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ORIGINAL

Characteristics of microfibrillated cellulosic fibers and paper sheets from Korean white pine

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Abstract Microfibrillated cellulosic fibrous product was successfully obtained from Korean white pine (*Pinus koraiensis* Sieb. et Zucc.) by using two alternative pretreatments (steam and ozone treatments) followed by disk milling (DM). The steam and ozone treatments were effective in extracting some of the hemicelluloses and degrading lignin, respectively, with both types of treatment resulting in the improvement of mechanical fibrillation as a result of loosening of the cell wall structure. The obtained products showed nanoscopic fibrous morphology even though hemicelluloses and lignin components remained. The specific surface area and filtration time were increased using the DM treatment after both treatments, and the values increased further with longer periods of DM. The paper sheets of the fibrillated products after both the alternative treatments had higher tensile properties at the same DM time scale than the sheets of the products obtained without treatment. Tensile strength was further increased by increasing sheet density showing the highest tensile strength and modulus of 125 MPa and 20 GPa, respectively.

Introduction

From the perspective of green growth, the research and development of eco-friendly materials are increasingly focused on utilizing forest products with the awareness of

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consumers and engineers for sustainability in the use of materials. In this context, recent research trends in forest product society have been mainly related to the production of cellulose nanofibers with economic feasibility and its applications for nanocomposite materials (Eichhorn et al. 2010; Medeiros et al. 2008). Cellulose nanofibers have extremely strong mechanical properties, for example, a Young's modulus of 130–140 GPa and tensile strength of 10 GPa, and a wide range of aspect ratios (Eichhorn et al. 2010; Samir et al. 2005). These properties are known to be stronger than glass, carbon, and aramid fibers, which are well-known high-strength fibers. A large number of preparation methods for cellulose nanofibers have been developed thus far, for example, mechanical treatments such as refiner and high-pressure homogenizer, and the combined method with chemical treatments such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation and acidified sodium chlorite-based delignification. (Chakraborty et al. 2005; Isogai et al. 2011; Jang et al. 2011; Kondo 2005; Taniguchi and Okamura 1998; Yano et al. 2005). Abe et al. (2007) introduced a method to prepare cellulose nanofibers with a uniform width of 15 nm from radiata pine by using disk milling after leaching hemicelluloses with 6 wt% potassium hydroxide and delignification with acidified sodium chlorite solution. The sample was kept in a water-swollen state, after the removal of the matrix polymers, to avoid the generation of hydrogen bonding between the microfibril bundles after the removal of the matrix. Research activities on TEMPO-oxidized cellulose nanofibers have been recently reviewed by Isogai et al. (2011). Individual cellulose microfibril can be easily separated by gentle mechanical treatment due to electrostatic and/or osmotic effects of C6 carboxylate groups of cellulose. The paper sheets from oxidized nanofibers are transparent and flexible with high tensile strength of 200–300 MPa and elastic moduli of 6–7 GPa. Hassan et al. (2010) reported the methods using dilute hydrochloric acid, dilute sodium hydroxide, cellulase or xylanase as a pretreatment to improve mechanical treatment. The effect of the pretreatment of bagasse pulp on the properties of isolated nanofibers and nanopaper sheets was investigated. The diameter of the obtained microfibrils was in the range of 7–30 nm; however, larger microfibrillar bands (up to 90 nm wide) were also observed in the pretreated pulps. Chang et al. (2012) also introduced a new approach to prepare lignocellulose microfibrils from bamboo fiber by using a combination of hot-compressed water treatment and mechanical disk milling (DM). Hot-compressed water treatment was effective at partially removing hemicelluloses, resulting in the loosening of the cell wall structure, thus enhancing subsequent fibrillation by DM.

In this study, the preparation method reported by Chang et al. (2012) was adopted, and in addition to HCW treatment, ozone treatment was also used as a pretreatment to remove lignin and loosen the cell wall structure. The ozone treatment is a well-known bleaching process in pulp and paper industry to remove mainly lignin. Ozone can react quite selectively with carbon–carbon double bonds in lignin (Kratzl et al. 1976; Sugimoto et al. 2009), but it can also react with carbohydrates by causing the cleavage of glycosidic linkages and by oxidizing alcohol groups to carbonyl groups and terminal aldehyde groups to carboxyl groups (Lemeune et al. 2004; Sakai and Uprichard 1991; Zhang et al. 1997). Even though ozonation may cause a reduction in the degree of polymerization of cellulose, delignification is expected to loosen the cell wall structure, resulting in the improvement of mechanical fibrillation. With this method, the fibrillated product will contain cellulose microfibrils as well as part of hemicelluloses and lignin, which remain after using HCW or ozone pretreatments. The objective of this paper is to investigate the mechanical properties of the paper sheets from microfibrillated cellulosic products with parts of hemicelluloses and lignin and to compare the properties of fibrillated products obtained with and without the two alternative treatments.

Experimental

Material

Korean white pine (*Pinus koraiensis* Sieb. et Zucc.) was obtained from the Research Forest of Kangwon National University in Korea and cutter-milled to 0.2 mm in size. Sodium chlorite ($NaClO_2$) and other chemicals used in this study were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan).

Steam and ozone treatments

Steam treatment (ST) was performed at 150 °C for 2 h by using an autoclave (MC-3032S, ALP Ltd, Japan). Eighty grams of wood powder was mixed with ten times the amount of water and kept at room temperature for 2 days before treatment. The steam-treated product was filtered to remove the water-soluble fraction, the amount of which was measured after evaporation and subsequent oven-drying.

Ozone treatment (OT) was conducted in a round flask at 40 °C for 3 h, with an oxygen flow of 0.5 L/min and ozone concentration of 204 g/m^3, which was generated from an ozone generator (D-DG-R5, Ecod Design Ltd., Japan). Sample moisture content was adjusted to 60 %. During OT, the color of the reactant became whiter indicating the ozonation effect on the lignin molecules. The pH of the treated samples decreased from 4.5 to 2.0, with several washes with water being required prior to mechanical grinding to avoid further degradation during the grinding treatment. The amount of the water-soluble fraction was also measured, and the amount of ozone consumption was found to be 9.77 wt% (based on the original wood weight).

Chemical composition

The chemical composition of Korean white pine was determined using the following methods. Holocellulose content was determined as the $NaClO_2$-delignified residue. A 0.5-g sample of the extracted sample was repeatedly (four times) treated with 0.2 g of $NaClO_2$ in 30 mL of 7.5 % acetic acid solution at 80 °C for 1 h. The delignified product, holocellulose, was filtered, washed with distilled water several times, vacuum-dried at 40 °C for 24 h, and weighed. The α-cellulose content was determined as the amount of insoluble residue in 17.5 % of NaOH aqueous solution. First, 5 mL of 17.5 % NaOH and 0.2-g sample of holocellulose were homogenized in a flask. After adding 5 mL of distilled water, the residue was filtered. Five milliliters of 10 % acetic acid solution was then added, filtered again, and washed with distilled water several times. After vacuum-drying the sample at 40 °C for 24 h, the α-cellulose residue was calculated. Klason lignin content was determined as the amount of insoluble residue in 72 % of aqueous sulfuric acid solution. First, 72 % of sulfuric acid solution was added to a 0.2-g sample extracted with EtOH: toluene solution. The mixture was then stirred at room temperature for 4 h. Subsequently, 112 mL of distilled water was added and refluxed for 4 h. The resultant product was filtered, washed with distilled water, dried at 105 °C for 24 h in vacuum, and weighed.

Mechanical grinding

The obtained filtered products were diluted in 2 % water suspension and subjected to DM (Supermasscolloider MKCA6-2, Masuko Sangyo, Japan). The rotational speed was set at 1,800 rpm, and the operation was repeated five times. The clearance between two disks was reduced to 20 μm, from the zero position at which the disks begin to rub. The milling time was calculated on the basis of the weight of the dried wood inserted into the mill. The energy consumption of each operation was calculated using the voltage, current, and operation time values.

Paper sheet preparation and measurements

The fibrillated product was diluted to a 0.5 wt% suspension (128 ml) and stirred for 10 min, followed by ultrasonication for 30 s to insure well-dispersed fibrillated products. The paper sheets were prepared by vacuum filtration with a polytetrafluoroethylene membrane filter (pore size, 0.2 um). The filtration time was measured at this stage, as a criterion of the degree of fibrillation. The obtained wet sheet was hot-pressed between two silicone-coated sheets of filter paper at 105 °C for 30 s at 50 Mpa pressure and then for 60 s at 150 Mpa pressure. The pressed sheets were further vacuum-dried at 40 °C for 24 h and kept for more than 1 day at a temperature of 23 °C and 50 % relative humidity before conducting the tensile test. Three dog-bone samples (5 $\text{mm}^3 \times 0.4\ \text{mm}^3 \times 50\ \text{mm}^3$) were cut from the sheets, and the tensile test was conducted using a Shimadzu Autograph (AG-1, 5kN load cell, Shimadzu Ltd, Japan), with a cross-head speed of 5 mm/min, according to JIS K7127. The morphological characteristics were observed using a field emission scanning electron microscope (SEM) (S-4800, Hitachi Co., Ltd., Japan). The fibrillated products were diluted to a 0.001 wt% suspension and then vacuum-filtered. The obtained product was immersed in ethanol for 30 min and transferred into *t*-butyl alcohol for 2 h, followed by freeze-drying for 24 h. For SEM observation, the samples were coated with a 1-nm-thick layer of osmium by using an osmium plasma coater (NEOC-AN, Meiwa Fosis, Tokyo, Japan). To measure the specific surface area (SSA), the wet fibrillated product was washed several times with *t*-butyl alcohol to remove water and then freeze-dried. The measurement was performed using BELSORP 18 (Bel Japan INC. Osaka, Japan), and the SSA was obtained by multi-point analysis of nitrogen gas adsorption–desorption isotherms at

77 K. The density of the paper sheets was measured using a gas pycnometer (AccuPycII 1340, Micromeritics Ltd., Japan). The sample was placed in the sample cell (capacity, 10 cm^3), and the volume was measured using a helium gas displacement technique via a series of degassing and pressurization cycles. The sample density was automatically calculated by the equipment software by using the cycle-based displacement volume and sample mass values.

Results and discussion

The changes in the amount of water-soluble fraction and chemical composition after the two alternative pretreatments, that is, steam treatment (ST) and ozone treatment (OT), are summarized in Table 1. The amount of water-soluble fraction was found to be 13.7 and 26.0 wt% for ST and OT, respectively, showing the partial degradation of the wood components. After ST, the product had more lignin content, indicating greater degradation of hemicelluloses. Hydrothermal treatment is a well-known process for the extraction of the hemicelluloses component of lignocellulosic materials. The acetyl groups of hemicelluloses and water itself in this treatment act as an acidic catalyst that facilitates the degradation of hemicelluloses (Ando et al. 2000). Previous studies that used eucalyptus wood and bamboo fiber found that the partial removal of hemicelluloses and lignin by hydrothermal treatment might result in a porous structure of the cell wall that loosens the cell wall morphology, thus facilitating mechanical fibrillation (Chang et al. 2012; Lee et al. 2010). In the current study, a pressure lower than that used in the previous two studies was used; however, the amount of water-soluble fraction was comparable. In contrast, the product after OT contained less lignin because of the strong delignification effect of ozonation. Ozone may react quite selectively with the carbon–carbon double bonds in lignin, most of which exist in the S2 layer between wood fibers. However, because of poor selectivity due to the formation of a large number of hydroxyl radicals, ozone may also react with carbohydrates. This may occur through the cleavage of glycosidic linkages, the oxidization of alcohol groups to carbonyl groups, and/or the oxidization of terminal aldehyde groups to carboxyl groups (Kaneko et al. 1983; Kratzl et al. 1976; Roncero et al. 2003; Sugimoto et al. 2009). Hence, a quantity of the carbohydrate, mainly hemicelluloses, was degraded by OT, as shown in Table 1.

Table 1 Amount of water-soluble fraction and chemical composition of the raw material and products after steam and ozone treatments

	Water-soluble fraction (wt%)[a]	Cellulose (wt%)	Hemicelluloses (wt%)	Lignin (wt%)
Raw material	–	57.2	25.5	26.5
Steam-treated product	13.7	64.8	10.0	33.2
Ozone-treated product	26.0	77.2	15.7	11.1

[a] Based on dried original wood weight

In general, most of the technologies used to isolate nanofibers from the lignocellulosic cell wall have used chemical or enzyme pretreatments prior to mechanical fibrillation to enhance the effect of fibrillation and reduce energy consumption (Hassan et al. 2010; Isogai et al. 2011; Saito et al. 2006; Wang and Sain 2007; Zuluaga et al. 2009). For example, Dufresne et al. (1997, 2000) used an alkaline treatment to isolate nanofibers from sugar beet and potato tuber cells. In addition, Hassan et al. (2010) reported the use of enzyme pretreatment before mechanical grinding and the use of high-pressure homogenization to isolate nanofiber from bagasse pulp.

In this study, ST and OT were used as alternative pretreatment techniques to improve the effect of fibrillation by DM. Figure 1 shows the effect of the DM time used for the nontreated product and treated product (both techniques) on power consumption during the operation. The energy consumption was calculated from the voltage, current, and operational time during the DM process.

To investigate the effect of the two alternative treatments on DM performance, filtration time and surface area were measured as the criteria for fibrillation degree and presented in Figs. 2 and 3, respectively. The filtration time of the fibrillated product after the two treatments was longer than that without treatment when using the same DM time, as shown in Fig. 2. This result indicated that fibrillation was improved by the two treatments. This outcome may be because the filtration of water in finer cellulose fibers takes longer because of its strong hydrophilicity and high surface area. Chang et al. (2012) reported similar results in a study by using bamboo fiber. The two treatments also increased specific surface area (SSA), as shown in Fig. 3. The SSA of the bamboo nanofiber obtained by DM after hydrothermal treatment at high pressure was reported to be 108.84 and 111.95 m^2/g, with a DM time of 139 and 274 min/kg, respectively (Chang et al. 2012). Moreover, 97 m^2/g of SSA was reported for bacterial cellulose by Ougiya et al. (1998). These values are comparable to those obtained in this study.

Fig. 1 Relationship of power consumption for DM operation versus DM time

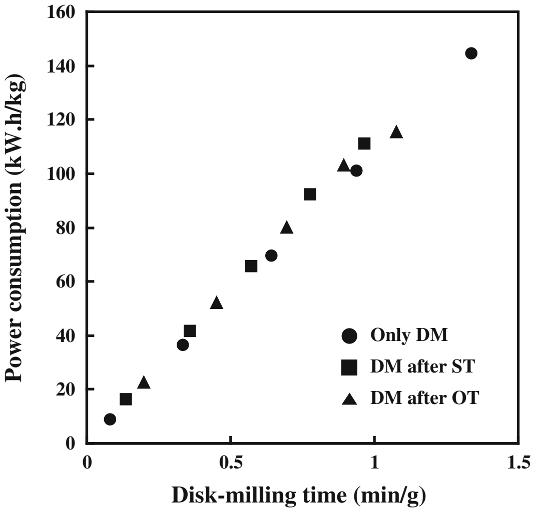


Fig. 2 Effect of DM time on the filtration time of the fibrillated product

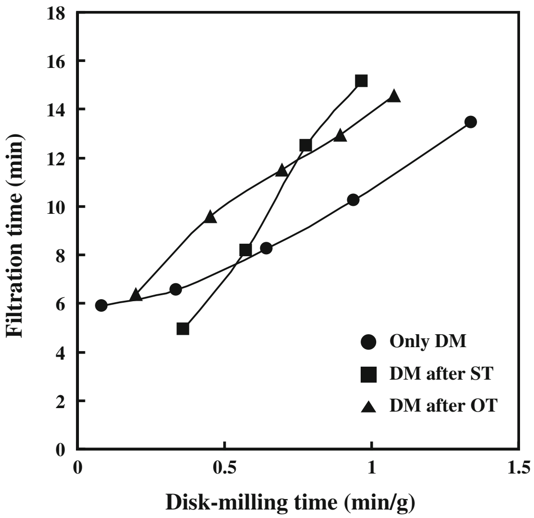


Fig. 3 Effect of DM time on the specific surface area of the fibrillated product

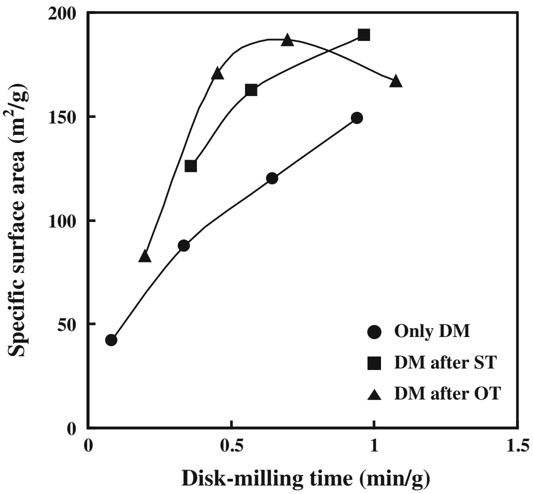


Figure 4 shows the morphology of the fibrillated products obtained from the original wood versus steam and ozone-treated products. It was found that the DM time required after using the two treatments was shorter than the time required to fibrillate the original wood to the same morphological scale. Both treated and untreated fibrillated products exhibited very fine morphology. In general, cellulose microfibrils exist as aggregates of nanosized elementary fibrils with a diameter of 3-5 nm in the cell wall of lignocellulosic materials. The size of elementary microfibrils depends on their origin (Awano et al. 2000; Schopfer 2006), and the diameter of these cellulose microfibril aggregates ranges from 12 to 16 nm (Klemm et al. 2005). Therefore, fibers with diameters obtained in the study are considered large microfibril aggregates that are bonded by matrix polymers, lignin, and

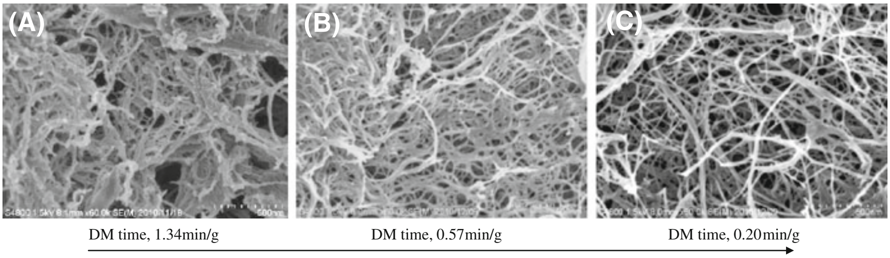


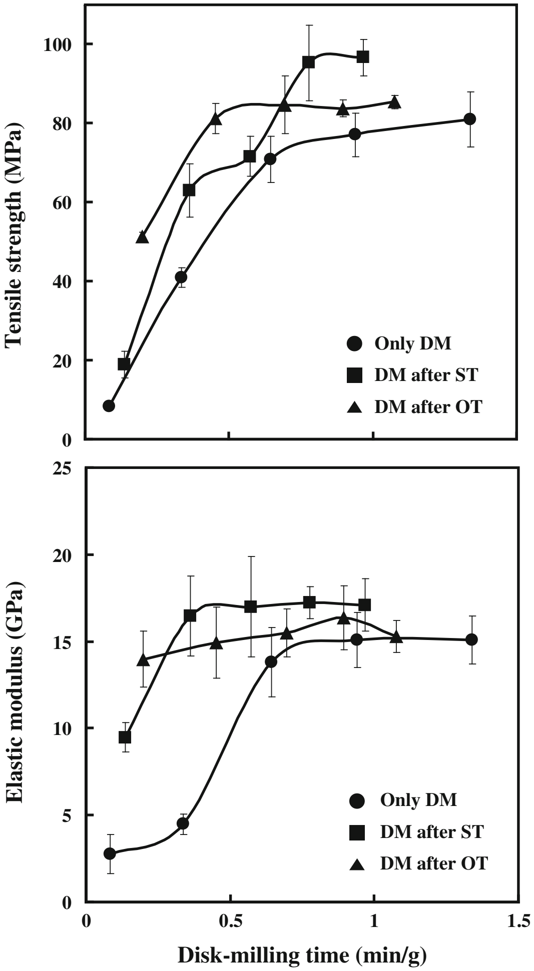
Fig. 4 Morphology of the fibrillated products from the original wood powder (**a**), steam (**b**), and ozone-treated (**c**) products

hemicelluloses. Even though the partial removal of matrix polymers by using the two treatments seemed to make it difficult to obtain uniform cellulose nanofibers, both treatments were still effective at improving the outcome of mechanical fibrillation.

The paper sheet was prepared by vacuum filtration of the fibrillated product. Figure 5 shows the effect of DM time on the tensile properties of the sheets. Tensile properties are expected to be mainly dependent on the degree of fibrillation, as well as the degree of polymerization (DP) of cellulose and hydrogen-bonding strength between the fibrils. In this study, the fibrillated product contained cellulose fibrils, in addition to matrix polymers, after ST or OT. Therefore, the effect of the chemical composition must be considered. The tensile strength and elastic modulus were significantly increased in all sheets with increasing DM time; this was due to an increase in the degree of fibrillation with DM time. The tensile strength of sheets obtained following treatment (ST or OT) was higher than that of untreated sheets for the whole range of DM time investigated in this study. In part, the higher tensile strength of the treated sheets was attributable to higher cellulose content, as shown in Table 1. The highest tensile strength was found to be 96.7 MPa at 0.97 min/g of DM time in sheets obtained from the ST fibrillated product.

The elastic modulus of sheets treated by OT was lower than that of sheets treated with ST. This is because OT was able to react with cellulose to decrease DP (Eriksson and Reitberger 1995; Gratzl 1992; Zhang et al. 1997); hence, this decrease might result in a lower modulus of the sheets. However, it should be kept in mind that it was difficult to measure the DP of cellulose in this study because of the complex chemical composition of the product with lignin and hemicelluloses. Lemeune et al. (2004) investigated the effects of ozone on the decrease in cellulose DP. The authors described that the ozonation of cellulose fibers resulted in a substantial reduction in cellulose DP. At an ozone charge of approximately 3 wt%, a 40 % reduction in DP was obtained, which was measured using cupriethylenediamine viscosity. This amount of ozone charge is less than three times the ozone charge obtained in this study (9.77 wt%), even though the authors used a fully bleached commercial hardwood kraft pulp. Despite the higher lignin content of the raw wood sample used in this study, a larger amount of ozone treatment might cause a decrease in cellulose DP, resulting in a decrease in the modulus.

Fig. 5 Tensile strength and elastic modulus of the sheets from the fibrillated product with different DM times



Hassan et al. (2010) reported the effect of different pretreatments (i.e., before the grinding process) of bagasse pulps on the tensile strength and modulus of nanopaper sheets made from isolated nanofibers. A tensile strength and modulus of 99.9–110.2 MPa and 5.6–6.1 GPa were obtained, respectively, for nanopaper sheets of nonpretreated pulp after 10–30 grinding passes. In contrast, a tensile strength and modulus of 80.7–138.2 MPa and 5.35–6.18 GPa, respectively, were obtained from the sheets of pulp pretreated with alkali and acid treatments. Although there was no information on the grinding time, tensile strength was comparable to the results obtained for DM times ranging from 0.6 to 1.34 min/g in the current study, whereas modulus values were less than twice that obtained here.

To further increase the tensile properties of the sheets, sheets of higher density were prepared by increasing the pressure of hot-pressing. Figure 6 shows the effect of sheet density on tensile strength and modulus. The obtained density of the nanopaper sheets ranged from 1,185 to 1,430 kg/cm^3, depending on the pressing pressure. In the published literature, the true density of a perfect cellulose crystal has been reported to be 1,582 and 1,599 kg/cm^3 for alpha and beta polymorphs, respectively (Kibbe 2000; Sugiyama et al. 1991), while that of microcrystalline cellulose was reported to be 1,512 kg/cm^3 (Sun 2005). Because the native cellulose of the lignocellulosic materials is a mixture of alpha and beta cellulose (VanderHart and Atalla 1984), the true density of 100 % crystalline natural cellulose is expected to be between 1,582 and 1,599 kg/cm^3. Ehrnrooth (1984) reported that the density of lignin and hemicelluloses of Asplund spruce in situ was 1,397 and 1,520 kg/m^3, respectively, assuming a density of 1,559 kg/m^3 for cellulose. Terashima et al. (2009) reported that the density of cellulose microfibril bundles, with hemicelluloses–lignin modules in the middle layer of the secondary wall of ginkgo tracheid cells, was approximately 1,450 kg/m^3. In the current study, when considering the chemical composition in the fibrillated product after ozone treatment (shown in Table 1), the obtained value of sheet density was lower than the reported true density; however, the highest value for sheet density obtained in this study (1,430 kg/m^3) was comparable to the value reported by Terashima et al. (2009).

As shown in Fig. 6, tensile strength and modulus of the fibrillated product obtained after ozone treatment for 3 h followed by DM (1.07 min/g) increased with increasing density. In particular, tensile strength was noticeably higher when the density was increased to more than 1,350 kg/cm^3. The product used for sheet preparation was subject to a long period of DM fibrillation (1.07 min/g) after partial delignification by OT; this led to fine nanoscopic morphology of the resultant product. The finer morphology may lead to the sheet being denser. Sun (2005) investigated the relationship between the density and tensile properties of sheets using microcrystalline cellulose. It was found that tensile strength significantly increased as density increased from 1,000 to 1,450 kg/cm^3 and then leveled off above 1,450 kg/cm^3. Henriksson et al. (2008) also investigated the effect of density on the tensile properties of nanopaper sheets prepared from softwood dissolving pulp. The density of the sheets from microfibrillated cellulose fibers was adjusted by drying the sheets from less polar solvents by using a solvent exchange process. It

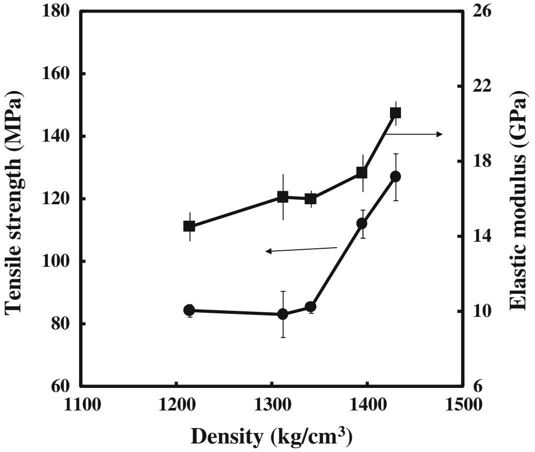


Fig. 6 Effect of sheet density on tensile strength and elastic modulus

was found that the specific modulus of porous networks of cellulose microfibrils increased with density. The authors explained that this phenomenon might be due to an increase in the hydrogen-bonding density of interfibrils in the more dense networks. The authors reported a tensile strength and modulus of 159–214 MPa and 10.4–13.7 GPa, respectively, depending on sheet density and cellulose DP. Comparing these values, in the current study, the highest tensile strength of 127 Mpa was lower; however, when also considering the chemical composition of the fibrillated product obtained in this study, the highest tensile strength of 127 Mpa and modulus more than 20 Gpa are comparable to previously reported values.

Conclusion

The aim of this study was to improve the efficiency of mechanical fibrillation of Korean white pine by using two alternative pretreatments, ST and OT. Both treatments were effective at loosening the cell wall structure and removing a quantity of hemicelluloses and lignin. The specific surface area and filtration time was increased by the two treatments and was further increased with longer DM periods. Furthermore, longer DM time was necessary to fibrillate nontreated samples to obtain the same morphology as the treated samples. When using a DM time of more than 0.57 and 0.20 min/g for ST and OT, respectively, most of the fiber diameter and length could be reduced to less than 20 nm and more than 1 μm, respectively. The tensile properties of the sheets from the fibrillated product after both treatments produced higher values than the nontreated product when using the same DM time scale. The highest tensile strength and modulus of 125 MPa and 20 GPa, respectively, were achieved in the paper sheet by OT by increasing sheet density, with these values being considered high, despite the fibrillated product containing some matrix polymers.

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