsions and latex particles) tend to adsorb on the pre-adsorbed layer of low-molecular weight substances.

13.2. Adhesion and kinetics of spreading

Van der Waals forces mainly determine the adhesion of lipophilic wood extractives in air. In solution, the surface hydrophilicity or hydrophobicity dominates the adhesion of extractives. The formation of Lewis acid-base or Brönsted acid-base bonds between the extractives and surfaces has only minor influence on their adhesion.

The adhesion of wood extractives is large on hydrophobic paper machine surface materials (like fluoropolymers) and small on hydrophilic surface materials in solution. From wood components, the largest adhesion of wood resin in solution was detected for

lignin. Therefore, the extractives tend to accumulate on hydrophobic paper machine parts and hydrophobic spots on paper web in the wet end. The increase of fiber hydrophilicity during bleaching of TMP pulp enhances the release of wood extractives, due to the lower adhesion of extractives when lignin content decreases. The adhesion of extractives on adsorbed polyDADMAC is small at high salt concentrations due to swelling of the polyDADMAC layer. Deswelling of the adsorbed PDADMAC in low salt concentrations decreases the adhesion of wood resin. This is one of the reasons why the operation of polyDADMAC as a pitch control chemical can be sensitive to the variations in process water salt conditions.

In solution, a water film is formed between the drop of extractives and the interface prior to spreading. The removal of this water film may take several seconds, which prevents the spreading of aggregated drops of extractives. An increase in surface roughness shortens the pre-wetting period significantly and enhances the contact of extractives. The delays before spreading begins will prevent the retention of aggregated pitch droplets in the web. Therefore, it is very important that the process water contain chemicals, fibres, fines and other material suitable for bridging the pitch droplets to the web. The occurrence of a pre-wetting period also enhances the cleanliness of smooth surfaces.

The observed wetting speeds in this study suggest that large pitch aggregates often have no time to reach the equilibrium contact angle in paper machine operations due the fast machine speeds. On the other hand, colloidal pitch droplets may reach the equilibrium angle in most papermaking operations.

13.3. Antifouling surfaces

The design of antifouling surfaces for the paper machine wet end is demanding. Hydrophilic and smooth process surfaces inhibit the collection of wood extractives. Also adsorbed water-swollen polymer layers may lower the tendency of resin to attach to wet surfaces (Paper IV). On the other hand, inorganic salts avoid nucleation on strongly hydrophobic surfaces (Järn 2006; Brecevic and Kralj 2000). Hydrophilic surfaces are

necessarily not very optimal against bacterial deposits (Raulio 2007). Instead hydrophobic fluoropolymer coatings are microbe –repellent[6]. In the press section the surface has to be somewhat rough in order to avoid fouling problems due to impaired web releasing. Another major difficulty is the adsorbed layer, which is formed easily since the process water contains both cationic and anionic substances. The adsorbed layers alter the surface properties of the antifouling surface.

In dry paper making conditions, surfaces must be strongly hydrophobic (fluorinated), before the fouling due to extractives can be reduced. Mildly hydrophobic surfaces are not especially repellent against the extractives.

For its self-cleaning and antifogging properties of UV illuminated TiO_2 can be useful when antifouling surfaces are developed. It was demonstrated that if the layer of extractives on TiO_2 is thin enough, the layer can be removed by using UV illumination. In solution oxygen diffusion and the penetration of oxygen and water through the fouling layer are the main factors that determine the rate of degradation. The main limitations of photocatalytic cleaning include the need for UV illumination and the inability to decompose thick layers of deposits.

14. Recommendations for future research

QCM-D and contact angle measurements give very useful information related to fouling. However, some aspects related to their use are unclear. For example, several scientific papers are focused on the viscoelastic behavior of adsorbed substances on QCM-D sensor surfaces. Is it certain that the observed dissipation and frequency shifts are due to the viscoelastic properties of the adsorbed layer? It is demonstrated in this study that the changes in surface roughness can also significantly alter dissipation and frequency shifts. This topic should be studied further experimentally. In the field of contact angles, the commonly applied GvOC method requires further research. The method does not take

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[6] Pinta-Clean Surfaces 2002-2006, Technology Programme Report, vol. 17, 2006, Tekes, Helsinki, p. 33.

into account e.g. the molecular asymmetricity of most test liquids. Partly for this reason the achieved results are often qualitative (Paper III).

The main research efforts related to fouling in paper making have so far been focused on those substances causing large macroscopic deposits (e.g. pitch, white pitch, hydrophobing agents etc.). Deposits may be presented as very thin adsorbed films, whose influence on paper machine operation is poorly understood. Thin adsorbed layers affect web releasing, corrosion, wetting, hydrodynamic and wearing properties of the process surfaces.

Other fields that need to be study further are the influence of hydrodynamics on fouling, spreading kinetics of liquid fouling substances and the interactions of microbes with process water components and surfaces. There are also several surface forces whose influence on fouling is still unknown. In addition, practical experiences related to fouling in paper mills are not well documented in scientific literature.

To develop antifouling technical solutions papermakers could learn from natural systems. After all, surfaces and other structures in living organisms are often antifouling.

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