Impact of Mechanical Refining on the Heat Tolerance of Cellulosic Paper

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Cellulosic paper is widely used in various applications, such as for decoration and in cold-rolled stainless steel. The thermal stabilities of cellulosic fibers were investigated with a thermogravimetric analyzer. Additionally, the impact of mechanical refining on the heat resistance of cellulosic paper was evaluated by testing the tensile strength and brightness of the samples derived from pulp with various beating degrees. The morphology of the paper was characterized with scanning electron microscopy and the monose content of the pulp samples was determined with high performance liquid chromatography. The results showed that the different pulps had different thermal stabilities. Because of pulp refining, the heat tolerance was enhanced in terms of the strength and optical properties. Compared with the original papers, the tensile strength and brightness of the 40°SR papers on average increased by 217% and 114%, respectively, all evaluated after heating at 240 °C. Therefore, the heat tolerance of cellulosic paper can be tuned with pulp refining.

Keywords: Cellulosic paper; Heat tolerance; Mechanical beating; Tensile strength; Brightness

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INTRODUCTION

It is very important to replace non-renewable resources with renewable ones, which is in line with the trend of social development (Fan *et al*. 2017). Cellulosic paper with its natural, renewable, and environmentally friendly properties is widely used in various applications. The paper properties will inevitably be affected by environment temperature in which they are used. Such effects can be expected especially when paper is used in higher temperature, resulting in the reduction of strength and whiteness. For example, the pattern on leather release paper is transferred to artificial or synthetic leather at temperatures in the range 160 °C to 200 °C, and food packing papers used in grilling and microwaving above 180 °C, so the thermal stability of the paper at 200 °C and above is very important (Chen *et al*. 2011). Thus, it is important to study the paper's strength and brightness thermal properties (Wu *et al.* 1997). In addition, the paper thermal properties mainly include flame resistance and high-temperature resistance. In recent years, studies have mainly focused on improving the flame resistance of paper by adding flame-retardants or other additives (An *et al*. 2007; Wang and Song 2010). To the knowledge of the authors, relatively few studies have been devoted to the high-temperature resistance mechanism of cellulosic paper and methods for improving the heat-tolerance of paper.

Pulp, which is widely used in the paper industry, is composed of cellulose, hemicellulose, and lignin, as well as extractives (tannins, fatty acids, and resins) and inorganic salts (Zhang *et al*. 2004, 2005). Cellulose is a polymeric compound composed of

D-glucose linked by β-1-4-glucosidic bonds and has a regular and orderly structure with a relatively high thermal stability (Soares *et al*. 1995; Bledzki and Gassan 1999; Klemm *et al.* 2005). Hemicellulose consists of many natural monosaccharides, such as glucose, mannose, galactose, xylose, and arabinose (Fengel and Wegener 1984; Shen *et al*. 2015). Unlike cellulose, hemicellulose has side groups in its chain structure. Different structures result in different thermal stabilities. The degradation of cellulose takes place from 250 °C to 400 °C, while hemicellulose degrades from 200 °C to 350 °C (Shen and Gu 2009; Lv *et al*. 2010; Giudicianni *et al.* 2013). Thus, the paper properties are influenced by the composition of the pulp.

The requirement for high quality paper has increased the demand for good quality pulp. Pulp refining is a promising approach to improve the pulp quality by changing the fiber characteristics (Hubbe 2014; Gharehkhani *et al.* 2015). It increases the area of contact between the fibre by increasing their surface through fibrillation and its flexibility so that most of the paper strength properties will improve. The main emphasis when observing heat tolerance is to record the changes in the strength, brightness, and their stability after heat treatment. For this purpose, four cellulosic materials were investigated with thermogravimetric analysis (TGA) and refined. Additionally, the morphology of the papers and the monose content of the pulp were characterized by scanning electron microscopy (SEM) and examined with high performance liquid chromatography (HPLC), respectively. This study provided the possibility to improve the heat tolerance of paper with refining process and expand application areas, such as the packing, heat-resistant label and so on.

EXPERIMENTAL

Materials

Bleached softwood pulps (A and B) and a bleached hardwood pulp (C) were supplied by China Tobacco Mauduit (Guangdong, China). Bleached jute pulp (D) was obtained from Shanghai Prema (Shanghai, China). These samples were slightly refined using a Mark VI type PFI refiner (Hamjern Maskjn, Hamar, Norway), according to the standard QB/T 1463-1992, and had beating degrees of 40°SR and 60°SR. The sources and properties of the various pulps are summarized in Table 1.

Table 1. Cellulose and Hemicellulose Contents in the Samples

Sample	A	B	C	D
Source	softwood	softwood	hardwood	jute
Cellulose Content (%)	92.46	91.61	92.76	94.64
Hemicellulose Content (%)	5.09	6.52	7.70	2.42

Methods

Thermogravimetric analysis

The TGA of the cellulosic materials was performed with a thermogravimetric analyzer (TGA209F3, NETZSCH Tarsus, Selb, Germany). During TGA, the samples were heated from 30 °C to 600 °C at a heating rate of 10 K/min under an oxidizing atmosphere.

Then, 5 mg of each sample was transferred in platinum crucibles. During the experiment, the cell of the thermogravimetric analyzer was flushed with air at a flow rate of 20 mL/min to maintain an oxidative atmosphere for the thermal decomposition of the samples.

The calculated thermogravimetric data was automatically output to the 209F3 thermogravimetric analyzer software and was initially analyzed using the NETZSCH Proteus software. Then, the data were analyzed and processed by origin as needed.

Paper-sheets formation and heat treatment

Paper sheets with a target basis weight of 90 g/m^2 were prepared with an Econo-Space automatic sheet former system (Model 1600, Réalisations Australes Inc., Quebec, Canada), according to TAPPI T205 (2002). The pressure for wet sheet pressing was kept at 200 kPa. The sheets were dried at 102 °C using a Formax 12 drum dryer (Thwing-Albert Instrument Company, New jersey, US).

After preparation, the papers that made from different materials and beating degree were treated at 25 °C, 160 °C, 180 °C, 200 °C, 220 °C, 240 °C, 260 °C, and 280 °C for 30 min with a heating plate (Wise Thermal HP-LP, Korea) under an air atmosphere.

Determination of the strength and optical properties

After heat treatment, the tensile index values and brightness of the paper sheets were measured using a L&W CE062 tensile strength tester and L&W Elrepho 070 brightness tester (Kista, Sweden) according to GB/T 12914-2008 and GB/T 7975-2005, respectively.

High performance liquid chromatography and scanning electron microscopy

Sugar components of the pulps were studied with a HPLC analyzer (AERS 500, DIONEX, Sunnyvale, US), (Wentz *et al*. 1982). SEM observations of the paper samples were performed using a FEI Quanta-200 environment microscope (Oberkochen, Germany).

RESULTS AND DISCUSSION

Thermogravimetric Analysis

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the four pulps (A, B, C, and D) are plotted in Figs. 1 and 2, respectively. The graphs show that the increase in the treatment temperature caused the weight of the pulp to be reduced gradually. When the pulp was heated from 30 °C to 100 °C, its mass decreased slightly, which accounted for a loss of up to 6 wt.% of the total mass and led to the formation of anhydrocellulose. The thermal decomposition of the four pulps started at approximately 230 °C, and the mass loss rates increased greatly with an increasing temperature and obtained maximum values at approximately 330 °C. When the temperature was above 330 °C, the weight loss rates decreased until the final temperature was reached.

There was a difference between the four materials according to TG and DTG curves that show the thermal decomposition. As the hemicellulose content decreased, both the TG and DTG curves exhibited a shift in the major weight loss temperature range (230 °C to 330 °C) towards a slightly higher temperature zone, and the maximum value of the weight loss rate increased slightly. Table 2 shows that the thermal decomposition of the A, B, C, and D pulps started at approximately 234.6 °C, 233.0 °C, 230.6 °C, and 238.5 °C, respectively.

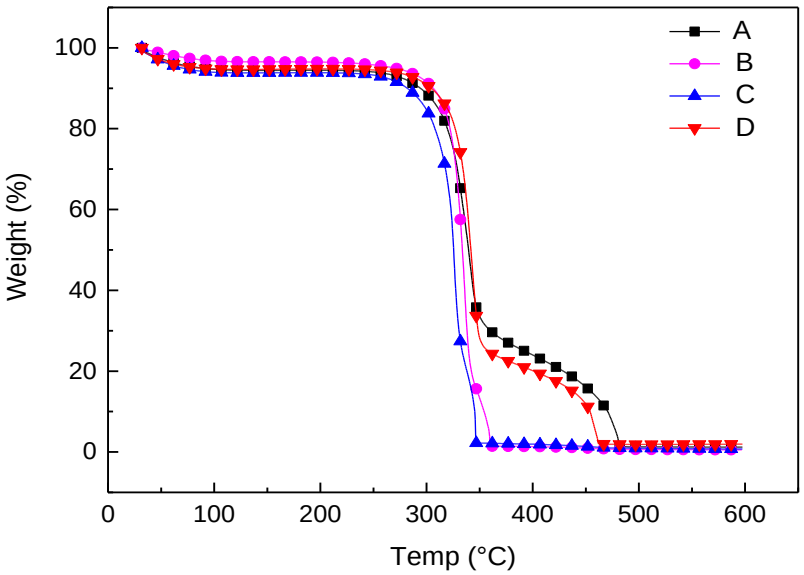

Fig. 1. TG curves of the various pulp samples (A, B, C, and D)

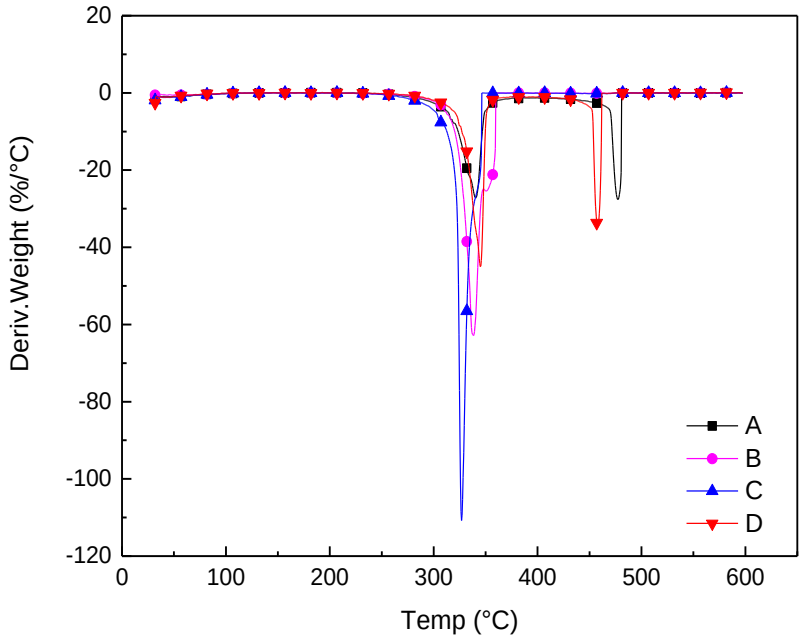

Fig. 2. DTG curves of the various pulp samples (A, B, C, and D)

Table 2. Characteristics of the Mass Loss of the Pulps

Pulp	T_0 (°C)	T_e (°C)	T_m (°C)
A	234.6	319.9	340.4
B	233.0	321.1	338.6
C	230.6	315.9	326.6
D	238.5	327.4	344.0

T_0: temperature of the commencement of pulp degradation after the drying stage
T_e: temperature of the commencement of extrapolated onset temperature
T_m: temperature at the first peak of the mass loss rate

Figure 3 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves of different beating degree of B pulp. It is clear that the temperature of initial degradation and maximum mass loss rate decreases and moves toward lower temperature with the increasing of beating degree. This implies that the thermal stability of pulp relates with the mechanical beating and decreases with the increasing of beating degree.

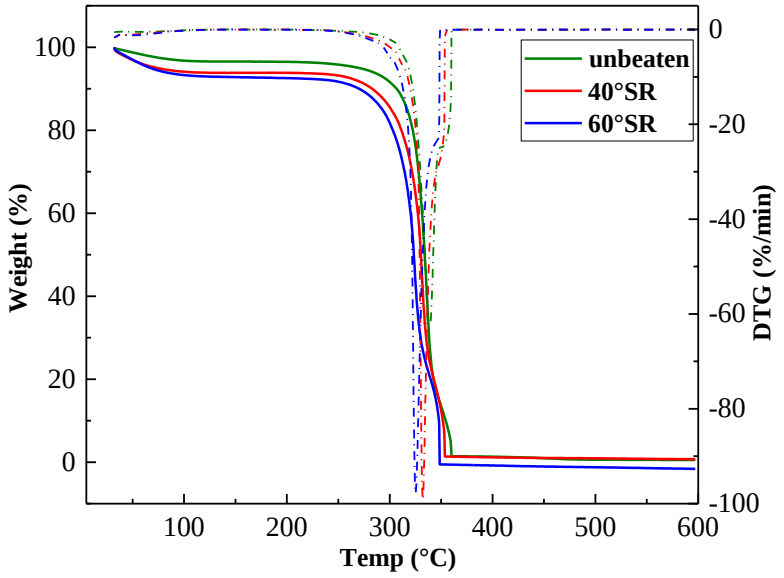

Fig. 3. TG and DTG curves of the B pulp sample

Impact of Mechanical Refining on the Heat Tolerance

The effect of mechanical beating on the heat tolerance of the paper was investigated using the four different papers (A, B, C, and D) by measuring the tensile strength and brightness. The beating degrees of the four papers included the unbeaten value (15 °SR), 40 °SR, and 60 °SR. The effect of refining on the paper properties often follows the same trend. Most properties are positively affected by refining (Afra *et al*. 2013; González *et al*. 2013). Figure 4 shows that the papers made from the beaten pulps had higher tensile strengths than the papers made from the unbeaten pulps. For example, the tensile strength of the B paper with a beating degree of 40°SR was 4.07 kN/m, which is 2.69 kN/m higher than unbeaten B paper even at 280 °C. Mechanical beating increases the area of contact between the fibers by increasing their surface through fibrillation and its flexibility (Dou *et al*. 2016; Zhao *et al*. 2017). However, the effects of refining are not always desirable and can be either advantageous or disadvantageous (Gharehkhani *et al*. 2015). Figure 4a shows the tensile strength of the paper prepared with 60 °SR pulp was 5.40 kN/m at room temperature, it decreased by 15.0% in comparison to the paper made from the 40 °SR pulp (6.35 kN/m). That was because the beating shortened the fibers and it decreased the fiber strength and the cohesion of the paper when the beating degree is too high (Chen *et al*. 2016). In addition, the thermal stability of the paper changed remarkably after beating with an increase in the heat treatment temperature. The tensile strength declined markedly, especially when the temperature exceeded 240 °C (Figs. 4a, 4b, and 4c). The tensile strength was still higher than that of the paper made from the unbeaten pulp. As for the beaten D paper (Fig. 4d), not only was the tensile strength higher than that of the unbeaten paper, but it also had a better strength stability. Thus, the heat tolerance of the handsheets, in terms of the mechanical strength, can be enhanced by adjusting the beating degree.

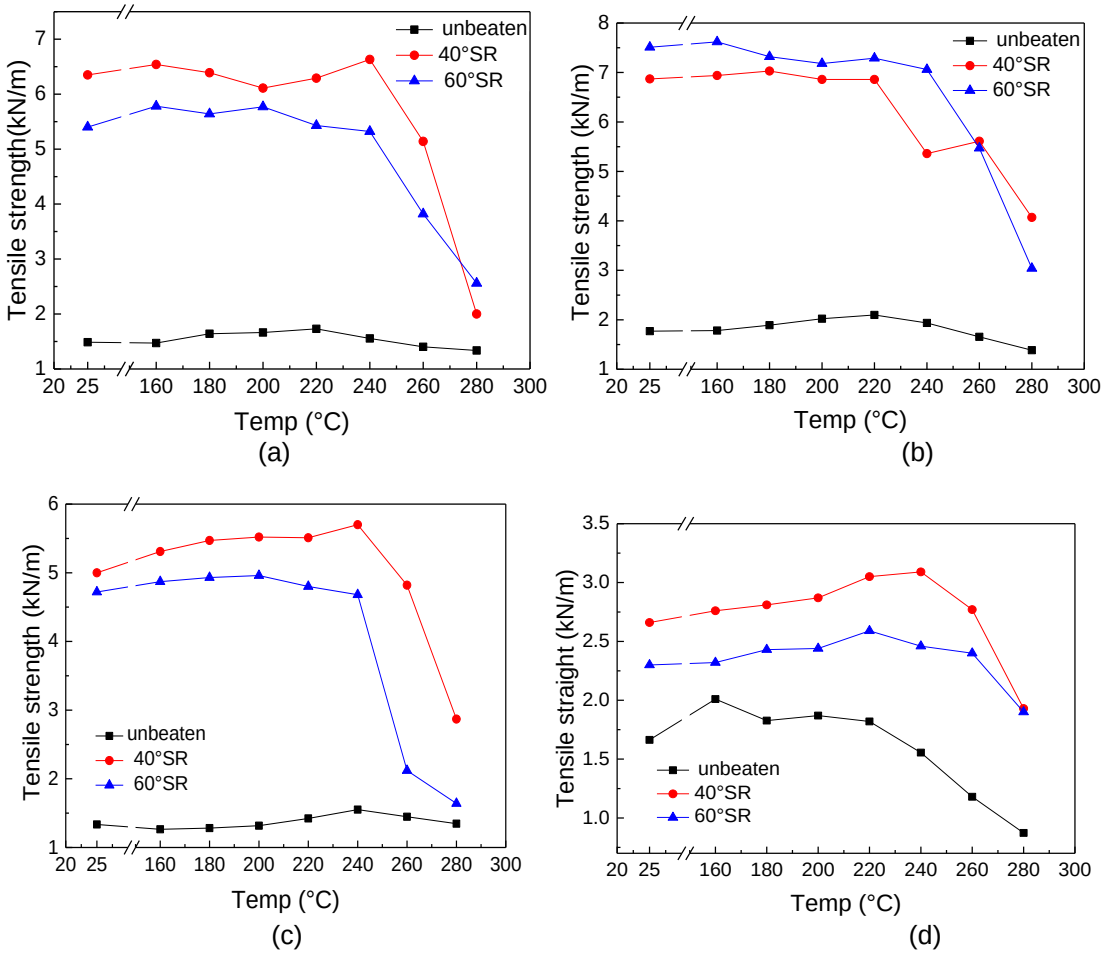

Fig. 4. Tensile strength of each paper with different beating degrees: (a) A, (b) B, (c) C, and (d) D

Brightness is also an important parameter to characterize the heat resistance of paper. The linear relationship between the brightness and temperature was investigated, and the results are shown in Fig. 5. The brightness of the paper generally decreased as the thermal treatment temperature increased. The influences of the beating degree on the paper brightness and brightness stability were examined. Figure 5 shows that the paper from pulp refined to 60 ºSR and heated to 160 or 180 °C had the higher brightness than the beaten paper at room temperature. This is attributed to the fact that the more highly beaten pulp, which is higher swelling ability, develops a greater fiber-to-fiber bonded area, and this consequently decreases the proportion of the light scattered from the sheet. Additionally, the brightness of the paper prepared using unbeaten pulp decreased faster with an increase in the treatment temperature. For example, the brightness retention value of the B paper with unbeaten pulp was 27.9%, which was lower than that of the 40 °SR paper (66.2%) and 60°SR paper (76.8%) at 240 °C. The other three papers (A, C, and D) showed the same trend as that of the B paper.

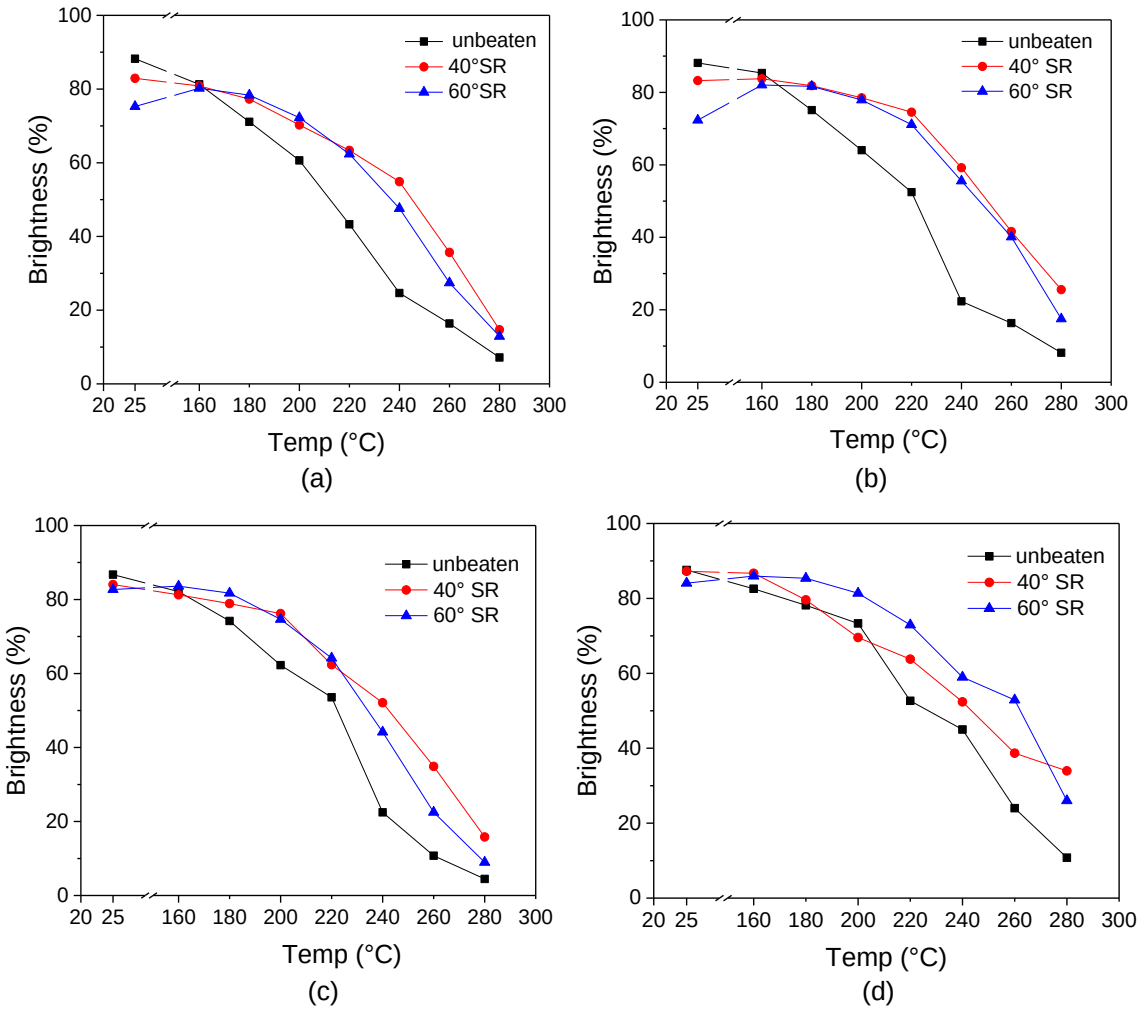

Fig. 5. Brightness of each paper with different beating degrees: (a) A, (b) B, (c) C, and (d) D

Surface Morphological Changes of the Cellulosic Paper

The morphology of each paper that had been subjected to heat treatment was analyzed by SEM. Figure 6 shows that the surface morphology of a single fiber did not change obviously, but there were fewer fines that coated the fibers and the surface of the paper became smoother with an increase in the treatment temperature. This phenomenon was the result of the fines having a lower pyrolysis temperature and poorer thermal stability compared with that of the fiber. The generation of fines occurred during refining (Jones *et al.* 2013), which led to the strength properties being positively affected because the connectivity within the fiber structure increased (Afra *et al.* 2013). Also, the strength stability was passively affected because the pyrolysis temperature decreased. This was consistent with the effect of the beating degree on the paper strength and strength stability that was discussed above.

Impact of Mechanical Refining on the Hemicellulose Content

Hemicellulose is the second major component after cellulose in lignocellulosic materials (Hamzeh *et al.* 2013). The effect of mechanical beating on the hemicellulose content of the material was therefore investigated (Jones *et al.* 2014). Table 3 shows that the sugars content from the hemicellulose decreased by various degrees after refining. For

example, the xylose produced in the unbeaten condition was 8.2%, and when the beating degree was 40°SR and 60°SR, the xylose content was 6.18% and 6.21%, respectively. This meant that mechanical beating decreased the hemicellulose content.

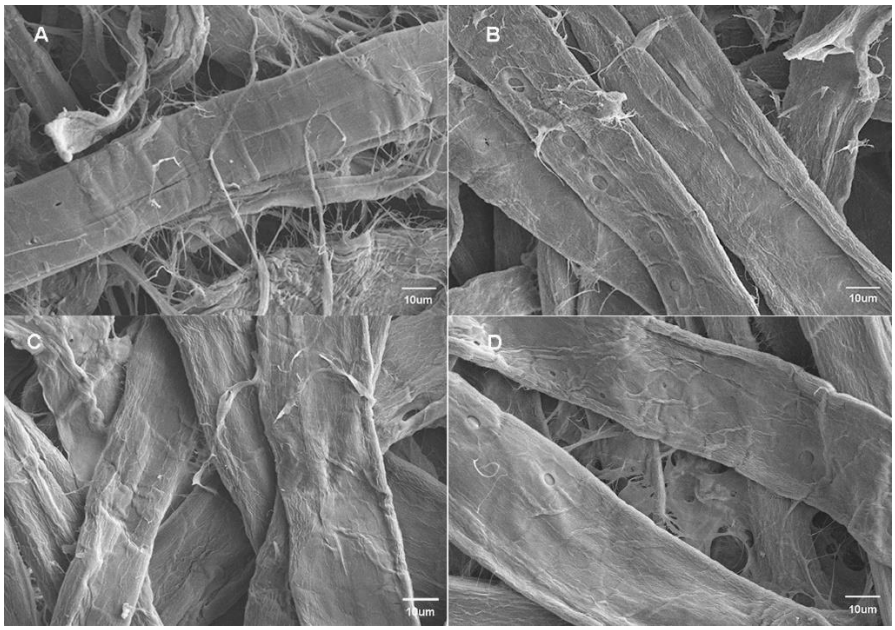

Fig. 6. SEM micrographs of the B paper (unbeaten) at different temperatures: (A) 25 °C, (B) 160 °C, (C) 220 °C, and (D) 280 °C

Table 3. Monose Content of B at Different Beating Degrees

Material	Beating Degree (°SR)	Arabinose (%)	Galactose (%)	Glucose (%)	Xylose (%)	Mannose (%)
B	15	0.62	0.21	86.32	8.20	4.64
	40	0.46	0.17	88.70	6.18	4.49
	60	0.44	0.18	88.51	6.21	4.66

CONCLUSIONS

1. Based on the thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the various pulp samples, clear correlations were found, and the thermal decomposition was dependent upon the material type and hemicellulose content.
2. When the pulps were treated with refining, fines were generated and the hemicellulose content decreased, which resulted in an improvement of the mechanical strength and optical properties.
3. Compared with the original paper, the tensile strength and brightness of the 40°SR papers averaged increases of 217.34% and 114.13% at 240 °C, respectively. Additionally, the brightness stabilization of the samples increased by 32.2% at 240 °C. Thus, it was concluded that the heat tolerance of the paper in terms of the mechanical strength and optical properties can be tuned by refining.

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REFERENCES CITED

Afra, E., Yousefi, H., Hadilam, M. M., and Nishino, T. (2013). "Comparative effect of mechanical beating and nanofibrillation of cellulose on paper properties made from bagasse and softwood pulps," *Carbohyd. Polym.* 97(2), 725-730. DOI: 10.1016/j.carbpol.2013.05.032

An, X.-h., Qian, X.-r., and Long, Y.-f. (2007). "Preparation of flame retardant paper based on *in-situ* synthesis of Mg-Al hydrotalcites," *China Pulp and Paper*.

Bledzki, A. K., and Gassan, J. (1999). "Composites reinforced with cellulose based fibres," *Prog. Polym. Sci.* 24(2), 221-274. DOI: 10.1016/S0079-6700(98)00018-5

Chen, H., Chen, K., Yang, R., and Yang, F. (2011). "Use of aluminum trihydrate filler to improve the strength properties of cellulosic paper exposed to high temperature treatment," *BioResources* 6(3), 2399-2410. DOI: 10.15376/biores.6.3.2399-2410

Chen, T., Xie, Y., Wei, Q., Wang, A., Hagman, O., Karlsson,.O and Liu, J (2016). "Effect of refining on physical properties and paper strength of *Pinus massoniana* and China fir cellulose fibers," *BioResources* 11(3), 7839-7848. DOI: 10.15376/biores.11.3.7839-7848

Dou, C., Ewanick, S., Bura, R., and Gustafson, R. (2016). "Post-treatment mechanical refining as a method to improve overall sugar recovery of steam pretreated hybrid poplar," *Bioresource Technology* 207, 157-165. DOI: 10.1016/j.biortech.2016.01.076

Fengel, D., and Wegener, G. (1984). *Wood: Chemistry, Ultrastructure, Reactions*, Walter de Gruyter Verlag, Berlin, Germany.

Fan, J., Li, T., Ren, Y., Qian, X., Wang, Q., Shen, J., and Ni, Y. (2017). "Interaction between two oppositely charged starches in an aqueous medium containing suspended mineral particles as a basis for the generation of cellulose-compatible composites," *Ind. Crop. Prod.* 97, 417-424. DOI: 10.1016/j.indcrop.2016.12.048

GB/T 12914-2008 (2008). "Paper and Board – Determination of tensile properties," China Standards Press, Beijing, China.

GB/T 7975-2005 (2005). "Paper and Board – Determination of color (c/2) - diffuse reflectance method," China Standards Press, Beijing, China.

González, I., Vilaseca, F., Alcalá, M., Pèlach, M. A., Boufi, S., and Mutjé, P. (2013). "Effect of the combination of biobeating and NFC on the physico-mechanical properties of paper," *Cellulose* 20(3), 1425-1435. DOI: 10.1007/s10570-013-9927-1

Giudicianni, P., Cardone, G., and Ragucci, R. (2013). "Cellulose, hemicellulose and lignin slow steam pyrolysis: Thermal decomposition of biomass components mixtures," *J. Anal. Appl. Pyrol.* 100, 213-222. DOI: 10.1016/j.jaap.2012.12.026

Gharehkhani, S., Sadeghinezhad, E., Kazi, S. N., Yarmand, H., Badarudin, A., Safaei, M. R., and Zubir, M. N. M. (2015). "Basic effects of pulp refining on fiber properties-A review," *Carbohyd. Polym.* 115, 785-803. DOI: 10.1016/j.carbpol.2014.08.047

Hamzeh, Y., Ashori, A., Khorasani, Z., Abdulkhani, A., and Abyaz, A. (2013). "Pre-extraction of hemicelluloses from bagasse fibers: Effects of dry-strength additives on paper properties," *Ind. Crop. Prod.* 43, 365-371. DOI: 10.1016/j.indcrop.2012.07.047

Hubbe, M. A. (2014). "Puzzling aspects of the hydrophobic sizing of paper and its inter-fiber bonding ability," *BioResources* 9(4), 5782-5783. DOI: 10.15376/biores.9.4.5782-5783

Jones, B. W., Venditti, R., Park, S., Jameel, H., and Koo, B. (2013). "Enhancement in enzymatic hydrolysis by mechanical refining for pretreated hardwood lignocellulosics," *Bioresource Technology* 147(7), 353-360. DOI: 10.1016/j.biortech.2013.08.030

Jones, B. W., Venditti, R., Park, S., and Jameel, H. (2014). "Comparison of lab, pilot, and industrial scale low consistency mechanical refining for improvements in enzymatic digestibility of pretreated hardwood," *Bioresource Technology* 167(3), 514. DOI:10.1016/j.biortech.2014.06.026

Klemm, D., Heublein, B., Fink, H., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Angew. Chem. Int. Edit.* 44(22), 3358-3393. DOI: 10.1002/anie.200460587

Lv, G.-J., Wu, S.-B., and Lou, R. (2010). "Kinetic study of the thermal decomposition of hemicellulose isolated from corn stalk," *BioResources* 5(2), 1281-1291. DOI: 10.15376/biores.5.2.1281-1291

QB/T 1463-1992 (1992). "PFI beating pulp mill laboratory method," China Standards Press, Beijing, China.

Soares, S., Camino, G., and Levchik, S. (1995). "Comparative study of the thermal decomposition of pure cellulose and pulp paper," *Polym. Degrad. Stabil.* 49(2), 275-283. DOI: 10.1016/0141-3910(95)87009-1

Shen, D. K., and Gu, S. (2009). "The mechanism for thermal decomposition of cellulose and its main products," *Bioresour. Technol.* 100(24), 6496-6504. DOI: 10.1016/j.biortech.2009.06.095

Shen, D., Zhang, L., Xue, J., Guan, S., Liu, Q., and Xiao, R. (2015). "Thermal degradation of xylan-based hemicellulose under oxidative atmosphere," *Carbohyd. Polym.* 127, 363-371. DOI: 10.1016/j.carbpol.2015.03.067

TAPPI T205 (2002). "Forming handsheets for physical tests of pulp," TAPPI Press, Atlanta, GA.

Wentz, F. E., Marcy, A. D., and Gray, M. J. (1982). "Analysis of wood sugars in pulp and paper industry samples by HPLC," *J. Chromatogr. Sci.* 20.8:349-352. DOI: 10.1093/chromsci/20.8.349

Wang, S. L., and Song, X. M. (2010). "Synthesize and application of Mg-Al hydrotalcite in flame retardant paper preparation," *Adv. Mat. Res.* 174, 362-365. DOI: 10.4028/www.scientific.net/AMR.174.362

Wu, C.-H., Chang, C.-Y., Lin, J.-P., and Hwang, J.-Y. (1997). "Thermal treatment of coated printing and writing paper in MSW: Pyrolysis kinetics," Fuel 76(12), 1151-1157. DOI: 10.1016/S0016-2361(97)00113-0

Zhang, M. Q., Rong, M. Z., and Lu, X. (2004). "All-plant fiber composites," in: *Proceedings of the Fourth Asian-Australasian Conference on Composite Materials (ACCM 4)*, Sydney, Australia, pp. 3-8.

Zhang, M. Q., Rong, M. Z., and Lu, X. (2005). "Fully biodegradable natural fiber composites from renewable resources: All-plant fiber composites," *Compos. Sci. Technol.* 65(15-16), 2514-2525. DOI: 10.1016/j.compscitech.2005.06.018

Zhao, D., Yang, F., Dai, Y., Tao, F., Shen, Y., Duan, W., Zhou, X., Tang, L. and Li, J (2017). "Exploring crystalline structural variations of cellulose during pulp beating of tobacco stems," *Carbohydrate Polymers* 174, 146-153. DOI: 10.1016/j.carbpol.2017.06.060

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