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The Effect of Internally-Filled Pulp on Recycling

By: Anne Spruit

A Thesis submitted in partial fulfillment of the course requirements for The Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
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Abstract

Recycling is an area of interest for much of the industry because of all the environmental concerns with the cutting down of trees, and the pulping operations to make paper. However, virgin fibers are still desired because they make stronger paper. Virgin fibers have a higher swelling capability than recycled fibers, that accounts for better bonding. Paper's physical properties also decrease rapidly as filler is substituted for fiber. Filler impairs interfiber bonding by preventing close contact with fibers. Filler is added to paper to increase opacity and brightness. However, there is a poor retention of filler in the sheet during papermaking, which is only partially solved with retention aids.

Never been dried softwood pulp was kneaded with a swelling agent and refined. Ten calcium carbonate runs and ten conventional runs were conducted. Pulp was kneaded with calcium chloride, refined, and then washed over a screen. Sodium carbonate and PEI were mixed together and then washed over a screen.

The ash content decreased with each recycle run for the calcium carbonate runs. The scattering coefficient also went down with each recycle. However, scattering coefficient goes up in the conventional recycle run, because less bonding occurs with each recycle. The amount of calcium carbonate in the sheet has a bigger effect on scattering coefficient than the degree of recycling.

Recycled fibers are less conformable than virgin fibers, which accounts for the big decrease between the 1st and the 2nd run in tensile index and burst index of both the conventional and the calcium carbonate paper. This happens because repeated drying of fibers produce a progressive deterioration of paper tensile strength. If the fiber lumens crack and the calcium carbonate is exposed, the fibers may not attach to the other fibers as well because the calcium carbonate particles are in the way.

With recycling, the tear index increases, passes through a maximum and then declines. The conventional run seems to continually increase, with the greatest increase between the 1st and 2nd run. At first, between the 1st and 2nd run, calcium carbonate has higher tear. A lumen loaded sheet has a lesser collapsed fiber, which offers more tearing resistance than a fully collapsed fiber.

Strength properties are not higher after four runs, but many interesting observations can be made from the recycling of lumen loaded pulp.
Introduction

Loading the pores with inorganic filler is an economically attractive concept. Unfilled recycled fibers become stiff and do not bond as well as virgin fibers. If these fibers were internally filled with a filler, the fiber wall may not be able to collapse and may rehydrate more quickly and more completely. This uncollapsed fiber will have different effects on strength properties.

In 1936, Haslam and Steele noted that following the beating of filler and fiber, a minor part of the filler was present in the lumens. It was also noted that, while leaving the exterior surfaces of the fiber free of filler, strength properties will increase when compared to conventionally filled pulp.

When recycled fibers are used to make paper, strength properties are decreased. Strength properties are decreased because of stiffness and collapsed fibers. The loss of fiber flexibility and plasticity is due to reduced swelling capacity of the fiber once it has been collapsed into a ribbon and made into paper. Large pores are closed up during drying and drying leads to a plastic flow at the crack interface that results in strain hardening of the fiber. Recycling also alters fiber curl or fines content, in which case recycled fiber pulp really is different from virgin pulp.

Bleaching the fibers tends to decrease lumen loading capacity of the fibers. Bleaching may affect the ionic structure of the fiber or possibly destroy crevices in the heavily lignified primary wall and middle lamella. However, for experimental purposes bleached fibers will be used because of its higher market value and need for recycling.

Refining the fibers will increase their ability to be lumen loaded. Refining will swell the fiber to increase the accessibility of the lumen for loading, but at the same time make it easier for the filler to be washed from the external structure of the fiber. During the refining stage, formamide is used because of its extremely high swelling power. Formamide swells the fibers by
about 125%, while water only swells the fibers 90%. Fibers beaten with formamide show fibrillation. The strength of formamide beaten fibers were equivalent to those beaten with water.

In the preliminary run, 20% formamide was compared to 20% sodium hydroxide. Sodium hydroxide was used because it is hydrophilic. In the concentration range of 2-4 N sodium hydroxide, the maximum swelling took place. The concentration at which maximum swelling took place was the same whether changes in width, volume, length, or cross-sectional area were followed. Sodium hydroxide increases beyond its limiting concentration which causes no change in the crystal lattice and only a slight increase in the amount of sodium hydroxide adsorbed up to a concentration of about 19-20% sodium hydroxide.

Economically, fillers are less expensive than fiber and enhance the brightness, opacity, and smoothness of the sheet, whether they are lumen loaded or conventionally loaded in the sheet. However, fillers decrease the strength properties, when conventionally loaded. There is also poor retention of filler in the sheet during papermaking. This problem is only partially solved with retention aids. Filler particles also cause two sidedness and dusting on the paper, an increase in the effluent load, and an overconsumption in the use of water, raw material, and energy.

Calcium carbonate was used to load the fiber lumens. Calcium carbonate has a cost/performance advantage over lower brightness fillers such as clay. Titanium dioxide is the other filler used for the filling of the lumen but cost is much higher. The calcium carbonate may also stay in the lumens of the pulp better than titanium dioxide, because the rough edges of the rosette shaped particles cause them to be lodged in the lumen.

Calcium carbonate is restricted to an alkaline environment, because it is easily reacted in acid. Alkaline papers have improved drainage, a more favorable rheology, greater productivity, a
lower cost for both paper coating and filling, higher brightness and a better printability. Alkaline papermaking also produces paper with a longer life span. Alkaline papers can exist for more than a century without a significant change, while acid paper's life span is about 50 years.

During the filling process, fiberization is carried out in the PFI mill, where the pulp is impregnated with a calcium salt to fill the micropores. A pumping action caused by the shearing forces during agitation, causes pigment to diffuse into the pits. The higher the concentration, the more rapid the entry of filler into the lumen and a higher loading. The degree of loading increases asymptotically with both the time of agitation and the concentration of filler. Also, increasing pulp consistency combined with the increase in mechanical action causes a more rapid entry of filler into the lumens and a higher loading. The rate of attachment of filler to the lumen wall is proportional to the concentration of filler in suspension and to the amount of free lumen surface area available for particle attachments. This is called the adsorption process.

In the precipitation process the calcium chloride and sodium carbonate, the sodium carbonate is used with a retention aid polyethyleneimine (PEI). PEI gives a 2 to 3 fold increase in lumen loading. PEI creates bonds to resist removal of the external filler during the washing stage. At a pH of 11, PEI causes flocculation of pigment and reduces the amount of filler which entered the lumen through the fiber pits. The calcium chloride reacts with the sodium carbonate to form the calcium carbonate filler and subsequent washing removes excess reagents.

\[ CaCl_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + NaCl(aq) \]

Highly filled sheets preserve stiffness and can be used in paperboard, where stiffness is needed. Most likely a small loss of strength of lumen loaded sheets can be attributed to reduced collapsibility and conformability of the lumen loaded fibers. Since there is no pigment on the
external fiber surface, interfiber bonding is not obstructed as in conventionally filled sheets.

Since filler is less expensive than pulp, it is desirable to increase the amount of filler. However, paper's physical properties decrease rapidly as filler is substituted for fiber. Filler impairs interfiber bonding by preventing close contact with fibers. With so many positive aspects to the loading of lumens, the aspects after recycling were also looked at.

The procedure was from an article by Allan, Negri, and Ritzenthaler. With the help of my thesis advisor, it was decided that the swelling of the fibers would be done using formamide. Also instead of using the British Disintegrator, the PFI mill would be used for the mixing of calcium chloride and the pulp. This was to increase the amount of calcium chloride in the lumens, before the sodium carbonate was added and calcium carbonate was precipitated.
Methods

Preliminary runs

Never been dried bleached softwood kraft fiber was used for this experiment. Softwood pulp contains more filler particles within the lumens than hardwood pulp, because softwood pulp has a greater area to be impregnated. There were six preliminary runs. Formamide and sodium hydroxide were compared to find the optimum swelling agent for the fibers in a PFI mill after approximately 7500 revolutions. There were three 25% sodium hydroxide in water and three 25% formamide, 75% water solution runs. Three formamide runs were tried because of formamide’s 125% swelling volume when compared to 90% swelling volume of water. Sodium hydroxide was tried because it is hydrophilic. The PFI mill was used according to TAPPI Standards (T248 cm-85) \(^{11}\). The PFI mill method has a roll and a bed plate to beat the fibers. The roll and bed plate move in the same direction but the roll moves faster. Only 30 grams of O.D. fiber is used at a time. The PFI mill was used at 7500 revolutions to obtain an approximate 400 freeness.

Thirty grams of softwood fiber was impregnated in solutions of calcium chloride for 5 minutes in the British Disintegrator. 120 g/L of calcium chloride was used. It was thickened by gravitational drainage on filter paper to an approximate 8% consistency. The pulp was then placed into three ziploc plastic bags and kneaded with 12 g/L of sodium carbonate and polyethylenimine (PEI). PEI was tried at values of 1, 5, and 10 ml at 1/1000 of the concentration in the bottle for each swelling agent run. PEI gives a 2 to 3 fold increase in lumen loading. The calcium salt reacts with the carbonate to form the calcium carbonate filler. The fibers are then placed on a 100 mesh screen and were washed with 3000 mL of water to remove excess reagents.
The ash content was used on the pulp after washing to find out how much calcium carbonate was inside the lumens. The ash content was used according to TAPPI Standards (T211 om-81 with ignition at 575°C)\textsuperscript{12}.

\textit{Final runs}

30 grams of never been dried softwood pulp was kneaded with 10 ml of 20\% formamide in a ziploc bag and again placed into a PFI mill. There was ten calcium carbonate runs and ten conventional runs. There was 7500 revolutions made with the PFI mill. Five PFI runs of pulp were then kneaded with 30 grams of calcium chloride for 5 minutes in a ziploc bag. The PFI mill was used for the 30 grams of pulp consecutively 4 times; 10 seconds refining and 60 seconds only turning. The 30 grams of pulp was then washed with 250 ml of water over a 100 mesh screen.

Five PFI runs of pulp were then placed into another ziploc bag with 30 grams of sodium carbonate and 5 ml of PEI at 1/1000 of the concentration. The pulp was then washed with 1000 ml of water on a 100 mesh screen. Ten conventional runs were also produced with a freeness of 434 compared to the 494 freeness of the calcium carbonate run.

When final sheets are made, handsheet formation, drying conditioning, and testing will be performed in accordance with standard TAPPI methods on the noble and wood handsheet maker located in Western Michigan Paper Science's wet lab. The ash content was used to provide the amount of filler retained in the lumens of the pulp. Most of the calcium carbonate will be lost at 900°C, so that method was not used. A scattering coefficient test of all runs was also obtained to find out how much calcium carbonate stayed in the sheet. The strength properties were measured on both internally filled recycled pulp and untreated recycled pulp. The tensile, burst, and tear tests will be used. This data will be analyzed to observe the difference internally filled recycled pulp makes on strength properties.
Step 1: 
Impregnation

Step 2: 
Dewatering

Step 3: 
Precipitation

Step 4: 
Washing

- Step 1: 30 grams of never-dried softwood pulp in a PFI mill
- Step 2: 30 grams of calcium chloride added to 30 g of pulp placed in the PFI mill
- Step 3: Removal of the excess solution with 250 ml of water over a 100 mesh screen
- Step 4: 5 ml of PEI at 1/1000 of the concentration also added.

Total:
7500 revolutions
4 times: 10 seconds of refining, 60 seconds only turning.

Five PFI runs were placed into a ziploc with 30 g of sodium carbonate.

1000 ml of water over a 100 mesh screen was used to wash the calcium carbonate off the outside.

Loaded softwood pulp.
**LUNEN LOAD ING PROCEDURE**

**Step 1**
- Impregnation
- 30 grams of never-dried softwood pulp in a PFI mill
- 7500 revolutions

**Step 2**
- Dewatering
- 30 grams of calcium chloride added to 5 runs and 30 g of pulp placed in the PFI mill
- Removal of the excess solution with 250 ml of water over a 100 mesh screen

**Step 3**
- Precipitation
- Five PFI runs were placed into a ziploc with 30 grams of sodium carbonate
- 5 ml of PEI at 1/1000 of the concentration also added

**Step 4**
- Washing
- 1000 ml of water over a 100 mesh screen was used to wash the calcium carbonate off the outside
- Loaded softwood pulp
Recycle Procedure

<table>
<thead>
<tr>
<th>Loaded fibers</th>
<th>Unloaded fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFI........... 7500 revolutions</td>
<td>PFI........... 7500 revolutions</td>
</tr>
<tr>
<td>Noble and Wood handsheet maker.............test (10 sheets)</td>
<td>Noble and Wood handsheet maker.............test (10 sheets)</td>
</tr>
<tr>
<td>British Disintegrator</td>
<td>British Disintegrator</td>
</tr>
<tr>
<td>Noble and Wood handsheet maker.............test (10 sheets)</td>
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<td>Noble and Wood handsheet maker.............test (10 sheets)</td>
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</tr>
<tr>
<td>British Disintegrator</td>
<td>British Disintegrator</td>
</tr>
</tbody>
</table>

Strength tests utilized:
- tear
- tensile
- burst

Other tests utilized:
- ash content (575°C)
- scattering coefficient
### Preliminary Run

<table>
<thead>
<tr>
<th>20% Caustic Soda</th>
<th>%CaCO₃</th>
<th>20% Formamide</th>
<th>%CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ml PEI</td>
<td>28.0</td>
<td>1 ml PEI</td>
<td>41.1</td>
</tr>
<tr>
<td>5 ml PEI</td>
<td>28.3</td>
<td>5 ml PEI</td>
<td>31</td>
</tr>
<tr>
<td>10 ml PEI</td>
<td>40.7</td>
<td>10 ml PEI</td>
<td>34.7</td>
</tr>
</tbody>
</table>

- PEI was used at 1/1000 of the concentration.

### Final Run

<table>
<thead>
<tr>
<th>Recycle Run</th>
<th>Average Ash Content (%)</th>
<th>Scattering Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp</td>
<td>26.25</td>
<td>N/A</td>
</tr>
<tr>
<td>1st CaCO₃ Run</td>
<td>11.89</td>
<td>37.12</td>
</tr>
<tr>
<td>2nd CaCO₃ Run</td>
<td>6.39</td>
<td>36.09</td>
</tr>
<tr>
<td>3rd CaCO₃ Run</td>
<td>3.83</td>
<td>35.14</td>
</tr>
<tr>
<td>4th CaCO₃ Run</td>
<td>2.66</td>
<td>34.83</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Recycle Run</th>
<th>Calcium Carbonate Run's Freeness</th>
<th>Conventional Run's Freeness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Run</td>
<td>494</td>
<td>434</td>
</tr>
<tr>
<td>2nd Run</td>
<td>685</td>
<td>587</td>
</tr>
<tr>
<td>3rd Run</td>
<td>627</td>
<td>678</td>
</tr>
<tr>
<td>4th Run</td>
<td>737</td>
<td>720</td>
</tr>
</tbody>
</table>
Tear Index

![Graph showing Tear Index for Conventional and Calcium Carbonate across four runs.]

- **Conventional**
- **Calcium Carbonate**

<table>
<thead>
<tr>
<th>Runs</th>
<th>Tear Index (Gfm/2g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Run</td>
<td>1.8</td>
</tr>
<tr>
<td>2nd Run</td>
<td>2.2</td>
</tr>
<tr>
<td>3rd Run</td>
<td>1.6</td>
</tr>
<tr>
<td>4th Run</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Discussion

Many interesting relationships were seen with the calcium carbonate and conventional recycle runs. The effects of tear and scattering coefficient are among the more intriguing.

Preliminary Run

The 25% formamide as a swelling agent was selected because it had the highest amount of calcium carbonate left in the fibers. The ash content showed this relationship between the different swelling agents. Formamide at a higher concentration is easier to work with than sodium hydroxide.

Freeness

Stock freeness generally showed a slight increase. The greater the initial degree of beating, the greater the loss of pulp recycling potential. This is due to the loss of internal swelling in the beaten fibers. Beaten pulp is more internally delaminated than is unbeaten pulp. After recycling, calcium carbonate should not escape from the lumens because, drying closes the delaminations which do not reopen during subsequent reslushing. Heavily beaten fibers may never fully recover their initial swelling.²

Ash Content

The ash content decreased with each recycle run for the calcium carbonate runs. The scattering coefficient also went down with each recycle. This portrays a good representation that the amount of calcium carbonate goes down so there is less rosette shaped calcium carbonate particles for light to scatter. The ash content in the final results is different from the preliminary results because procedure was different and more washing was initiated.
Scattering Coefficient

Scattering coefficient must be defined as a structure factor which expresses the relative decrease in light intensity of the transmitted light which has its cause in the reflection of the light. It is a measurement of the area of free nonbonded surfaces in the paper. The light scattering ability depends on the difference in refractive index between air, cellulose, and filler. The scattering coefficient increases with increasing specific surface. An increase in the number of bonds in the paper reduces the scattering coefficient. As less bonding occurs with each recycle, scattering coefficient goes up which is shown in the conventional recycle run. However, the amount of calcium carbonate has a bigger effect on scattering coefficient than recycling.

When light passes through the paper fibers a certain amount of absorption takes place, but very little scattering. Scattering occurs at the fiber surfaces. Some of the light is reflected by both external surfaces and internal cracks. Two fibers which are tightly bonded together have no free surfaces between them, so that light is not scattered in the interface between them.

Tensile Index

Recycled fibers are less conformable than virgin fibers, which accounts for the big decrease between the 1st and the 2nd run in tensile index of both the conventional and the calcium carbonate paper. This happens because repeated drying of fibers produce a progressive deterioration of paper tensile strength. The properties important to the strength of paper made from recycled fibers are the fiber strength, fiber length, fiber swelling/plasticity and fiber bonding potential. Fiber swelling determines how well the fibers conform to one another which in turn determines the relative bonded area. When fibers lose their swelling capabilities they do not bond as well. It was hoped that this would be minimized by filling the lumens. Multiple recycles
increase cellulose crystallinity and gives rise to a reduction in swelling and interfiber bonding. Loss of swelling and reduction of pore size control fiber flexibility \(^2,14\).

Fiber-fiber bonding is influenced by fiber swelling or plasticity and specific bond strength. It is suggested that the loss of fiber flexibility and plasticity is due to the reduced swelling capacity of the fiber once it has been made into paper. The specific bond strength has to do with the mechanics of hydrogen bonding and dried fibers have a lower potential for hydrogen bonding. Coarseness will affect the rigidity of the fibers and the number of fiber contacts. Fibers become stiffer and possibly more brittle with each recycle. If the fiber lumens crack and the calcium carbonate is exposed, the fibers may not attach to the other fibers as well because the calcium carbonate particles are in the way \(^2,14\).

Strength of paper derives from both the tensile strength of individual fibers in the network and the strength of the forces that hold them to other fibers. The loss in interfiber bonding was much more pronounced than the loss in fiber strength. Bonds tend to break before the fiber does, which makes bond strength the limiting and controlling factor. The findings of Bobalek and Chaturvedi showed that zero span tensile strength remained constant after three recycles so with increased bonding weakness, fiber weakness shows a very little change \(^2,14\).

Polymeric chains of cellulose are oriented along the lengths of fibers so that fiber strength may be expected to originate from strong covalent linkages within the cellulose molecules where as fibers adhere to one another in paper by much weaker intermolecular hydrogen bonding. Tensile strength of a random two dimensional sheet does not exceed 1/3 of the strength of individual component fibers. As the point of failure is approached more bonds fail in the rupture region and the remaining fibers take more of the load until the fibers lying in the direction of loading reach
their rupture strain. The stress is transferred from certain fibers to the remaining ones and secondly a catastrophic failure of the load bearing fibers $^{2,14}$.

**Burst Index**

Burst index showed the same representation as the tensile index showed. This decrease in the amount of strength in the calcium carbonate and the conventional run is also due to the decrease in the amount of bonding. A loss of sticky hemicellulose at the fiber surface reduces the bonding potential of the fiber. Reduced bonding has been described as irreversible hornification, which implies a stiffening or hardening of the fiber. It is suggested that the larger pores closed up during drying and that drying may lead to hardening of the fiber $^{2,14}$.

**Tear Index**

With recycling, the tear index increases, passes through a maximum and then declines. The conventional run seems to continually increase, with the greatest increase between the 1st and 2nd run. The 2nd run is the 1st recycle run and is when the fibers are the most damaged and lose most of their bonding capability $^{2,15}$.

The two concepts that are known for how tear reacts on the paper are the stretching of individual fibers until they break in tensile failure and the pulling of individual fibers out of the network against frictional forces. The work of fiber failure was small compared with the work of fiber pull out, since the frictional forces act successively along the entire length of each fiber as it is withdrawn from the sheet. In a lightly bonded sheet, the work of pull out is low, so that the tear strength is low. Tear strength first rises with recycling, but passes through a maximum as the proportion of fibers that are broken increases. The energy of pull out far exceeds the energy of fiber failure so that the tear strength drops as bonding is increased further and more fibers fail
Conclusion

There are many areas of interest that can be considered in the area of lumen loading. This experiment was important because recycling of lumen loaded pulp had not been looked at before. Now certain properties have been found and hopefully better understood.

The ash content decreased with each recycle run for the calcium carbonate runs. The scattering coefficient also went down with each recycle. As less bonding occurs with each recycle, scattering coefficient goes up which is shown in the conventional recycle run. However, the amount of calcium carbonate has a bigger effect on scattering coefficient than recycling.

Recycled fibers are less conformable than virgin fibers, which accounts for the decrease in tensile index and burst index of both the conventional and the calcium carbonate paper. This happens because repeated drying of fibers produce a progressive deterioration of paper tensile strength. If the fiber lumens crack and the calcium carbonate is exposed, the fibers may not attach to the other fibers as well because the calcium carbonate particles are in the way. This reduces bonding because the fiber/ fiber bond is higher than the fiber/ particle bond.

Tear index is inversely related to bonding and increased by the number of recycles. With recycling, the tear index increases with degree of bonding, passes through a maximum and then declines. The conventional run seems to continually increase.

At first, calcium carbonate has higher tear, because a lumen loaded sheet has a lesser collapsed fiber and offers more tearing resistance than a fully collapsed fiber. The higher tear in these runs may be due to more swollen fibers because the calcium carbonate pieces were lodged in the lumens and the use of formamide increased the swelling. The calcium carbonate run, however, seems to have reached its maximum tear before the conventional recycle run. Tear increases with a decrease in the degree of bonding, passes through a maximum and then declines. Tear strength is greater the higher the fiber length and fiber strength. If the lumen broke and the calcium carbonate was exposed the fibers would bond to it. The calcium carbonate particle is acting as a fiber with a smaller shape and lesser strength. If the sheet has smaller fiber strength and lower fiber length, tear index will go down. This causes a lightly bonded sheet so the ease of pull out has increased. With the decrease in strength of the calcium carbonate particle, this particle would break more easily when it was pulled on.

Many interesting observations can be made from the recycling of lumen loaded pulp.
Appendix I

CaCO₃ Run

1st Run  2nd Run  3rd Run  4th Run

Conventional Run

1st Run  2nd Run  3rd Run  4th Run
References


11. "Laboratory beating of pulp (PFI mill method) TAPPI Test Methods, T248 cm-85.


13. Class notes for Paper Physics class at Western Michigan University


Bibliography


21. Class notes for Paper Physics class at Western Michigan University