Physical Properties of Pulp and Paper: A Comparison of Forming Procedures

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Abstract

In this work, we used the conventional wet papermaking process and the solution casting procedure to make paper sheets and optimized the relative content of eucalyptus and Simao pine pulps using the mechanical properties of the paper sheet as the evaluation index. The chemical composition, water retention value, zeta potential, carboxyl content, and drainage behavior of the pulp created using the optimal mass ratio for each method were measured, and the resulting paper sheets were characterized via Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and nitrogen adsorption/desorption isotherms. We found that for a ratio of eucalyptus to Simao pine pulps of 94:6 using the wet papermaking process, the mechanical properties of sheets took their optimal values, and the tear, tensile, and burst indexes and the folding endurance were equal to 4.43 $mN \cdot m^2 \cdot g^{-1}$, 27.47 $N \cdot m \cdot g^{-1}$, 1.13 $kPa \cdot m^2 \cdot g^{-1}$, and 11.38 times, respectively, whereas the ratio leading to the best possible mechanical performance in the solution casting process was 88:12, and the corresponding paper sheets had tear, tensile, and burst indexes and the folding endurance of 11.73 $mN \cdot m^2 \cdot g^{-1}$, 23.03 $N \cdot m \cdot g^{-1}$, 0.68 $kPa \cdot m^2 \cdot g^{-1}$, and 25.50 times, respectively. The cellulose, hemicellulose, and lignin contents of the pulp treated by the solution casting method were lower by 1.88, 3.11, and 2.67 percent, respectively, compared to that obtained via the wet papermaking process. However, the water retention value, zeta potential, and carboxyl content of the pulp obtained via solution casting were higher by 50.31, 123.41, and 50.15, percent, respectively, compared to that obtained via the wet papermaking process. The drainage time obtained via the solution casting method was one-fifth of that obtained via the wet forming process. The paper sheet prepared via the solution casting method was found to exhibit weaker hydrogen bonding, a decreased level of crystallinity (26.64% lower), and an increased compactness and N_2 gas adsorption capacity (19.55% and 66.7% higher, respectively) compared to the sheet obtained via the wet papermaking process. This work shows that the physical properties of the paper prepared via the two processes considered here, using their respective optimal weight ratios of the different types of pulp, have their own advantages.

In order to improve the mechanical properties of paper sheets, the pulp fibers that are to be manufactured into paper are pretreated using physical and/or chemical methods. Beating (or refining) is one of the most common physical means of fiber pretreatment. Via beating or refining, the fiber can be split to improve the swelling capacity of the pulp fibers and enhance the fiber–fiber bonding properties, which improves the mechanical properties of the paper (Garcia et al. 2002, Seo et al. 2002, Nazhad 2004). Biological methods also effectively alter the properties of pulp fibers, including drainage characteristics, softness, fiber strength, and the degree of hornification, through enhancing the fiber–fiber bonding properties (Bhardwaj et al. 1996, Pastor et al. 2001, Wolfaardt 2003, Zhang et al. 2008, Bajpai 2010). Chemical treatment methods, especially those utilizing NaOH aqueous solutions, are another more effective and rapid way to change the fiber bonding properties and fiber strength through rapidly inducing significant lateral swelling of the fiber (Jie Cai et al. 2015). Freeland and Hrutfiord (1994) treated different recycled fibers with a NaOH solution; the short span compression index of the old corrugated containers, the linerboard, and the medium that were created from fibers

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subject to this treatment were found to increase by 10.6, 20.4, and 11.3 percent, respectively. Gurnagul (1995) also used a NaOH aqueous solution to treat a thermomechanical pulp as well as bleached and unbleached unbeaten low-yield kraft pulps; the increase in the swelling of the thermomechanical pulp fibers was found to be mirrored by the increase in the handsheet strength, but no correlation was found between the level of fiber swelling and handsheet strength in the case of the kraft pulps. Zanuttini et al. (2009) employed alkaline treatments on unbleached recycled softwood kraft pulp; it was found in this work that the alkaline treatment reduced the freeness of the pulp but improved the papermaking properties: the tensile strength and short column compressive strength were found to be enhanced by more than 50 and 5 percent, respectively, by this treatment.

Jie Cai (2005) reported that a NaOH/urea aqueous solution precooled to −13°C could quickly dissolve cotton linter pulps (α-cellulose content > 95%) with a polymerization degree of less than 700. It has also been reported that dissolved cellulose can be regenerated via hydrogen bond reconstruction in many systems, including water, inorganic salt solution, and organic solution systems (Zhang et al. 2005). In previous work (Miao et al. 2018), unbleached eucalyptus hardwood kraft pulp was treated in a NaOH/urea aqueous solution that was precooled to −13°C and reconstructed via hydrogen bonding in a 5 wt% H_2SO_4/5 wt% Na_2SO_4 solution; it was found not only that an amount of cellulose film filled among the fiber network but also that each fiber could plump completely; thereby, the water retention capacity of the pulp and the mechanical properties of the resultant paper were significantly improved. However, in the process whereby the pulp was disintegrated into individual fibers, a large quantity of fine cellulose film was generated, and these films were removed in the white water used in the conventional papermaking process, resulting in a large amount of fiber losses and an increased cost of wastewater treatment. It can thus be concluded that fibers treated with a NaOH/urea aqueous solution precooled to −13°C are not suitable for use in the conventional papermaking procedure, but the solution casting method should be selected to form sheets via the self-assembly of fibers in the cellulose solution alongside solvent evaporation, which induces a phase separation for hydrogen bond reconstruction and sheet curing and avoids the fiber losses and whitewater treatment problems. In another study, the optimal process (fixing the ratio of NaOH to urea, solution precooled temperature, and regeneration system) involving a NaOH/urea aqueous solution was investigated; this process did not produce cellulose films but instead significantly swelled the fibers (Miao et al. 2019). The pulp fibers used in both the above works (Miao et al. 2018, 2019) were unbleached eucalyptus kraft pulp fiber. Pulp fibers come from different plants, and their morphological properties and chemical composition can vary significantly; the mechanical properties of the resulting paper produced from these pulp fibers can also vary significantly (Wangaard and Williams 1970, Wangaard and Woodson 1972, Kiaei and Samariha 2011). How the length and strength of fibers obtained from different plants influence the properties of pulp handsheets has been discussed by many authors. Numerous inconsistencies in experimental findings have also been reported.

Morais et al. (2019) reported that the eucalyptus pulp with high coarseness and deformations, low fines content, and low pentosan content is more suitable for making high-softness tissue paper. Wangaard and Woodson (1973) reported that for a given sheet density, both fiber strength and fiber length have a positive correlation with both the breaking length and the burst properties of the sheet, and that, as the sheet density increases, increasing fiber length leads to an increase in these properties until the maximum tear factor values are obtained at sheet densities at or beyond 0.50 g/cm^3. However, Mittal et al. (1978) reported that properties such as tensile and burst strengths are largely independent of the fiber length and that the folding endurance of the sheet is only slightly affected by the length of the fiber; this work found that fiber length has a significant impact on paper tear strength. Eucalyptus kraft pulp is characterized as a rigid and short broadleaf hardwood (Morais et al. 2019), and Simao pine fiber is a softwood fiber; softwood fibers are typically longer and more flexible than hardwood fibers (Jicheng Pei and Li 2012). In the present work, the effect of the dosage of eucalyptus and Simao pine pulps treated with different processes on the properties of the pulp and resultant paper sheet is investigated. The chemical composition, water retention value, zeta potential, carboxyl content, and drainage behavior of the pulps were measured, and the resulting paper sheets were characterized via Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption/desorption isotherms.

Materials and Methods

Materials

Unbleached eucalyptus kraft dry pulp (UEKP) sheets (commercially available) and unbleached Simao pine kraft dry pulp (USKP) sheets (commercially available) were provided by Yunnan Yunjing Forestry and Pulp Mill Co., Ltd (Jinggu, China). The water retention values (WRVs) of UEKP and USKP were determined according to the Chinese standard GB 29286-2012 and were found to be 92.16 ± 1.08 percent and 97.58 ± 1.42 percent, respectively. Sodium hydroxide, urea, and ammonium sulfate were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd (Shanghai, China). All chemical reagents used were analytical grade and used as received. Deionized water was used to prepare all the solutions throughout the experiment; for other processes requiring water, tap water was used.

Methods

Pulp treating and handsheet forming.—First, UEKP and USKP sheets were torn into approximately 0.3 by 1-cm^2 pieces and mixed to achieve uniform distributions composed of different mass ratios. In accordance with our previous works (Miao et al. 2018, 2019), the above mixed pulp fibers were treated with different NaOH/urea aqueous solutions; the resultant pulps were then processed using different procedures to form sheets. Each sheet had a basis weight of 60 g/m^2, and six sheets were prepared for each weight ratio considered here. The pulp treatments and sheet forming procedures used here are as follows.

Wet papermaking process (Miao et al. 2019).—Approximately 10 g of the above-mentioned mixed fiber was soaked in 100 g of 1.0-wt% NaOH/8.0-wt% urea aqueous

solution and stored for 24 hours at 0°C in a refrigerator; the mixture was then mechanically stirred at 2,500 rpm for 5 minutes at room temperature; 200 mL of 7.0-wt% $(NH_4)_2SO_4$ was then added while the mixture was stirred for a further 30 minutes. The resulting pulp slurry was then drained, washed, and filtered with tap water through a Buchner funnel sealed using a 200-mesh filter cloth at a vacuum level of 0.08 MPa until the pH of the pulp was neutral. A proportion of the as-prepared pulp was then used to test the physical properties of the pulp, and the remaining pulp was used to make handsheets according to Chinese standard GB/T24324-2009 on a standard apparatus (G 8E; Gockel & Co. GmbH, Munich, Germany). The wet handsheets were placed for 5 minutes on the drying plate of the standard apparatus at 95°C.

Solution casting method (Miao et al. 2018).—At room temperature, maintaining a solid–liquid weight ratio of 1:50, the mixed fibers described above were immersed in a 7.0-wt% NaOH/12.0-wt% urea aqueous solution that was precooled to −13°C and mechanically stirred at 2,500 rpm for 5 minutes. The resulting mixed pulp slurry was then divided into two parts. Part of the slurry was added to 200 mL of 7-wt% $(NH_4)_2SO_4$ aqueous solution (with a ratio of dry fibers to solution of 2 g:200 mL) and was continuously stirred at 2,500 rpm for 5 minutes; this mixture was then drained and washed until the pH of the pulp was neutral. The pulp properties were measured from this sample. The remaining part of the mixed pulp slurry was poured into a square acrylic mold with a side length of 200 mm; it was then shaken, defoamed, and placed into a preheated electro-thermostatic blast oven for 4 hours at 60°C to solidify the sample and form a sheet. The formed sheets were soaked in 200 mL of the 7-wt% $(NH_4)_2SO_4$ aqueous solution for 5 minutes and then washed with tap water until the pH of the sheets was neutral; they were then placed for 5 minutes on the heated plate of the standard apparatus at 95°C for drying.

Determination of the mechanical properties of the handsheets.—The mechanical properties of the handsheets (tear, burst, and tensile indexes and folding endurance) were measured according to standards GB/T 455-2002, GB/T 454-2020, GB/T 12914-2018, and GB/T 457-2018, respectively. The tests were repeated six times for each sample; the standard deviation was calculated and is shown as the error bars in the plots from Figures 1 to 3.

Evaluation of the properties of the pulp.—The cellulose, hemicellulose, and lignin content of the as-prepared pulps were determined according to laboratory analytical procedures reported by the National Renewable Energy Laboratory (Sluiter et al. 2010).

The WRVs of the above as-prepared pulps were measured according to Chinese standard GB 29286-2012. The WRVs were calculated as the difference between the weights of the wet pulp and dry pulp per unit weight of dry pulp,

$$\mathrm{WRV}\,(\%) = \frac{w_\mathrm{w} - w_\mathrm{d}}{w_\mathrm{d}} \times 100$$

where w_w represents the weight of the wet pulp after centrifugation (g) and w_w is the weight of the dry pulp (g).

The drainage behavior of the above as-prepared pulps was determined using a dynamic drainage jar (Mütek DFR-05; BTG, Säffle, Sweden); 1,000 mL of pulp suspension with 0.2 percent of content of dry fiber was poured into the dynamic drainage jar and stirred for 30 seconds at 750 rpm

at 25°C; water filtration was then started, and the time required for 800 g of filtrate to be collected was determined.

The zeta potential values of the as-prepared pulps with a 0.2 percent content of dry fiber were measured in the sample cell of the Mütek SZP-10 System Zeta Potential (BTG) at a temperature of 25°C.

The carboxylate content of the as-prepared pulps was determined via the conduct metric titration method (Chen et al. 2013).

All measurements were conducted on three samples (in addition to the drainage behavior); the standard deviations of the measurements were calculated and are shown in the tables.

Characterization of the handsheets.—The functional group structure of the handsheets was recorded using an FT-IR spectrometer (Bruker Equinox 55; Bruker Spectroscopy Corp., Ettlingen, Germany). The sheet sample was clamped and placed in the spectrometer. The IR spectra were recorded in the range from 4,000 to 400 cm^{-1} with a resolution of 4 cm^{-1} over 32 scans. The obtained data were corrected to account for the presence of H_2O and CO_2 in the atmosphere using the software supplied with the spectrometer.

The crystalline structure of the handsheets was determined using an X-ray diffractometer (X'Pert 3; Panalytical Co. Ltd, Almelo, Netherlands) in the range of $2\theta = 5°$ to $80°$ using a scanning speed of 13.77 s/step, a step size of 0.01313°, and an operating voltage and current of 40 kV and 40 mA, respectively. The sample tablets for the XRD measurements were prepared by taping the sheet to the mold.

The cross section and surface morphology of the handsheets was observed using cold field emission SEM (SU8010; Hitachi High-Technologies Corp., Tokyo, Japan) operating at 1 kV.

Specific surface area and pore volume measurements of the handsheets were conducted at 77 K using a surface area and pore size analyzer (TriStar II 3flex; Micromeritics Instruments Corp., Norcross, GA, USA). Prior to all measurements, all the samples were degassed for 12 hours at 110°C under vacuum conditions.

Results and Discussion

Paper strength

Figures 1 and 2 show the effect of the mass ratio of the eucalyptus and Simao pine pulps on the mechanical properties of the paper sheets prepared via the wet paper forming and solution film casting processes. As can be seen from the figures, for a given ratio of eucalyptus and Simao pine, the mechanical properties of paper sheets observed differ due to the different processes used in their construction.

As shown in Figure 1, with increasing amounts of Simao pine pulp fiber in the mixture, the mechanical properties of the paper are generally improved. Since Simao pine fibers are longer and more ductile, whereas eucalyptus fibers are shorter and harder, when the amount of Simao pine fiber exceeds 6 wt%, increasing quantities of Simao pine fiber leads to the mechanical properties of the paper sheets first decreasing before increasing, with the exception of the tensile strength, which was seen to increase slightly and then decrease. From the perspective of the paper strength, the optimal mass ratio of eucalyptus pulp to Simao pine pulp for
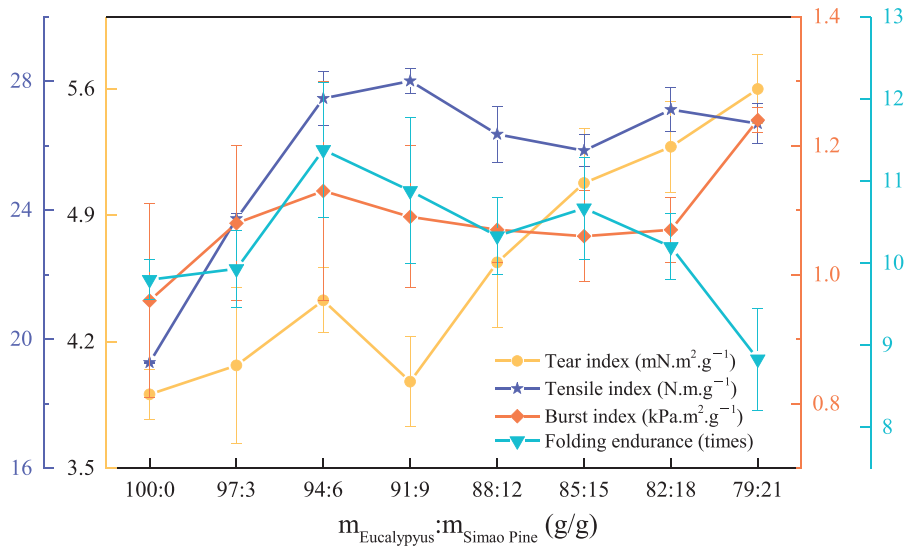
Figure 1.—Mechanical properties of the paper sheets prepared via the wet papermaking process.

use in this procedure is concluded to be between 94:6 and 85:15.

Figure 2 shows the effect of the amount of Simao pine pulp added to the eucalyptus pulp on the mechanical properties of paper sheets prepared via the solution film casting method. The mechanical properties of the paper prepared via this method are significantly different from those prepared via the wet papermaking process, which shows that the paper forming process has a notable influence on the mechanical properties of the resulting paper. As can be seen from the figure, with the increase in the content of Simao pine, the paper strength initially increases before decreasing. For a Simao pine fiber content of 12 wt%, the tensile and tear strength reached their maximum values of 23.03 N·m·g^{-1} and 11.73 mN·m^2·g^{-1}; the maximum burst strength and folding endurance were 0.68 kPa·m^2·g^{-1} and 25.50 times for a Simao pine content of 15 and 18 wt%, respectively. The mass ratio of eucalyptus pulp and Simao pine pulp is in the range 88:12 to 85:15 mirrored to the

paper strength relatively high, so from the perspective of paper strength, the most suitable mass ratio of eucalyptus pulp and Simao pine pulp for use in this procedure is between 88:12 and 85:15.

In order to better understand the influence of the two procedures on the paper strength, we selected tensile strength as the primary evaluation index and the other mechanical properties as auxiliary evaluation indexes to establish the most suitable process parameters. When the mass ratios of eucalyptus and Simao pine pulps is 94:6 for the wet paper papermaking and 88:12 for the solution casting methods, the tensile index of the resulting paper sheets is relatively high and the tear, burst, and folding endurance still increasing. Therefore, we selected the pulp and its resulting paper sheets treated with these two ratios for further analysis and characterization. The following sections, unless otherwise mentioned, refer to the paper or pulp obtained using these two ratios.
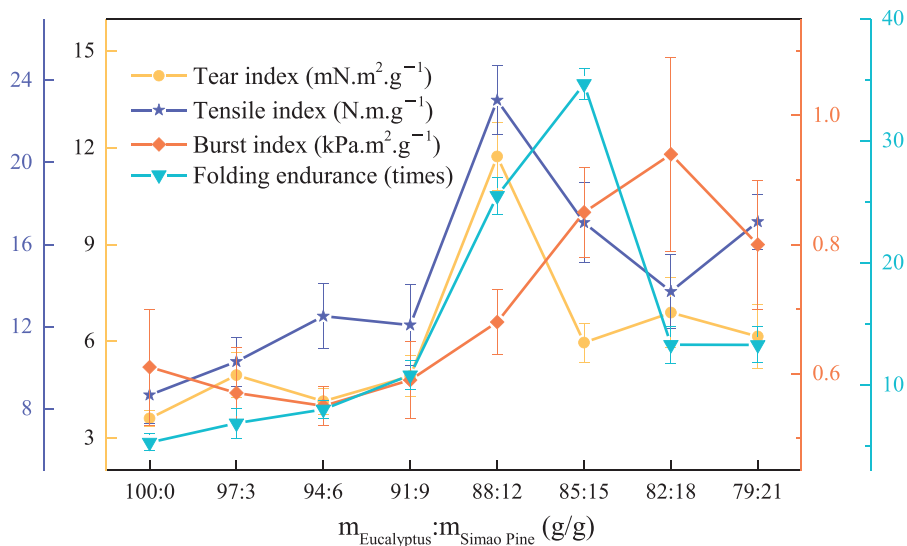

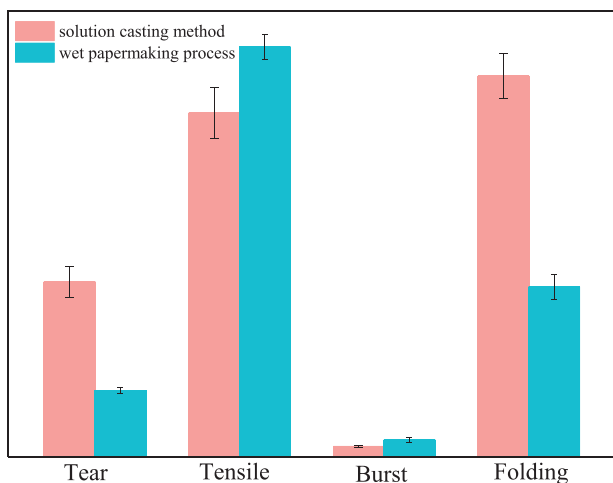*Figure 2.—Mechanical properties of paper sheets prepared via the solution casting process.*

Figure 3.—Comparison of the mechanical properties of the paper sheets prepared via the wet paper papermaking and solution casting processes.

Figure 3 provides a comparison of the mechanical properties of paper sheets prepared with two previously mentioned optimal parameters. It can be seen that the paper prepared via the wet papermaking process has superior tensile and burst strengths, but the tear strength and folding endurance are superior for the paper fabricated via the solution casting method. This finding can be attributed to the fact that more flexible and longer fibers lead to a higher folding endurance and tear strength in paper sheets (Mittal et al. 1978).

In order to better understand the difference in mechanical properties of the paper fabricated via the two processes investigated here, we evaluated the microphysical properties of the paper sheets for ratios of eucalyptus to Simao pine pulps of 94:6 in the wet papermaking method and 88:12 in the solution casting method.

Pulp properties

Table 1 shows the cellulose, hemicellulose, and lignin compositions of the pulps with the selected mass ratios obtained via the previously described processes. The cellulose, hemicellulose, and lignin contents of the pulp fiber obtained via the solution casting method are slightly lower than in the pulp obtained via the wet papermaking process (the pulp obtained via the solution cast method showed cellulose, hemicellulose, and lignin contents that were lower by 1.88, 3.11, and 2.67 percent, respectively, compared to the values obtained via the wet papermaking process). This may be due to the fact that the pulp washing procedure used in the wet papermaking process requires direct contact between the single fiber and deionized water while the mixture is subject to stirring, whereas the solution casting method relies on a concentration difference to induce molecular diffusion from the inside to the outside of

the paper sheet. In order to fully remove the sodium hydroxide and urea from within the sheet, considerably more washing would be required than the amount used in the wet papermaking process considered here, which would result in a further decrease in the cellulose, hemicellulose, and lignin contents.

Table 2 shows the WRVs, zeta potentials, and carboxyl group contents of the pulps with optimized mass ratios treated using the aforementioned processes. The WRV of a given pulp is known to have a positive correlation with the mechanical properties of the resulting paper sheet; that is, the mechanical properties of the paper sheets obtained from pulps with high WRV values are better. The WRVs of the solution casting pulp were found to be 56.02 percent higher than that of the wet papermaking process pulp, indicating that the solution casting process leads to considerably higher water retention of the pulp. The WRV of the pulp treated by the solution casting process is higher than those of the pulps treated using the wet papermaking process, and the corresponding mechanical properties of the paper were also found to be superior (as shown in Fig. 3). The zeta potential test is a measure of the electric charge at the surface of the fibers, which is an indirect assessment of the physical stability of the paper in water. The negative charge of the pulp obtained via the solution casting process is more than twice that of the pulp obtained via the wet papermaking process, indicating that the solution casting process dissociates more functional group fibers carrying ionizable negative charges to the fiber surface and improves the stability of the fiber in water. The negative charge on the fiber surface comes primarily from the carboxyl group, and the carboxyl group in the plant fiber exists mainly in hemicellulose. It can be seen from Table 2 that the carboxyl group content of the pulp obtained via the solution casting process is 50.15 percent higher than that of the pulp obtained in the wet papermaking process. It is thus hypothesized that the solution casting process detaches a larger quantity of hemicellulose from the plant cell wall, thereby increasing the carboxyl group content of the fiber surface. This hypothesis is supported by the results of the zeta potential tests performed on the fibers. These results indicate that the increase in carboxyl content enhances the swelling and/or bonding capacity of the cellulosic fibers and improves the bonding of the pulp fibers in paper; thus, the increased carboxyl content increases the strength of the resultant paper, which is consistent with previous reports in the literature (Zhang et al. 2007, Chen et al. 2010).

Figure 4 shows the drainage performance of the pulps with the optimal mass ratio of eucalyptus and Simao pulps obtained via the aforementioned processes. Under the same filtration conditions, 800 mL of suspension with a solid content of 0.2 percent (dry fiber) was found to require 335 seconds for the wet papermaking process pulp but only 66 seconds for the solution casting film process pulp; furthermore, the maximum drainage rate was obtained after 24 seconds in the case of the solution casting film and 44 seconds in the case of the wet papermaking process. This

Table 1.—Composition of the pulp samples treated according to the wet papermaking process and the solution casting method.

Sheet forming process	Sample ($m_{Eucalyptus}$:$m_{Simao\ pine}$)	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)
Wet papermaking process	94:6	87.05 ± 0.85	5.69 ± 0.16	0.15 ± 0.02
Solution casting method	88:12	85.41 ± 0.23	3.92 ± 0.12	0.11 ± 0.03

Table 2.—Water retention values (WRVs), zeta potentials, and carboxyl contents of the pulp samples with the optimal mass ratios of eucalyptus and Simao pine pulps obtained via the wet papermaking and solution casting procedures.

Sheet forming process	Sample ($m_{Eucalyptus}$:$m_{Simao\ pine}$)	WRVs (%)	zeta potential	COO^- (mmol·kg^{-1})
Wet papermaking process	94:6	111.35 ± 0.48	−171.3	6.54
Solution casting method	88:12	167.37 ± 1.35	−382.7	9.82

indicates that the solution casting process leads to improved drainage performance of the pulp, which can be attributed to the increased negative charge on the surface of the fibers obtained via this method.

Sheet characterization

FT-IR spectroscopy.—Figure 5 shows the infrared absorption spectra of the sheets prepared using the selected mass ratios of the constituent pulps. The absorption bands of the paper sheets prepared using the processes considered here show a large degree of similarity, but there are some notable changes regarding some functional groups. Specifically, it is can be observed that the peaks that were present at 3,341 cm^{-1} in the case of the sheet made via the wet paper papermaking process, corresponding to the stretching of the –OH group, shifted to a higher wave number (approximately 3,447 cm^{-1}) for the sheet made via the solution casting method; this shift indicates that the hydrogen bonds were weaker in the latter method (GC Pimentel 1960, Marechal and Chanzy 2000), which can be explained by the fact that the cellulose with a degree of polymerization less than 700 in the fiber was dissolved in NaOH/urea aqueous solution (Jie Cai 2005); this dissolved cellulose then coagulated in the $(NH_4)_2SO_4$ aqueous solution, leading to a lower degree of hydrogen bond reconstruction. This is consistent with reports in the literature that state that the degree of polymerization of cellulose decreases after dissolution and regeneration. Furthermore, peaks observed at 1,720 cm^{-1} in the sheet obtained via the wet paper papermaking process, which corresponds to the C=O stretching vibration, were seen to be translated to a lower wave number (approximately 1,637 cm^{-1}) in the case of the sheet obtained via the solution casting method; this change can be attributed to the carbonyl oxygen in the carboxyl group and to hydroxyl

hydrogen in the hydroxyl group within the fiber forming intramolecular hydrogen bonds; the peak is also noted to be stronger in the latter case, which is due to more hemicellulose detaching from the plant cell wall. These results are consistent with the carboxyl contents determined above. Moreover, the peak observed at 1,113 cm^{-1} in the spectrum corresponding to the sheet obtained via the wet papermaking process, which corresponds to the C–O–C antisymmetric stretching vibration, disappeared as a result of the solution casting process; this indicates that the crystal phase of the cellulose changed from I to II due to the rotary isomerism of the oxymethyl groups (Zhbankov et al. 2002, Li et al. 2015), indicating that the solution casting process induces a more complete transformation of the cellulose.

In addition, we used the PeakFit software to perform Gauss peak fitting for the infrared hydrogen bond region of 3,000 to 3,800 cm^{-1} (Oh et al. 2005, Popescu et al. 2009); the fitting curves are shown in Figure 5, and the fitting results are detailed in Table 3.

In the range 3,800 to 3,000 cm^{-1} of the spectra shown in Figure 6, four bands assigned to different hydrogen-bonded –OH vibrations can be observed. The band at approximately 3,152 cm^{-1} is related to the intermolecular hydrogen bonds of the cellulose chains 6-OH...O-3′, and the other three bands, which can be observed at approximately 3,330, 3,500, and 3,620 cm^{-1}, correspond to intramolecular hydrogen bonds at 3-OH...O-5, 2-OH...O-6, and 3-OH...O-6, respectively (Roy et al. 2009). The energy of the hydrogen bonds and hydrogen bonding distance were calculated for these bands. The energy of the hydrogen bonds was calculated using Equation 1 (Struszczyk 1986), and the hydrogen bonding distances were obtained by
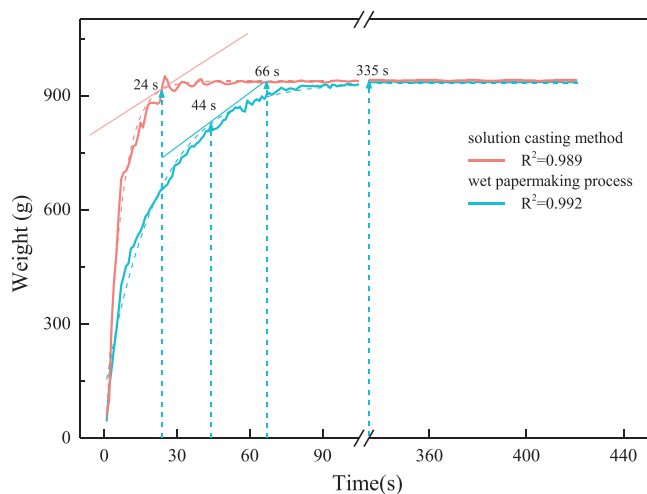

Figure 4.—Drainage behavior of the pulps with the optimal mass ratios of eucalyptus and Simao pine pulps.
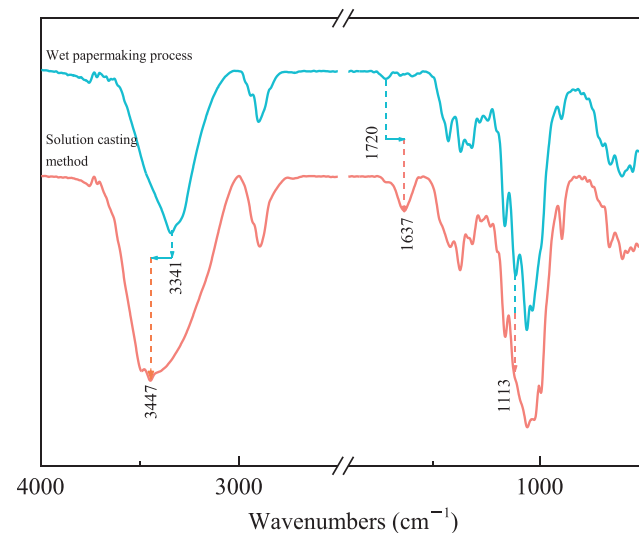

Figure 5.—Fourier-transform infrared spectroscopy spectra from the paper sheets prepared from the pulps with the optimal mass ratios.

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Table 3.—Hydrogen bond energy (E_H), hydrogen bond distance (D), and the Gaussian fitting results for the paper sheets.

Sheet forming process	Sample ($m_{Eucalyptus}$:$m_{Simao\ pine}$)	Peak	Wave number (cm^{-1})	Area (%)	r^2	Hydrogen bonding energy, E_H (kJ·mol^{-1})	Hydrogen bonding distance, D (Å)
Wet forming process	94:6	1	3,151.98	3.77	0.9995	35.72	2.74
		2	3,319.94	72.86		23.67	2.78
		3	3,480.21	23.06		12.18	2.81
		4	3,659.26	0.31		0.05	2.85
Solution casting method	88:12	1	3,153.48	10.88	0.9994	35.61	2.74
		2	3,336.10	60.22		22.51	2.78
		3	3,503.77	28.42		10.49	2.82
		4	3,627.28	0.48		1.63	2.85

considering Equation 2 (Pimentel and Sederholm 1956):

$$E_H = \frac{1}{k} \times \frac{v_N - v}{v_N} \qquad (1)$$

Here, E_H represents the energy of the hydrogen bonds (kJ·mol^{-1}), v_N represents the standard frequency corresponding to free –OH groups (3,650 cm^{-1}), v is the frequency of the bonded –OH groups of the sample (cm^{-1}), and k is a constant equal to 3.82×10^{-3} (mol·kJ^{-1}):

$$\Delta v = 4.43 \times 10^3 (2.84 - D) \qquad (2)$$

Here, $\triangle v = v_0 - v$ (cm^{-1}), v_0 is the monomeric –OH stretching frequency (3,600 cm^{-1}), v represents the stretching frequency observed in the infrared spectrum of the sample (cm^{-1}), and D is the hydrogen bonding distance (Å).

The calculated energy of the hydrogen bonds and hydrogen bonding distance are given in Table 3. As can be seen from Table 3, the hydrogen bonding distances are similar for both the pulps obtained here. Moreover, the intermolecular hydrogen bond distances (~2.74 Å) of the two samples were less than the intramolecular hydrogen bonds (2.78 to 2.85 Å), and the corresponding intramolecular hydrogen bond energies (~23.00 to 0.05 kJ·mol^{-1}) are smaller than the intermolecular hydrogen bond energy (~35.70 kJ·mol^{-1}) (Struszczyk 1986), indicating that the stability of the cellulose chains depends primarily on intermolecular hydrogen bonds. It can also be seen that the energy of the hydrogen bonds corresponding to peaks 1 to 3 (see Table 3) undergoes a small decrease in the case of

the solution casting method with respect to the wet forming procedure, but a small increase in bond energy is observed for peak 4. This result is hypothesized to be related to the pulp processing in the solution casting method leading to more cellulose with a polymerization degree of less than 700 being dissolved in the NaOH/urea solution, which leads to a smaller number of hydrogen bonds being created.

XRD analysis.—The XRD patterns obtained from the paper sheets are dominated by the pattern that corresponds to cellulose, and the diffraction peaks at $2\theta \approx 15.88°$ and $22.59°$ in the (110) and (200) planes are characteristic of the cellulose I crystal in the raw materials (Popescu et al. 2009, Miao et al. 2018). Figure 7 shows the XRD spectra of the paper sheets obtained via both methods. The cellulose crystal structure of the paper sheet prepared via the wet forming process shows a large degree of similarity to that of the raw fiber; however, the patterns characteristic of cellulose crystals of the paper sheet obtained via the solution casting method are significantly shifted from being characteristic of cellulose I to cellulose II (French and Cintron 2013, French 2014, Jin et al. 2016), and the corresponding peak can also be seen to have decreased and broadened with respect to that observed in the spectrum of the raw materials. We used the Jade 6.5 software to quantitatively calculate the X-ray crystallinity indexes for both samples, and we also used the empirical equation derived by Nelson and O'Connor (1964) to calculate the infrared crystallization index based on the infrared data.

The crystallinity of the samples was calculated using Segal's method (Segal et al. 1959) according to
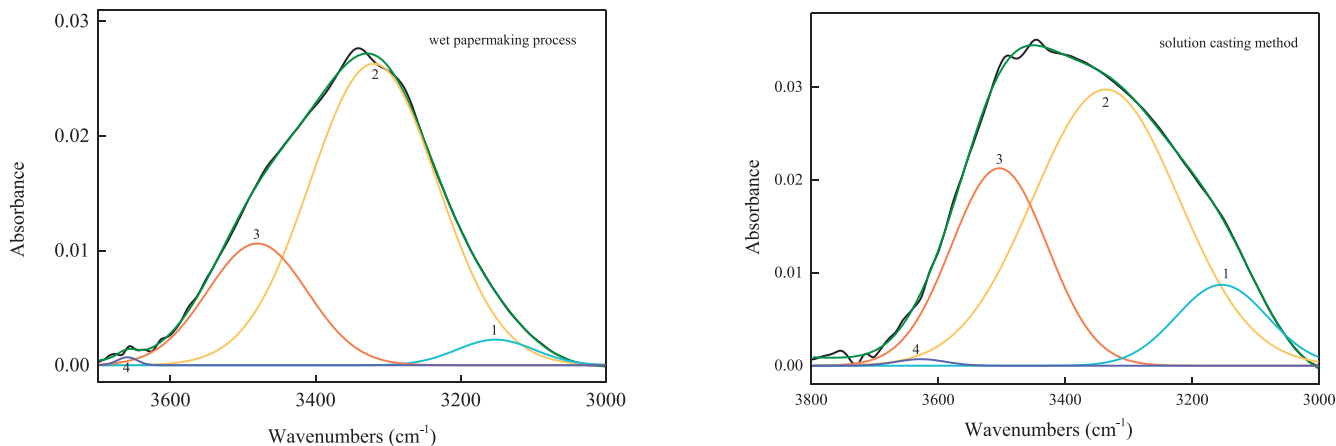

Figure 6.—Gaussian fitting curves of the hydrogen bond zones of the Fourier-transform infrared spectroscopy spectra obtained from paper sheets prepared using the pulps containing the optimal ratios of eucalyptus and Simao pine pulps.
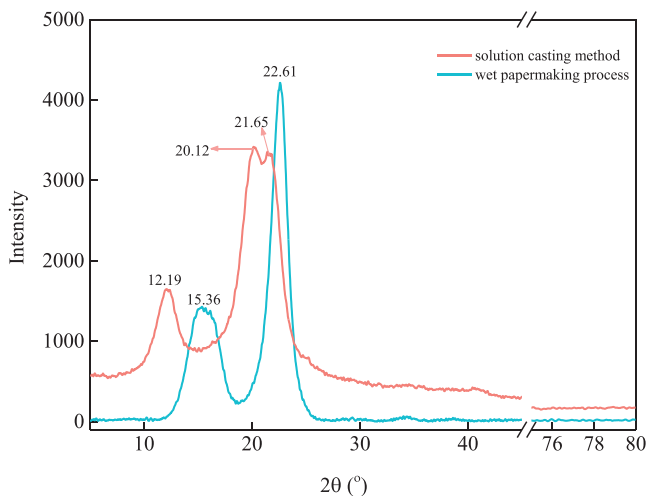
Figure 7.—X-ray diffraction spectra of paper sheets prepared via the two methods considered here.

$$Cr\,(\%) = \frac{I_{200} - I_{Am}}{I_{200}} \times 100 \qquad (3)$$

where Cr represents the crystallinity (%), I_{200} is the reflection intensity of the (200) plane diffraction, and I_{Am} represents the minimum intensity close to the 2θ angle of 18.58°.

The index of crystallinity was calculated according to the empirical method developed by Nelson and O'Connor (1964) according to

$$N \cdot O'KI - \frac{\delta_{1372}}{\delta_{2900}} \qquad (4)$$

where $N{\cdot}O'KI$ represents the infrared crystallinity, δ_{1372} is the peak intensity of the peak that corresponds to C–H bending (1,372 cm^{-1}), and δ_{2900} represents the peak intensity of the peak that corresponds to C–H stretching (2,900 cm^{-1}).

The results of the calculations of the crystallinity and infrared crystallinity are shown in Table 4. The crystallization indexes of the sheets obtained via both procedures were found to decrease due to the presence of the dissolved cellulose with a lower degree of hydrogen bond reconstruction; the decline in the infrared crystallization index was not significant, whereas there was a large decrease in the X-ray crystallization index (26%); these results are consistent with previous studies (Matsuda 1994).

SEM analysis.—Figure 8 shows the SEM images of the surface and cross section of the paper sheets. All the paper sheets formed using the two methods considered here are formed via fiber self-assembly in a disorderly manner (see Figs. 8a and 8b), and there is no significant difference in terms of the manner in which the fibers are deposited. However, in terms of the single fiber shape (Figs. 8a and 8b)

and the extent of filling and weaving observed within the paper sheets (Figs. 8c and 8d), the sheets show significant differences. For the paper sheet prepared via the wet forming method, each fiber in the network making up the paper sheet is flat and loosely woven, whereas the paper sheets prepared via the solution casting procedure exhibit fibers that are plump and form a compacted weave pattern. This illustrates that the compactness of the paper sheet obtained using the solution casting method is higher than that of the sheet obtained via the wet forming process. The compactness of the paper sheets was calculated to be 0.399 g/cm^3 for the sheet obtained via the wet forming method and 0.477 g/cm^3 for the sheet obtained via the solution casting method. In general, better mechanical properties, such as higher tear and burst indexes, of paper sheets are associated with higher compactness. It is likely the higher compactness of the paper sheet prepared via the solution casting method explains its superior mechanical properties.

Nitrogen adsorption isotherms and pore structure.— Nitrogen adsorption/desorption isotherms at −77 K obtained from both samples are shown in Figure 9. The isotherms of both samples were similar: The nitrogen adsorption capacities of the two samples are very small (a maximum of 2.5 cm^3/g for the sample obtained via the solution casting method and 1.5 cm^3/g for the sample obtained via the wet forming method), which indicates that there is not a strong interaction between either material and adsorbed gas and that adsorptive molecules gather around the most attractive sites on the surface. The two samples are largely nonporous, with the exception of a small number of micropores with a characteristic size of 2.5 nm. Due to a slight increase in the number of micropores, the nitrogen gas adsorption capacity of the paper sheets prepared by the solution casting method was 66.67 percent higher than that of the sheets prepared via the wet papermaking process; this is consistent with the analysis of the SEM results.

Conclusions

In this work, paper sheets were prepared via a wet forming process and a solution casting method, and the mechanical properties of the sheets were used as the evaluation index for the optimization of the contents of eucalyptus and Simao pine pulps in the two processes considered. The optimal ratio of eucalyptus pulp to Simao pine pulp was found to be 94:6 when considering the wet forming process; at this ratio, the tear, tensile, and burst indexes and the folding endurance were found to be 4.43 mN·m^2·g^{-1}, 27.47 N·m·g^{-1}, 1.13 kPa·m^2·g^{-1}, and 11.38 times, respectively. In the solution casting process, the optimal ratio of eucalyptus to Simao pine pulps was found to be 88:12, and at this ratio, the paper exhibited tear, tensile, and burst indexes and folding endurance of 11.73 mN·m^2·g^{-1}, 23.03 N·m·g^{-1}, 0.68 kPa·m^2·g^{-1}, and 25.50 times, respectively.

We measured the properties of the pulps and the physical characteristics of the resulting paper generated via these two processes with their respective optimal mass ratios. The

Table 4.—Infrared and X-ray crystallinity indexes of paper sheets.

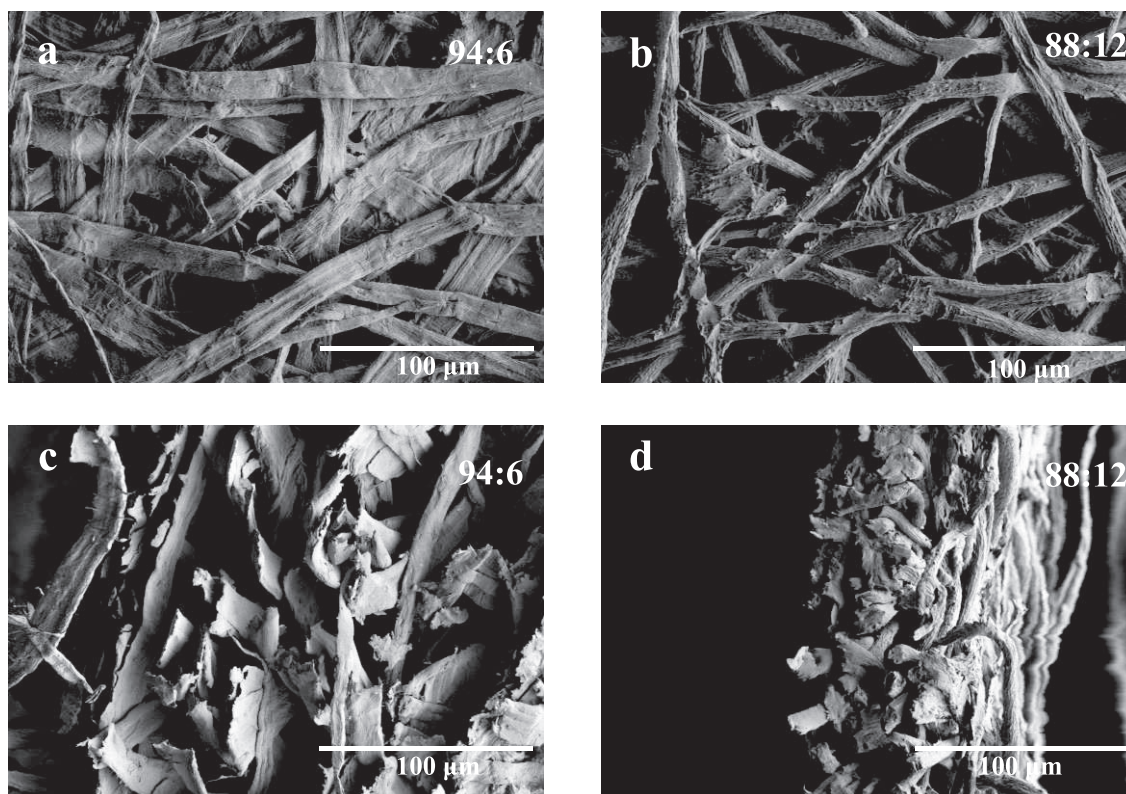| Sheet forming process	Sample ($m_{Eucalyptus}$:$m_{Simao\ pine}$)	Infrared index $N{\cdot}O'KI$	X-ray crystallinity index (%)
Wet forming process	94:6	1.0025	46.69
Solution casting method	88:12	1.0015	34.25

Figure 8.—Surface (a and b) and cross sections (c and d) of the paper sheets prepared from the two pulps (a and c correspond to sheets obtained via the wet papermaking process, and b and d correspond to sheets obtained via the solution casting method).

cellulose, hemicellulose, and lignin contents of the pulp treated via the solution casting method were lower by 1.88, 3.11, and 2.67 percent, respectively, compared to the values obtained from the pulp treated by the wet papermaking process, but the water retention value, zeta potential, and carboxyl content were larger by 50.31, 123.41, and 50.15 percent, respectively, using the former process; the drainage time of the material obtained via the solution casting method was one-fifth that of the material obtained via the wet forming process. The paper sheet prepared via the solution casting method exhibited weaker hydrogen bonding and decreased crystallinity but a higher compactness and

nitrogen gas adsorption capacity (19.55% and 66.7% higher, respectively) than that obtained via the wet papermaking process. This was hypothesized to be due to the single fibers being more plump and the cellulose with a polymerization degree of less than 700 having been dissolved and regenerated in solution cast process.

This work shows that the physical properties of the paper prepared via the two processes considered here, using their respective optimal weight ratios of the different types of pulp, have their own advantages. To obtain a paper with a higher tensile and burst strength, the wet forming method should be used; with the aim of creating sheets with other
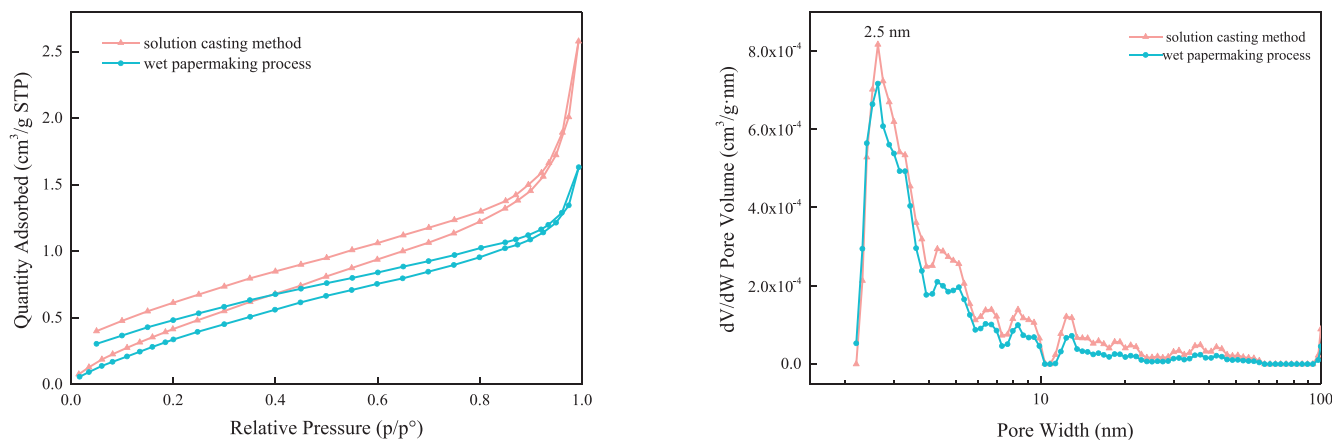

Figure 9.—Nitrogen adsorption/desorption isotherms (left) and the corresponding pore size distributions curves (right) from the paper sheets prepared from the pulps considered in this work.

mechanical properties being higher, the solution casting process should be selected. However, it is noted that the solution casting process limits the possibility of large-scale continuous production.

Acknowledgments

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