Chapter 13

THE ATTRACTION OF MAGNETICALLY SUSCEPTIBLE PAPER

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Abstract

We have imparted magnetic susceptibility to lignocellulosic fibers by adding iron powder to the fibers during hydrogen peroxide bleaching chemistry. We have, therefore, generated carboxylic acid groups in the fibers by deliberately inducing cellulose degradation through Fenton catalysis of the hydrogen peroxide during the chemical oxidation process at a specified level of iron. The iron particles consequently have an exposed layer of iron oxide that allows ionic neutralization of the negatively charged fiber acid groups. After removal of non-attached excess iron, these fibers have been cast into two-dimensional sheets with two different original iron concentrations and tested for physical and chemical properties. Physical tests included tensile, zero-span tensile, caliper, and surface resistivity. Chemical tests included surface charge, kappa, and viscosity. Scanning electron microscopy (SEM) and inductively coupled plasma (ICP) emission spectroscopy were also conducted. Remarkably, the magnetically susceptible sheets with incorporated iron were able to retain a tensile strength similar to the unbleached sheets despite attenuation in fiber strength. This is likely due to a chemical refining phenomenon that allowed for increased fiber–fiber bonding. The introduction of the retained iron also significantly alters the surface resistivity of the paper sheets. Such fibers may have a use in applications where charge conduction or dispersion is necessary.

Keywords: magnetic susceptibility; lignocellulosics; iron

13.1 Introduction

Imparting specific functionality to lignocellulosic fibers potentially offers great promise to increasing the attractiveness and utility of related materials. Recently, a number of research groups have focused on chemically manipulating these fibers for controlled applications or unique functionality. For

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example, lignocellulosics, in general, have been at the "core" of several material processing applications such as lignosulfate-based hydrogels, polyurethane foams, bimorphous ceramics, photocatalysis supports, and thermoplastic extrusions.

On a similar front, fiber modification with a view toward developing new functionality is currently witnessing a renaissance. Choplin has demonstrated the feasibility of using cellulose as a support for a catalyst (Pd-based) for allylic alkylations [1]. Basso has shown lignocellulosics as feasible biosorbents of trace toxic metals [2]. Ghosh was able to photofunctionalize fibers with photoactive acids for grafting and property modification [3]. Induction of magnetic susceptibility in lignocellulosics, however, has received very little research attention.

The work presented here has examined the nature of lignocellulosics as platforms that support the force of magnetism. Recently, we have explored the induction of magnetic susceptibility in lignocellulosic fibers through the generation of fiber carboxylic groups as a result of iron-catalyzed hydrogen peroxide bleaching. Using titration measurements as an elementary probe for the accretion of carboxylic acid functionalities, we observed an increase of ca. 20% in acid functionalities on the surface (55 μeq/g of pulp). The increase is lower than expected due to a substantial loss in carbohydrates through the degradation process. We have found from previous work that hydrogen peroxide bleaching is typically a very effective method to introduce carboxylic acid groups in kraft pulps.

13.2 Experimental

All work was conducted using standard hydrogen peroxide bag bleaches. Bleaches were conducted at 15% peroxide for 2 h in which trace peroxide residuals were determined after the bleach. All bag bleaches were outfitted with several bags due to extensive gas production during the bleach. All runs were done at temperatures of 90 °C and conducted at 10% iron. A caustic solution of pH 12 was used for all make-up water, which was added to maintain all pulp-water solutions at a 10% solid level (mass of pulp/mass of pulp and water). A base-bleached sample was designated, as the H_2O_2 sample had the iron separated by several days of mixing on a magnetic stir plate in which the iron was extracted. Iron could not be easily extracted with normal washing. "25%" iron level sheets (m/m) were made by adding additional iron powder to the bleached pulp to achieve the mass balance ratio required. Tensile strength was tested using the TAPPI standard method on random handsheets. SEM was conducted using standard operational conditions. Surface carboxylic acid group levels were determined by standard potentiometric acid titration procedures. All percentages of iron were determined *via* ICP. Volume and surface resistivity

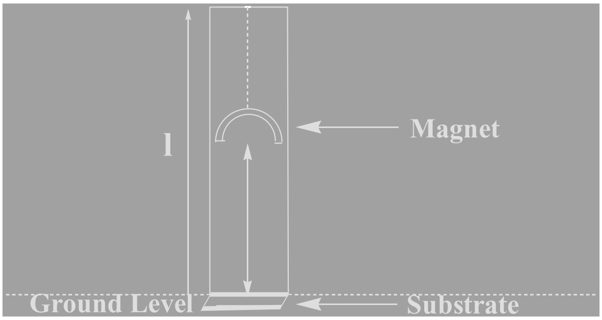

Figure 13.1. Setup for measure of magnetic susceptibility

were determined by ASTM D4949-94 and determination of DC resistivity of writing paper (Keithley Method). Magnetic susceptibility was determined using the setup depicted in Figure 13.1. The interpolar distance, *l*, for threshold of attractive adherence to the poles of the magnet was measured.

13.3 Results

Once it was discovered that the iron was intractably bound to the sheets and could not be readily removed, a study was designed to determine the properties of sheets made from the magnetically susceptible fibers. Initial efforts focused on studying the nature of the adherence of the iron particles to the fibers using SEM. The iron particle distributions appeared heterogeneous and also were found to bound to fiber surface as opposed to physically entrapped between fibers. A sample micrograph can be seen in Figure 13.2. The iron particles were found to be physico-chemically adsorbed to the surface of the fibers. These fibers were washed extensively with deionized water, but demonstrated fair adsorption of the small iron particles across the fiber surface.

The next step in our investigations was to determine the levels of iron contained in each pulp. All iron addition levels were made on the basis of unbleached fiber. It was clear there was significant degradation and yield loss during bleaching since the final levels of iron, as determined by ICP, were significantly higher than the projected amounts based on raw fiber. It was also clear that our method of removing the iron from the bleached pulp over several days of magnetic stirring was effective since the levels of iron contained could be reduced to the levels found in the base pulp. The ICP measurements are shown in Table 13.1.

The next step was to determine the impact of degradation and iron incorporation in the sheets on the sheet strength. It was determined that the overall sheet strength was not significantly affected. This was most likely due to a chemical

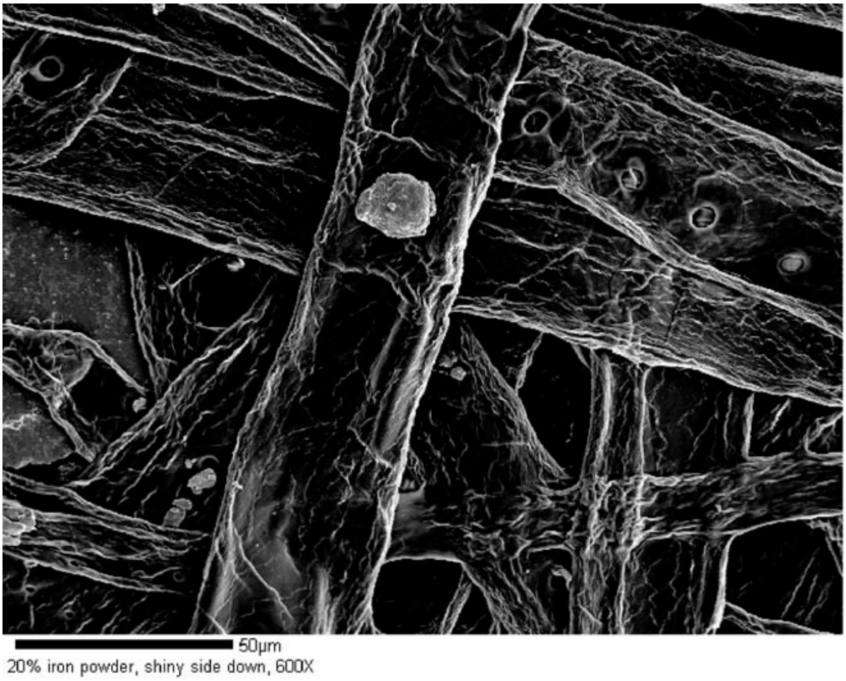

Figure 13.2. A typical SEM micrograph of a 20% iron powder sheet at 600× magnification

refining effect allowing for greater fiber bonding, even though individual fiber strength was most likely decreased. Tensile measurements can be seen in Figure 13.3.

The finding in Figure 13.4 was remarkable and extremely important for the further evaluation of this process. Although not unprecedented, it demonstrated that bonding could be improved *via* chemical means.

It was important to understand the level of magnetic susceptibility imparted to the pulp and compare this to a full-metal substrate. As expected, when the percentage of iron was increased, the magnetic susceptibility was increased.

Table 13.1. The iron addition levels that were found in the pulps from ICP evaluation

Substrate	Fe (mg/kg)	Percentage (iron/pulp)
Base pulp	3830	0.4
H_2O_2 bleached	2160	0.2
10% Fe^0 H_2O_2 bleached	130,000	13
25% Fe^0 H_2O_2 bleached	317,000	32

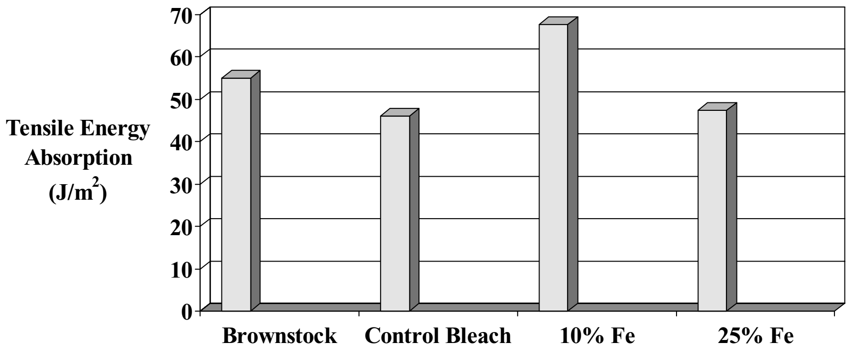

Figure 13.3. Tensile energy absorption comparison

Interestingly, the magnetic susceptibility was proportional to the level of iron. This work can be seen in Figure 13.4.

In addition to magnetic susceptibility, the iron addition also imparted another interesting property: a significant decrease in the electrical resistivity. The volume resisitivity was cut in half for the 10% sample and almost to one-third in the 25% sample. The surface resistance was even more greatly impacted. The bleached sample with the iron removed actually had a higher resistance than the base stock. The 10% and 25% iron samples had near equal resistivity that was about 1/250th of the original base stock. This could have significant implications on new products where electrical properties are important such as computers. A graph comparing surface and volume resistivity for all samples can be seen in Figure 13.5.

From these results, it is possible to impart meaningful magnetic susceptibility to pulp using hydrogen peroxide bleaching, without significant changes in tensile strength. This iron addition has the welcome side effect of changing

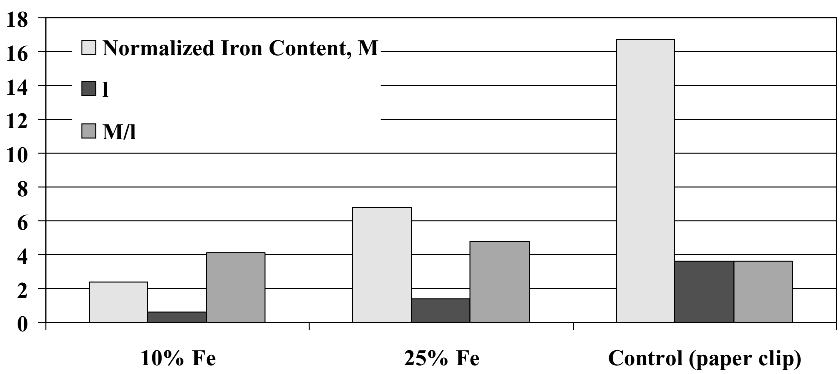

Figure 13.4. Comparison of magnetic susceptibility

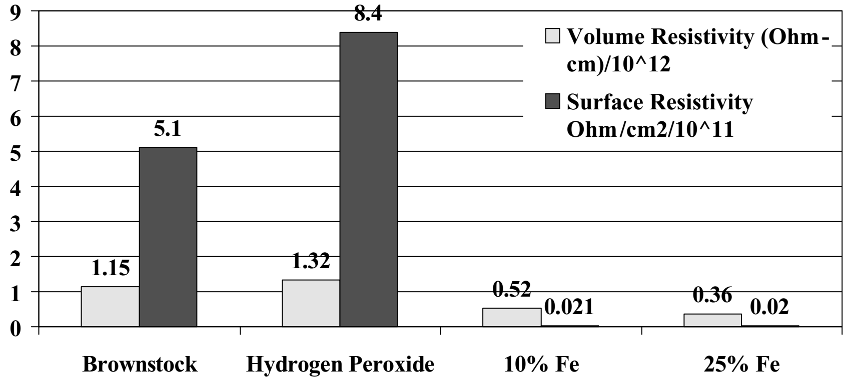

Figure 13.5. Comparison of surface and volume resistivity

the electrical resistance of the sheet. Such fiber modification could allow for use in unique end products and increase pulp value.

13.4 Conclusions

Iron powder was successfully incorporated into peroxide-bleached sheets resulting in magnetic susceptibility. The level of magnetic susceptibility was proportional to the level of iron incorporated. The magnetically susceptible sheets, with incorporated iron powder, were able to retain a tensile strength similar to the base (unbleached) stock. The magnetically susceptible sheets also had dramatically decreased volume and surface resistivity. This new substrate has great promise for future pulp and paper products.

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