Facile preparation of nanofiller-paper using mixed office paper without deinking

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ABSTRACT: Mixed office paper (MOP) pulp without deinking with an ash content of 18.1 ± 1.5% was used as raw material to produce nanofiller-paper. The MOP pulp with filler was mechanically fibrillated using a laboratory stone grinder. Scanning electron microscope imaging revealed that the ground filler particles were wrapped by cellulose nanofibrils (CNFs), which substantially improved the incorporation of filler into the CNF matrix. Sheets made of this CNF matrix were densified due to improved bonding. Specific tensile strength and modulus of the nanofiller-paper with 60-min grinding reached 48.4 kN·m/kg and 8.1 MN·m/kg, respectively, approximately 250% and 200% of the respective values of the paper made of unground MOP pulp. Mechanical grinding duration did not affect the thermal stability of the nanofiller-paper.

Application: Cogrinding fiber with filler has practical significance for high-value use of MOP without costly deinking.

Cellulose nanomaterials have received a great deal of attention from the scientific community in the past decade because they are renewable and biodegradable and possess good mechanical properties [1,2]. Extensive research in nanocellulose-based composites has been conducted for developing biodegradable polymeric materials [3-6]. A number of nanocellulose-based polymers have been prepared [7-9]. These engineered biodegradable materials are being considered for applications, including structural materials, barrier films, and packaging composites.

Biomimic techniques have been used to develop strong, tough, and stiff organic–inorganic hybrid composites [10,11]. Nanocellulose-inorganic clay hybrid materials with high mechanical and electronic functionality and barrier properties have also been developed [12-17]. The inorganics were embedded in a nanocellulose matrix, which forms a nanolayered structure. Because of the strong interaction of nanocellulose and inorganics, the nanocellulose-inorganic clay hybrid composites exhibit excellent mechanical and gas barrier properties, as well as thermal stability. Calcium carbonate has also been used to prepare nanocellulose-filler composites [10,16,18]. Typically, these nanocellulose-inorganics composites were prepared by addition of a low amount of inorganics to the nanocellulose matrix. In other words, inorganics such as clay or calcium carbonate were not applied during mechanical fibrillation of cellulose fibers. The main challenge in such preparation is the dispersions of the inorganics in the matrix [19], which results in layer-composite structure.

Waste paper is a potential lignocellulosic biomass feedstock for the bioproducts industry. In 2012, about 51.1 million tons of waste paper and paperboard were recovered in the United States [20]. Secondary fibers recovered from mixed office paper (MOP) or old corrugated containers (OCC) have very high cellulose content (approximately 50%-70%). Paper filler such as lime ($CaCO_3$) and kaolinite clay ($Al_2Si_2O_5(OH)_4$), accounts for approximately 15% of the total weight of MOP. Filler content is even higher in papers made in Europe. Currently, MOP is recycled as a source of secondary fibers through pulping and flotation deinking, a process that often loses a significant amount of fibers and fillers [21].

Here, for the first time, we evaluate the feasibility of using MOP as a raw material for nanofiller-paper production by cogrinding cellulose fibers together with inorganics. We use the term nanofiller-paper or nanofiller-composite to differentiate nanocellulose-filler composites reported in the literature that simply mixed filler with cellulose nanofibrils (CNF) rather than cogrinding with cellulose fibers during nanofibrillation. The filler containing MOP pulp was fed into a laboratory grinder without deinking or separation steps. Nanofiller-paper was prepared using the resultant CNF and nanofiller mixture from grinding of MOP pulp by ultrafiltration, pressing, and drying. The mechanical, optical, and thermal properties of the films were characterized. The resultant nanofiller-paper has substantially improved mechanical properties over properties of paper made of unground MOP pulp.

MATERIALS AND METHODS

Raw material

Laboratory MOP sheets were produced using A4 copy paper with 30% recycled-fiber content. The paper sheets were printed both sides. Each side was printed with 46 lines, each line containing 52 letters (A-Z) in black using a Sharp MX3100N laser printer (Sharp; Osaka, Japan). The printed papers were

shredded into small pieces and soaked in deionized (DI) water overnight. The soaked paper was then pulped in a laboratory pulper (Formax Model 450H, Adirondack Machine Corp.; Queensbury, NY, USA) at 15% solid consistency for 10 min at room temperature without any chemicals. Pulp was dewatered using a nylon bag and kept at 5ºC for future use. The collected pulp has an ash (filler) content of 18.1%±1.5% determined by a literature protocol [22].

Mechanical fibrillation

The pulp was mechanically fibrillated using a MKZA6-2, disk model MKGA6-80# (Masuko Sangyo Co. Ltd.; Kawaguchi, Japan) super mass colloider as described previously [23]. Pulp at 2% consistency was fed continuously into the colloider at 1,500 rpm using a peristaltic pump (Cole Parmer; Chicago, IL, USA). The gap of the two disks was set at -100 µm. The zero position was determined by slight contact of the disks before loading pulp. There was no direct contact between the disks even at the negative setting because of the presence of pulp slurry in the grinding operation. Fibrillated CNF samples were collected periodically and the time-dependent energy consumption was recorded.

Preparation and testing of nanofiller-paper

The CNF slurry was diluted to 0.1% consistency and continuously stirred for 1 h using a model RZR-50 mechanical stirrer at 2000 rpm (Caframo Ltd.; Wiarton, ON, Canada). Nanofiller-paper was formed by ultrafiltration of the slurry using a 9-in. filtration system with a polyvinylidene fluoride membrane of 0.45 µm pore size (Millipore; Billerica, MA, USA). Nanofiller-paper together with blotter paper was pressed at 207 kPa (30 psi) for 3 min and pressed for another 3 min at 345 kPa (50 psi). Pressed sheet was dried in a 5-in. dry ring in a conditioned room (23ºC and RH 50%) with a 22.7-kg (50-lb) load on top. Tensile tests were carried out using a model 5865 system (Instron; Norwood, MA, USA) equipped with a LX500 laser extensometer for precise displacement determination (MTS System Corp.; Eden Prairie, MN, USA). Film opacity, basis weight, and thickness were tested using TAPPI methods T 519 om-06.26 "Diffuse opacity of paper (d/0 paper backing)," T 410 om-08 "Grammage of paper and paperboard (weight per unit area)," and T 411 om-10 "Thickness (caliper of paper, paperboard, and combined board)," respectively.

Analyses

The transmittance of CNF slurry was measured using a model 8453UV-Vis spectrophotometer (Agilent Technologies; Palo Alto, CA, USA). A thoroughly mixed aliquot of CNF slurry was diluted to 0.1 wt% and placed in a 10-mm quartz cuvette. The spectrum of the cuvette filled with water was used as a reference.

Mixed office paper fibers and CNFs were imaged using a Leo EVO 40 scanning electron microscope (SEM) (Carl Zeiss NTS; Peabody, MA, USA) under ultrahigh vacuum conditions. Specimens were prepared by drying drops of the aqueous slurry of 0.2 g/L on polished aluminum mounts. The samples were sputter-coated with gold to provide adequate conductivity. Handsheets made of unground MOP fibers and nanofiller-paper samples were imaged by a Hitachi S3400N SEM with energy dispersive X-ray spectroscopy (EDAX AMETEK Inc.; Mahwah, NJ, USA) at an acceleration voltage of 15 kV. Cross-sections of sheets were prepared by carefully cutting the sample with a sharp knife. The samples were fixed to an aluminum stub with carbon glue, gold-plated with a vacuum electroplating machine for about 60 s, and then observed with SEM. Thermogravimetric analysis (TGA) was carried out with a Perkin Elmer TGA 4000 (Perkin Elmer; Waltham, MA, USA) with a heating rate of 10ºC/min under nitrogen atmosphere (10 mL/min).

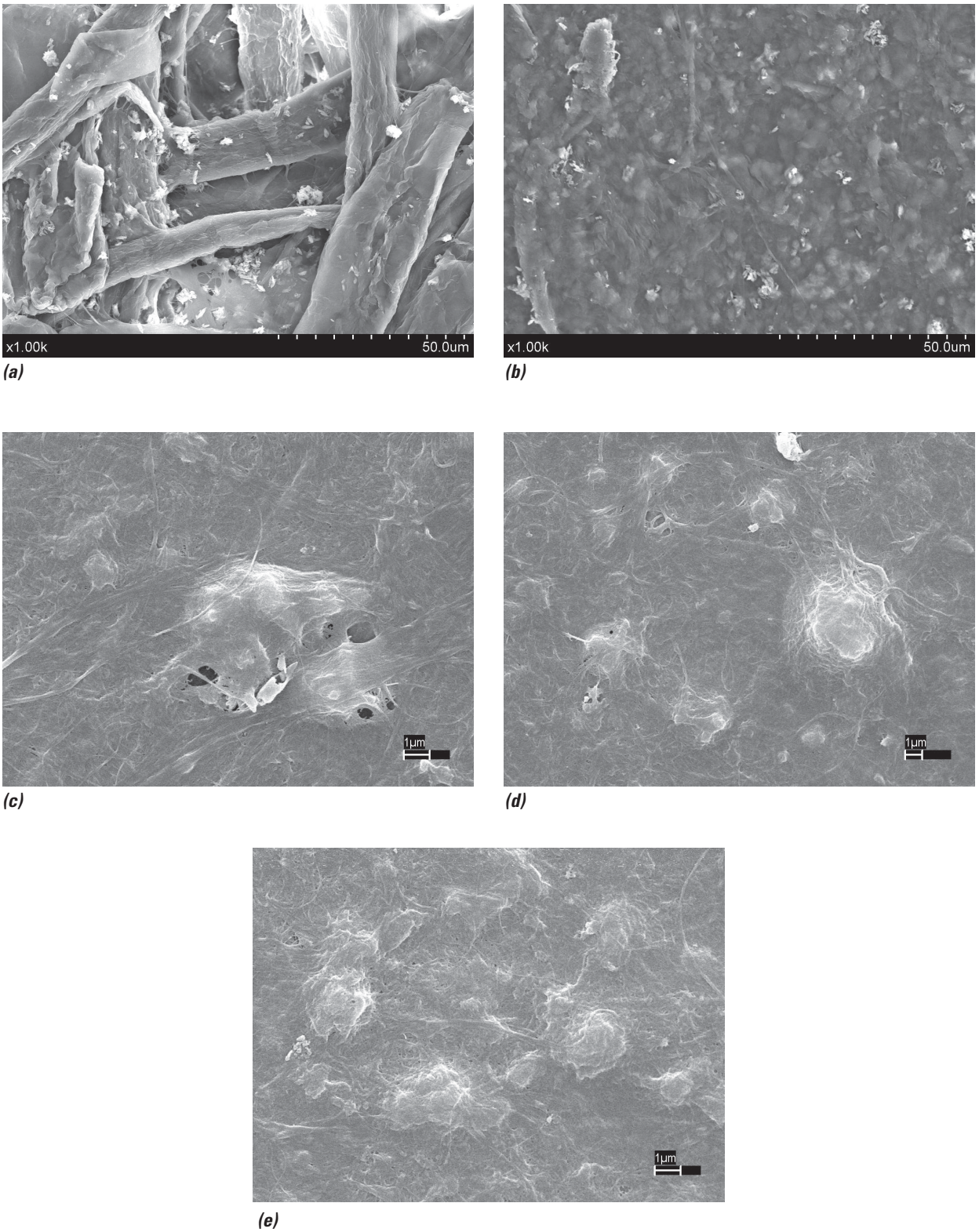
RESULTS AND DISCUSISON

Mechanical fibrillated MOP pulp

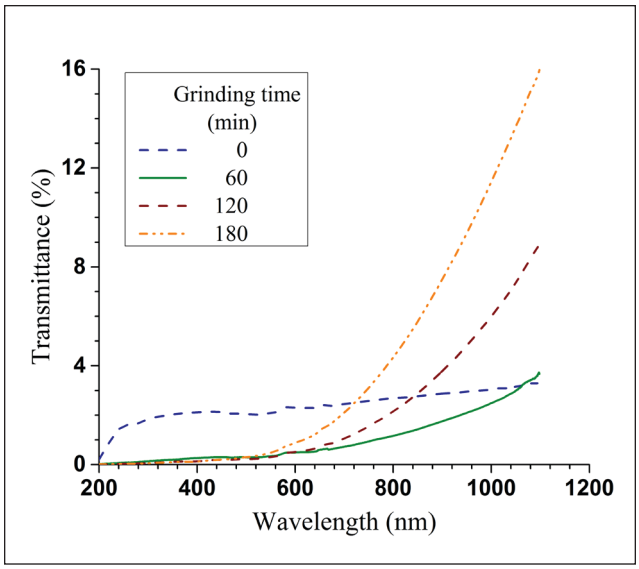
The average width of the MOP fibers was approximately 15 µm, with many carbonate particles and aggregates (1–7 µm) on their surfaces, as shown in **Fig 1**. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) was used to verify the presence of high concentration of calcium carbonate in the prepared MOP pulp.

Mixed office paper CNFs were also examined by SEM to observe morphological development during mechanical fibrillation by grinding. Fibers were broken up into fines or fibrils through 60 min of internal and external fibrillations [23,24] by mechanical shearing and compression. Some fibers were mildly fibrillated into micron size while others were highly fibrillated into submicron size and nanofibrils (Fig. 1). The fibrils and ground filler particles were well mixed together due to their interactions during grinding, and most filler particles were wrapped around by fibrils. Most particles appeared to be approximately 2 µm, suggesting grinding separated the filler particle aggregates. Further grinding resulted in more fragmentation and separation of microfibers [23]. Grinding to 180 min made no apparent variations in fibril-filler morphology as indicated by SEM imaging (Fig. 1).

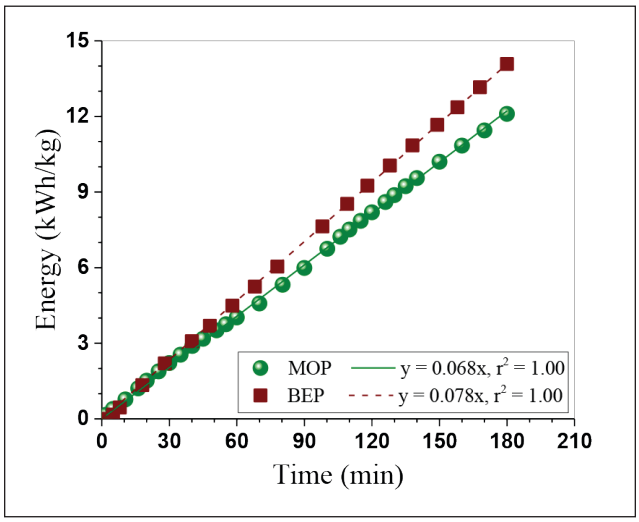
The light transmittances of the CNF slurries from different grinding duration are shown in **Fig 2**. Mixed office paper pulp suspension without mechanical fibrillation was easily flocculated despite extensive mixing. Settling of fibers was observed at the bottom of the cuvette. The sample was not well dispersed to make good measurements. The results shown in Fig. 2 were light transmittance above the settling region. The MOP CNFs were well dispersed and not optically transparent. The light transmittance of the CNF slurries with 60-min fibrillation was the lowest. The spectral transmittance of the CNF slurry was increased in the long wavelength range with grinding time, suggesting the reduction in fibril size. As expected, the highest light transmittance recorded was from the fibrils with 180-min fibrillation, despite no visible differences observed between 120-min and 180-min grinding from SEM imaging (Fig. 1). The low transmittances shown in Fig. 2 were also due to the ink and filler particles in the MOP CNF slurries.



1. Morphologies of mixed office paper (MOP) at different fibrillation times revealed by scanning electron microscope (SEM) imaging: (a) initial MOP fibers, scale (each division) = 5 µm; (b) 60 min, scale (each division) = 5 µm; (c) 60 min, scale = 1 µm; (d) 120 min, scale = 1 µm; and (e) 180 min, scale = 1 µm.



2. Spectral transmittance of nanofibrillated MOP fibril suspensions from different fibrillation times at 0.1% consistency.

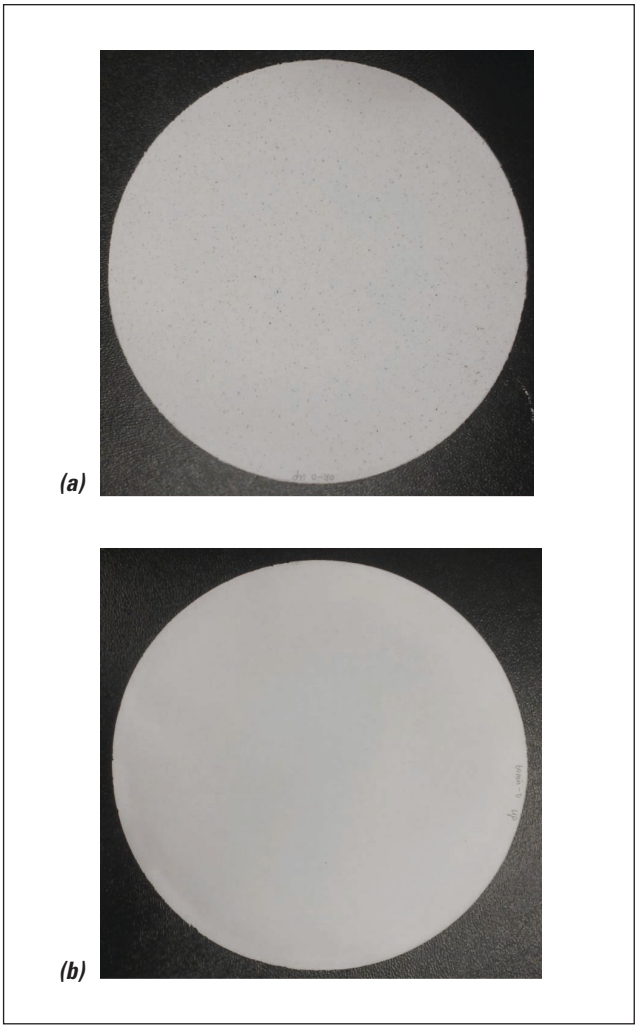


3. Time-dependent energy consumption for mechanical fibrillating MOP compared with that for fibrillating a bleached eucalyptus kraft pulp.

Energy inputs for fibrillation of MOP pulp were increased linearly with time (**Fig. 3**), in agreement with a previous study [23]. Energy consumption for grinding MOP was 2 kWh/kg or 17% lower than that consumed for fibrillating a bleached kraft eucalyptus pulp sample after 3 h. This perhaps was due to the presence of filler (18%) that effectively reduces the amount of fibers that tends to be more intensive than filler (carbonate) for breakup.

Visual appearance and structure of nanofiller-paper

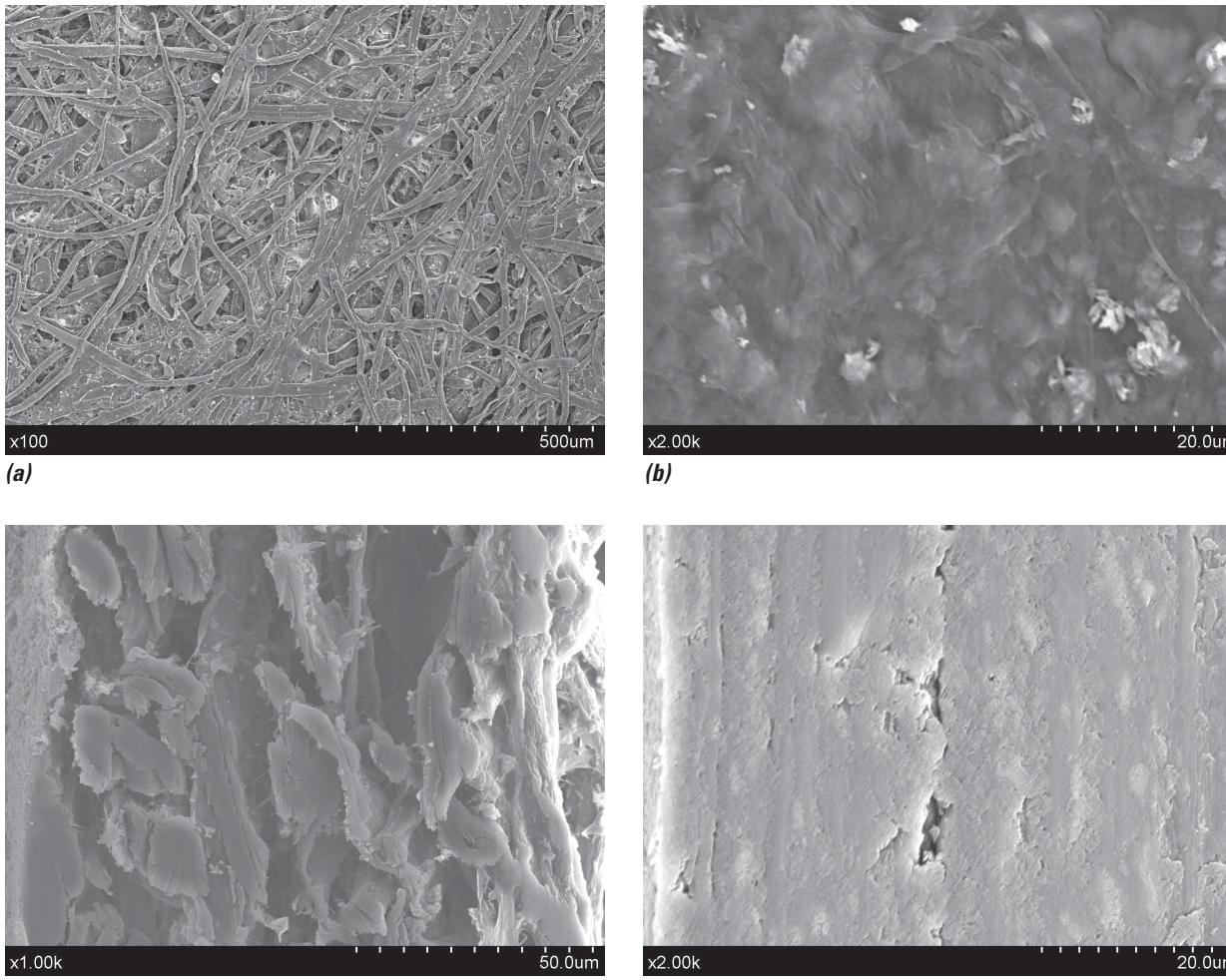
The visual appearance of a handsheet made from MOP pulp without grinding is shown in **Fig. 4**. A large amount of residual ink particles can be seen from the sheet surface as inks tends to be localized on paper coatings and fillers [25]. Mechanical



4. Visual images of sheets made from (a) unground MOP fibers, and (b) cellulose nanofibrils from 60-min mechanical grinding of MOP (sheet diameter = 16 cm).

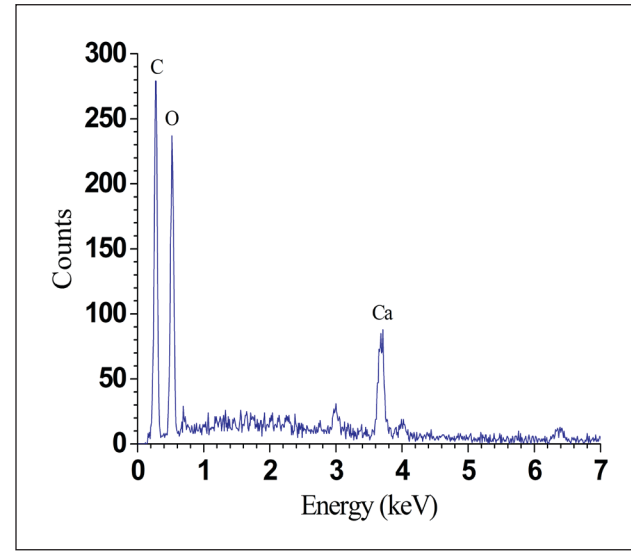
grinding not only fibrillated fibers into microfibrils or nanofibrils, but also fragmented ink and filler aggregates. The fragmented ink and filler particles were homogeneously dispersed into the fibril matrix. As a result, no obvious residual ink particles were observed in nanofiller-paper (Fig. 4). The size reduction of ink particles can also be verified by the reduction in optical brightness (ISO) from 80% of the sheet made of unfibrillated MOP pulp to 60% of the nanofiller-paper.

Scanning electron microscope images show differences in the surface morphology between the handsheet of unground MOP pulp and nanofiller-paper. Fibers with 15 µm diameter can be seen on the surface of the MOP pulp handsheet (**Fig. 5**). The filler particles appeared to be simply coated (i.e., sitting) on the fiber surfaces. Void spaces with sizes of approximately 10–100 µm were present. The nanofiller-paper showed a smooth surface with smaller void spaces (Fig. 5). The filler particles were wrapped by CNFs and well incorporated into the CNF matrix; that is, filler particles are not simply mixed with CNFs but are part of CNFs and cannot easily be separated.

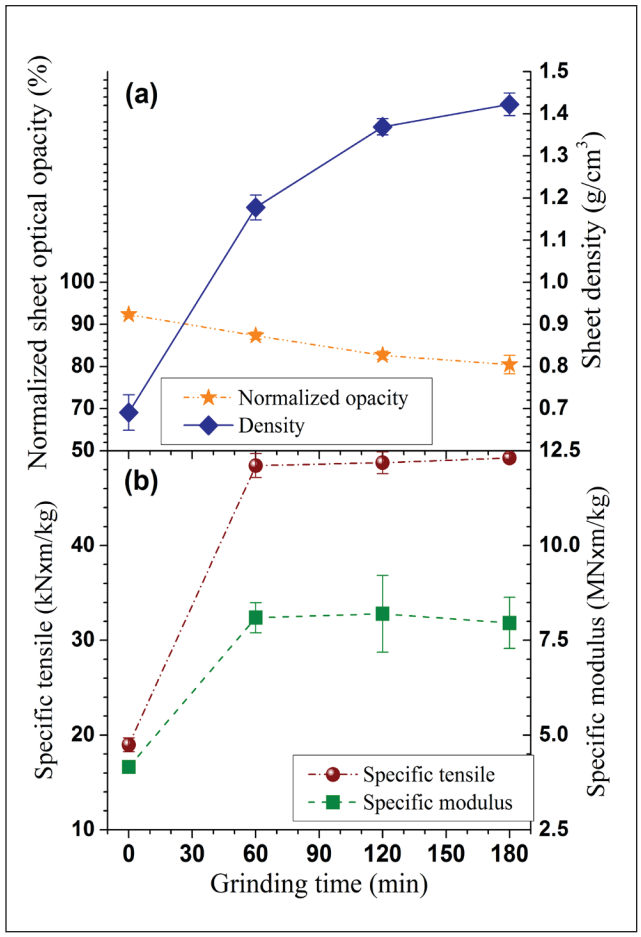


5. SEM images of the surface and cross-section of MOP handsheet and nanofiller-paper from 60-min grinding of MOP: (a) MOP handsheet surface; (b) nanofiller-paper surface; (c) cross-section of MOP handsheet; and (d) cross-section of nanofiller-paper.

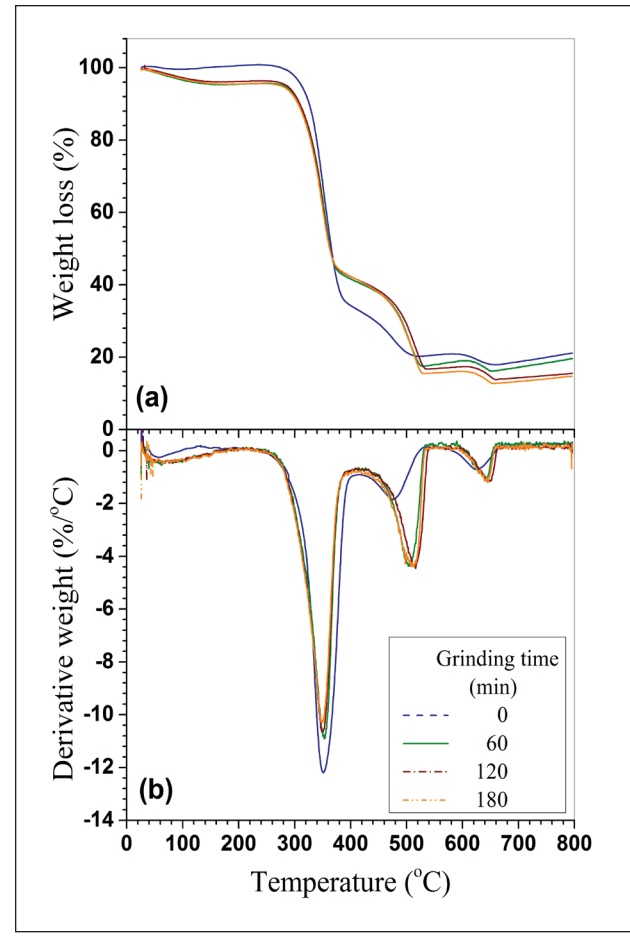
Scanning electron microscope images of the cross-sections of the handsheet of unground MOP pulp and nanofiller-paper further validated the observations from the surface SEM imaging. Simple mixing of inorganic particles with cellulose nanomaterials often produces a layered structure [17,26,27], which was also observed from the sheet made of MOP pulp in this study (Fig. 5). A lot of void spaces created by interfiber gaps were present in different layers, which resulted in a low sheet density. In contrast, mechanical grinding disintegrated fibers into nanofibrils without lumens that facilitated the incorporation of ground filler particles into the CNF matrix with much smaller voids (Fig. 5), which resulted in high sheet density. Energy dispersive X-ray spectroscopy verified the presence of calcium carbonate in the nanofiller-paper (**Fig. 6**).



6. Energy dispersive X-ray spectrum of the nanofiller-paper made of fibrillated MOP pulp.



7. Optical and mechanical properties of nanofiller-paper with different fibrillation times: (a) normalized sheet opacity (by sheet density) and sheet density, and (b) specific tensile strength and Young's modulus.



8. Thermal stabilities of nanofiller-papers from MOP pulp with different fibrillation times: (a) thermogravimetric analysis, and (b) derivative thermogravimetric curves.

Mechanical and optical properties

The handsheets made of unground MOP fibers had high opacity of over 90% primarily because of the void space in the sheet, as discussed in the previous section (Fig. 5). The densification of the sheet that reduced the void spaces due to improved incorporation of ground filler particles into the CNF matrix reduced the sheet opacity (**Fig. 7**). Furthermore, normalized (by density) sheet opacity was decreased with increased grinding time. However, the reduction in opacity is not significant after 120 min of grinding.

Sheet density was calculated by the measured weight, area, and thickness of the sheets. Mechanical fibrillation disintegrated fibers to result in fibrils without lumens (Fig. 5) and increased surface area, therefore improving the bonding. The improved incorporation of ground filler particles into the CNF matrix filled in interfibril void spaces (Fig. 5). Both improved bonding and incorporation of fillers increased sheet density (Fig. 7). The increase was most significant with 60-min grinding. The density of the nanofiller-paper with 180-min grinding was close to the density of cellulose (approximately 1.5 g/cm^3).

Specific tensile strength and specific tensile modulus of the nanofiller-paper were compared with those of the sheet made from the MOP fibers without grinding. The nanofiller-paper with 60-min grinding had specific tensile strengths and specific tensile modulus of 48.4 kN·m/kg and 8.1 MN·m/kg, respectively, compared with 19 kN·m/kg, and 4.1 MN·m/kg, respectively, of the sheet made of unground MOP fibers (Fig. 7). Filler loss was noticed during sheet forming based on TGA measurements, which may also contribute to increased tensile strength of the nanofiller-paper. The filler content of the MOP sheet made of unground fibers was 18%, same as that of the initial MOP. The filler content of the nanofiller-paper sheets made with 60-, 120-, and 180-min grinding were reduced to 16%, 14%, and 13%, respectively. However, the observed strength improvements can be primarily attributed to the improved fibril bonding as evidenced from the reduced void spaces (Fig. 5). No obvious improvement in mechanical strength was observed with continued grinding after 60 min, perhaps because further reduction of fibrils did not improve bonding (Fig. 7) while shortening of fibrils can reduce the sheet strength.

Thermal properties

Thermogravimetric analysis of nanofiller-paper was carried out as a measure of thermal stability and antiflammability. These properties are important for processing and for self-extinguishing packaging composites. The thermal degradation of nanofiller-paper involves the complex decomposition of organic and inorganic components from MOP. On the basis of weight loss as a function of temperature, the TGA curve of the sheet from unground MOP fibers can be divided into four regions (**Fig. 8**). The first mass loss stage in the range of 25°C to approximately 250°C was due to moisture loss through evaporation. The second stage occurred from 250°C to approximately 400°C with rapid mass loss. The third stage occurred from this point to 540°C where mass loss rate was decreased. The second and third mass loss stages are mainly attributed to the decomposition of cellulose in MOP fibers. The temperatures at the maximum degradation in each stage can be easily identified using the derivative thermogravimetric (DTG) curve (Fig. 8), i.e., 352°C and 505°C for stages 2 and 3, respectively. The weight losses for stages 2 and 3 were 66% and 14%, respectively. Different cellulose degradation mechanisms were proposed [28-30]. The last stage of mass loss from 540°C to the final testing temperature of 800°C corresponded to the degradation of calcium carbonate. The thermal degradation of calcium carbonate is well known and led to the formation of CaO, releasing carbon dioxide [31].

Similar trends were also observed for TGA curve of the nanofiller-paper with different grinding times (Fig. 8). The weight loss in the first stage was higher than the weight loss of the sheet made of unground MOP fibers, suggesting more moisture in the nanofiller-paper because of significantly increased fibril pore volume by mechanical nanofibrillation. A very similar sharp decrease in mass was also observed in the second stage. However, a relatively lower amount of mass loss in the first half of the third stage was observed, perhaps because of improved incorporation of ground calcium carbonate particles in the CNF matrix that enhanced thermal stability. The increased mass loss in the final stage compared with the mass loss of the sheet from unground MOP fibers suggests the reduction in the particle size of the filler particles facilitated the decomposition of calcium carbonate. Furthermore, the nanofiller-paper made with 180-min grinding showed the most mass loss (Fig. 8). Overall, however, grinding time had very limited effect on the TGA curves of nanofiller-paper, which indicates that further grinding longer than 60 min had limited effects on the structure and thermal decomposition of nanofiller-paper. This is consistent with the findings from the SEM analyses (Fig. 1). The DTG curves clearly show the temperature range of each mass loss stage (Fig. 8).

CONCLUSIONS

Mixed office paper with filler content of 18% was used to produce nanofiller-paper through mechanical grinding. The cogrinding of filler with cellulose fibers substantially improved the incorporation of filler into the cellulose nanofibril matrix; that is, the ground filler particles were wrapped around by cellulose nanofibrils rather than sitting on fiber surfaces when filler was simply mixed with CNFs. The nanofiller-paper made of this biopolymer matrix had substantially improved mechanical properties with a specific tensile strength and modulus of 48 kN·m/kg and 8 MN·m/kg, respectively, or increased by approximately 250% and 200%, respectively, over those of the sheet made of unground MOP pulp fibers. This improvement is mainly attributed to the improved bonding among cellulose fibrils and the improved incorporation of filler particles into the fibril matrix compared with interfiber bonding in conventional papers due to the presence of fibers lumens. The nanofiller-paper also exhibited good thermal stability. The study presented a potential avenue for use of waste paper for high value added products without deinking. **TJ**

ACKNOWLEDGEMENTS

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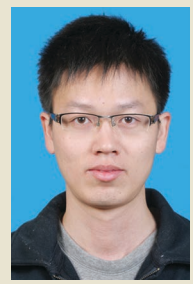

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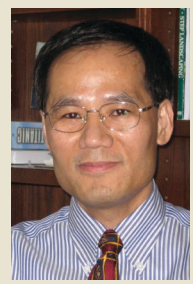

Zhu

High-value use of mixed office paper (MOP) can provide substantial economic return, and the secondary fiber is a sustainable resource. Our focus was on recovering and using secondary fibers for cellulose nanofibril (CNF) production with the incorporation of filler.

The laboratory study was relatively easy. However, practical issues such as dewatering and low-consistency grinding will need to be addressed in commercial settings. An interesting finding was that visible ink particles disappeared without deinking after grinding, and paper strength was substantially increased.

At mills, cogrinding of cellulose fibers with filler can compensate paper strength loss due to filler application. This practice can increase filler loading to reduce fiber usage in papermaking. The next step would be to conduct large-scale runs using either MOP or adding filler into virgin pulp.

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