NOVEL USE OF WASTE KERATIN AND COTTON LINTER FIBERS FOR PROTOTYPE TISSUE PAPERS AND THEIR EVALUATION

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Corporate environmental sustainability calls for sustainable product manufacturing with less creation of waste material or increased reuse of waste materials. One example is the use of keratin fiber from the poultry industry and cotton linter from the textile industry for paper and tissue manufacturing. In this paper, the feasibility of using these waste fibers to make paper was demonstrated in handsheets. The properties of these handsheets were compared to the properties of handsheets made with standard bleached eucalyptus tropical hardwood fibers. A blend of cotton linter and keratin fibers at 80/20 and 60/40 ratios showed a 59% and 73% improvement in sheet bulk, respectively, compared to eucalyptus handsheets. Similarly, air permeability of the cotton / keratin fiber handsheets improved 414% and 336%, respectively, versus the eucalyptus. However, the tensile index of the cotton and keratin fiber blends was lower than the eucalyptus sheets. There was no remarkable difference in water absorbency up to 20% keratin fiber. Above 20% of keratin fibers the water absorbency started to decrease, which is likely attributable to the hydrophobic nature of the protein-based keratin fiber.

Keywords: Cotton; Feather; Keratin; Handsheet; Tissue; Fiber; Renewable; Sustainable

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INTRODUCTION

Keratin is a group of fibrous proteins occurring in hair, feathers, hooves, and horns. Keratin has coiled polypeptide chains that combine to form supercoils of several polypeptides linked by disulphide bonds between adjacent cysteine amino acids. It is a tough, insoluble protein substance that is the chief structural constituent of the outer-layer of the skin and horny tissue (Rouse and Van Dyke 2010). For example, chicken feather is a processing waste material from the poultry industry, containing about 90% keratin. Keratin fiber can be processed from chicken feathers and thus can be considered as a renewable and sustainable source of alternative natural fibers.

In the US alone, there are about two to four billion pounds of feathers produced annually (El-Nagar et al. 2006). Current utilization of this alternative natural material is limited to a few pilot plants reported by Featherfiber Corporation, and most chicken feather fibers are disposed of in landfills. Although it is abundantly available, significant challenges exist in developing ways to effectively utilize this natural material, and in developing industrially acceptable methods to process, market, and use avian feather fibers (Karthikeyan et al. 2007).

Barone and Schmidt (2004) made keratin films by mixing glycerin with keratin in a Brabender mixing head at 40 ^{o}C for 40 minutes, followed by film press using a Carver Press. Barone et al. (2005) further demonstrated the production of films using keratin plasticized by glycerin. US patent 2006/0084728 to Barone and Schmidt disclosed polymer composites containing keratin and at least one synthetic polymer such as polyolefin, thermoplastic polyurethane, polyesters, etc. The process to make the composites relied on dissolving synthetic polymer in organic solvents such as acetone to create a polymer with a "dough-like" consistency, and then chicken feather fiber was added. The resulting material was further processed by rolling it with aluminum bars on a flat surface. Although these processes proved the concept of using chicken feather, they are not exactly suitable for a large industrial line of production commonly used for plastic manufacturing. In addition, the biodegradability of these composite materials was verified using a modified ASTM D5338 composting method (Barone and Arikan 2007).

Winandy et al. (2003) describe production of medium density wood fiberboard composites using from 20 to 95% chicken feather fibers and a 5% phenol formaldehyde resin as adhesive. The physical properties of the feather-wood fiber mixtures showed a marked improvement in resistance to water absorption and thickness swell, probably related to the hydrophobic keratin in the feather fiber. Dweib et al. (2004) made nonwoven mats comprising recycled newspaper cellulose and keratin fiber using a wetlaid process. Using an acrylated epoxidized soybean oil (AESO)-based resin as a binder, the chicken feather fiber can be added up to 60% to make low-cost and environmentally-friendly composites for use in industries such as construction, automotive, and trucking. US patent 2005/0153118 to Licata describes paper and paper composites made from wood pulp and fibrous protein such as keratin, fibrin, collagen or elastin with the help of a cross-linking agent or an oxidizing agent. However, the invention used commodity wood pulp, which still creates a negative forestry impact. The desire of the environmental sustainability movement is tree-free product design. A recent review by Rouse and Van Dyke (2010) indicates a wide range of keratin-based biomaterials for potential medical-related applications.

Cotton linters are created in the mechanical process of separating the cotton from its seeds. The linters are short fibers attached to the seeds and other areas of the cotton boll which fall out during the separation process. These fibers are viewed as a lower value by-product or waste in the production of textile-grade fibers. Linters used in tissue and wipe products are well known, as illustrated in EP patent 1058751 to Paterson-Brown et al. (2003). The use of an abundant cotton linter residue as raw material is very attractive to sustainable manufacturing. There are about 17 states, located in southern part of the United States, which have suitable climate to grow cotton. This large scale of cotton plantation contributes significantly to the cotton industry and makes the U.S. the fourth largest cotton grower worldwide (Wakelyn et al. 2007).

Historically, few applications in paper and tissue products are seen using a blend of cotton linter and keratin fiber, although both materials are available. It is believed that keratin fiber is morphologically akin to cotton fiber and capable of forming useful tissues derived from these two biodegradable and renewable sources (Sczostak 2009). However, the basic mechanical properties of such samples have virtually never been studied and reported to encourage more research activities in this direction.

Recovered fibers from wastepaper is a good example of waste fibrous materials that are extensively used in tissue, corrugated paper, and other applications. Both poultry and cotton industries have sufficient bases to support scale-up needs, and several cotton fiber-based products such as wipes and tissues are already in the marketplace (http://www.cottonbabies.com/ and http://www.saveatree.com.au/). Therefore, products containing cotton linter and keratin fiber are expected to marketable.

This paper discusses utilization of the above two waste fibrous materials for paper and tissue manufacturing and evaluation of the mechanical properties of handsheets made from blends of these two fiber sources. The results are compared to handsheets made from a commodity pulp – *Eucalyptus grandis*. The information from this technology assessment provides insights into the applicability of these two materials for sustainable paper and tissue manufacturing. The main objective is to prove the concepts about how to use keratin fibers, to understand unique properties of keratin materials, and to provide business recommendations.

EXPERIMENTAL

Materials

Keratin fiber was purchased from Featherfiber Corporation (Nixa, MO). It was thoroughly cleansed in a proprietary cleaning system to remove all soluble protein and contaminants, followed by mechanical shredding and shearing to obtain fibers separated from the feather shaft (Gassner et al. 1998). The molecular formation is approximately two thirds β-sheet, and one third aligned in repeating rope-like α-helices. The keratin "fiber length" ranges from 3 to 9 mm with a typical aspect ratio of 16 to 1.

Cotton linter (*Gossypium hirsutum*) dry lap pulp with an average fiber length of 3 to 5 mm was provided by ADM (Decatur, IL). These fiber lengths are within the range reported by Hurter (2006), but slightly shorter than those reported by Han (1998) and Wakelyn et al. (2007). It is a total-chlorine-free grade pulp bleached to 88%+ ISO brightness.

A Fiber Quality Analyzer (OpTest Equipment Inc., Hawkesbury, Ontario, Canada) was used to characterize cotton linter and keratin fibers according to the method outlined by Robertson et al. (1999).

Commodity *Eucalyptus grandis* (hybrids) dry lap pulp was supplied by Aracruz, Brazil. It is a fast-growing exotic tree that is suitable for use as raw material in the pulp and paper industry. The tree plantation in Brazil relies on cloning processes. *E. grandis* is normally harvested for pulping in 6 to 7 years. The fiber length ranges from 0.8 to 1.0 mm, which increases with tree age (Bhat et al. 2006).

Ethanol was purchased from Sigma-Aldrich Corporation (St. Louis, MO), and used as received.

Methods

Handsheet preparation

Handsheets were prepared according to a standard operating procedure 2016 (SOP 2016), which is the proprietary method Kimberly-Clark (K-C) modified and approved in 2007. The major difference, in comparison to TAPPI T205 (2006), is that the sheet is pressed one at a time and only once without a plate during the K-C sheet making procedure. The sheet is then dried at steam temperatures instead of air dried with a plate. All other general procedures are the same, unless otherwise noted below.

To make handsheets, a slurry suspension of each fiber was prepared. The keratin fiber suspension was prepared by disintegrating eight grams of keratin fiber in a beaker containing 400 mL of ethanol and water (1:1) solution. Ethanol was used as a wetting agent initially in order to soak keratin fiber into water (Choudary et al. 2009). Once it was submerged, 3600 mL water was then added to form 4000 mL of keratin fiber suspension. Commercially, alternative wetting agents are outlined in US patents to Jansma and Smith (1993) and Polat et al. (2007), which can be used in tissue manufacturing. The cotton fiber suspension was made according to SOP 2016 (2007).

The appropriate amount of slurry of cotton and keratin fiber was taken to make handsheets comprising cotton / keratin at 80/20 and 60/40 ratios at a target basis weight of 60 gsm. Five replicate handsheets were prepared for each mixture. The resultant handsheets were soft, bright, and smooth. These handsheets were used to conduct several mechanical property tests for technical evaluation.

Tensile testing

All testing was done under laboratory conditions of 23.0 ± 1.0 °C, 50.0 ± 2.0 % relative humidity, and after the sheet had equilibrated to the testing conditions for a period of not less than four hours. The testing was done on a tensile testing machine maintaining a constant rate of elongation, and the width of each specimen tested was 2.54 cm. The specimens were cut into strips having a 2.54 ± 0.04 cm width using a precision cutter. The "jaw span" or the distance between the jaws, sometimes referred to as gauge length, was 12.7 cm. The crosshead speed was 1.27 cm per minute. A load cell or full scale load was chosen so that all peak load results fell between about 20 and about 80 percent of the full scale load. Suitable tensile testing machines include those such as the Sintech QAD IMAP integrated testing system (Rockford, IL), recording at least 20 load and elongation points per second.

Specific Absorbent Capacity (SAC)

Specific absorbent capacity was measured by cutting a 7.62 cm by 7.62 cm sample from handsheets that had been equilibrated under standard TAPPI conditions for 4 hours. The sheet dry weight (*SDW*) was weighed to the nearest 0.001 grams. After weighing, the sheet was soaked in a shallow 22.86 cm by 30.48 cm or approximate sized pan filled with about 2.54 cm of water. The sample was soaked for about 10 seconds, after which the sample was removed from the pan by carefully picking up the sample at the corner. The sample was then held by the corner in an elevated position above the water surface and allowed to drain for 30 seconds. After 30 seconds the sheet wet weight (*SWW*) was weighed to the nearest 0.001 grams and the *SAC* in g/g determined from Equation (1):

$$SAC = \frac{SWW - SDW}{SDW} \tag{1}$$

Basis Weight (BW)

Samples were conditioned at standard TAPPI conditions for a minimum of 4 hours prior to basis weight testing. Handsheets were cut to 19.05 cm by 19.05 cm ± 0.03 cm size. Five handsheets were weighed and total mass (W) of the handsheets recorded. The BW in g/m^2 was then calculated from Equation (2):

$$BW = \frac{W}{5} \times 27.56 \tag{2}$$

The numerical value of 5 represents five handsheets in the stack and 27.56 is an inverse of dimensional conversion factor to change from square centimeters to square meters.

Caliper

Caliper is the handsheet thickness, which was measured using a Lorentzen and Wettre Code SE 050 micrometer (Alpharetta, GA) on a single sheet using the following settings: lifting Height: 3.0 mm, lower speed: 1.00 mm / second, upper measuring surface: 2 cm^2, and pressure: 50 kPa. The caliper of 5 handsheets was measured in inches, and the average was reported for calculations of other parameters.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy images of the handsheets containing cotton and keratin fiber at 100/0 and 60/40 ratios were obtained using a JSM-6490LV scanning electron microscope (Peabody, MA). The surface images are generated at 170X for all samples that were coated with gold of about 15 nanometer thickness prior to taking any observations.

Statistical analysis

All data represented the mean of five independent experiments and measurements. Error bars shown in figures are standard deviations calculated using a method outlined by Young (1996).

RESULTS AND DISCUSSION

Waste Fiber Characterization

Arithmetic average fiber length is the sum of all of the individual fiber lengths divided by the total number of fibers measured. In comparison, cotton linter fiber length (2.1 mm) was shorter than keratin fiber (2.6 mm). The results from this study for fiber lengths are slightly lower than waste fiber data provided by suppliers.

Fiber curl is the deviation from straightness of the fiber axis. The arithmetic mean curl for cotton linter was 16.7%. For keratin quill, it was 6.2%. Therefore, cotton linter showed much greater curl value than keratin fiber, mostly due to softness of cotton linter (Gopalakrishnan and Aravindhan 2005) and rigidity of keratin fiber (Yu and Liu 2006).

The fines are defined as objects that are less than 0.20 mm in length, and reported fines as a total percentage of fiber was based on an arithmetic basis or length weighted basis. The percentage of fines on an arithmetic basis is the number of fines divided by the total number of fibers (fines included) multiplied by 100. The fines value was 38.9% for cotton linter and 57.6% for keratin fiber, indicating more fines for keratin fiber than cotton linter. It is believed that intensive processing and alcohol washing of chicken feather fiber is a direct cause of the observed level of fines.

Specific Volume

The specific volume (*V*) is the volume occupied by a unit of mass of a material. It is equal to the inverse of density (ρ). The specific volume may be expressed in $\frac{m^3}{kg} or \frac{ml}{g}$, which can be calculated using Equation (3):

$$V(ml/g) = \frac{1}{\rho} = \frac{Caliper(in) \times 2.54(cm/in)}{BasisWeight(g/m^2)} \times 10000(cm^2/m^2) \times 1000^{-1}(ml/cm^3) \quad (3)$$

The caliper and basis weight of the handsheets can be determined, respectively. An average value for caliper or basis weight of five duplicates was obtained and used to figure out the specific volume for each code of the sample.

Figure 1 shows the changes in handsheet specific volume as keratin fiber was increased from zero to 40%. In comparison to the neat eucalyptus tissue, the specific volume for cotton alone increased by 54%, the cotton / keratin (80/20) handsheet increased 59%, whereas specific volume for the cotton / keratin (60/40) handsheet increased 73%. The increase in specific volume with addition of keratin suggests that keratin fiber wall thickness is relatively high, producing higher specific volume in the blended tissue sheets.

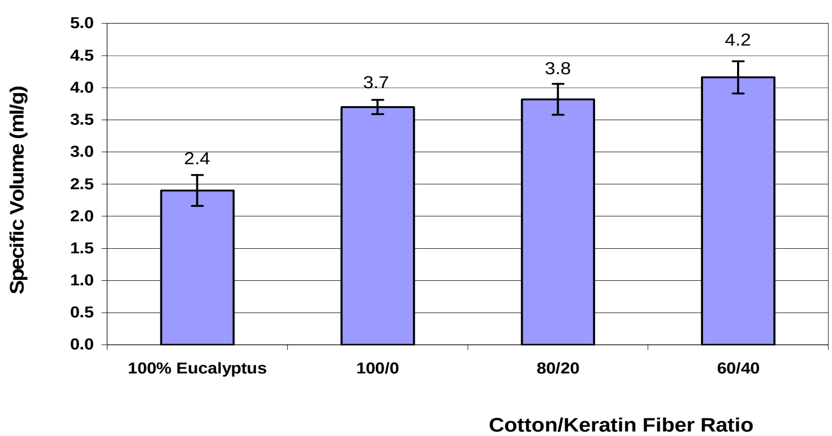

Figure 1. Cotton / keratin and eucalyptus handsheet specific volume

In comparing the eucalyptus, 100% cotton, and the 80/20 blend, there was a good linear relationship between the tensile strength and specific volume, suggesting that the increase in bulk was due to in part a decrease in relative bonded area of the fibers. However, the 60/40 blend had the greatest specific volume yet the highest tensile strength of any of the cotton / cotton blend samples. This suggests that keratin fibers have some bulk-building capability beyond simple reduction of the relative bonded area of the sheet.

Air Permeability

Air permeability is a measure of the rate of air flow passing perpendicularly through a known area under a prescribed air pressure differential between the two surfaces of a tissue material. It is generally expressed in $cm^3/s/cm^2$.

Regardless the percentages of keratin fiber in the composite handsheets, their air permeability values were dramatically greater than the neat eucalyptus, as shown in Fig. 2. A plausible explanation is due to tight hydrogen bonding in the neat eucalyptus, which results in lower air permeability, whereas hydrogen bonding among cotton and keratin fiber is weak, inducing more air flow through the handsheets. Tensile index data may further support this point of view. Within the cotton/keratin fiber system, air permeability decreased as more keratin fiber was incorporated into the handsheets. At 20% of keratin fiber, air permeability was 10% less than the neat cotton linter handsheets, and at 40% of keratin fiber, air permeability was 24% less than the neat cotton linter handsheets. However, air permeability should increase as handsheets get bulky at high keratin fiber incorporation, as shown in Fig. 1. This abnormality is likely due to keratin fiber surface features, which are quite different from those of cotton linter fibers seen from Fig. 6. Relatively large keratin fibers block air passage through the handsheets, resulting in a decrease in air permeability.

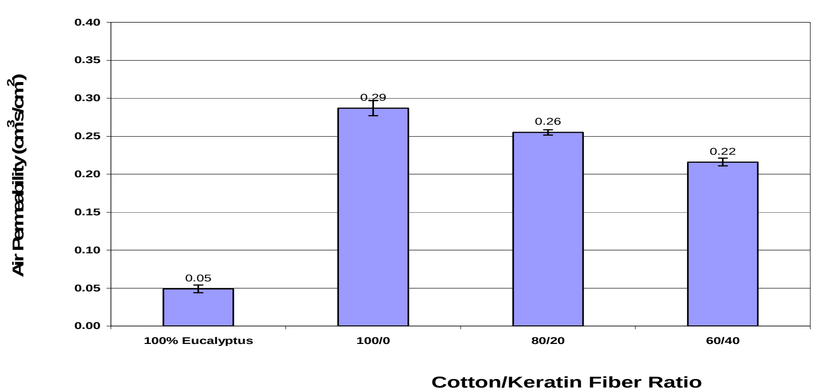

Figure 2. Cotton / keratin and eucalyptus handsheet air permeability

Tensile Index

Tensile index is a measure of the tensile strength (N/m) divided by tissue basis weight (g/m^2). Figure 3 presents tensile index for cotton/keratin and eucalyptus handsheets. The tensile property for the cotton/keratin handsheets was weaker in all cases than the neat eucalyptus, which is attributed to less hydrogen bounding energy among keratin and cotton fibers. The use of ethanol in the keratin fiber slurry preparation may have a negative impact on fiber interactions as well (Normakhamatov et al. 2009).

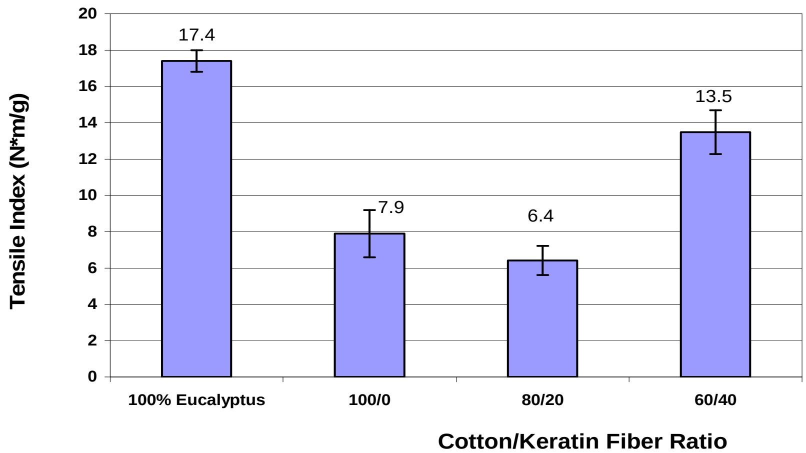

Figure 3. Cotton / keratin and eucalyptus handsheet tensile index

Specific Absorbency

For absorbency testing, a piece of the sample (7.62 cm x 7.62 cm) was cut and weighed as described earlier. Keratin fiber is a protein-based fiber, showing a tendency of hydrophobic behavior. At 20% of keratin fiber, the specific absorbency capacity was not impacted, because the dominate component in the handsheet was cotton fiber. However, absorbency decreased 20% when 40% of keratin fiber was present in the handsheet, as shown in Fig. 4. Obviously, the keratin fiber surface is relatively hydrophobic.

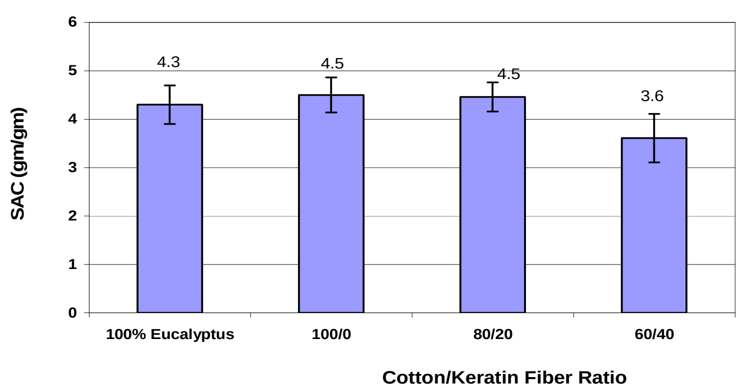

Figure 4. Cotton / keratin and eucalyptus handsheet specific absorbency capacity (SAC)

Tissue products such as facial tissue, paper towel, and bath tissue are designed to include several important properties. For example, the products should have good bulk, soft feel, and good integrity. Moreover, it is desirable to provide such tissues with high absorbency characteristics, particularly when used in certain applications such as paper towel. The current results indicate tissue absorbency was not impacted up to 20% keratin fiber content. The actual amount of keratin fiber incorporation can be selected depending on a particular application.

Scanning Electron Microscopy (SEM) Study

Figure 5 is the SEM for 100% cotton handsheets, where some of fibers are open and flat, and in some cases fiber surface twist is visible. Figure 6 is the SEM for cotton and keratin (60/40), where there were ribbons stripped from quill and shaft, barbs and barbules, flakes that might be sheath or collapsed ribbons, and micrometer-sized spheres.

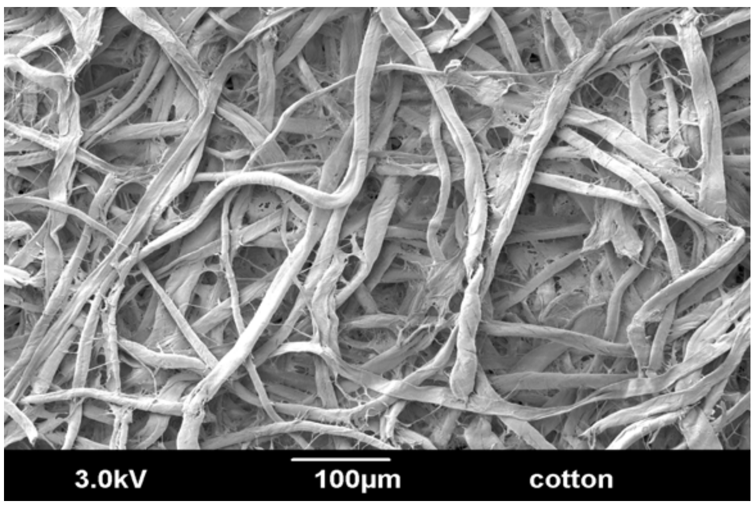

Figure 5. 100% Cotton handsheet SEM at 170X

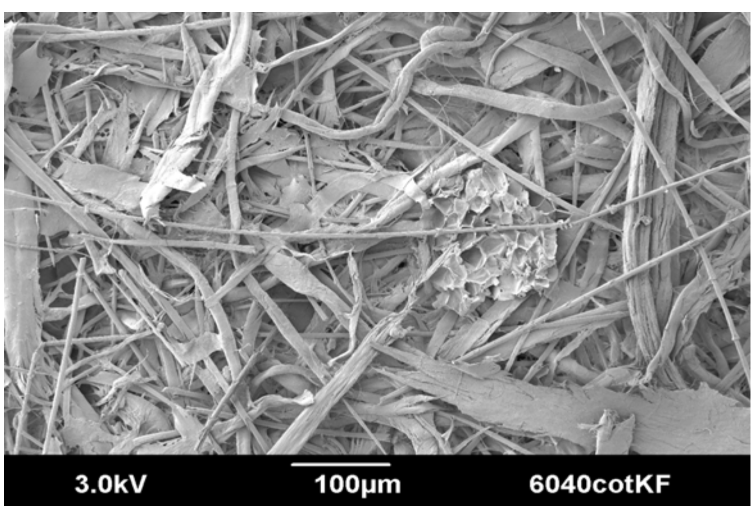

Figure 6. Cotton and keratin fiber (60/40) SEM at 170X

CONCLUSIONS

1. It is feasibility to use waste cotton linter and keratin fibrous materials for tissue product manufacturing.
2. The specific volume of the handsheet made from the blend was higher than that of the neat eucalyptus handsheet, whether cotton was blended with keratin fiber or not.
3. The air permeability for cotton and keratin fiber was enhanced by more than 4 times.
4. The specific absorbency capacity values did not indicate significant differentiation, whereas the tensile index for cotton and keratin fiber handsheets was lower than the neat eucalyptus.
5. These handsheet mechanical properties can be judiciously tailored in order to meet product specifications.

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