1 Introduction

Paper is one of the oldest and most abundant materials used in our daily life. This lightweight, highly porous and flexible materials has been used for over 2000 years as a writing medium and also for other applications, including packaging, printing or filtration.[1] The technology of paper-making has been improved over several decades and to date the paper fabrication is one of the most optimized industrial processes.[1] Hence, different standard paper grades can be produced in large quantities in a very economic fashion making it a comparable cheap material.

However, in recent years paper became less important as a material for simple applications (e.g. writing, printing) due to the digital revolution and therefore novel paper-based materials that can be used for more sophisticated applications need to be developed.[1] The use of paper as a substitute for other materials (e.g. based on glass or silicon) is highly attractive, because paper exhibits various, unique properties: (i) paper consists of (almost) 100 % cellulose, the most abundant, degradable and renewable biopolymer,[1] (ii) the fabrication of porous fiber mats, which are chemically and thermally stable, is simple compared to wovens (e.g. textiles)[1] and (iii) the fiber mats as well as cellulose fibers itself can be easily modified with organic or inorganic compounds to implement novel functions, leading to changes in the hydrophilicity, permeability or reactivity of the material.[2,3] Thereby, it should be mentioned that the fibrous network of which paper consists has a complex structure and the relationship between the structure of the material and the resulting properties is only partly understood and further investigations need to be performed in order to understand the complex structure of paper and paper-derived materials in more detail.

Due to the above-mentioned advantages, paper has recently gained a considerable interest as a low-cost substrate for the fabrication of paper-based sensors,[4-6] electronics,[7,8] and actuators.[9-11] Thereby, paper-based functional devices are typically easy-to-fabricate, easy-to-use and biodegradable, especially compared to other devices based on glass or polymers.[3,12]

In the following sections, a brief discussion of functional paper materials, based on the modification of paper with organic compounds (section 1.1.1) as well as a combination of organic and inorganic compounds will be given (hybrid materials, section 1.1.2). The focus will be placed on the development of paper-based magnetic materials. In section 1.2, the methods that have been employed for the fabrication of paper-based actuators (with emphasis on magnetic paper actuators) will be introduced.

1.1 Functional Paper Materials

1.1.1 Organic Papers

During the last decade, there is a tremendous interest, both from academia and industry, in the development of novel paper-based materials by modifying paper with organic compounds (combining of paper with other functional materials). In case of organic-modified papers, the organic material is either non-covalently absorbed to the cellulose fibers or chemically bond to the cellulose fibers. On an industrial scale, the modification of paper with organic moieties is typically performed in order to increase the hydrophobicity of paper or paper board, since untreated, hydrophilic paper is sensitive to water and moisture and therefore not suitable e.g. for food or drink packaging applications.[13] A simple method to achieve hydrophobic coatings (also known as paper sizing) is the modification of paper sheets with small organic molecules, which are either absorbed to the cellulose fibers (e.g. paraffin wax) or covalently attached to the cellulose fibers (e.g. alkyl ketene dimers (AKD) or alkenyl succinic anhydride (ASA)).[14]

Although the modification of paper with small organic molecules is widely applied in industry to alter the properties of paper sheets (i.e. wetting behavior), this approach has also some drawbacks, because the molecules are attached to the cellulose fibers only with one chemical bond. Hence, the molecule can be detached from the fiber if the bond is cleaved by a thermal or chemical treatment. One possible approach to circumvent this problem is the use of synthetic polymers where several covalent bonds are being established between the polymer chain and the cellulose fiber. The use of functional, organic polymers for the modification of paper materials is of great interest due to their high flexibility with respect to the possible design/composition of the polymer. Synthetic polymers are typically used in the papermaking industry to improve the dry strength or wet strength of commercial paper grades. Dry strength additives are typically based on polyacrylamides (PAMs) that are copolymerized with a various other monomers to achieve e.g. charged copolymers (cationic or anionic).[15] The wet strength of paper is typically increased by applying poly(amidoamine-epichlorohydrine) (PAAE) polymers. PAAE acts as a wet strengthening additive via the formation of covalent bonds between the polymer and the cellulose fibers. The latter are established upon a thermal treatment of the PAAE-modified paper sheets.[15,16]

In a recent publication, Jocher et al. introduced a novel approach for the fabrication of wet-strengthened paper grades that involve the use of photo-reactive polymers and light instead of head as energy source for the covalent attachment and crosslinking of the polymer.[16]

For this, preformed copolymers, which consist of a hydrophilic, poly(dimethylacrylamide) (PDMAA) matrix and carry defined amounts of photo-reactive benzophenone moieties, have been covalently attached to the cellulose fibers via a one-step photochemical reaction between the benzophenone groups and aliphatic C-H groups present on the cellulose fiber (for details on the photochemical reaction, see chapter 3). Furthermore, the excited benzophenone groups can also react with aliphatic C-H groups from polymer chains in close vicinity. Hence, this approach leads to the formation of a surface-attached polymer network.[16] By changing the matrix component of the polymer to hydrophobic monomers (e.g. methyl methacrylate- or styrene-based) the resulting copolymers can be used to achieve the formation of hydrophobic paper materials.[17-19]

Besides the photochemical attachment of functional polymers, such macromolecules have been successfully immobilized to cellulose fibers by applying the “grafting to” or “grafting from” approach (Note, the photo-attachment of functional polymers can also be described as “grafting to” approach). In the “grafting to” approach, preformed polymers that are end-functionalized are brought to reaction with appropriate functional groups located at the surface of the cellulose fibers (e.g. O-H groups) (Figure 1-1).[20,21]

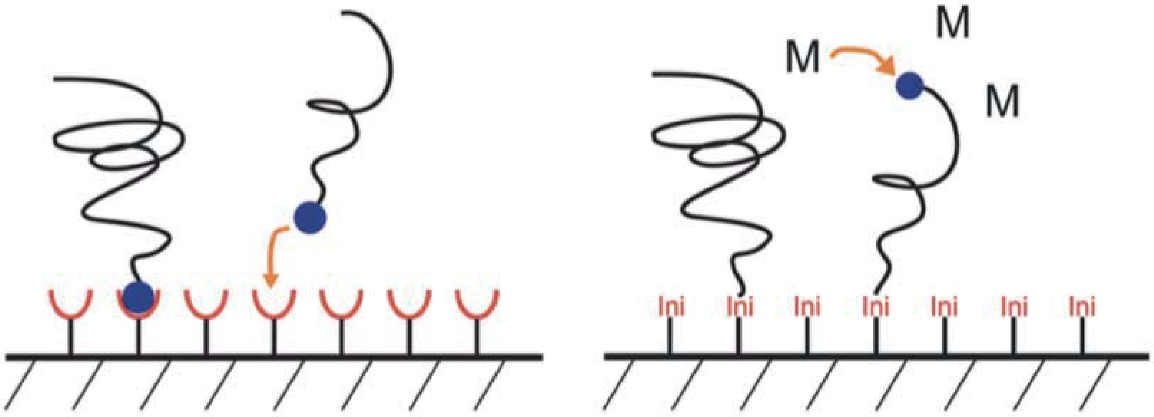

Figure 1-1: Schematic illustration of two different grafting techniques for the covalent attachment of functional polymers to cellulose fibers: attachment of preformed polymers that contain functional groups, which can react with appropriate groups on the cellulose fiber surface (“grafting to”, left); surface-initiated polymerization from cellulose-immobilized initiators (“grafting from”, right) (Figure adopted from reference [1]).

The advantage of this approach (as for the photochemical attachment of polymers) is the comparable easy analysis of the polymer with respect to its molar mass etc. before its attachment to the cellulose fibers.[20,21] However, the “grafting to” approach also has some limitations, including a low final grafting density. The low grafting density can be explained by the fact that surface-attached polymer chains hinder the diffusion of additional polymer chain ends to the surface for a further attachment of polymer chains.[20,21]

It should be noted that this drawback does not count for the photochemical approach, because (i) the polymer chains are not end-functionalized and carry several functional groups (i.e. benzophenone moieties) that can potentially react with aliphatic C-H groups present on the surface of the cellulose fiber and (ii) polymer chains that can not diffuse to the surface of the cellulose fibers can still be covalently attached to the polymer chains that are covalently attached to the cellulose fibers, since the present benzophenone moieties can react with any kind of aliphatic C-H groups. As a result, significant higher grafting densities can be achieved by using this approach (amounts of surface-attached polymers of > 50 mg polymer/gram cellulose fibers can be obtained by using this approach).[17] Due to the limitations of the “grafting to” approach, only a few reports on the modification of cellulose via this technique exist in the literature.

Besides the “grafting to” approach, the “grafting from” technique has been widely used for the modification of paper substrates with functional, organic polymers (Figure 1-1).[20,21] Thereby, the modification of paper either aims on an improvement of the paper properties (e.g. dimension stability, water/heat resistance etc.) or on the implementation of new functions to the paper substrate.[21] In case of the “grafting from” approach, the cellulose fiber is modified with functional groups that can act as initiators, followed by a subsequent polymerization from the surface of the cellulose fiber.[20,21] By using this approach, significantly higher grafting densities can be achieved if compared to the “grafting from” approach, because the small monomers can easily be attached to the end of the growing polymer chains and the adsorbed amount is not thermodynamically or kinetically hindered.[20,21] The grafting of functional polymers from cellulose fibers is typically based on controlled radical polymerizations (ATRP, NMP or RAFT) with a focus placed on ATRP.[20,21] In a first step, the hydroxyl groups present on the surface of the cellulose fibers are converted into initiating moieties, which allow a grafting of functional polymers from the fiber surface in a second step. If methyl acrylate is being used as monomer, this approach can be utilized to render paper hydrophobic (Figure1-2 a).[22] In further studies by Malmström et al. and later also by other working groups, different, functional polymers have been grafted to cellulose fibers for the development of paper materials with special properties, including paper materials with antibacterial properties,[23], superhydrophobic surfaces,[24], or materials that can react to external stimuli (e.g. temperature or pH value) (Figure 1-2 b, c).[25]

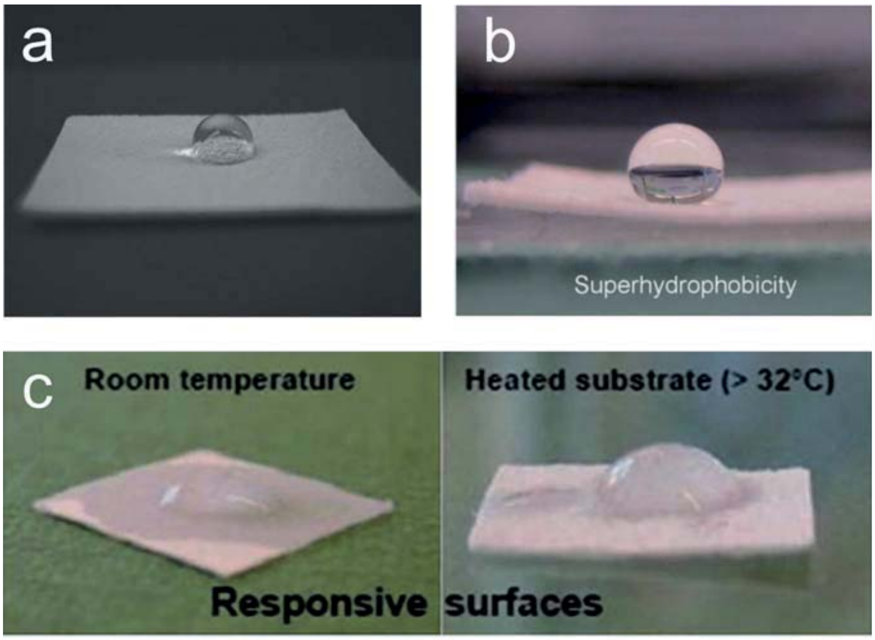

Figure 1-2: (a) A droplet of water on a filter paper that has been rendered hydrophobic via the grafting of poly(methyl acrylate); (b) Water droplet on a superhydrophobic filter paper. Superhydrophobic cellulose was synthesized via the grafting of poly(glycidylmethyl methacrylate), followed by a ring-opening of the epoxide groups and subsequent reaction with pentadecafluorooctanoyl chloride; (c) Water droplets placed on a thermoresponsive paper (obtained via the grafting of poly(N-isopropylacrylamide) at room temperature (left) and on a heated substrate (right). (Figure adopted from reference [21]).

Besides the surface modification of paper substrates with organic materials for the implementation of novel functions, the organic modification of paper materials has also been applied for the development of low-cost analytical tests for point-of-care diagnostics.[12] The confinement of fluid streams inside paper channels is very interesting, because paper as a porous material enables a capillary-driven fluid transport, i.e. no external pumps are needed for the transport of fluids. To achieve a spatially resolved fluid transport within a paper sheet, hydrophobic barriers have to be implemented within the paper matrix.[12] The formation of hydrophobic barriers can be achieved by various means including the physical blockage of the pores by using a photoresist[4], poly(dimethylsiloxane) (PDMS) polymers[26] or paraffin wax.[e.g.27,28] Other approaches include the chemical hydrophobization of the cellulose fiber surface by using small organic molecules (e.g. AKD) that can covalently bind to the hydroxyl groups of the cellulose fibers.[29,30] In addition to small organic molecules, functional polymers have been used for the generation of hydrophobic barriers, which can be covalently attached to the paper matrix by ultraviolet (UV) irradiation.[17-19] Possible applications for micro structured paper materials progress from paper-based filters (e.g. for the separation of red blood cells from the blood plasma[31]), to paper-based immunoassays and sensors (e.g. for the detection of glucose, proteins or metal ions).[32,33]

1.1.2 Paper-based Hybrid Materials

Besides the modification of paper with organic materials, hybrid paper-based materials that also contain inorganic compounds (small molecules, nanoparticles etc.) have been reported recently. Paper-based hybrid materials have been used in various applications, progressing from (bio)sensors, light and flexible paper-based electronics, materials that amplify the surface enhanced Raman scattering to magnetic paper materials. The development of biohybrid materials is a research field of growing interest because those materials combine the properties of inorganic (nano-) compounds with the low environmental impact of biodegradable materials (e.g. paper).[34]

Paper-based sensors

An extensively studied application for the paper-based hybrid materials is their use as sensors or biosensors. In case of biosensors the paper surface is typically functionalized with a compound (e.g. nanoparticles), which is either physically absorbed or covalently attached to the cellulose fibers. The obtained biosensors are used e.g. for cancer screening[35] or for the detection of target molecules in biological systems.[36]

Amongst others, (antibody-conjugated) gold nanoparticles are widely used for the detection of the desired analyte, because gold nanoparticles exhibit very high extinction coefficients if compared with common organic dyes.[37] In addition, monodisperse latex particles that are coupled with dark colors or fluorescent dyes are being used, since they exhibit a strong contrast to the nitrocellulose membrane or paper substrate.[37] However, colloidal gold particles are favored due to their smaller size and can be homogeneously dispersed in high volume fractions inside the test zone of the device. In addition, colloidal gold has a higher color intensity compared to latex particles.[37] Abe et al. firstly reported on the development of a paper-based immunochromatographic device using colloidal gold-labeled anti-human IgG solutions and human IgG as model analyte.[38] To date, the use of gold nanoparticles for the detection of metabolites, bacterial agents, maleria proteins, HIV, DNA, tuberculosis and for the detection of metal ions (e.g. Cu(II) or Hg(II)) has been reported.[37]

Besides the modification of paper substrates with inorganic nanoparticles, paper materials have been modified with carbon nanotubes (CNTs) for the development of paper-based gas sensors. After the CNTs have been deposited via different methods, including ink-jet printing, drop-casting, spray- or dip-coating, flexible and universally applicable gas sensors can be obtained.[39,40]

Paper-based gas sensors obtained by mechanically drawing of single-walled carbon nanotubes (SWCNTs) could be used e.g. for the detection of chemically aggressive vapors, including nitrogen dioxide or chlorine, or environmental toxins.[40,41] The gas detection is based on the formation of a weak charge-transfer complex between the gas molecule (NO_2 or Cl_2) and the CNTs.

The latter leads to a change in the resistance of the paper/CNT films that can be measured to calculate the vapor concentrations.[40]

In addition, paper sheets have been modified with multi-walled CNTs (MWCNTs) that can be used for the detection of different alcohols (e.g. methanol, ethanol, 1-propanol and 1-butanol) (Figure 1-3 b).[42] The detection is again based on a change in the resistance once the sensor comes into contact with the alcohol vapor.

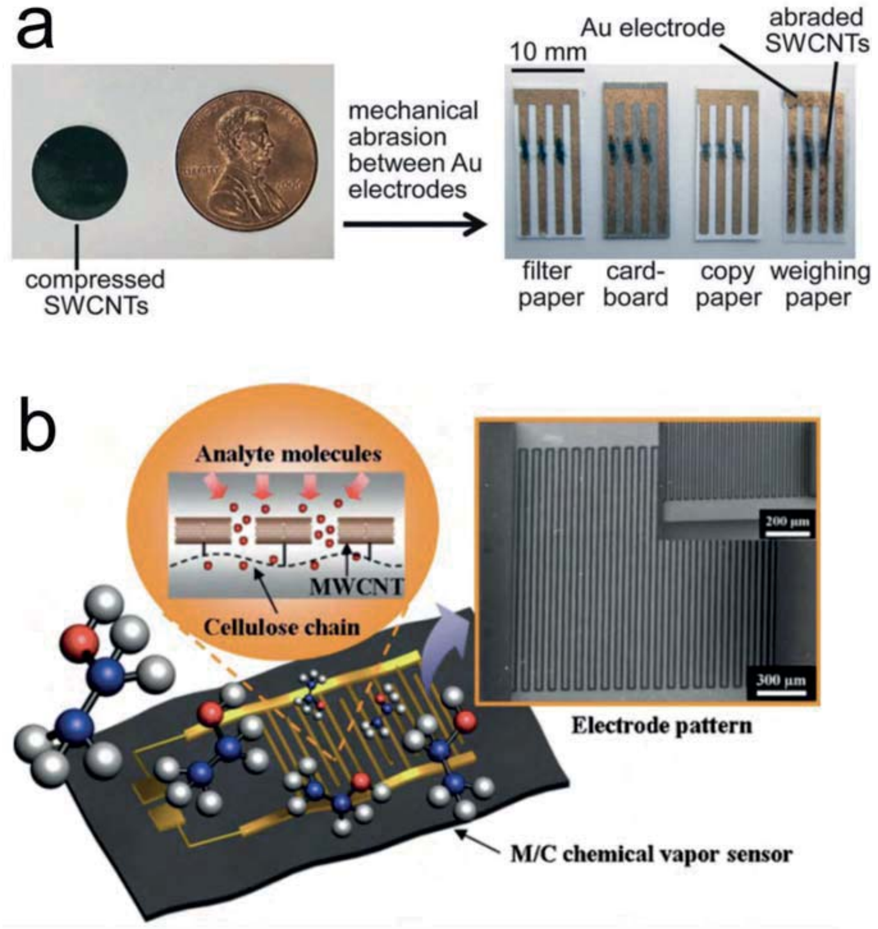

Figure 1-3: (a) Fabrication of sensors on various types of paper by the mechanical abrasion of a pellet of compressed SWCNTs, (b) Schematic of chemical vapor sensor made with M/C paper and IDT shaped electrode. (Figure adopted from references [42] and [43]).

Sarfraz and coworkers developed a low-cost H_2S sensor by drop casting a deprotonated emeraldine base poly(aniline) (PANI)-copper chloride film onto paper substrates that contains printed silver electrodes. The detection is based on the formation of CuS and the concurrent protonation of PANI after the sensor has been exposed to H_2S.[44]

Paper-based electronic devices

Paper has been also used as a substrate for electronic devices. The fabrication of electronic devices such as paper-based organic diodes or transistors directly on top of common paper substrates is challenging, because these devices typically require a smooth surface on a molecular level.[7] Paper substrates usually exhibit a rough surface and show only poor chemical and mechanical barrier properties. Furthermore, paper absorb materials easily due to its porous nature and contains chemical compounds that can act as impurities for the fabrication of electronic devices.[7] Thus, paper electronics typically involve the use of plastic covered paper substrates or the lamination of a plastic film containing electronics between two paper sheets.[7] However, the surface of paper can be made impermeable to different liquids by coating the paper surface with different polymers, including polyethylene (PE), polypropylene (PP) or polyethylene terephthalate (PET).[7] Polymer-coated paper substrates have been used for electrochemical displays.[7]

Besides the use of functional polymers, the surface properties of paper (i.e. roughness, porosity, surface energy) can also be tuned via the coating of aqueous dispersions of pigments and binders.[8] Thereby, recyclable paper substrates that exhibit a relatively high surface smoothness and good barrier properties can be obtained.[8] Bollström et al. developed a multilayer coated paper substrate that is suitable for printed electronics.[8] For this, a base paper, which had been precoated with ground calcium carbonate (GCC), was coated with kaolin in order to decrease the surface roughness of the paper sheet. Subsequently, a polymeric barrier layer, consisting of acrylic or styrene-acrylic copolymer latexes, was coated on top of the kaolin layer (Figure 1-4).[8] The polymer latex was typically blended with precipitated calcium carbonate (PCC) in order to increase the polarity of the surface to enable the coating of an aqueous top layer. After the paper had been multilayer coated, the drying and penetration behavior of a drop of a polymeric semiconductor (poly(3-hexylthiophene)) solution was investigated. The authors could show, that the coated paper shows superior barrier properties and the ink spreading could be much better controlled if compared to commercially available paper grades (Figure 1-4).[8]

As mentioned above, the fabrication of (printed) electronics typically requires a very smooth and non-absorbing substrate. However, it should be noted, that recently some interesting reports of electronic devices, which were fabricated directly onto the paper substrate have been published. Thereby, it turned out that sometimes the rough paper surface might be even advantageous (e.g. if the cellulose paper structure is used as an “active” material in sensors and actuators).[7]

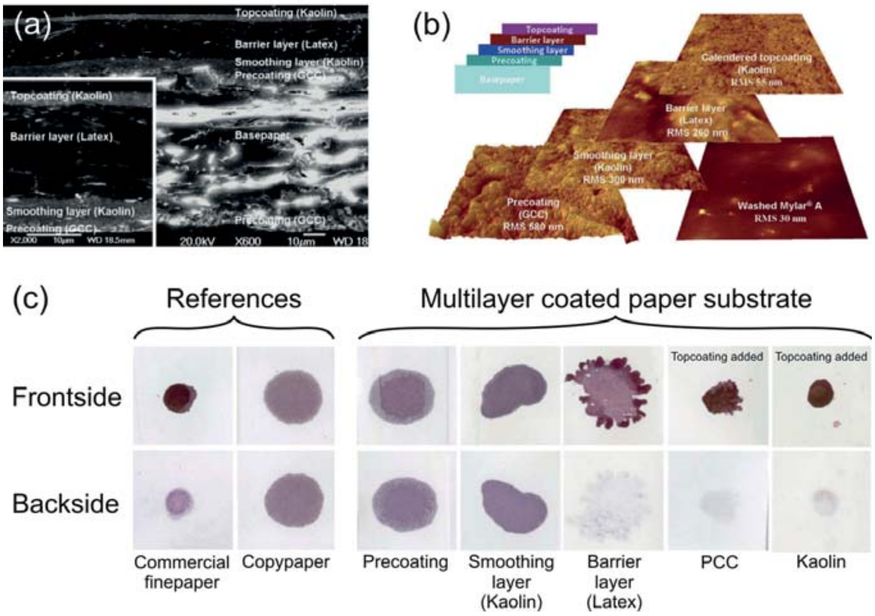

Figure 1-4: Characterization of a multilayer-coated paper substrate suitable for printed functionality: (a) Cross-section electron microscope (SEM) image showing the layer structure of the substrate. The insert shows a higher magnification. (b) Atomic force microscope (AFM) images (20 x 20 µm^2) of each layer showing the changes in the surface roughness. The RMS roughness was measured from 100 x 100 µm^2 images. (c) Drop tests with the organic semiconductor P3HT in DCB. The visible spots on the backside indicate that the active material has penetrated through the paper substrate. The multilayer-coated paper shows superior barrier properties that allow a controlled spreading of the polymer solution (Figure adopted from reference [8]).

A further modification of the coated paper with different polymers can be used to build up a hygroscopic insulator field effect transistor (HIFET).[8]

Besides the use of functional paper as transistors, paper substrates have also been used for various other electronic applications, including displays, RFID tags and sensors.[7] Siegel and coworkers fabricated a thermochromic display that consists of micro patterned, conductive wires on one side of the paper and a coated thermochromic ink on the other side of the photopaper. Once a current runs through the wires, resistive heating causes the thermochromic ink to turn transluscent, revealing a preprinted message behind the thermochromic layer.[45]

Magnetic paper materials

Magnetic cellulose fibers or magnetic paper sheets are a third class of very interesting hybrid materials. Among other inorganic constituents in biohybrid materials, magnetic (nano)particles can impart very interesting properties from a technological point of view.[34] The incorporation of magnetic nanoparticles into cellulose fibers or paper sheets enables the development of magnetic (fiber) materials, which can respond to an external magnetic field.

Those hybrid materials have a number of potential applications such as magnetic paper for anti-counterfeiting[46], loudspeaker membranes, magneto-responsive actuators, flexible data storage materials[47] or filtration/purification. [34,48]

For the fabrication and application of magnetic paper materials it is important to know that different materials respond differently to an applied, external magnetic field depending on their structure and nature.[46] For example, anisotropic, natural cellulose fibers intrinsically show a negative diamagnetic behavior and can align perpendicular to the direction of the applied magnetic field.[46] However, this behavior is only found if very strong magnetic fields (~20 T) are being applied and only a few reports exist on this topic.

Besides, researchers have also focused on the use of cellulose fibers as substrates to keep or synthesize magnetic particles. In general, two different methods have been employed for the fabrication of magnetic cellulose fibers: (i) lumen loading and (ii) in situ synthesis of magnetic particles.[49] In case of the first approach, careful mixing of an aqueous solution containing the pulp fibers as well as the magnetic particles leads to an introduction of the particles (e.g. magnetite, Fe_3O_4, or maghemite,γ-Fe_2O_3) into the lumen of the fiber, whereas the external surface of the fiber is almost free of magnetic particles (Figure 1-5).[50]

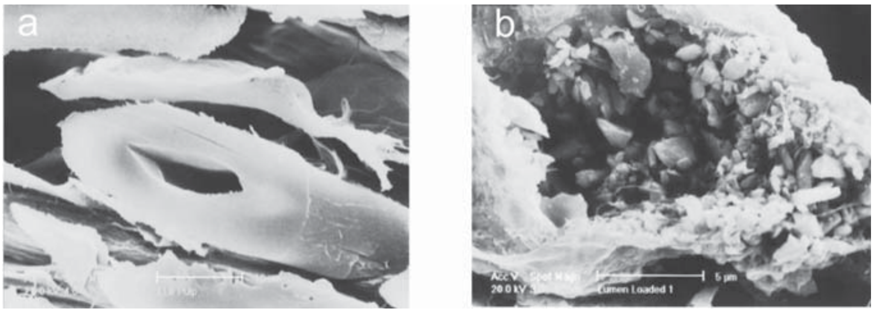

Figure 1-5: (a) Scanning electron micrograph of a cross section of a pulp without lumen-loaded particles, (b) Scanning electron micrograph of a cross section of an unbleached kraft pulp lumen-loaded with Fe_3O_4 showing pigment particles adhering to the lumen surface (Figure adopted from reference [50]).

The introduction of the magnetic particles into the lumen allows the establishment of a strong inter-fiber bonding between the cellulose fibers and therefore the modified fibers can be used for the preparation of magnetic paper sheets. However, it should be noted that an increasing loading (loading degree > 5%) will result in a decreasing tensile strength, because of the loss of fiber-fiber bonding sites due to the deposition of magnetic particles on the fiber surface (besides the fiber lumen).[51] It was found that the retention of the magnetic particles inside the fiber lumen could be improved by using cationic polyelectrolytes (e.g. polyethylenimine, PEI) as retention aid.[50]