Ultrasound-assisted Xylanase Treatment of Chemi-Mechanical Poplar Pulp

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Xylanase treatment can be an environmentally friendly way to improve the formability and drainability of chemi-mechanical pulp (CMP). Improvements in xylanase treatment efficiency are possible with application of an ultrasonic wave *via* the cavitation effect. Results showed that the specific surface area (SSA) of the combined treated pulp increased by 14.6% at an ultrasonic treatment of 30 min and xylanase dosage of 10 U/g, in comparison to xylanase treatment alone. Also, the drainability of xylanase-treated pulp increased from 450 to 500 mL, and it further increased to 775 mL with ultrasonic-assisted xylanase treatment. Morphological characterization of pulps showed an enhanced fibrillation for the combined treatment, as shown by scanning electron microscope (SEM) images. In addition, the dimensions of treated fibers were negligibly affected.

Keywords: Chemi-mechanical pulp; Xylanase treatment; Ultrasonic treatment; Specific surface area

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INTRODUCTION

From a global perspective, full utilization of native or local wood stores to produce biomass-based products is of strategic significance. Chemi-mechanical pulp (CMP) production technology fits well into the above concept by virtue of its high yield production (approximately 85%) (Xing *et al.* 2010). Furthermore, because CMP provides high-bulk and high-opacity paper sheets (Hu *et al.* 2015), it has found increasing applications in many paper grades (Georgieva *et al.* 2008). However, its physical strength is lower than chemical pulps, which hinders widespread application.

The weak physical strength of CMP is probably due to the high content of lignin, which hampers the intermolecular hydrogen bonding and Van der Waals forces between fiber surfaces. Xylanase treatment is one of the alternative and efficient technologies to improve the physical properties of pulps (Mansfield *et al.* 1997; Zhao *et al.* 2002). For example, the physical strength of corn bran dietary fiber can be improved by activating the fiber bonding modes (Hu *et al.* 2008). The xylanase treatment is expected to cleave the xylose chains around cellulose and thus improve the fibrillation process (Yang *et al.* 2011; Liu *et al.* 2012). In addition, xylanase and ultrasonic waves were used to treat wheat straw pulping to achieve maximum reduction in lignin content (Dedhia *et al.* 2012). Also, xylanase can increase the specific surface area (SSA) of fibers and thus improve the conformability (Rustamov *et al.* 2014). Others have reported that the tensile strength of xylanase-treated pulps increased from 179.53 to 208.26 N (Zhuang *et al.* 2014).

Ultrasonic wave treatment may be a favorable approach to further enhance the enzymatic modification *via* the cavitation effect (Pu *et al.* 2010; Zhao *et al.* 2013; Subhedar and Gogate 2014). It is a purely physical method enabling microjets and shockwaves to impinge on the fiber surface, causing changes in surface morphology (Li *et al.* 2014; Renouard *et al*. 2014). These changes not only increase the xylanase accessibility onto fibers, but also accelerate fibrillation. Ultrasonic wave treatment has been applied in waste paper recycling to produce recycled cellulose fibers (Xing *et al.* 2010; Guo *et al.* 2015). Also, the ultrasonic wave technique has been used to improve the sheet density, tensile strength, and brightness properties of recycled pulp fibers (Daisuke *et al.* 2000). The potential of high-power ultrasound to smooth paper surfaces in a volume-preserving way was studied (Ehrlich and Grossmann 2013). In other work, ultrasound treatment was able to provide similar results than kneading but at higher specific energy consumption (Wanske and Grossmann 2011).

Ultrasonic wave-amplified xylanase treatments of CMP pulp have not yet been reported. The objective of this study was therefore to investigate the effect of ultrasonic-assisted xylanase treatment of CMP pulp. The specific surface area (SSA) and drainability of pulps were evaluated in addition to fiber surface morphology and fiber quality.

EXPERIMENTAL

Materials

CMP pulp was supplied by Shandong Sun Paper Industry Joint Stock Co., Ltd. located in eastern China. The chemical composition (based on mass) of the CMP was as follows: cellulose 53.3% according to TAPPI T429 cm-84 (1984), hemicellulose 22.5% according to TAPPI T223 cm-84 (1984), acid-insoluble lignin 14.4% according to TAPPI T222 om-88 (1988), and ash 0.7% according to TAPPI T211 om-93 (1993).

Xylanase was purchased from Novozymes Biotechnology Co. Ltd., China.

Experimental Procedure

Xylanase treatments were performed according to previous reports (Yang *et al.* 2011) as follows: 40 °C, 30 min, pH 7 to 8, and pulp consistency 3%. The xylanase dosages were 10, 20, 30, 40, and 50 U/g (enzymatic activity unit) (based on oven-dried pulp). A temperature-controlled water bath (HH-8, Changzhou Guohua Electric Co. Ltd., China) was used.

Ultrasonic-assisted xylanase treatment was carried out in a sonicator (JY98-DN, Ningbo Scientz Biotechnology Co. Ltd., China) at 120 W in the time range of zero to 40 min. The pulp consistency was set at 3%, whereas other conditions were kept the same as in the xylanase treatment process.

Once the reaction was completed, the pulp was boiled for 5 min to inactivate the enzyme, followed by washing and drying.

Specific Surface Area Analysis

The specific surface area (SSA) of the pulp was determined by nitrogen absorption experiments using a surface area and porosimetry analyzer (v-sorb2800p, Beijing Jin Aipu Technology Co., Ltd.) in liquid nitrogen temperature. Before testing, the sample was dried in an oven (105 °C, 4 h) to remove the absorbed moisture and then placed in the analyzer for 3 h for testing.

Canadian Standard Freeness

Canadian standard freeness (CSF), indicating the drainability of pulp, was carried out in a Canadian standard freeness tester (33-23-00, Holland TMI Group) according to TAPPI T 227 (1984).

Surface Morphology

An environmental scanning electron microscope (SEM) (QUANTA 200, Holland FEI Co., Ltd.) was used to observe the fiber surface morphology. All samples were coated with a thin layer of gold (SCD 005, Switzerland BAL-TEC Corporation) under an accelerating voltage of 15 kV.

Fiber Quality

The average length and width, and the amount of fines were measured by a Fiber Quality Analyzer (FQA, Optest equipment Inc., Canada) according to TAPPI T271 (1991).

RESULTS AND DISCUSSION

Effect of Treatment on the Specific Surface Area of Pulps

The specific surface area (SSA) directly relates to the physical properties of pulps, *i.e.*, increasing SSA increases the fiber conformability (Mert *et al.* 2014; Rustamov *et al.* 2014). Figure 1 shows the SSA of pulps under different treatment conditions. As can be seen from Fig. 1(a), the SSA of pulps increased with increasing of xylanase dosage for both xylanase treated and ultrasonic-assisted xylanase treated samples. Furthermore, the ultrasonic-assisted xylanase-treated pulp showed a larger increment in SSA than its control counterparts under the same conditions. This phenomenon may be caused by the cavitation effect, which not only increases the fiber fibrillation through opening of additional external and internal surfaces, but also enhances xylanase adsorption onto the fiber.

Figure 1(b) shows the effect of ultrasonic time on the SSA values. For those samples without xylanase, the SSA of fibers increased with ultrasonic time treatment. Interestingly, the SSA increased more for ultrasonic-assisted xylanase treated samples, specifically beyond 20 min. All these results support the notion that the ultrasonic-assisted process displays a synergistic effect. Xu *et al.* (2014) reported that the internal bond strength and adsorption of pulp fibers increased by 4.07% and 23.49% when using ultrasonic-wave treatments. Li *et al.* (2015) also reported that pulps having a high crystallinity (78.9%) and low average fiber length of 37 μm can be obtained from ultrasonic pretreatment when coupled with HCl-$FeCl_3$ as a catalyst.

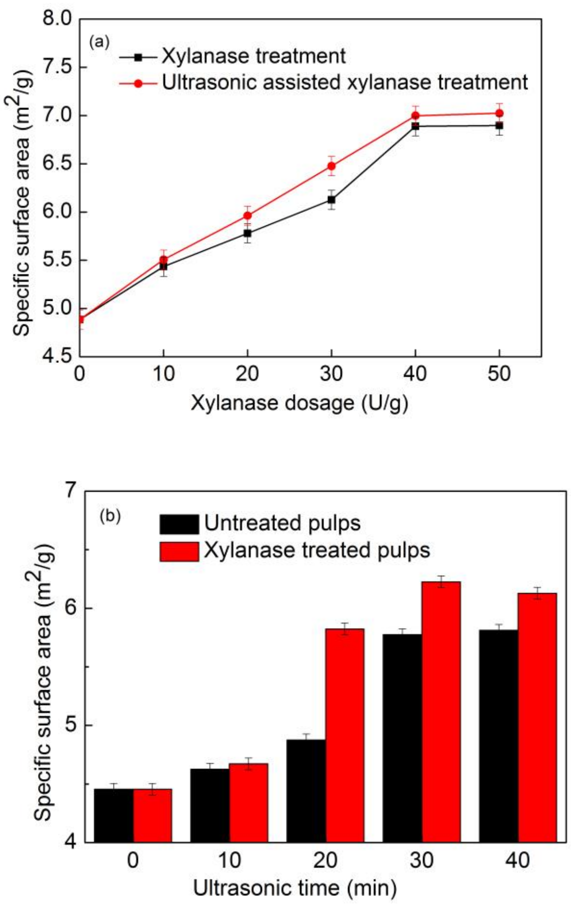

Fig. 1. Effect of xylanase dosage and ultrasonic treatment time on specific surface area of pulps: (a) xylanase treatment at 40 °C for 30 min, ultrasonic time 30 min; (b) xylanase dosage of 10 U/g, 30 min

Effect of Treatment on the Canadian Standard Freeness

Pulp drainability was obtained by the Canadian standard freeness (CSF) test. The effect of xylanase and ultrasonic-assisted xylanase treatment is presented in Fig. 2(a). The CSF of xylanase-treated pulp was 500 mL, which was an increase from 450 mL for the original untreated CMP. Furthermore, the CSF increased to 775 mL for the ultrasonic-assisted xylanase treatment after 10 min. However the CSF became constant when the ultrasonic time was increased beyond 10 min. This can be explained by the removal of fines after xylanase digestion. Furthermore, the xylanase efficiency could be further improved by ultrasonic treatment through loosening of the compact structure of cell wall, thus enhancing the accessibility of enzyme onto fibers. Others have also reported improvement of drainability of pulps after xylanase treatment based on the average fiber length increase and fines percent decrease (Luo *et al.* 2012).

The comparison of xylanase and ultrasonic-assisted xylanase treatment on CSF is shown in Fig. 2(b). The CSF of pulps increased with increases in xylanase dosage in the range of 10 to 50 U/g for both xylanase and ultrasonic-assisted xylanase treatments. This verified the improvement in pulp drainability after xylanase treatment. Also, the CSF of ultrasonic-assisted xylanase treated pulps showed higher values than the untreated samples. It should be note that the pulp yield was kept above 97.5% for all runs.

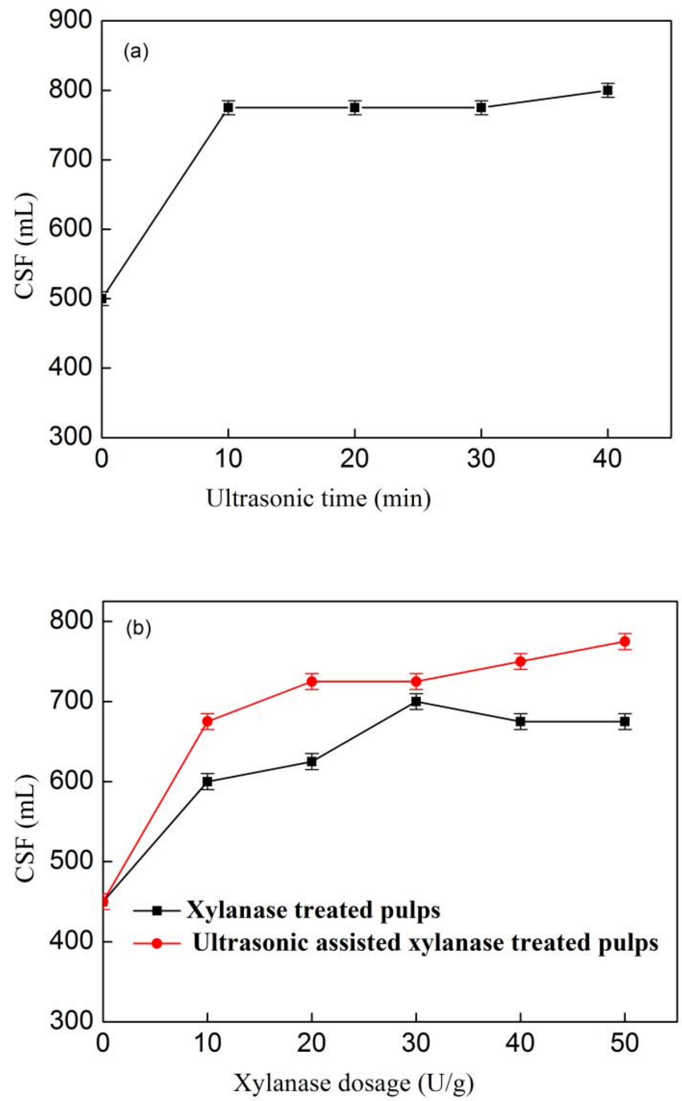

Fig. 2. Effect of ultrasonic treatment time and xylanase dosage on CSF: (a) xylanase treatment at 10 U/g and 40 °C; (b) 40 °C and 30 min

Surface Morphology of Untreated and Treated Pulps

Figure 3 shows SEM images of untreated and treated CMP pulps. In relation to the smooth and compact surface of untreated pulp (Fig. 3(a)), the xylanase-treated pulp (Fig. 3(b)) presents more pockets and asperities on the fiber surface, caused by the "etching" of xylanase. Furthermore, Fig. 3(c) shows ultrasonic-assisted xylanase treated pulp with stronger fibrillation. All of these results demonstrated that ultrasonication enhances xylanase treatment.

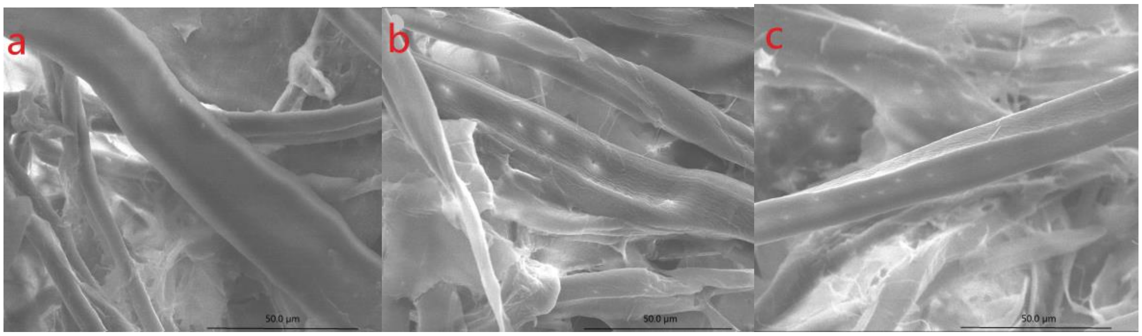

Fig. 3. SEM images of (a) untreated pulp, (b) pulp treated with xylanase at 10 U/g for 30 min, and (c) ultrasonic-assisted xylanase treated pulp at 30 min with xylanase dosage of 10 U/g for 30 min

Effect of Treatment on Fiber Quality

The fiber quality of untreated and treated pulps is listed in Table 1. Dimensions including fiber length and width were constant for all three kinds of pulp, which suggests that a gentle xylose chain cleavage for both xylanase and ultrasonic-assisted xylanase treatments. However, the fines content decreased gradually for xylanase and ultrasonic-assisted xylanase treated pulps, which may be explained by xylanase digestion of the fines, which may be amplified by ultrasonication. In other studies, fines content decreased from 27.21% to 23.64% when studying xylanase pretreatments for wood pulp (Lei *et al.* 2008).

Table 1. Effect of Xylanase Treatment on Fiber Quality

	Untreated pulp	Xylanase-treated pulp[1]	Ultrasonic-assisted xylanase-treated pulp[2]
Length (mm)	0.550	0.574	0.567
Width (μm)	21.2	21.3	20.9
Fines (%)	18.26	16.54	12.18

Note: [1]Xylanase dosage of 10 U/g, [2]ultrasonic time of 30 min and xylanase dosage of 10 U/g

CONCLUSIONS

1. Ultrasonication enhanced xylanase treatment to improve chemi-mechanical poplar pulp properties.
2. The specific surface area (SSA) was increased by 14.6% for ultrasonic-assisted xylanase treatment over 30 min and xylanase dosage of 10 U/g from xylanase treatment alone. The drainability also was increased from 500 mL to 775 mL.
3. Ultrasonic-assisted xylanase treatment enhanced the fibrillation of fibers, as determined by SEM. The fiber length and width were negligibly affected; however, the fines content decreased during ultrasonic-assisted xylanase treatment.

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REFERENCES CITED

Daisuke, T., Takashi, H., Shinya, K., and Takayoshi, M. (2000). "Ultrasonic treatment to improve the quality of recycle pulp fiber," *Japan Wood Research Society* 46(5), 405-409. DOI: 10.1007/BF00776405

Dedhia, B. S., Csoka, L., and Rathod, V. K. (2012). "Xylanase and ultrasound assisted pulping of wheat straw," *Applied Biochemistry and Biotechnology* 168(4), 731-741. DOI: 10.1007/s12010-012-9813-6

Ehrlich, P., and Grossmann, H. (2013). "Deinkability: Ultrasound-assisted deinking of cross-linked inks," *Internatianal Papierwirts*. 2013(2), 47-51.

Georgieva, N., Spiridonova, R. B., Petkova, E., and Yotova, L. (2008). "Application of improved chemical-mechanical pulp from poplar wood in the packing paper composition," *Holz Als Roh-Und Werkstoff* 66(1), 75-76. DOI: 10.1007/s00107-007-0196-2

Guo, X. Y., Jiang, Z. G., Li, H. X., and Li, W. T. (2015). "Production of recycled cellulose fibers from waste paper via ultrasonic wave progress," *Applied Polymer* 132(19), 1-9. DOI: 10.1002/app.41962

Hu, Y. B., Wang, Z., and Xu, S. Y. (2008). "Treatment of corn bran dietary fiber with xylanase increases its ability to bind salts, in vitro," *Food Chemical* 106(1),113-121. DOI: 10.1016/j.foodchem.2007.05.054

Hu, G. C., Fu, S. Y., Liu, H., and Lucia, L. A. (2015). "Adsorption of cationized eucalyptus heteropolysaccharides onto chemical and mechanical pulp fibers," *Carbohydrate Polymers* 123, 324-330. DOI: 10.1016/j.carbpol.2015.01.057

Lei, X. C., Lin, L., and Li, K. C. (2008). "Effect of xylanase pretreatment of wood chips on fiber separation in the CTMP refining process," *BioResources* 3(3), 801-815. DOI: 10.15376/biores.3.3.801-815

Luo, Q., Li, X. P., Liu, Y., and Liu, J. H. (2012). "Effects of enzymatic modification of masson pine mechanical pulp on fiber morphology and pulp properties," *Applied Mechanics and Materials* 117-119, 1593-1596. DOI: 10.4028/www.scientific.net/AMM.117-119.1593

Li, P. L., Guo, Y., and Zhang, B. B. (2014). "The effects of ultrasonic wave on the properties of flax fiber treated in alkali," *Advanced Materials Research* 1037, 11-15.

Li, J. B., Zhang, X. R., Zhang, M. Y., Xiu, H. J., and He, H. (2015). "Ultrasonic enhance acid hydrolysis selectivity of cellulose with HCl-$FeCl_3$ as catalyst," *Carbohydrate Polymers* 117,917-922. DOI: 10.1016/j.carbpol.2014.10.028

Liu, L. F., Cheng, L. D., Huang, L. Q., and Yu, J. Y. (2012). "Enzymatic treatment of mechanochemical modified natural bamboo fibers," *Fibers and Polymers* 13(5), 600-605. DOI: 10.1007/s12221-012-0600-3

Mansfield, S. D., Jong, E. D., Stephens, R. S., and Saddler, J. N. (1997). "Physical characterization of enzymatically modified kraft pulp fibers," *Biotechnology* 57, 205-216. DOI: 10.1016/S0168-1656(97)00100-4

Mert, B., Tekin, A., and Demirkesen, I. (2014). "Production of microfluidized wheat bran fibers and evaluation as an ingredient in reduced flour bakery product," *Food Bioprocess Technology* 7, 2889-2901. DOI: 10.1007/s11947-014-1258-1

Subhedar, P. B., and Gogate, P. R. (2014). "Enhancing the activity of cellulase enzyme using ultrasonic irradiations," *Journal of Molecular Catalysis B: Enzymatic* 101, 108-114. DOI: 10.1016/j.molcatb.2014.01.002

Pu, J. W., Lin, J. H., Zhao, Q., Zhou, S. K., Yao, S., and Xing, M. (2010). "The influence of ultrasonic treatment on the bleaching of CMP revealed by surface and chemical structural analyses," *BioResources* 5(3), 1353-1365.

Rustamov, M. K., Gafurova, D. A., Karimov, M. M., Rustamova, N. M., Bekchonov, D. Zh., and Mukhamediev, M. G. (2014). "Application of ion-exchange materials with high specific surface area for solving environmental problems," *Russian Journal of Chemical* 84 (13), 2545-2551. DOI: 10.1134/S1070363214130106

Renouard, S., Hano, C., Doussot, J., Blondeau, J. P., and Laine, E. (2014). "Characterization of ultrasonic impact on coir, flax and hemp fibers," *Materials Letters* 129, 137-141. DOI: 10.1016/j.matlet.201405.018

TAPPI T211 om-93 (1993). "Ash in wood, pulp, paper and paperboard: Combustion at 525 ^{o}C," TAPPI Press, Atlanta, GA.

TAPPI T222 om-88 (1988). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T223 cm-84 (1984). "Pentosans in wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T227 (1994). "Freeness of Pulp (Canadian standard method)," TAPPI Press, Atlanta, GA.

TAPPI T271 (1991). "Fiber length of pulp and paper by automated optical analyzer," TAPPI Press, Atlanta, GA.

TAPPI T429 cm-84 (1984). "Alpha-cellulose in paper," TAPPI Press, Atlanta, GA.

Wanske, M., and Grossmann, H. (2011). "High power ultrasound treatment smoothes paper," *Internatianal Papierwirts*. 2011(5).

Xing, M., Yao, S., Zhou, S. K., Zhao, Q., Lin, J. H., and Pu, J. W. (2010). "The influence of ultrasonic treatment on the bleaching of CMP revealed by surface and chemical structural analyses," *BioResources* 5(3), 1353-1365.

Xu, Y. J.,Yan, Y., Yue, X. P., Zhu, Z. F., Zhang, D. J., and Hou, G. Q. (2014). "Effect of ultrasonic wave pretreatment on the fibrillation of cellulose fiber," *Tappi Journal* 13(4), 37-43.

Yang, G. H., Chen, K. F., Chen, J. C., Meng, L., and Zhang, F.S. (2009). "Improvement of alkline peroxide mechanical pulp properties of fast-growing poplar by xylanase treatment," *Chemistry and Industry of Forest Products*. 29(2), 105-109.

Yang, G. H., Lucian A. Lucia, Chen, J. C., Cao, X. D., and Liu, Y. (2011). "Effect of enzyme pretreatment on the beatability of fast-growing poplar APMP pulp," *BioResources* 6(3), 2568-2580.

Zhao, H. J., Wei, C. Y., Cui, Y. Z., Lv, L. H., and Wang, X. (2013). "The effect of ultrasonic wave pretreatment of reed leaf cellulose dissolved in ionic liquids," *Advanced Materials Research*. 821-822, 47-50. DOI: 10.4028/www.Scientific.net/AMR.821-822.47

Zhao, J., Li, X. Z., Qu, Y. B., and Gao, P. J. (2002). "Xylanase pretreatment leads to enhanced soda pulping of wheat straw," *Enzyme and Microbial Technology* 30(6), 734-734. DOI: 10.1016/S0141-0229(02)00050-9

Zhuang, L. H., Zheng, C. L., Sun, J., Yuan, A., and Wang, G. W. (2014). "Performances of ramie fiber pretreatment with dicationicimidazolium ionic liquid," *Fibers and Polymers* 15(2), 226-233. DOI: 10.1007/s 12221-014-0226-8

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