# Physical handsheet properties of pulp furnishes containing attritor-treated fibers

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**ABSTRACT:** Several articles have been published during the past 30 years on different methods to produce micro- to nanosize cellulose particles from pulp. Unfortunately, a general lack of information exists on the impact of differing manufacturing process methods upon the product properties obtained from these differing methods. Literature data show that wet processing of small-sized cellulosic fibers generates handsheets with approximately equal or higher density and modulus of elasticity than controls for a given amount of added microcellulose. The current work evaluated small particle generation from pulp fibers via dry processing methods and compared the physical properties of dry versus wet processed particles. Dry processing to obtain microcellulose gave considerably lower sheet density and modulus as compared with wet processed microcellulose. The lower modulus can be compensated for by refining base fibers more aggressively to obtain higher density and higher modulus sheets. Dry processing methods for making microcellulose and their impact on final board properties, including modulus and smoothness, will be discussed.

***Application:*** The impact of attritor-processed fiber on handsheet physical properties might have potential for commercial applications.

Ball milling of cellulosic fibers has historically been performed as a method to change the crystalline structure of cellulose [1]. Later work determined that changes in the cellulose crystal structure could be accomplished with or without enzymatic or chemical pre- or cotreatments [2]. These treatments were designed to accelerate the desired changes in crystalline structure and to deconstruct cellulose-based fiber and wood to analyze their chemical constituents. More recently, research has focused upon enzymatic-assisted ball milling deconstruction of fibers to make the cellulose more reactive toward fermentation for biorefinery applications [2–7]. Milling of cellulose has also been claimed to be a scalable method of obtaining nanocellulose from aqueous solutions [8,9]. Ball milling imparts significant amounts of energy into the fibers or wood being studied, resulting in an alteration of the cell wall components. Because the cell wall components are modified during processing, direct ball milling is not necessarily a suitable method for obtaining pure lignocellulosic components of the cell wall. However, ball milling can be a useful analytical method when combined with other analytical methods. The amount of chemical degradation or other physical transformations that occurs during ball milling is often cited as part of experimental studies. For the current work, ball milled fibers resulting in effects on board properties will be reported, not specific fiber modifications resulting from the ball milling process.

Previous research has been done on ball milling of fibers to elucidate chemical and structural issues related to different wood species. These types of data may provide future collaborative information, which supports how these materials behave in product applications related to paperboard [10,11]. In this light, it is essential to understand that while fundamental aspects of cellulose fiber milling are known, board based applications of the cellulose from this process have not been fully explored. Wood flour applications in paperboard have been examined [11]; however, to the extent that the wood flour is generally provided as an unbleached residual material at a relatively large particle size, wood flour is not directly of interest with respect to bleached board where high brightness materials would be needed. Wood flour has been semibleached to reasonable brightness levels, but the incorporation of a secondary wood flour bleaching process into a mill would not likely be economical.

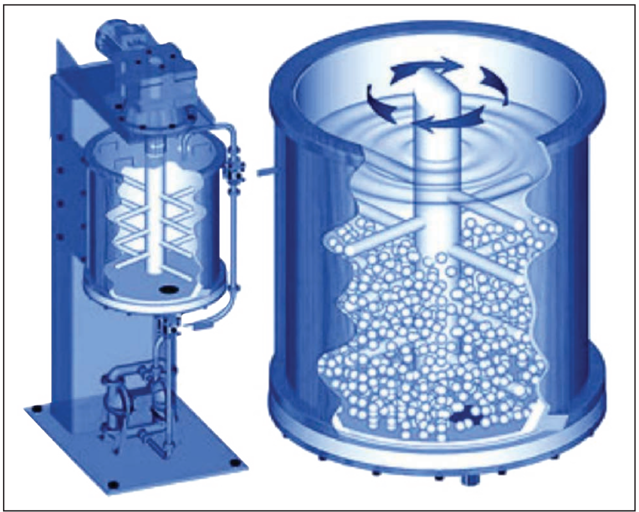
The current study examines the role of dry pulverized pulp fibers in the production of lower density bleached board. Our focus on dry grinding was driven by previous work in wet grinding of cellulosic fibers to micro- and nanosize materials, which imparted well-known effects such as drainage reduction, board densification, and material handling problems. Our purpose is not to discuss many of the relevant factors of pre- and primary mechanical treatments on fibers. Recent work has attempted to categorize several factors of importance [12,13].

### *Preparation of attritor-treated fibers*

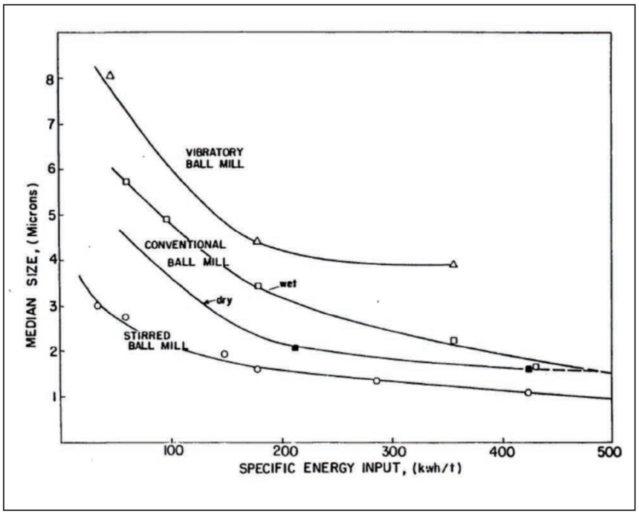
The current work used attritor-based technology for dry grinding of cellulose fibers. Attritor-treated pulp fibers were prepared using stirred ball mill devices from Union Process Inc., Akron, OH, USA. A diagram of the basic attritor unit used in this study is shown in **Fig. 1**.

Several key variables for use of attritors include shaft rotation speed; rod size, angle and geometry; grinding ball size; grinding temperature; and input power. Many attritors are equipped with temperature control, but for the attrition of cellulose in this study, we allowed the mechanical energy of the attritor to raise the temperature of the system and did not attempt to thermostatically control the system temperature.

The efficiency of particle size reduction for a given specific energy input for an attritor as compared with other types of ball mills is shown **Fig. 2** for the ultrafine girding of copper ore concentrates (chalcopyrite) [14]. While Fig. 2 illustrates that attritors are designed to handle and pulverize materials in the smaller size ranges (i.e., 1–2 $\mu$m or less), they are available for milling of cellulosic materials if the appropriate sized material is introduced into the devices.



*1. Schematic of attritor used for micronizing cellulose.*




*2. Comparative particle size reduction for attritor (stirred ball) versus ball milling.*

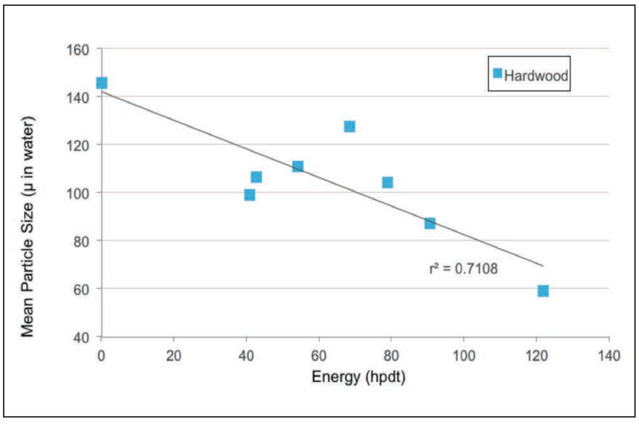
Attritors are used for the production of ultrafine pigments for paints, pyrotechnics, and fine-powder metal applications, including catalysts. Additional information regarding attritor operation variables, as well as how attritors differ from other grinding devices (e.g., vibrator ball mills), is available [15].

Attritors may be run in batch, semibatch, or continuous modes, depending on the applications. For the current work, cellulosic pulp fibers were prepared in semicontinuous mode with a pulp flake of 3/4 in. x 3/4 in. being added to the attritor for a given period (usually 15 min), allowing the resultant powder to be sieved through the bottom opening. The pulp powder was then weighed and a corresponding amount of additional pulp flake was added to the unit.

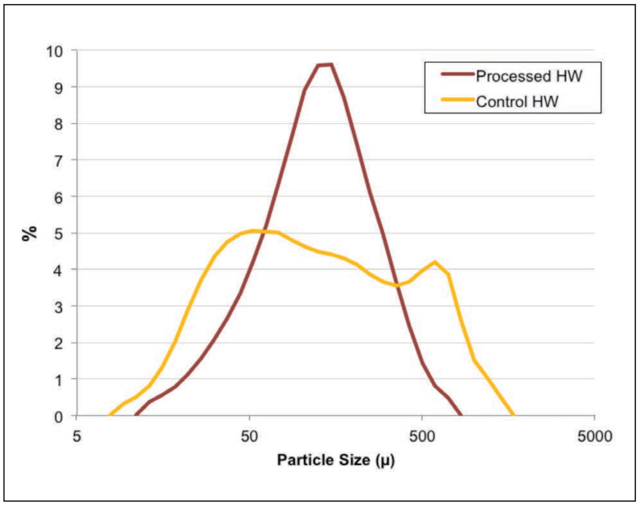
All work was conducted at nearly 100% (nominal) solids. Because of the energy imparted to the pulp during the attrition process, the unit would generally heat to >115°C, so it was anticipated that except for tenaciously bound water, all the residual moisture would be evaporated.

**Figure 3** shows the correlation between energy input in the attritor and the particle size reduction of a commercial once-dried hardwood market pulp. No dispersants were added during measurement of the particle size distribution, so agglomeration tendencies may be greater than what is sometimes seen in protocols where dispersants are added before measurement. A relatively good correlation was obtained for the particle size range shown with higher energy input resulting in smaller materials. Some deviation was noted in these semicontinuous experiments. These deviations could be related to agglomeration during particle size analysis or to minor variations in the semicontinuous experimental protocol. In general, these results suggest that one can very likely tailor the energy inputs to a desired particle size and then use that particle for building a board product, depending on paper machine dynamics and product requirements.

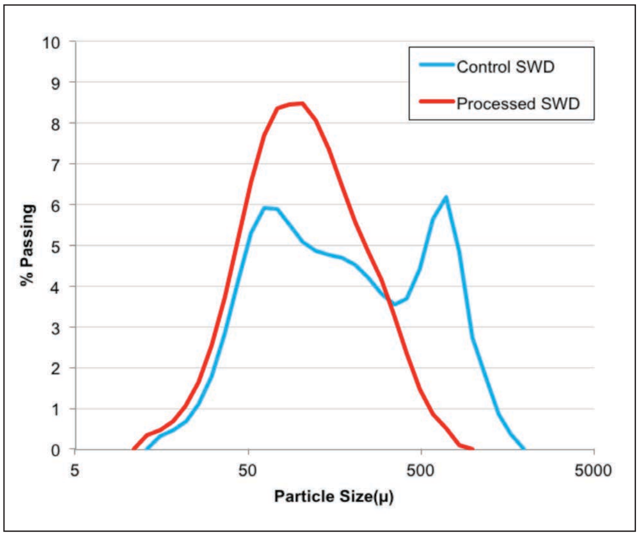
**Figure 4** shows the mean particle size for standard hardwood and semicontinuous attritor treatment of hardwood fi-




*3. Particle size reduction for hardwood pulps (hpdt = horsepower-days/short ton).*




*4. Particle size distribution for control hardwood and processed hardwood at 70 hpdt.*




*5. Particle size distribution for control softwood and processed softwood at 100 hpdt.*

bers processed at approximately 70 hp-days/short ton (hpdt). Particle size distributions (PSD) were measured using a Microtrac S3500 (Microtrac, Montgomeryville, PA, USA) particle size analyzer (PSA). For the analysis conditions used, we saw a significant diminution of the higher end (long fiber) peak. The large spike in material around 100 μm is likely explained by particle agglomeration phenomena occurring in the aqueous solution that was used as a carrier during the measurement process. All samples were diluted to an approximate 1% solution and then tested in the PSA instrument. Each sample was sonicated for 1 min before being introduced into the measurement cell and no dispersant was added. Even with the potential for particle agglomeration during the measurement and analysis, a significant reduction in the hardwood fiber particle size resulting from the attritor process was noted.

For softwood, a typical PSD reduction curve is shown in **Fig. 5**. The results show a large decrease in the high-end

| Sample | Catalyst | Energy, hpdt | Mean Particle Diameter, μm |
|---|---|---|---|
| 1 | 0 | 0 | 443 |
| 2 | 0 | 57 | 375 |
| 3 | 0 | 85 | 268 |
| 4 | A | 78 | 84 |
| 5 | B | 79 | 114 |
| 6 | A+B | 82 | 69 |
| 7 | A+B | 120+ | Aerosol |

*I. Mean particle size of softwood samples after attritor treatment with and without catalysts at given grinding energy inputs.*

particle size of pine fiber and a shift toward the lower end (about 100 μm) range. These data are for energy inputs of about 100 hpdt.

The application of catalysts during attritor processing also appears to have a positive impact on size reduction of the pine fibers. Two different catalysts were employed individually and concomitantly. As expected, the experimental data for samples 1–3 (**Table I**) show that increasing energy inputs results in a reduction in the measured mean particle size diameter. Comparing sample 3 with samples 4–6 demonstrates that the use of one or two catalysts is quite effective in terms of particle size reduction at essentially equivalent energy inputs. Combining the two catalysts resulted in more effective particle size reduction for a given energy input.

It was possible to make exceptionally finely ground softwood fibers (sample 7). If the milling time with the attritor is extended for the conditions of sample 6 (i.e., higher energy input), then the material became small enough to become electrically charged and to form an aerosol. This was an interesting outcome; however, it is a condition to avoid as it could result in a dust explosion. We report this observation as a precautionary warning to have proper grounding and collection devices for this type of material when applying these processing conditions.

## METHODS

Bleached hardwood and bleached softwood pulp samples were refined with a Valley beater to freeness targets; 120 g/m$^2$ and 240 g/m$^2$ handsheets were made of each pulp type as received and at each level of refining for physical testing. The paper property tests performed on the handsheets included caliper, tensile, and elastic modulus. The test samples were allowed to condition in a controlled humidity environment and were tested in that same environment. Testing was performed according to TAPPI Standard Test Methods (**Table II**).

### *Impact of attritor-treated fibers on handsheet properties*

Because of the high cost of hardwoods in selected mill locations, the handsheet investigation was conducted with handsheets made of a combination of attritor-treated and untreated

| Test Method | Title |
|---|---|
| T 402 | Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products |
| T 200 | Laboratory beating of pulp (Valley beater method) |
| T 205 | Forming handsheets for physical tests of pulp |
| T 220 | Physical testing of pulp handsheets |
| T 410 | Grammage of paper and paperboard |
| T 494 | Tensile properties of paper and paperboard (using constant rate of elongation apparatus) |

***II. TAPPI Standard Test Methods used for testing.***

| Condition, 120 g/m² | CSF, mL | Density, lb/mL/3000 ft² | Modulus of Elasticity, ksi | Sheffield Smoothness |
|---|---|---|---|---|
| RL 0 | 745 | 8.51 | 439 | 370 |
| RL 0 + 10% AP | 755 | 7.98 | 351 | 388 |
| RL 0 + 20% AP | 750 | 7.54 | 325 | 396 |
| RL 1 | 670 | 9.56 | 677 | 315 |
| RL 1 + 10% AP | 675 | 8.62 | 603 | 379 |
| RL 1 + 20% AP | 700 | 8.37 | 489 | 395 |
| RL 2 | 625 | 9.94 | 767 | 280 |
| RL 2 + 10% AP | 650 | 7.61 | 614 | 386 |
| RL 2 + 20% AP | 650 | 8.01 | 499 | 399 |
| RL 3 | 570 | 10.29 | 834 | 271 |
| RL 3 + 10% AP | 590 | 8.58 | 721 | 365 |
| RL 3 + 20% AP | 620 | 8.21 | 600 | 390 |

***III. Data for softwood furnishes and handsheet properties that contain various levels of attritor-treated pulp fibers (RL = refining level on the untreated softwood pulp; AP = attritor-treated softwood pulp fibers).***

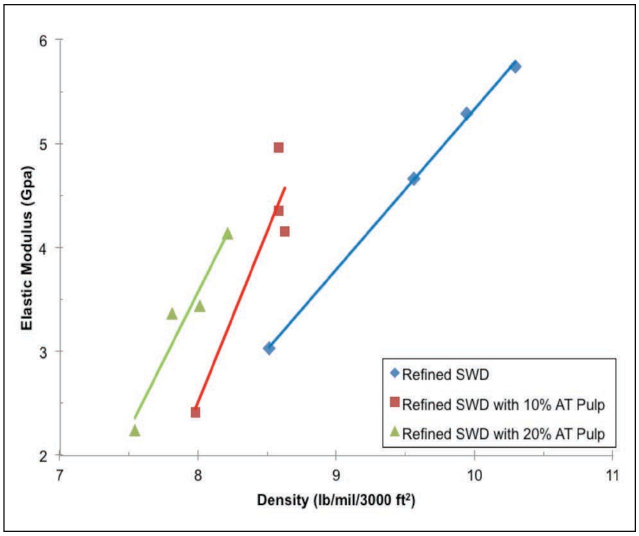
softwood pulp fibers. These handsheets were prepared and tested according to TAPPI Standard Test Methods (Table II).

Initial efforts were made to enhance the properties of attritor-based fibers using refining. These efforts were not successful because the attritor-treated fibers had no propensity to hydrate. It is speculated that attritor-treated fibers, having been once dried and ground, have become fully hornified. Additional work would be needed to fully understand these effects. In lieu of developing methods for refining the attritor-treated fibers, we opted to refine the untreated softwood pulp and then added the attritor-treated fibers (as is) to the refined softwood pulp. The CSF values for the different softwood pulps employed in this study are shown in **Table III**, as are freeness values for the combined pulps and the sheet densities and moduli values. In Table III, RL stands for refining level on the untreated softwood pulp and AP stands for attritor-treated softwood pulp fibers.

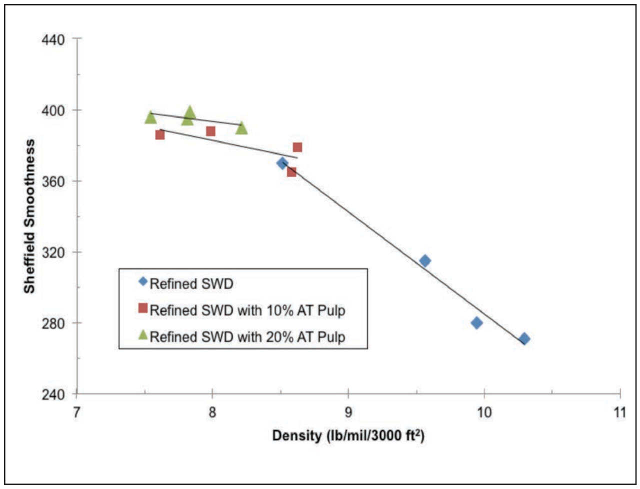
Table III shows the various conditions that were used to demonstrate the impact of attritor-treated fiber addition on the densities and moduli of softwood pulp furnishes refined to different levels. For these examples, we used a pine pulp that was processed in an attritor at approximately 85 hpdt. No attempt was made to examine the effects of catalysts on the resulting attritor treatment of pine fibers when it was added to untreated pine pulp furnishes in the handsheet studies.

For the laboratory handsheets, we refined the base softwood pulp to a given CSF value and then added either 10% or 20% of the attritor-treated fibers; tests were conducted on handsheets for sheet density, modulus, and smoothness (Sheffield units). Obviously, the CSF can be related to the modulus and other sheet properties, but because the industry tends to sell paperboard on caliper and resultant stiffness, which is related to the modulus, we focused on the density and the modulus for these handsheets.

**Figure 6** shows the relationship between density and modulus for the handsheets in this study. Each curve represents a series of refined softwood pulp sheets with a certain percentage of attritor-treated fibers. The data for each linear series that is the nearest to the graph's origin correspond to refined softwood pulp at RL 0 (lowest level), whereas the data for each series that is the most distant correspond to refined softwood pulp at RL 3 (highest level).




***6. Density versus elastic modulus for refined softwood and refined softwood with attritor treatment.***

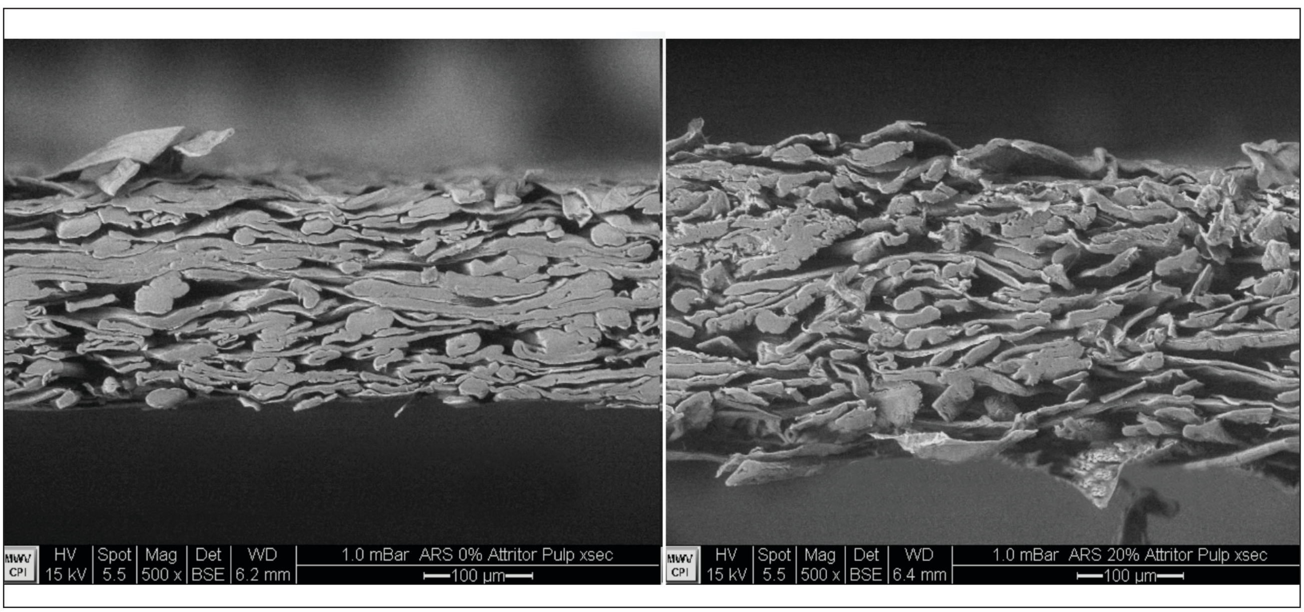



***7. Sheffield smoothness versus density for refined softwood and refined softwood with attritor treatment.***

Figure 6 shows that the addition of the attritor-treated fibers to the softwood pulp causes a decrease in sheet modulus and density. However, it is important to note that the sheet modulus can be increased by refining the untreated softwood pulp that contains attritor-treated fibers. While this was done for laboratory handsheets, the fact that the CSF goes up for attritor-containing pulp furnishes offers the intriguing option of putting small particle size pulps into the sheets without affecting drainage.

The current work only considers the in-plane modulus; while out-of-plane modulus would likely change, we are continuing to examine this variable. Nonetheless, over the range of 0% to 20% addition to the untreated softwood pulp, the use of attritor-treated fibers can lower sheet density at a given modulus. Also, if a product paperboard can withstand a decrease in modulus of 20%, then a 10% attritor-treated fiber addition could be tolerated with little additional refining of the untreated softwood pulp. A potential 10% reduction in fiber usage and lower bulk could be realized with a 10% addition and some additional refining. Thus, it may be possible to substitute shorter fiber pulps (e.g., hardwood pulps) with attritor-treated softwood fibers in certain circumstances for paperboard pulp furnishes.

As more attritor-treated fibers are added to the softwood furnish, the handsheet density decreases and the surface of the handsheets becomes rougher. **Figure 7** shows the results of Sheffield smoothness for the various handsheets. These data are for raw handsheets, which were not coated or calendered, and only represent the potential impact of this type of additive on sheet properties in a laboratory setting. Surface properties are a prime qualifier for many paperboard




***8. Side scanning electron microscopy view of pulps containing 0% attritor and 20% attritor.***

products, so the option to re-engineer a top ply or coating to regain smoothness needs to be carefully examined. The fact that the addition of attritor-treated fibers to the pulp furnish caused an appreciable increase in surface roughness is a strong indicator that additional investigation would be required before it could be feasible in commercial applications.

Visually, the results of our study are evident from the side-on scanning electron microscopy photos (**Fig. 8**). The micrograph of softwood furnish without attritor-treated fibers is shown on the left, whereas the furnish containing 20% attritor-treated fibers is shown on the right; the scale bar represents 100 $\mu$m. The handsheets with 20% attritor-treated fibers are noticeably thicker (less dense) than the control sheets with only untreated softwood pulp.

## CONCLUSIONS

We have shown that blending dry grinding of softwood fibers (once dried) to a softwood pulp furnish can yield handsheets with lower density as compared with a control softwood pulp furnish without attritor-treated fibers. While this lowers the sheet modulus, it is possible to refine the base softwood pulp furnish to regain sheet modulus. Balancing these effects offers an option to use less fiber in paperboard construction, depending upon product specifications.

Handsheets containing attritor-treated fibers, which have lower sheet densities, have appreciably rougher surfaces, as quantified by Sheffield smoothness values, than control without attritor-treated fibers. This was observed regardless of the level of refining of the base softwood pulp furnish.

Additional research is needed to understand the energy inputs and particle sizes obtained with attritor processing of pulp fibers, as well as how attritor-treated fibers when blended with pulp furnishes affect paper machine drainage. Control of sheet surface roughness to allow for graphic printing requirements would also have to be investigated before this technology could be implemented on the industrial scale. **TJ**

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## ABOUT THE AUTHORS

Several different wet techniques have been employed in the manufacture of nanofibrilated cellulose (NFC). In our work, we attempted to determine how dry processed NFC would affect the physical properties of paper.

A substantial body of work exists that examines NFC from wet processing methods. The current work used an attritor (dry) processing method. Rehydrating the attritor-processed NFC was difficult. Eventually, we resorted to some pulp refining on the attritor pulp included in the blend to get the material into the sheet.

The attritor-processed material had a significant impact on bulk at similar stiffness. The impact on sheet smoothness was unexpected and unfortunate. Attritor-processed pulps might have the ability to alter the bulk-stiffness relationship of some board grades. In addition, attritor processing requires less energy than several other methods of processing.

Our next step is to examine the impact of attritor processing on different fiber sources and how these pulps affect handsheet physical properties. Another objective is to perform a full financial cost-benefit analysis for the resulting products.

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