Evaluation of Cellulase Effect on the Refining Process of Softwood Bleached Kraft Pulp

Sung Gyu Park,[a] Ji Hyun Tak,[a] Ji Young Lee,[b,]* Kyoung Sik Shin,[c] and Se Il Park [c]

As interest in the use of eco-friendly enzymes increases in the paper industry, an energy-intensive industry, the development of a wide range of enzyme application technologies is required. This study evaluated the effects of cellulase on the refining efficiency, fiber properties, and sheet strength of softwood bleached kraft pulp (Sw-BKP). The pulp was enzyme-dosed with cellulase for 6 h and refined using a laboratory beater for 15 min. The freeness and physical properties of the Sw-BKP fibers were analyzed. The pulp freeness decreased linearly as the refining time and enzyme dosage increased, indicating that the cellulase promotes refining efficiency by inducing fiber shortening and internal fibrillation during refining. Handsheets were prepared from 15-min refined enzyme-dosed and non-enzyme-dosed Sw-BKP. The strengths of the enzyme-dosed handsheets were lower than those of the non-enzyme-dosed handsheets because fiber shortening due to the cellulase activity was dominant during the refining. Therefore, cellulase effectively reduces refining energy consumption. However, it is essential to determine the correct enzyme dosage and refining time to balance the desired refining energy reduction with the resulting paper strength.

DOI: 10.15376/biores.20.1.1059-1068

Keywords: Cellulase; Enzyme treatment; Bleached kraft pulp; Refining energy; Beating; Paper strength

*Contact information: a: Department of Forest Products, Gyeongsang National University, Jinju 52828, Republic of Korea; b: Department of Environmental Materials Science/IALS, Gyeongsang National University, Jinju 52828, Republic of Korea; c: Dong Jin Industry CO., LTD., Gyengsan 38537, Republic of Korea; * Corresponding author: paperyjy@gnu.ac.kr*

INTRODUCTION

Global efforts to reduce energy, such as minimizing carbon emissions, earning eco-friendly certificates, and making climate change agreements, are accelerating progress toward a low-carbon economy. To achieve sustainable growth and enhance national competitiveness in the international community, Korea must promote the realization of carbon neutrality and contribute to such policies. According to Statistics Korea, the paper industry accounted for 0.65% of the domestic manufacturing industry in 2019 and recorded an annual export performance of 2.4 billion dollars as of 2021. According to the Korea Paper Industry Association, although the paper industry accounted for only 0.65% of the domestic manufacturing industry in 2019, it emitted approximately 5.5 million tons of greenhouse gases in 2018, accounting for 1.4% of industrial and 0.8% of total national emissions. Therefore, in an international environment where countries declare carbon neutrality to reduce greenhouse gases, urgent efforts to reduce greenhouse gases are required for the paper industry in Korea to survive.

Due to low pulp self-sufficiency and limited water resources, Korean papermakers are experiencing a vicious cycle in which low-grade pulp and low-quality process water are used for papermaking (Jo *et al.* 2020; Kim *et al.* 2021; Lee and Yoon 2022; Kim and Goo 2024). Efforts to improve paper quality have resulted in high electricity and drying energy consumption. Therefore, the Korean paper industry has suggested technologies to reduce energy consumption, including modifying refining and drying processes and equipment and applying new raw materials. However, hardware approaches involve increased cost and time, and the applicability of new raw materials varies depending on the paper grade. Thus, it is necessary to develop eco-friendly technologies that can be rapidly applied to a wide range of papermaking processes, such as manufacturing printing paper and paperboard.

The use of enzymes in the papermaking process can reduce the consumption of synthetic polymer chemicals and electrical and drying energy. Cellulase and xylanase, enzymes that act on cellulose and hemicellulose, the main components of pulp fibers, cause swelling and hydrolysis of pulp fibers (Wong *et al.* 2000; Shojaei *et al.* 2012; Verma *et al.* 2016; Tanveer *et al.* 2023; Barrios *et al.* 2024). In addition, if cellulase, which selectively acts on water-soluble colloidal substances and cellulose fibers, is applied to improve the drainage defect caused by excessive fines (Cao and Tan 2002; Lecourt *et al.* 2010; Min *et al.* 2015), the wet moisture content can be rapidly reduced, and a reduction in drying energy can be expected. Cellulase and hemicellulose can also help save energy if the enzyme dosing is conducted before refining (Oksanen *et al.* 2011; Przybysz *et al.* 2016; Buzata *et al.* 2018). Although many studies have reported the effects of enzyme application, there is not enough information on changes in fiber properties and paper strength according to the enzyme dosage and pulp type in the refining process.

This study evaluated the effect of cellulase on refining energy savings of Sw-BKP, which is widely used for producing printing and writing paper grades, by plotting freeness curves according to the refining (beating) time and enzyme dosage. Changes in the physical properties of the fibers and the sheet strength based on the enzyme dosage were also determined to investigate a mechanism for improving refining efficiency.

EXPERIMENTAL

Materials

The softwood bleached kraft pulp (Sw-BKP) was supplied by Moorim Paper Co., Ltd., Jinju, Republic of Korea. The enzyme was supplied by Sunson Industry Group Co., Ltd., Beijing, China, and its specifications are shown in Table 1.

Table 1. Cellulase Specifications

Items	Specifications
Model Name	SUN65
Component	Cellulase
Appearance	Liquid with low subsidence
Color	Brown
Odor	Normal fermentation odor
Enzymatic Activity (u/mL)	1,080

Methods

Enzyme dosage and refining treatment of bleached softwood kraft pulp (Sw-BKP)

The disintegration of the Sw-BKP was performed at a consistency of 2.0% using a laboratory disintegrator (Daeil Machinery Co., Ltd., Daejeon, Republic of Korea) with 30,000 revolutions. The pulp slurry was kept in a water bath for 6 h and adjusted to the manufacturer's recommended optimum reaction conditions (pH 6.0 and 50 °C). Then, 0.00%, 0.01%, 0.02%, and 0.03% of the enzyme relative to the mass of the oven-dried fibers were added to samples of the pulp slurry. The samples were vigorously mixed to distribute the enzyme. The enzyme-dosed samples were refined for 15 min with a laboratory Hollander beater (FRANK-PTI; GmbH, Birkenau, Germany). Sub-samples were collected at 0, 5, 10, and 15 min during the refining for freeness testing using a Canadian freeness tester (33-23-00; Messmer Büchel, Netherlands). The equipment used for these procedures is shown in Fig. 1.

Table 2. Enzyme Treatment Condition

Items	Condition
Enzyme dosage (% on oven-dried fibers)	0.01, 0.02, 0.03
pH	6.0
Temperature (°C)	50
Reaction time (h)	6

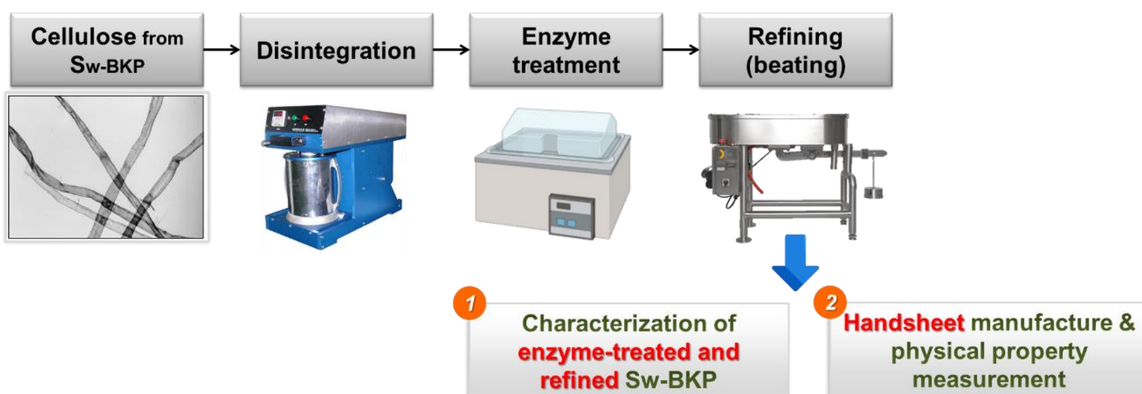

Fig. 1. Flow diagram of the experimental procedure

Characterization of enzyme-dosed and refined Sw-BKP

A fiber analyzer (FQA-360; OpTest Equipment Inc., Hawkesbury, Canada) was used to measure the length and width of the pulp fibers. The water retention value (WRV) of the pulp fiber was measured according to ISO 23714 (2007) to determine the swelling of their cell walls, which is also referred to as internal fibrillation. To analyze the shapes of the pulp fibers after the enzyme dosing and refining, microscopic images were captured at 100× magnification using an optical microscope (BX51; Olympus, Tokyo, Japan).

Handsheet manufacture and physical property measurement

Handsheets with a grammage of 80 ± 5 g/m^2 were produced according to TAPPI T205 sp-06 (2006). The enzyme-dosed, 15-min refined samples were diluted to a 0.7% consistency, wet pressed at 345 kPa for 5 min using a laboratory wet press (model 326; Wintree Corporation, Japan), and dried at 120 °C using a cylinder dryer (Daeil Machinery

Co., Ltd., Daejeon, South Korea). The handsheets were conditioned at 23°C and 50% relative humidity to maintain moisture content of 8%. Grammage (TAPPI T410 om-08 2013), tensile strength (TAPPI T494 om-06 2006), burst strength (TAPPI T403 om-10 2010), and tear strength (TAPPI T511 om-08 2008) were measured to determine the effect of the enzyme dosing on the physical properties of the handsheets.

RESULTS AND DISCUSSION

Effect of Enzyme Dosing on the Freeness and Physical Properties of Sw-BKP Fibers

Figure 2 shows the freeness curves of the enzyme-dosed Sw-BKP samples according to the refining time. The freeness of the pulp fibers decreased with increased refining time, and for the same refining time, the freeness of the pulp reduced with increasing enzyme dosage. As freeness is an operating indicator of the refining process, which consumes large amounts of electrical energy, electrical energy can be saved if the target freeness can be obtained within a shortened refining time. The freeness of the non-enzyme-dosed Sw-BKP sample was approximately 510 mL CSF after 15-min of refining. When 0.03% of the cellulase was added to the pulp before refining, a 20% reduction in refining time was observed in approximately 12 min.

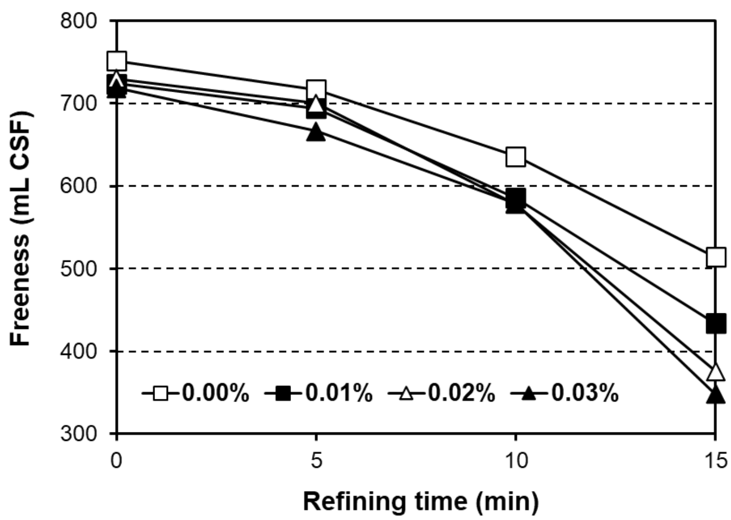

Fig. 2. Pulp freeness depending on the refining time and enzyme dosage

The average fiber lengths of the enzyme-dosed, 15-min refined Sw-BKP samples are shown in Fig. 3. The fiber length of the samples decreased with increased enzyme dosage, and the fiber length of the sample dosed with 0.03% cellulase decreased considerably. However, no significant change in the fiber width was observed when the enzyme dosage was increased to 0.03%. As the WRV of the fibers is proportional to their internal fibrillation, it is an important index that can be used to determine changes in fiber properties during refining. The WRV of the fibers tended to increase as the enzyme dosage increased. The WRV increased by 11% when the enzyme dosage was increased from zero to 0.03% after refining for 15 min (Fig. 4). Therefore, the enzyme effectively promoted fiber shortening and internal fibrillation. However, because the ratio of the fiber shortening was greater than that of the internal fibrillation, more fiber shortening occurred than internal fibrillation during the refining after the enzyme dosing.

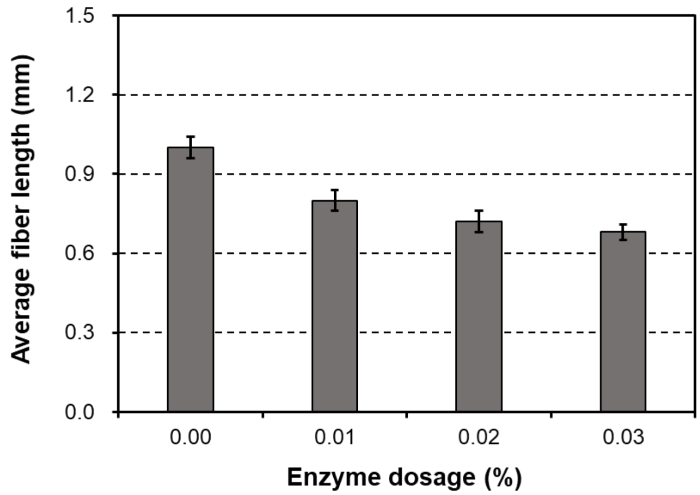

Fig. 3. Average fiber length of the 15-min refined pulp depending on the enzyme dosage

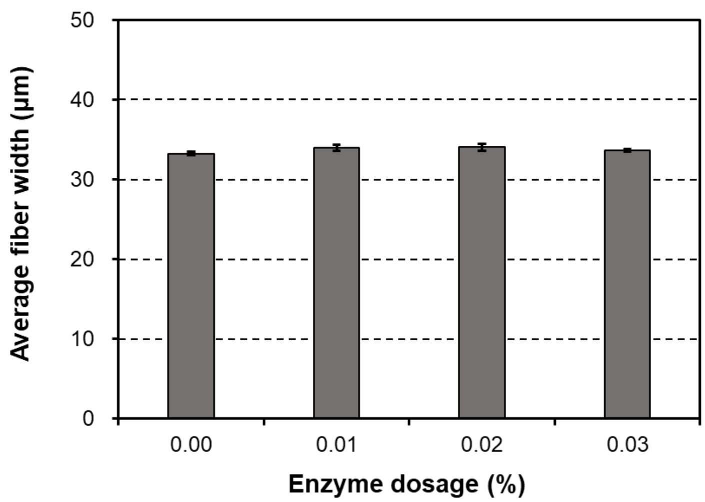

Fig. 4. Average fiber width of the 15-min refined pulp depending on the enzyme dosage

To confirm these measurements, microscopic images of the enzyme-dosed 15-min refined, and non-refined samples were examined (Fig. 5 through 7). Although no significant changes in the morphology of the enzyme-dosed unrefined fibers were observed, it appeared that the long fibers had been cut into short fibers after the enzyme dosing and refining. Higher the enzyme dosage, shorter the fibers observed after refining. In addition, fibrils were observed on the surface of the short fibers after the enzyme dosing and refining. These results are consistent with the fiber length, width, and WRV results.

Therefore, it was confirmed that if enzyme dosing was performed before refining, the fiber length decreased, and internal fibrillation was promoted during refining, which could reduce the refining time required to obtain the desired pulp freeness.

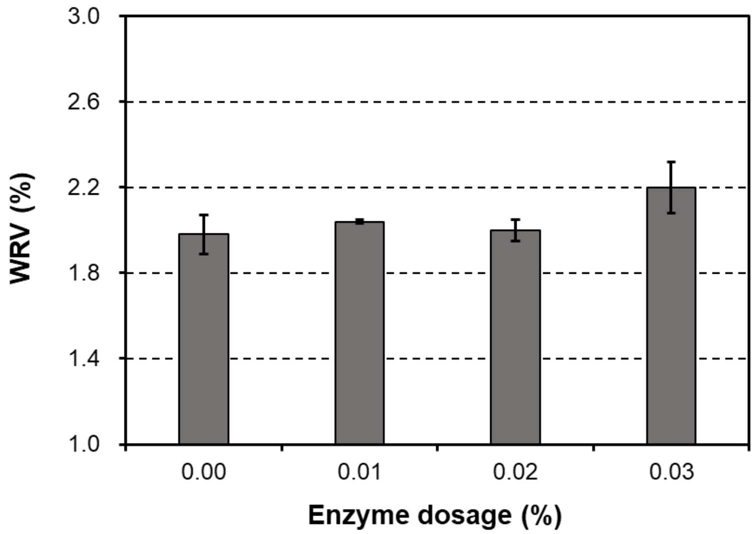

Fig. 5. Water retention value (WRV) of the 15-min refined pulp slurry according to the enzyme dosage

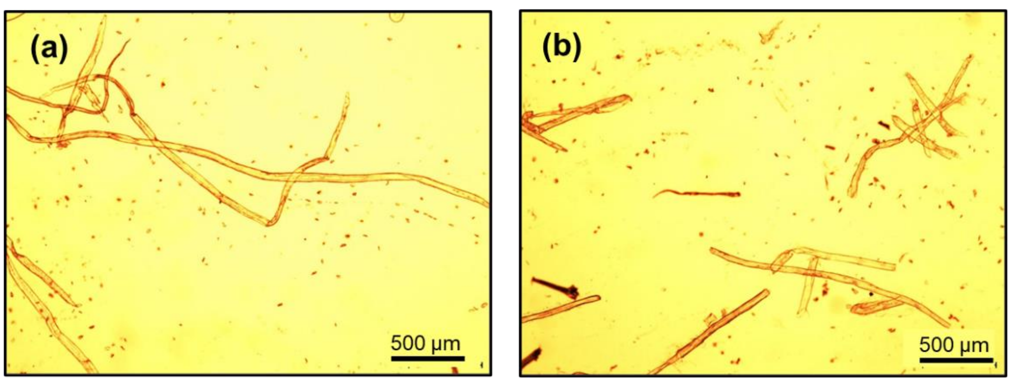

Fig. 6. Micrographs of the 0.01% enzyme-dosed pulp slurries: (a) unrefined and (b) refined for 15 min

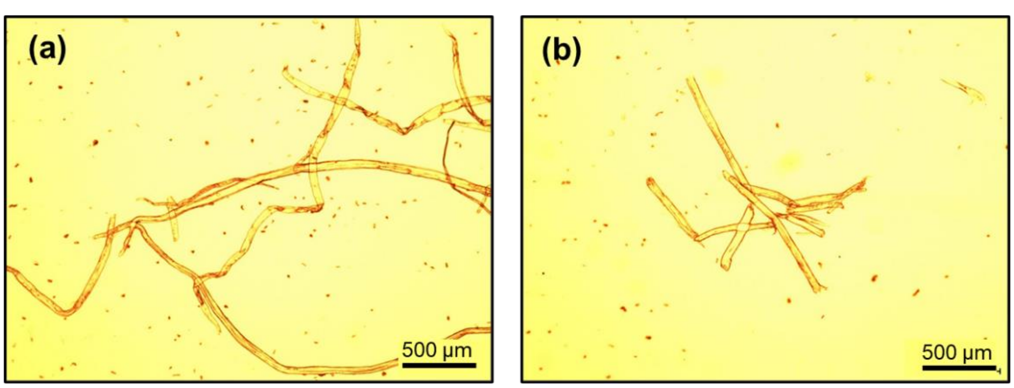

Fig. 7. Micrographs of the 0.02% enzyme-dosed pulp slurries: (a) unrefined and (b) refined for 15 min

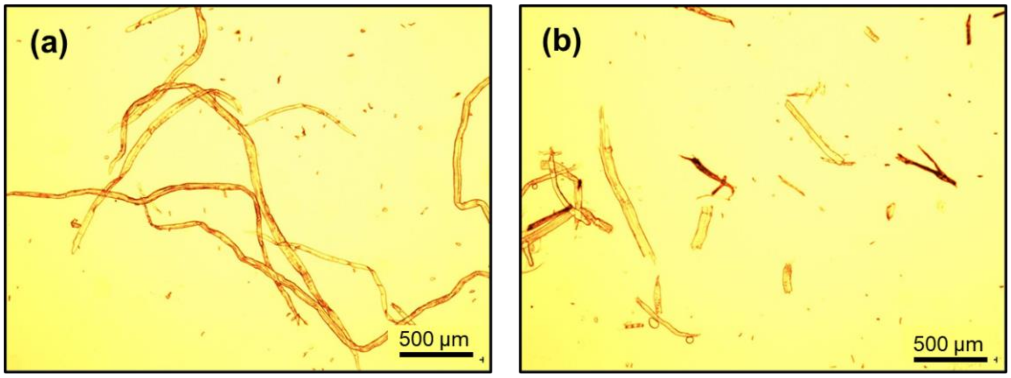

Fig. 8. Micrographs of the 0.03% enzyme-dosed pulp slurries: (a) unrefined and (b) refined for 15 min

Effect of Enzyme Dosing on the Physical Properties of Handsheets

Handsheets were prepared from the enzyme-dosed, 15-min refined samples, and their strengths were measured. Figures 9 through 11 show the tensile, bursting, and tear indices of the handsheets. As the enzyme dosage increased, the tensile, bursting, and tearing strengths of the handsheets decreased. The changes in fiber length and cell wall swelling (internal fibrillation) during the refining directly affect the strength properties of the paper (Hartman 1985; Nordström and Hermansson 2017; Motamedian *et al.* 2019; Mandlez *et al.* 2022).

According to the effect of the enzyme on the physical properties of Sw-BKP described in the previous section, the fiber shortening and cell wall swelling (internal fibrillation) occurred simultaneously. However, the fiber shortening was dominant, and, in particular, the increased enzyme dosage tended to promote fiber shortening (Clark 1978).

Cellulase doping can shorten the refining time required for target freeness, reducing the electrical energy required. However, strength reduction due to fiber shortening must be avoided. Therefore, controlling the enzyme dosage and refining time is essential to balance desired refining energy savings and paper strength.

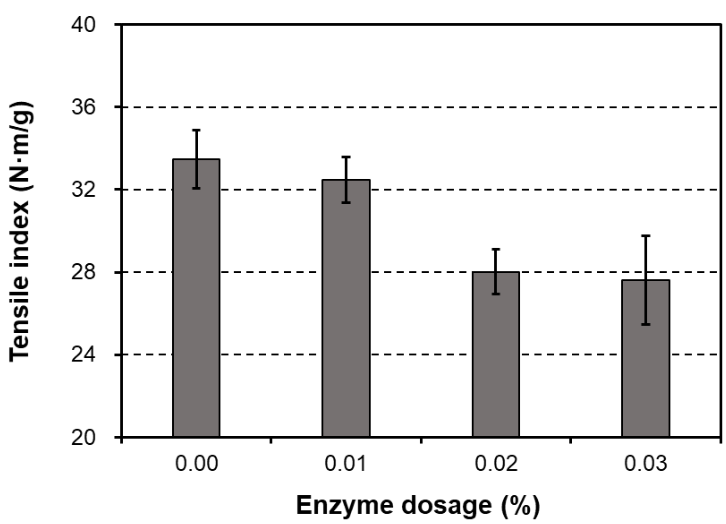

Fig. 9. Tensile indices of the handsheets prepared from the enzyme-dosed, 15-min refined pulp slurry depending on enzyme dosage

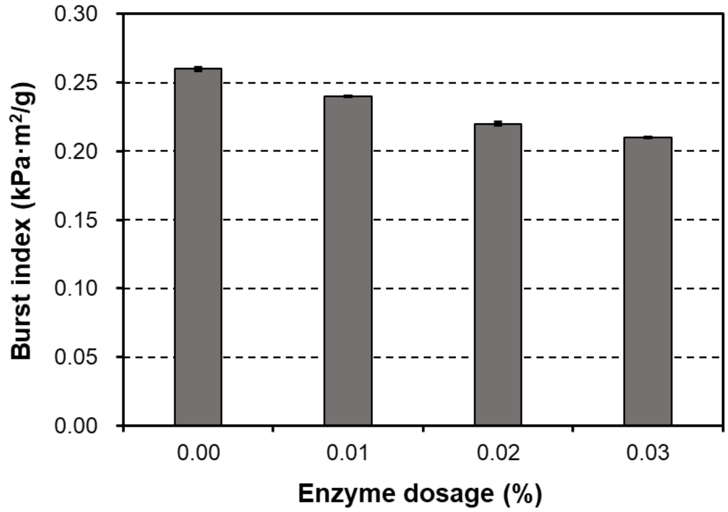

Fig. 10. Burst indices of the handsheets prepared from the enzyme-dosed, 15-min refined pulp slurry depending on enzyme dosage

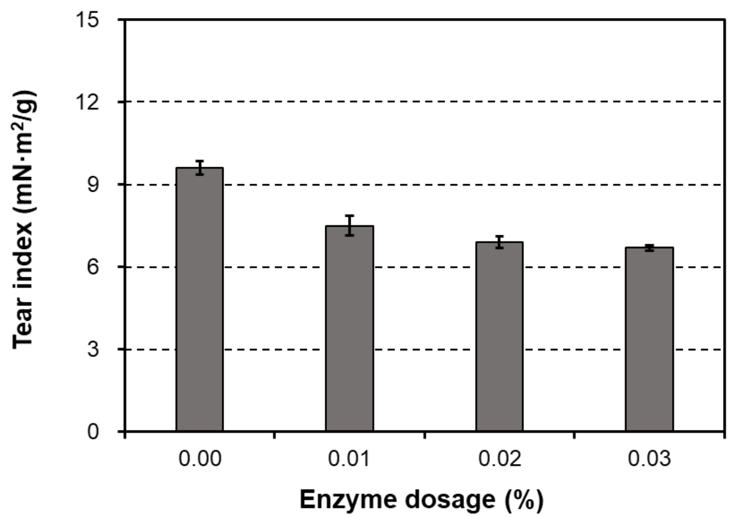

Fig. 11. Tear indices of the handsheets prepared from the enzyme-dosed, 15-min refined pulp slurry depending on enzyme dosage

CONCLUSIONS

1. The cellulase promoted the fiber shortening and swelling of the cell walls (internal fibrillation) of the softwood bleached kraft pulp (Sw-BKP) during the refining process and reduced the refining time required to obtain the target freeness. This indicates cellulase can effectively reduce the refining energy used in the papermaking process.
2. The strengths of the handsheets prepared from the enzyme-dosed, refined Sw-BKP were lower than those of the non-enzyme-dosed, refined Sw-BKP because

fiber shortening was dominant during the refining because of the enzyme.

3. Determining the correct enzyme dosage and refining time is essential to balance reduced refining energy consumption with target paper strength.

ACKNOWLEDGMENTS

Following are results of a study on the "Leaders in INdustry-university Cooperation 3.0" Project, supported by the Ministry of Education National Research Foundation of Korea.

REFERENCES CITED

Barrios, N., Smith, M. M., Venditti, R. A., and Pal, L. (2024). "Enzyme-assisted dewatering and strength enhancement of cellulosic fibers for sustainable papermaking: A bench and pilot study," *Cleaner Production* 434(1), 1-14. DOI: 10.1016/j.jclepro. 2023.140094

Buzata, K. P., Kalinowska, H., Borkowski, J., and Przybysz, P. (2018). "Effect of xylanases on refining process and kraft pulp properties," *Cellulose* 25, 1319-1328. DOI: 10.1007/s10570-017-1609-y

Cao, Y., and Tan, H. (2002). "Effect of cellulase on the modification of cellulose," *Carbohydrate Research* 337(14), 1291-1296. DOI: 10.1016/s0008-6215(02)00134-9

Clark, D. (1978). *Pulp Technology and Treatment for Paper*, Miller Freeman Publications, San Francisco. DOI: 10.1007/978-3-030-79139-1_6

Hartman, R. R. (1985). "Mechanical treatment of pulp fibres for paper property development," *Papermaking Raw Materials*, FRC, Manchester, pp. 413-442. DOI: 10.15376/frc.1985.1.413

ISO 23714 (2007). "Pulps – Determination of water retention value (WRV)," International Organization for Standardization, Geneva, Switzerland.

Jo, H. M., Lee, J. Y., and Lee, Y. H. (2020). "Strength improvement of the coloring paper for fruit bag by using non-woody bamboo kraft pulp," *Journal of Korea TAPPI* 52(6), 132-139. DOI: 10.5814/JKTAPPI.2020.12.52.6.132

Kim, S. W., Lee, S. L., and Yoon, B. S. (2021). "Time series characteristics of the imported pulp prices," *Journal of Korea TAPPI* 53(6), 98-105. DOI: 10.7584/JKTAPPI.2021.12.53.6.98

Kim, S. N., and Goo, Y. W. (2024). "Determinants of pulp producer prices in Korea: Focused on exchange rate and import prices," *Journal of Korea TAPPI* 56(1), 3-10. DOI: 10.7584/JKTAPPI.2024.2.56.1.3

Lecourt, M., Meyer, V., Sigoillot, J. C., and Conil, M. P. (2010). "Energy reduction of refining by cellulase," *Holzforschung* 64, 441-446. DOI: 10.1515/hf.2010.066/html

Lee, S. L., and Yoon, B. S. (2022). "Dynamic causal relationships among import price, import quantity and ocean freight rate index in the chemical pulp market," *Journal of Korea TAPPI* 54(4), 94-102. DOI: 10.7584/JKTAPPI.2022.08.54.4.94

Mandlez, D., Koller, S., and Eckhart, R. (2022). "Quantifying the contribution of fines production during refining to the resulting paper strength," *Cellulose* (29), 8811-8826. DOI: 10.1007/s10570-022-04809-x

Min, B. C., Bhayani, B. V., Jampana, V. S., and Ramarao, B. V. (2015). "Enhancement of the enzymatic hydrolysis of fines from recycled paper mill waste reject," *Bioresources and Bioprocessing* 40(2), 1-10. DOI: 10.1186/s40643-015-0068-2

Motamedian, H. R., Halilovic, A. E., and Kulachenko, A. (2019). "Mechanisms of strength and stiffness improvement of paper after PFI refining with a focus on the effect of fines," *Cellulose* (26), 4099-4124. DOI: 10.1007/s10570-019-02349-5

Nordström, B., and Hermansson, L. (2017). "Effect of fiber length on formation and strength efficiency in twin-wire roll forming," *Nordic Pulp & Paper Research Journal* 32(1), 119-125. DOI: 10.3183/npprj-2017-32-01-p119-125/html

Oksanen, A., Edelmann, K., Kataja-aho, J., and Suurnakki, A. (2011). "Enhancing dewatering of thermo-mechanical pulp (TMP) based papermaking through enzymatic treatment," *Holzforschung* 65, 787-795. DOI: 10.1515/HF.2011.083

Przybysz Buzata, K., Przybysz, P., Kalinowsaka, H., and Derkowska, M. (2016). "Effect of cellulases and xylanases on refining process and kraft pulp properties," *PLOS ONE* 11(8), 1-14. DOI: 10.1371/journal.pone.0161575

Shojaei, K. M., Dadashian, F., and Montazer, M. (2012). "Recycling of cellulosic fibers by enzymatic process," *Applied Biochemistry and Biotechnology* 166, 744-752. DOI: 10.1007/s12010-011-9463-0

Tanveer, A., Gupta, S., Dwivedi, S., Yadav, K., Yadav, S., and Yadav, D. (2023). "Innovations in papermaking using enzymatic intervention: An ecofriendly approach," *Cellulose* 30. 7393-7425. DOI: 10.1007/s10570-023-05333-2

TAPPI T205 sp-06 (2006). "Forming handsheets for physical tests of pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T410 om-10 (2013). "Grammage of paper and paperboard (weight per unit area)," TAPPI Press, Atlanta, GA, USA.

TAPPI T494 om-06 (2006). "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)," TAPPI Press, Atlanta, GA, USA.

TAPPI T403 om-10 (2010). "Bursting strength of paper," TAPPI Press, Atlanta, GA, USA.

TAPPI T511 om-08 (2008). "Folding endurance of paper (MIT tester)," TAPPI Press, Atlanta, GA, USA.

Verma, P. K., Bhardwaj, N. K., and Singh, S. P. (2016). "Improving the material efficiency of recycled furnish for papermaking through enzyme modifications," *The Canadian Journal of Chemical Engineering* 94(3), 430-438. DOI: 10.1002/cjce.22410

Wong, K. K. Y., Richardson, J. D., and Mansfield, S. D. (2000). "Enzymatic treatment of mechanical pulp fibers for improving papermaking properties," *Biotechnology Progress* 16(6), 1025-1029. DOI: 10.1021/bp000064d

Article submitted: October 7, 2024; Peer review completed: November 2, 2024; Revised version received and accepted: November 13, 2024; Published: December 4, 2024.
DOI: 10.15376/biores.20.1.1059-1068