SOYBEAN MEAL-BASED ADHESIVE REINFORCED WITH CELLULOSE NANO-WHISKERS

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Cellulose nano-whiskers were used to enhance the performance of soybean meal-based adhesive. Soybean meal flour, cellulose nano-whiskers (CNW), sodium hydroxide (NaOH), and polyethylene glycol (PEG) were used to develop different adhesive formulations. The effect of adhesive components on water resistance of the adhesive was measured on the three-ply plywood (three cycle soak test). The viscosity and solid content of the adhesive were measured. The cross section of the cured adhesives was evaluated using scanning electron microscopy (SEM). The effect of the hot press parameters on the water resistance of the plywood bonded by soybean meal/CNW/NaOH/PEG adhesive was investigated. The results showed that using the CNW in the adhesive formulation improved the water resistance of the plywood by 20%. The plywood bonded by the soybean meal/CNW/NaOH/PEG adhesive met the interior plywood requirement (2000 (ANSI/HPVA HP-1)). Fewer holes and cracks, as well as a smooth surface were observed on the cross section of the cured adhesive after the incorporation of CNW. In the hot press process, the water resistance of the plywood bonded by the soybean meal/CNW/NaOH/PEG adhesive increased as the hot press temperature and time increased.

Keywords: Soybean meal; Cellulose nano-whiskers; Plywood; Water resistance; Viscosity

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INTRODUCTION

In the 21st century, renewable raw materials have drawn attention because of their environmentally friendly nature and sustainability. Formaldehyde-based adhesives, such as phenol-formaldehyde resin, urea-formaldehyde resin, and melamine-formaldehyde resin, are playing a dominant role in the wood composites industry. The issues of formaldehyde emission and the dependency on petroleum resources require more effort on the development of wood adhesives from renewable resources. Protein is a "green" material. It is low cost, renewable, and eco-friendly. As one of the most important forms of natural protein, soybean protein is abundant, low price, and sustainable. Using soybean flour as a wood adhesive can be traced back to 1923 (Liu 1997). But the low water resistance and the high viscosity of the conventional soybean-based adhesive limit its applications.

In recent years, most researchers have focused on chemical modification on soybean protein to increase the water resistance and reduce the viscosity of the soybean based adhesive. The major chemicals used for the modification can be classified into

three categories. The first category is a protein denaturing agent, such as alkali (Hettiarachchy *et al.* 1995), urea (Zhang and Hua 2007), sodium dodecyl sulfate (SDS) (Huang and Sun 2000), guanidine hydrochloride (Zhong *et al.* 2003), *etc*. A second is cross-linker, such as maleic anhydride (Liu and Li 2007), DOPA (Liu and Li 2004), glutaraldehyde (Wang *et al.* 2007), and phenol formaldehyde resin (Zhong and Sun 2007). The last one is viscosity reducer, such as sulfites (Kalapathy *et al.* 1996) and proteolytic enzyme (Kumar *et al.* 2004).

Soybean is an important agricultural crop worldwide because of its unusually high contents of oil and edible protein. Soybeans are defatted so that the soy oil is removed by crushing or solvent extraction to obtain soybean meal. The industrial-grade soybean meal generally has a uniform protein content of 44% to 55%, depending on the source (Pizzi 1989). Most of the soybean meal has been used in feeding animals and poultry.

Natural fiber is another abundant and renewable biomass material, which could be obtained from vegetal resources, such as wood and cotton. Fiber consists of cellulose chains with amorphous and crystalline regions, combining with some lignin and hemicellulose. Cellulose nano-whiskers can be obtained by removing the lignin and hemicellulose, reducing the amorphous regions, and breaking the fiber down into nano-scale components by chemical (Eichhorn 2011) or mechanical (Siro and Plackett 2010) methods. Because of a much higher cellulose content, the percentage of the crystalline component is also higher, so that cellulose nano-whiskers can present much higher mechanical properties, which implies that they may have great potential in different applications including tissue engineering, nano-composites, and nano-devices. In recent years, cellulose nano-whiskers have been widely researched (Eichhorn *et al.* 2010), but the application on soybean based adhesive has not been reported.

In this study, soybean meal flour, cellulose nano-whiskers (CNW), sodium hydroxide (NaOH), and polyethylene glycol (PEG) were used to develop a soybean meal/CNW/NaOH/PEG adhesive. The effects of adhesive components on water resistance, viscosity, and solid content were measured. Three-ply plywood specimens were made by the different adhesive formulations. Water resistance of the plywood specimens was measured in accordance with the procedure described in American National Standard (2000 (ANSI/HPVA HP-1)) related to the three cycle soak test. The cross sections of the cured adhesives of different formulations were examined by scanning electron microscope (SEM). The effect of hot press parameters (temperature and time) on water resistance of the plywood bonded by the soybean meal/CNW/ NaOH/PEG adhesive were measured.

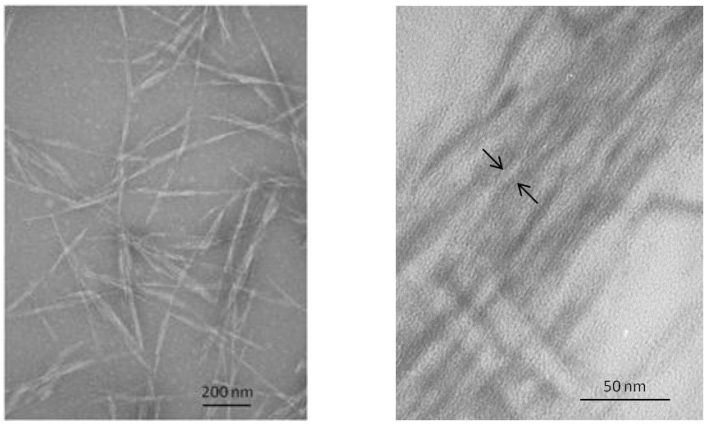
EXPERIMENTAL

Materials

Soybean meal (43% soy protein content) was obtained from Ware Milling Incorporated Company in Mississippi State of USA. Sodium hydroxide (NaOH) and polyethylene glycol – 400 (PEG) were purchased from Fisher Scientific. Pine veneer (150 × 150 × 8 mm) was provided by a local plywood mill.

Preparation of Cellulose Nano-whiskers (CNW)

Cellulosic nano-whiskers were prepared hierarchically from kenaf bast fibers by an all-chemical process (Shi *et al.* 2011). The process began with a hermetical alkaline (5 wt%) retting for one hour, followed by a bleaching treatment with 10% H_2O_2 at 70 °C for 1 hour. A hermetic reactor was used in those processes. The bleached fibers were hydrolyzed with an inorganic acid (30 wt% of H_2SO_4) at 80 ^oC for four hours, from which CNW was fabricated. The lengths of the fabricated CNWs were in a range from 100 to 1400 nm, and the diameters ranged from 7 to 84 nm. The aspect ratios ranged from 5 to 450, with an average value of 19.5. The transmission electron microscope (TEM) images of the CNWs are shown in Fig. 1.



(a) 50000× (b) 370000×

Fig. 1. TEM images of CNWs (Shi *et al.* 2011).

Preparation of Different Adhesives

Four different soy based adhesive formulations were obtained:

1) Soybean meal adhesive: Soybean meal flour (30 g) was added into water (70 g) and mixed in a beaker for 30 minutes at 20 °C to obtain the soybean meal adhesive.
2) Soybean meal/CNW adhesive: The soybean meal flour (30 g) was added into 0.5% cellulose nano-whiskers solution (70 g) and mixed in a beaker for 30 minutes at 20 °C.
3) Soybean meal/CNW/NaOH adhesive: The NaOH solution 40 wt% was added into soybean meal/CNW formulation and adjusted to pH 9.
4) Soybean meal/CNW/NaOH/PEG adhesive: The PEG (10 g) was incorporated into soybean meal/CNW/NaOH formulation (90 g).
5) Soybean meal/NaOH/PEG adhesive: The NaOH solution (40wt%) was added into soybean meal adhesive and adjusted to pH 9, and then 10% of PEG was incorporated.

Solid Content Measurement

The solid content of the adhesive was measured based on an oven-drying method. About 5 g (weight α) of the adhesive was placed into an oven at a temperature of 100 ±

2 °C until a constant weight (weight β) was obtained. The solid content was calculated using the following equation. An average of three replicates was used.

$$\text{Solid content (\%)} = \frac{\beta \text{ (g)}}{\alpha \text{ (g)}} \quad (1)$$

Viscosity Measurement

The viscosity of the adhesive was measured using a Brookfield viscometer with a spinning rate of 1 rpm and determined by averaging the data collected – 5 measurements in 2 minutes at 20 °C.

Plywood Preparation

Three-ply plywood samples were made under the following conditions: 180 g/m^2 of glue spreading; 15 minutes of hot pressing time; 160 °C of hot pressing temperature; 1.0 MPa of hot pressing pressure. After the hot pressing, the plywood was stored under ambient conditions (20 ^{o}C and 12% relative humidity) for at least 24 h before testing. Five plywood panels were made using each adhesive formulation.

The water resistance of the interior plywood panels (Type Ⅱ) was determined using a three-cycle soak test in accordance with the procedure described in American National Standard for Hardwood and Decorative Plywood; Hardwood Plywood & Veneer Association; 2000 (ANSI/HPVA HP-1). Ten plywood specimens (2 inch × 5 inch) cut from five plywood panels were submerged in water at 24 ± 3 °C for 4 h, and then dried between 49 °C and 52 °C for 19 h with sufficient air circulation. All specimens were inspected after the first cycle to determine whether delamination occurred and again after the third cycle, if applicable. This soaking/drying cycle was repeated until the three cycles were completed.

The criterion for interior application, as described in the standard, is that 95% of the specimens should not delaminate after the first soaking/ drying cycle, and 85% of specimens should not delaminate after the third soaking/drying cycle. A specimen shall be considered as failing when any single delamination between two plies is greater than 2 inches in continuous length, over 0.25 inches in depth at any point, and 0.003 inches in width.

Scanning Electron Microscope Testing

The samples were dried in an oven at 120 ± 2 °C until a constant weight was obtained. The samples were then placed on an aluminum stub. A coating of 10 nm Au/Pd film was applied to the samples using a Q150T S Turbo-Pumped Sputter Coater/Carbon Coater (Quorum Technologies Ltd., UK). The coated samples were then examined and imaged by using a JSM-6500F field emission scanning electron microscope (FESEM) (JEOL USA Inc., Peabody, MA).

RESULTS AND DISCUSSION

Water Resistance Analysis

The water resistance is one of the most important properties for wood adhesive. Compared to formaldehyde-based adhesives, soybean-based adhesive may present a

lower water resistance. Table 1 shows the water resistance of plywood bonded by different soybean-based adhesive formulations.

Table 1. Water Resistance of Plywood Bonded with Adhesives in Different Formulations

	Adhesives	1st cycle	2nd cycle	3rd cycle	**P**ass or **F**ail
A	Soybean meal adhesive	4/10 *	7/10	10/10	**F**
B	Soybean meal/CNW adhesive	2/10	5/10	8/10	**F**
C	Soybean meal/CNW/NaOH adhesive	0/10	2/10	4/10	**F**
D	Soybean meal/CNW/NaOH/PEG adhesive	0/10	0/10	1/10	**P**
E	Soybean meal/NaOH/PEG adhesive	0/10	1/10	3/10	**F**
* The left number is the delamination specimen number after the first cycle of water resistant test and the right number is the total specimen number in the experiment.					

For the pure soybean meal adhesive, seven out of ten specimens delaminated after the second cycle, and all of the specimens delaminated after the third cycle of soak test. The incorporation of CNW improved the water resistance of the plywood (see adhesive B in Table 1). The number of delaminated specimens was reduced from 10 to 8 after the third cycle of the soak test. NaOH is able to denature soy protein and unfold the secondary helical structure of a protein to expose the non-polar groups, so that the water resistance of the soybean based adhesive could be improved (Hettiarachchy *et al.* 1995; Kalapathy *et al.* 1996).

Table 1 shows that only four out of ten specimens bonded by adhesive C delaminated after the third cycle of the soak test. PEG is strongly hydrophilic and can be used as a dispersing agent to improve the distribution of the adhesive components. The incorporation of PEG into the soybean meal/CNW/NaOH formulation increased the water resistance of the plywood, showing only 1 out of 10 specimens delaminated after the 3rd cycle, which met the interior plywood requirements described in the American National Standard (2000 (ANSI/HPVA HP-1)). Compared to the adhesive E, the number of delaminated specimens after the 3rd cycle was reduced from 3 pieces to 1 piece, indicating a reinforcement effect when the CNW was incorporated.

Apparent Viscosity Analysis

Figure 2 shows the apparent viscosity of the different adhesive formulations. Adding 0.5% CNW increased the viscosity of adhesive B by 85.7% from 42,000 cP to 80,000 cP, which can be attributed the good distribution of the CNW in the adhesive system. The well-distributed CNW entangled the intermolecular hydrogen bond between soy protein and CNW, which increased the viscosity of adhesive B. After denaturing, the unfolded molecule chain of protein further increased the entanglement among the protein molecules and dramatically increased the viscosity of the adhesive C.

After being denatured by NaOH, the viscosity of adhesive C was 220,000 cP, which was 175% higher than that of adhesive B. Because of the elevated viscosity of the adhesive, adhesive C lost the flow ability and was difficult to stir. To reduce the viscosity of the adhesive, one of the most effective methods is to decrease the intermolecular forces in the protein.

PEG was used in the adhesive formulation as a lubricant to reduce the intermolecular forces. After the incorporation of PEG, the viscosity of adhesive D was reduced by 70.5% to 65,000 cP, which was 18.8% lower than that of soybean meal/CNW

adhesive. When comparing with the viscosity of adhesive E, the viscosity of adhesive D was improved by 80.5% from 36,000 cP to 65,000 cP because of the distribution of CNW.

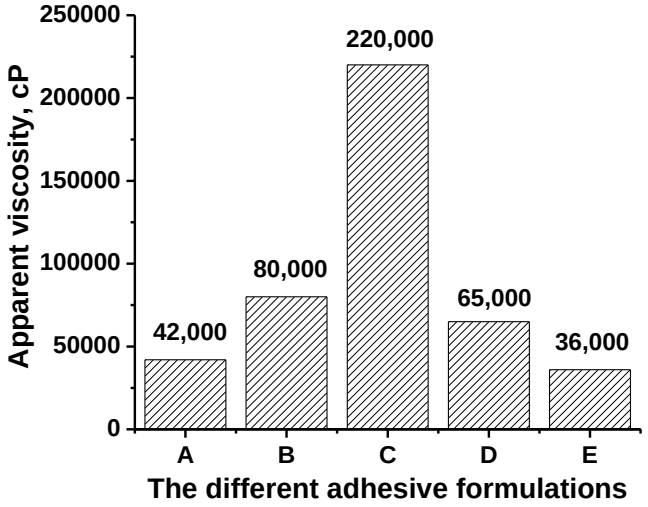


Fig. 2. Apparent viscosity of the adhesives in different formulations: A (Soybean meal adhesive), B (Soybean meal/CNW adhesive), C (Soybean meal/CNW/NaOH adhesive), D (Soybean meal/CNW/NaOH/PEG adhesive), E (Soybean meal/NaOH/PEG adhesive)

Solid Content Analysis

Figure 3 shows the solid content of adhesives in different formulations. The experimental results showed that the viscosity of soybean meal adhesive would be greatly increased if a solid content was more than 30%. The solid content of adhesive A was 28.4%, which would not be suitable for the hot pressing process since more than 70% of water content in the adhesive needed to be removed.

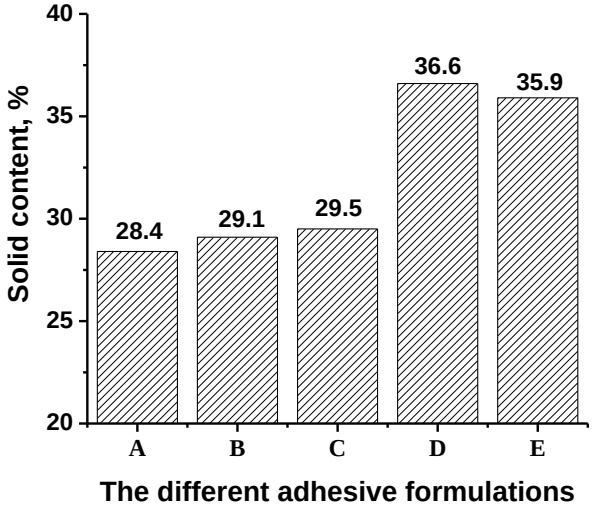
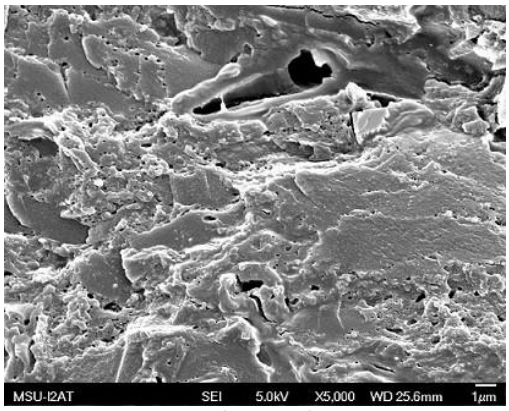


Fig. 3. Solid content of adhesives in different formulations: A (Soybean meal adhesive), B (Soybean meal/CNW adhesive), C (Soybean meal/CNW/NaOH adhesive), D (Soybean meal/CNW/NaOH/PEG adhesive), and E (Soybean meal/NaOH/PEG adhesive)

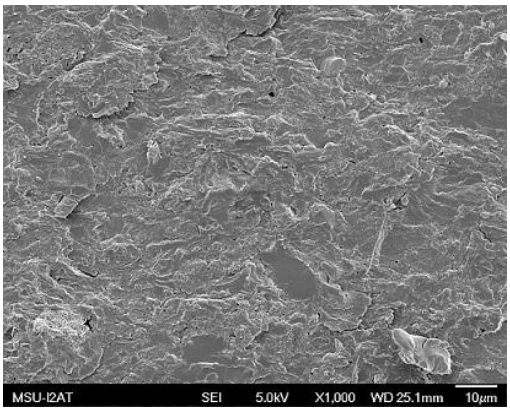
After adding the CNW and denaturation by NaOH, the solid content of adhesive C was increased from 28.4% to 29.5%. The solid content of adhesive D was improved by 24% from 29.5% to 36.6% by the incorporation of PEG. Compared with adhesive E, for which the solid content was 35.9%, using CNW increased the solid content of the adhesive by 2%.

SEM Analysis

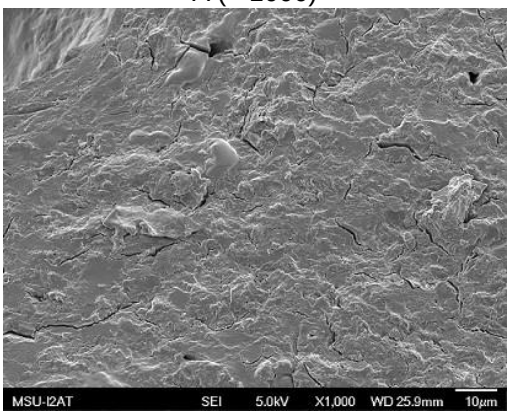
Figure 4 shows the cross sections of the cured adhesives in different formulations. From the cross section of the cured adhesive A, holes and cracks were observed. These holes and cracks would be caused by the gasification of water in the adhesive during the hot pressing, which reduced the water resistance of the adhesive.



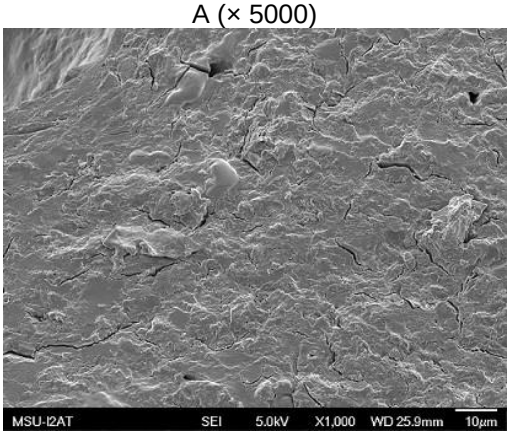
A (× 1000)



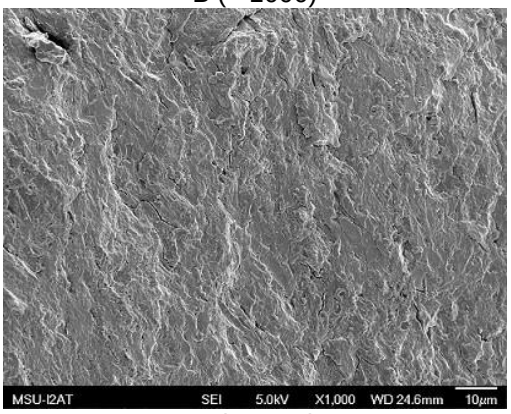
A (× 5000)



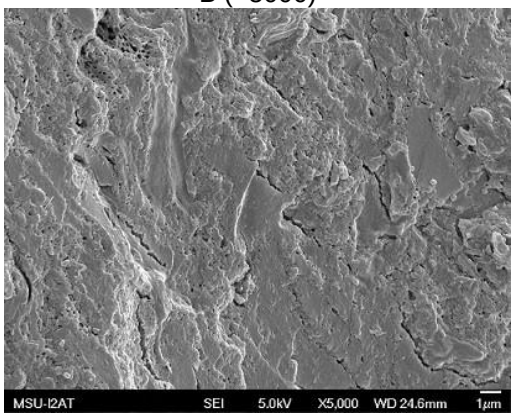
B (× 1000)



B (×5000)



C (× 1000)



C (× 5000)

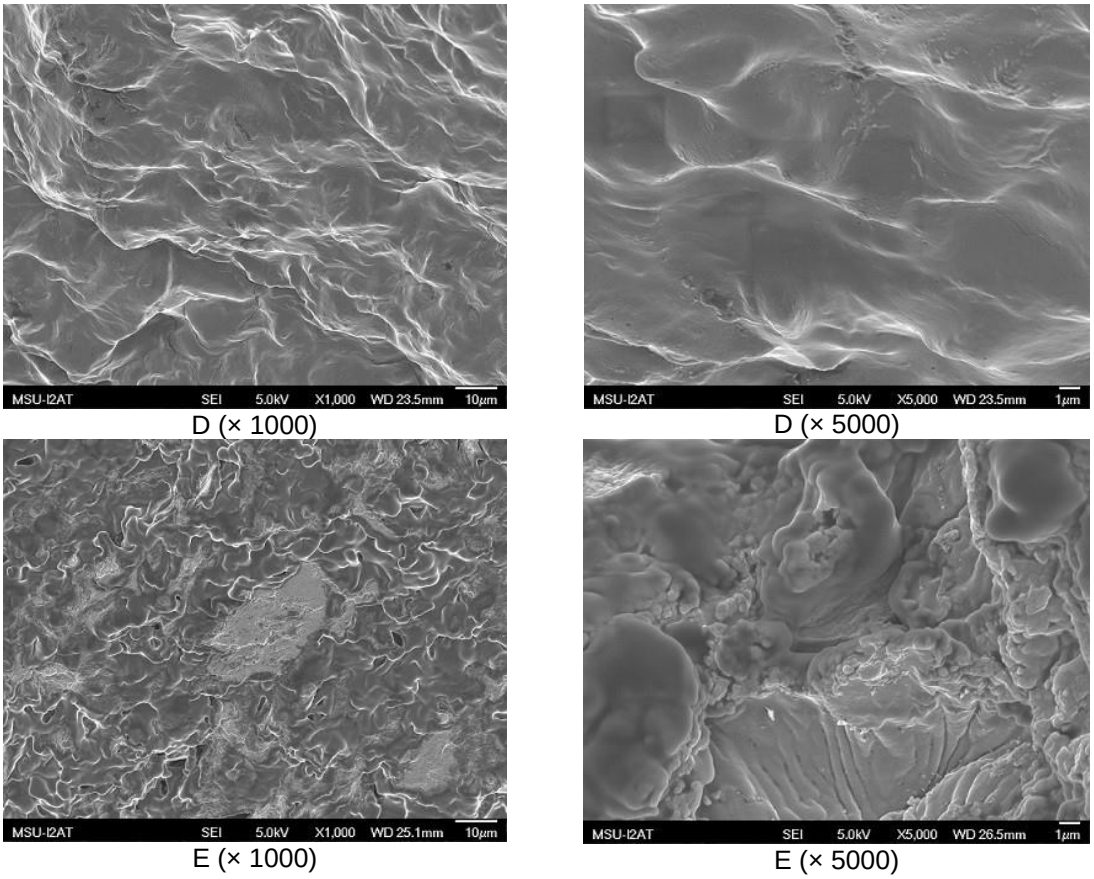


Fig. 4. The cross sections of the cured adhesives in different formulations: A (Soybean meal adhesive), B (Soybean meal/CNW adhesive), C (Soybean meal/CNW/NaOH adhesive), D (Soybean meal/CNW/NaOH/PEG adhesive), and E (Soybean meal/NaOH/PEG adhesive)

Water or moisture was easily intruded into holes and cracks of the cured adhesive layer and broke the bonding. After the incorporation of CNW, fewer holes and cracks were observed on the cross section of cured adhesive B, indicating that the use of CNW reduced the water gasification in the adhesive. After adding NaOH, a smoother surface was observed in the cross section of the cured adhesive compared with that of adhesives A and B, which could prevent water and moisture invading and improve water resistant of the adhesive. Mixing PEG in the adhesive formulation could further reduce the water gasification in the adhesive because no holes and cracks were observed on the cross section of cured adhesive D. In addition, the surface at the cross section of the cured adhesive D became much smoother when compared with that of adhesive C, which could further improve water resistance of the adhesive. For the cross section of the cured adhesive E, folds were observed on the surface, indicating adhesive E exhibited less water resistance compared to adhesive D.

Hot Pressing Temperature Analysis

The hot press temperature is one of the important hot press parameters benefitting the water resistance of the plywood bonded by soybean meal based adhesive. Figure 5 shows the effect of hot press temperature on the water resistance of plywood bonded by adhesive D. The water resistance of the plywood increased as the hot press temperature

increased. At 120 °C, all of the specimens bonded by adhesive D delaminated after the third cycle of soak test, indicating that adhesive D could not cure completely at that temperature, irrespective of the other hot press parameters. Elevated temperature could make the adhesive curing more completely. For the specimens made from a hot pressing temperature of more than 165 °C, one out of ten specimens delaminated after the third cycle of soak test, which met the requirement of the interior plywood.

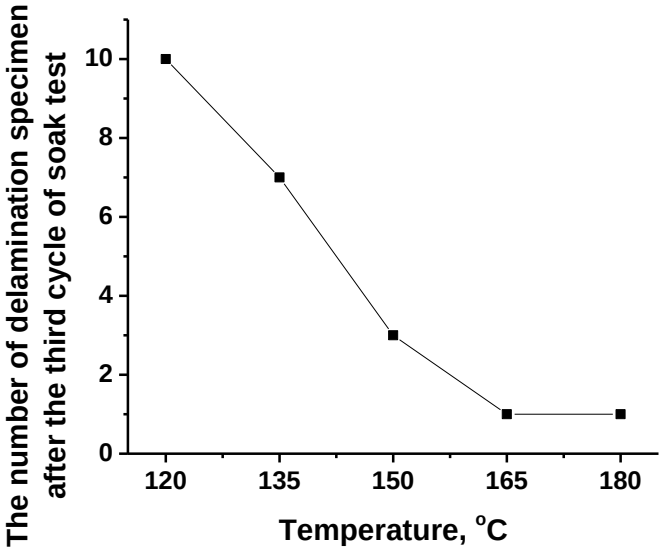


Fig. 5. The effect of hot press temperature on the water resistance of plywood bonded by adhesive D (soybean meal/CNW/NaOH/PEG adhesive, hot press parameters: 15 min of hot press time; 1.0 MPa of hot pressing pressure; 180 g/m^2 of glue spreading)

The well distributed CNW possibly filled gaps in the cured adhesive during the hot press process, which could prevent moisture intrusion to increase the water resistance of the adhesive. It may also reduce the gasification of the water in the adhesive, which could accelerate the curing process of the adhesive. According to literature data, the hot press temperature required for adhesive D was lower than that of synthetic latex modified soy protein based adhesive (170 °C) (Qi and Sun, 2011), but higher than highly reactive cross-linker modified soy protein based adhesive (120 °C) (Liu and Li 2004) at the same hot press time. The differences could be attributed to the fact that CNW is a functional additive for the soybean meal-based adhesive, rather than a reactive additive. But, compared to the cross-linker, the CNW reinforcer comes from natural resources and does not rely on petroleum resources.

Hot Pressing Time Analysis

Hot press time is another important hot press parameter. Generally, the specimens made with a long pressing time benefited from improved water resistance of the plywood bonded by the soybean meal-based adhesive. Figure 6 shows the effect of hot press time on the water resistance of plywood bonded by adhesive D. The water resistance of the plywood specimens increased with hot-press time. At 5, 10, and 15 minutes of hot pressing time, the number of delaminated specimens after the third cycle of soak test was

more than 1, indicating that the adhesive D could not cure completely within 15 minutes hot pressing time. However, when the hot pressing time was increased to 20 to 25 minutes, the specimens showed only one piece and no delamination after the third cycle of soak test, which met the requirement of the interior plywood. The widely used hot press time in plywood industry was from 60 s/mm to 70 s/mm. The hot press time of adhesive D was from 50 s/mm to 62.5 s/mm, which met the hot press time requirement for the plywood industry.

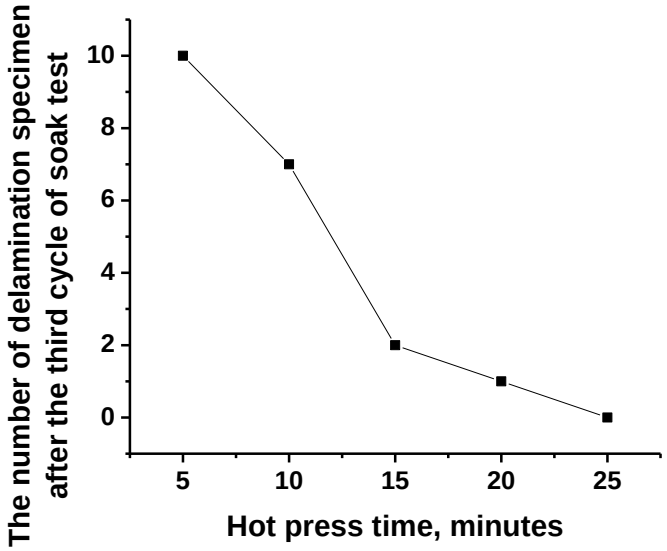


Fig. 6. The effect of hot press time on the water resistance of plywood bonded by adhesive D (soybean meal/CNW/NaOH/PEG adhesive, hot press parameters: 150 ^{o}C of hot press temperature; 1.0 MPa of hot pressing pressure; 180 g/m^2 of glue spreading)

CONCLUSIONS

1. Using cellulose nano-whiskers (CNW) in the adhesive formulation improved the water resistance of a plywood specimen by 20%.
2. Plywood bonded by a soybean meal/CNW/NaOH/PEG adhesive met the interior plywood requirement described in the American National Standard (2000 (ANSI/HPVA HP-1)).
3. Fewer holes and cracks, as well as a smooth surface were observed on the cross-section of the cured adhesive after the incorporation of CNW, which could prevent moisture intrusion, thus improving the water resistance of the adhesive.
4. In the hot press process, the water resistance of the plywood bonded by the soybean meal/CNW/NaOH/PEG adhesive increased with the hot press temperature and time. By 165 ^{o}C of hot press temperature with 15 minutes of hot press time or 150 ^{o}C hot press temperature with 20 minutes of hot press time, the plywood bonded by the soybean meal/CNW/NaOH/PEG adhesive met the interior plywood requirement described in the American National Standard (2000 (ANSI/HPVA HP-1)).

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REFERENCES CITED

Eichhorn, S. J. (2011). "Cellulose nanowhiskers: promising materials for advanced applications," *Soft Matter* 7(2), 303-315.

Eichhorn, S. J., Dufresne, A., Aranguren, M., Marcovich, N. E., Capadona, J. R., Rowan, S. J., Weder, C., Thielemans, W., Roman, M., Renneckar, S., Gindl, W., Veigel, S., Keckes, J., Yano, H., Abe, K., Nogi, M., Nakagaito, A. N., Mangalam, A., Simonsen, J., Benight, A. S., Bismarck, A., Berglund, L. A., and Peijs, T. (2010). "Review: current international research into cellulose nanofibres and nanocomposites," *Journal of Materials Science* 45(1), 1-33.

Hettiarachchy, N. S., Kalapathy, U., and Myers, D. J. (1995). "Alkali-modified soy protein with improved adhesive and hydrophobic properties," *J. Am. Oil Chem. Soc.* 72(12), 1461-1464.

Huang, W. N., and Sun, X. Z. (2000). "Adhesive properties of soy proteins modified by sodium dodecyl sulfate and sodium dodecylbenzene sulfonate," *J. Am. Oil Chem. Soc.* 77(7), 705-708.

Kalapathy, U., Hettiarachchy, N. S., Myers, D., and Rhee, K. C. (1996). "Alkali-modified soy proteins: Effect of salts and disulfide bond cleavage on adhesion and viscosity," *J. Am. Oil Chem. Soc.* 73(8), 1063-1066.

Kumar, R., Choudhary, V., Mishra, S., and Varma, I. K. (2004). "Enzymatically-modified soy protein. Part 2: Adhesion behaviour," *J. Adhes. Sci. Technol.* 18(2), 261-273.

Liu, K. S. (1997). *Soybeans: Chemistry, Technology, and Utilization*, Aspen Publication, Inc., New York.

Liu, Y., and Li, K. C. (2004). "Modification of soy protein for wood adhesives using mussel protein as a model: The influence of a mercapto group," *Macromol. Rapid Commun.* 25(21), 1835-1838.

Liu, Y., and Li, K. C. (2007). "Development and characterization of adhesives from soy protein for bonding wood," *Int. J. Adhes. Adhes.* 27(1), 59-67.

Pizzi, A. (1989). *Wood Adhesives, Chemistry and Technology*, Vol. 2, Marcel Dekker, Inc., New York.

Shi, J. S., Shi, S. Q., Barnes, H. M., and Pittman, C. U. (2011). "A chemical process for preparing cellulosic fibers hierarchically from kenaf bast fibers," *BioResources* 6(1), 879-890.

Siro, I., and Plackett, D. (2010). "Microfibrillated cellulose and new nanocomposite materials: A review," *Cellulose* 17(3), 459-494.

Wang, Y., Mo, X., Sun, X. S., and Wang, D. H. (2007). "Soy protein adhesion enhanced by glutaraldehyde crosslink," *J. Appl. Polym. Sci.* 104(1), 130-136.

Zhang, Z. H., and Hua, Y. F. (2007). "Urea-modified soy globulin proteins (7S and 11S): Effect of wettability and secondary structure on adhesion," *J. Am. Oil Chem. Soc.* 84(9), 853-857.

Zhong, Z., and Sun, X. S. (2007). "Plywood adhesives by blending soy protein polymer with phenol-formaldehyde resin," *Journal of Biobased Materials and Bioenergy* 1(3), 380-387.

Zhong, Z. K., Sun, X. S., Wang, D. H., and Ratto, J. A. (2003). "Wet strength and water resistance of modified soy protein adhesives and effects of drying treatment," *J. Polym. Environ.* 11(4), 137-144.

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