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A novel and efficient approach for imparting magnetic susceptibility to lignocellulosic fibers

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Abstract

We have imparted magnetic susceptibility to lignocellulosic fibers by adding iron powder in a heterogeneous manner 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, lignin content (kappa) and viscosity. SEM and ICP 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 which 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

1. Introduction

Imparting specific functionality to lignocellulosic fibers potentially offers great promise in 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 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 (Quignard & Choplin, 2001). Basso has shown lignocellulosics as feasible biosorbents of trace toxic metals (Basso, Cerrella, & Cukierman, 2002). Ghosh was able to photofunctionalize fibers with photoactive acids for grafting and property modification (Ghosh & Gangopadhyay, 2000). Induction of magnetic susceptibility in lignocellulosics, however, has received very little research attention.

The work presented here has examined the potential of lignocellulosics as platforms to 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 in acid functionalities on the surface from a starting value of 46 μequiv./g of pulp to a final level of 55 μequiv./g of pulp,

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equivalent to a 20% increase. This increase is lower than that 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.

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 experiments were outfitted with several bags due to the 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% solids 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. 'Twenty-five percent' 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 a modified potentiometric acid titration procedure described as follows: methyl glycol chitosan polymer (Wako Pure Chem. Ltd, Japan) was used as the adsorption cationic polymer whose charge density was measured to be 2.24×10^{-3} equiv./g by UV/VIS spectroscopy. This determination was done as follows: before the adsorption experiment, 1.5 g by dry mass of each of the pulps was treated with 300 mL 0.1 N HCl for 1 h to remove resident metal ions and these pulps were then washed thoroughly with deionized water. The resident carboxyl groups were then converted to their Na^+-form by treatment with 250 mL of 5 mM $NaHCO_3$ and addition of NaOH to achieve pH 9. To remove excess electrolyte, the pulps were washed with deionized water (pH 5.5) to pH 7.5. Different amounts of chitosan were added to a series of samples and deionized water was added to make the volume of the pulp suspension 300 mL. This mixture was then stirred for 40 min. Finally, the pulp suspension was filtered using a vacuum flask and fritted glass filter funnel. The filtrate was then collected for further chitosan and iodine ion concentration measurements. The residual concentration of chitosan found in the filtrate after the surface charge density adsorption is called the equilibrium concentration and was determined by titration with potassium polyvinyl sulfate (KPVS, Wako Pure Chem. Ltd, Japan) with a cationic indicator, orthotoluidine blue (OTB) [13]. UV/VIS spectroscopy was used to determine the iodide ion in the solution and the charge density of chitosan. All UV/VIS absorption measurements were performed using a UV160 UV/VIS recording spectrophotometer (Shimadzu) using the absorbance peak of 226 nm for quantitative measurements of the iodide ion. Every electroneutralization event between positively charged sites on chitosan and the negatively charged site on the pulp fibers stoichiometrically releases an iodide ion. In control experiments, we determined that there was no dissolution of lignin or other chromophores from the bleached pulp that interfered with the absorbance maximum of the iodide ion. From knowledge of the total amount of chitosan added to the suspension, the equilibrium concentration of the chitosan and iodide ion concentration in the adsorption solution, and the adsorbed amount of the chitosan, the surface charge density of the pulps and their adsorption stoichiometry can be calculated as follows

$$\mathrm{AD} = \frac{(N_0 - N_\mathrm{E})V}{W} \tag{1}$$

$$\mathrm{CD} = \frac{(N_\mathrm{IE} - N_\mathrm{E})V}{W} \tag{2}$$

$$\mathrm{AS} = \frac{\mathrm{CD}}{\mathrm{AD}} \tag{3}$$

where AD is the adsorbed amount of the chitosan, equiv./g of pulp; CD is charge density of pulps, equiv./g of pulp; AS is the adsorption stoichiometry; N_0 and N_E are the normal concentrations of chitosan in adsorption solution before and after adsorption, respectively, equiv./L; N_IE is the normal concentrations of iodide ion in the solution after adsorption, equiv./L; V is the volume of adsorption solution, L.

All percentages of iron were determined via ICP. Volume and surface resistivity were determined by ASTM D4949-94 and determination of D-C resistivity of writing paper (Keithley method). Magnetic susceptibility was determined using the setup depicted in Fig. 1. The interpolar distance, *l*, for threshold of attractive adherence to the poles of the magnet was measured.

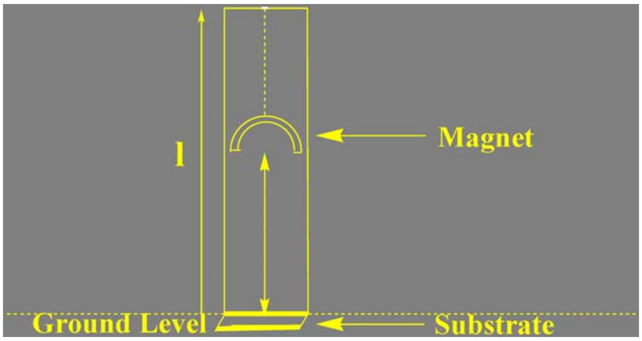

Fig. 1. Setup for measure of magnetic susceptibility.

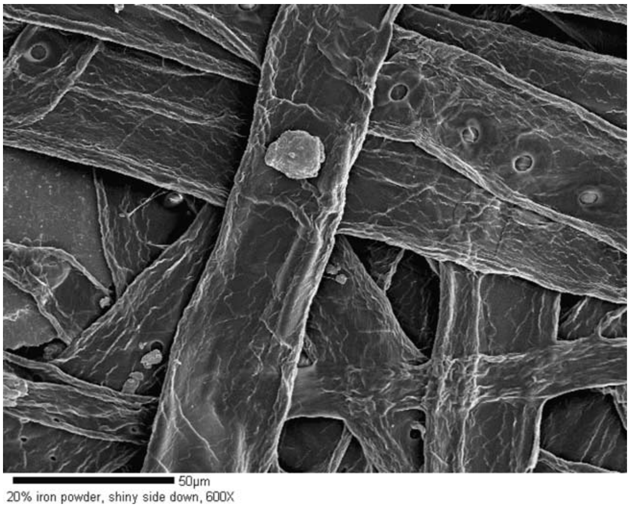

Fig. 2. A typical SEM micrograph of a 20% iron powder sheet at 600 times magnification.

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 neutral iron ($4Fe^0$) particles to the fibers using SEM. These iron particles were between 5 and 25 μ in diameter and were in general oxidized at the surface by a monolayer or more of iron(II) oxide. The iron particle distribution on the lignocellulosic surface was heterogeneous and also found to bind to fibers surface as opposed to be physically entrapped among fibers. A sample micrograph is shown in Fig. 2. The iron particles were found to be physico-chemically adsorbed to the surface of the fibers due to iron(II) oxide to cellulose hydroxyl group interactions as well as Lewis acid interactions. Since iron acts as a catalyst in the decomposition of hydrogen peroxide, it is likely that the iron(II) oxide outside layer was dissolved exposing fresh iron(0) which was oxidized to iron(II) during the disproportionation of hydrogen peroxide. It is likely that this iron(II) form solubilized as an iron(II) chloride salt in the bulk, whereas the remaining iron particles remained entangled in the fibers. These fibers were washed extensively with deionized water, but demonstrated strong adsorption of the iron particles across the fiber surface. Since the iron(II) oxide form of iron that catalyzed the decomposition of the peroxide is insoluble in water, the iron particles did not ionize.

Table 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% $Fe^0H_2O_2$ bleached	130,000	13
25% $Fe^0H_2O_2$ bleached	317,000	32

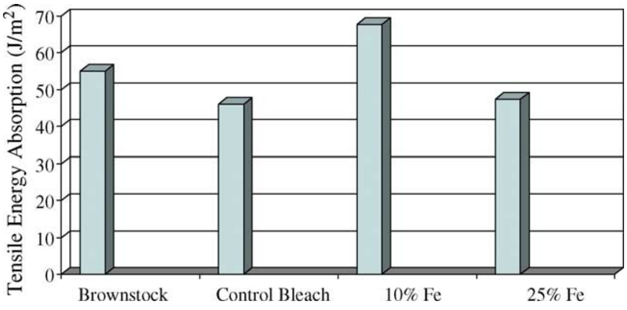

Fig. 3. Tensile energy absorption comparison.

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 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 refining effect allowing for a greater fiber bonding, even though individual fiber strength was most likely decreased. Tensile measurements can be seen in Fig. 3.

The finding in Fig. 4 was remarkable and extremely important for the further evaluation of this process (see Experimental section for description of experiment). 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. Interestingly, the magnetic susceptibility was proportional to the level of iron. This work can be seen in Fig. 4.

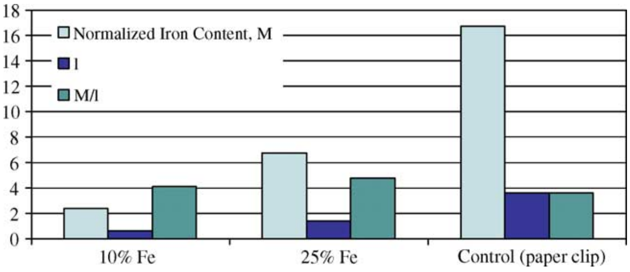

Fig. 4. Comparison of magnetic susceptibility.

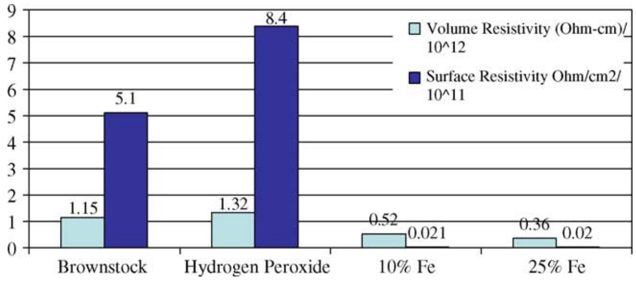

Fig. 5. Comparison of surface and volume resistivity.

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 a 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 Fig. 5.

From these results it appears that it is possible to impart meaningful magnetic susceptibility to pulp using hydrogen peroxide bleaching, without significant changes in tensile strength. Unfortunately, the issue of homogeneously distributing the iron particle network across the fiber is not possible at this time. TOF-SIMS (Time of Flight-Secondary Ion Mass Spectrometry) measurements that were done previously demonstrated that a 'hotspotting' phenomenon is unavoidable in bleaching conditions (Mancosky & Lucia, 2001). This 'hotspotting' leads to an uneven distribution of carboxylic acid functionalities across the lignocellulosic surface and thus provide pockets of metal accumulation from carboxylic acid–metal chelation, such as observed with the heterogeneous distribution of iron in this study. Nevertheless, this iron addition has the welcome side effect of changing the gross electrical resistance of the sheet. Such fiber modification may allow for use in unique end products and increase pulp value.

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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References

Basso, M. C., Cerrella, E. G., & Cukierman, A. L. (2002). Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater. *Industrial and Engineering Chemistry Research*, *41*(15), 3580–3585.

Ghosh, P., & Gangopadhyay, R. (2000). Photofunctionalization of cellulose and lignocellulose fibres using photoactive organic acids. *European Polymer Journal*, *36*(3), 625–634.

Mancosky, D. G., & Lucia, L. A. (2001). Use of TOF-SIMS for the analysis of surface metals in H_2O_2-bleached lignocellulosic fibers. *Pure and Applied Chemistry*, *73*, 2047–2058.

Quignard, F., & Choplin, A. (2001). Cellulose: a new bio-support for aqueous phase catalysis. *Chemistry Communications*, 21–22.