THE INFLUENCE OF NANOCELLULOSE AND SILICON DIOXIDE ON THE MECHANICAL PROPERTIES OF THE CELL WALL WITH RELATION TO THE BOND INTERFACE BETWEEN WOOD AND UREA-FORMALDEHYDE RESIN

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Abstract. Urea-formaldehyde (UF) resin is used as an adhesive in the most wood-based composite plants in China. The quality of such composites is strongly affected by the mechanical properties of the cell wall in relation to the interface between UF resin and wood. This research investigates the mechanical properties of the cell wall in the bond interface of wood and UF resin with nanocellulose and silicon dioxide, and compares the mechanical properties of wood-adhesive interface cell walls to their gluing strength. The hardness and reduced modulus of the cell wall were investigated by means of nanoindentation. The test results show that there was a close relationship between the mechanical properties of the cell walls at the wood-adhesive interface and the percentage of nanocellulose or SiO_2 in the UF. The shear strength of UF resin with nanofibrillated cellulose (NFC) or nano-SiO_2 in bonded wood also gradually increased when the content of these two kinds of nanomaterials was increased from 0% to 2%.

Keywords: Cell wall, bond interface, nanocellulose, nano-silicon dioxide, urea-formaldehyde.

INTRODUCTION

Urea-formaldehyde (UF) resin is a main binder for wood composite boards and widely used in most wood-based composite plants in China (Dunky and Pizzi 2002). UF resin is thermosetting that can be acid cured and heat accelerated to form a rigid, crystalline-like polymer. In general, urea resins are noted for their fast cure speed, high strength, and cost-effectiveness. However, the water resistance of the hardened resin is unsatisfactory owing to the reversibility of the aminomethylene link and hence the susceptibility to hydrolysis. Moreover, as a thermosetting polymer, UF resin is brittle compared with thermoplastic resin. It has been observed that wood cell walls are harder, stiffer, and more brittle in contact with UF resin (Stöckel et al 2010).

It was investigated whether the UF and polymeric diphenylmethane diisocyanate adhesives could penetrate into the wood substrate as far as to the cell wall level, creating an interphase region whose mechanical properties would potentially greatly influence the macroscopic quality of the bond (Stöckel et al 2012). In good agreement with early nanoindentation studies (Gindl and Gupta 2002; Gindl et al 2004a and b), cured UF located in the adhesive bond line showed a modulus comparable to that of the wood cell wall. However, with regard to hardness and toughness, UF showed characteristics very different from those of the wood cell wall. The comparably high hardness and low toughness justified the classification of UF as an adhesive with a distinctly brittle character. Liu et al (2014) reinforced phenol formaldehyde (PF) with three kinds of nanofibers, concluding that cellulose nanomaterials could improve the mechanical properties of both adhesives as well as the cell wall structure. Although the control PF resin glue line had an elastic modulus and hardness of 9.33 and 0.687 GPa, commercial cellulose nanofibrils had the most obvious reinforcing effect on the elastic modulus and hardness within the glue line.

To increase the mechanical properties of the gluing interface of composites, a number of recent studies have related to nanocellulose and silicon, both of which are used to improve the properties of some high-polymer materials, including some resins. One important advantage of nanocellulose-reinforced polymer composites

is that they are more eco-friendly than traditional carbon- and glass-fiber-based composites (Pandey et al 2012); in addition, the polymer composites have low toxicity and can be used as reinforcing agents for industrial biocomposites (Lam et al 2012). Cellulose nanocrystal is one type of these renewable biomaterials (Peng et al 2011). It has been proven that cellulose nanocrystal can increase the strength of some wood adhesives (Kaboorani et al 2012). Wang and Xing (2010) have shown that oriented strand board (OSB) properties can be improved by reinforcing the bond line strength, preventing PF resin from penetrating into wood pores, and increasing resin coverage on the strand surface. Just 3-4% of nano-material filler is enough to improve resin performance and OSB properties. When 3% of cellulose nanofiber (CNF) (based on the oven-dried weight of resin) was added, the elastic modulus of resin increased 31.6% and the strength increased 24.1% (from 79 to 98 MPa). The elastic modulus of OSB panels increased 12.1% to 3605 MPa with the addition of 4% CNF into the resin (based on the oven-dried weight of the resin). In addition, the bending strength increased 14.5% to 30.8 MPa. Another key property, internal bond strength increased as well.

Nano-silicon is an attractive material that has been studied by many researches. A study of silicon-cellulose nanocomposite showed that it has an efficient and stable photoluminescence (Pikulev et al 2012). The addition of nano-SiO_2 may improve the age-resistant properties of starch and polyvinyl alcohol films (Yao et al 2011). When nano-SiO_2 is added in percentages from 0.75% to 1%, the interfacial shear strength of ultrahigh-molecular-weight polyethylene fibers increases from 1.29 to 1.83 MPa (Zhang et al 2010). In other studies, it has been found that added nano-SiO_2 particles can improve the mechanical properties and water resistance of starch and polyvinyl alcohol blend films (Xiong et al 2008; Tang et al 2009).

As discussed above, there may be a strong relationship between the quality of these kinds of composites and the mechanical properties of the cell wall in the bond interface for UF resin gluing wood. The objective of this study was to investigate the mechanical properties of the cell wall at the interface between wood and UF resin containing a small amount of nanocellulose and SiO_2, and to establish a correlation between the mechanical properties of wood-adhesive interface cell walls and their adhesive strength.

MATERIALS AND METHODS

Sample Preparation

The wood species of the sample was Larch (*Larix gmelinii*) from Heilongjiang Province of China. After oven drying, its MC was between 10% and 12%; the wood was then cut into a 200 mm (L) by 10 mm (W) by 10 mm (T) sample using a saw. Its surface was sliced to the smoothness required for bonding.

The UF resin was obtained from a wood composites factory and used to bond samples. Its solid content was about 60%, and the adhesive rate was 150 $g \cdot m^{-2}$ applied to only on one surface. The nanocellulose came from Intelligent Chemicals Ltd. (Shanghai, China). Its length was 400-600 μm and its diameter was 10-50 nm. Finally, the nano-SiO_2 was prepared by means of controlled hydrolysis and condensation of tetraethyl orthosilicate with ammonia as a catalyst at 323 K. Its diameter was about 50 nm (see Fig 1).

All the samples were hot pressed at a temperature of 120°C and pressure 1.5 or 2.0 MPa, for 10 min. After hot pressing, the two bonded samples were set aside for about 3 da indoors, and then were sawn into two blocks: one was for testing the mechanical properties of the cell wall in the bond interphase of wood by nanoindentation, and the other was for testing the gluing strength using mechanical testing instruments. The first block measured 20 mm (L) by 10 mm (W) by 10 mm (T); after sawing, it was then cut into a pyramidal shape—four inclined planes from the adhesive bond region on the one end (as shown in Fig 2); the adhesive bond line interface was located in the center. The other

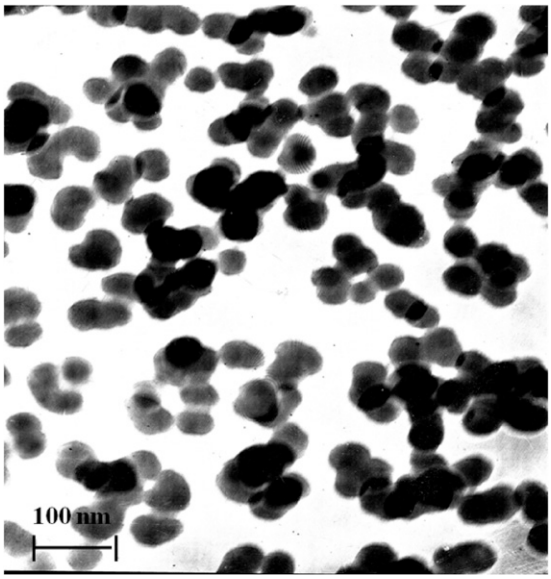

Figure 1. Size of nano-SiO_2 compared with 100-nm scale bar.

sample measured 50 mm (L) by 10 mm (W) by 10 mm (T); after sawing, it was cut into a 15 mm (L) by 10 mm (W) by 5 mm (T) shape, with an adhesive bond region on both ends to test the adhesion strength. It was necessary that the top of the pyramidal specimen should be cut successively with three kinds of knives to get a very smooth surface—an ordinary sharpened blade, a glass knife, and a diamond knife. The smoothed specimens were conditioned at 21°C and 60% RH in the nanoindentation test room for at least 24 h before testing.

Nanoindentation Testing Method

A TriboIndenter® system manufactured by Hysitron, Inc. (Minneapolis, MN) was used for the nanoindentation testing. A Berkovich indenter with a three-sided pyramidal shape and with an area-to-depth function was loaded for all experiments (Oliver and Pharr 1992). All experiments were conducted with a closed-loop feedback control to provide precise control of the nanoindentation probe in its load-controlled modes. A drift monitoring time of 40 s was set to measure the system's drift before any of the tests were initiated. The single indentation procedure included four steps. First, a 2 μN set-point force was established between the probe and sample surface. The indentation test did not start until the 2 μN preload force was detected by the transducer. Second, the peak load (250 μN) was set to be achieved at a loading rate of 30 μN s^{-1}. Third, at this peak load, the loading was held for 5 s to avoid the effect of creep occurring in viscous material during the unloading (Liu et al 2006). Finally, the unloading was executed at the same loading rate. The scanning probe microscopy (SPM) assembly in the TriboIndenter system is capable of accurately positioning the bond line interface. Using a scan size of 40 μm by 40 μm, interesting indent positions were marked on the specimens on the SPM image; 44 indentations were implemented and checked by rescanning the image (as shown in Fig 3). Only indentations in the middle of the bond line interface layer, including the cell walls, were

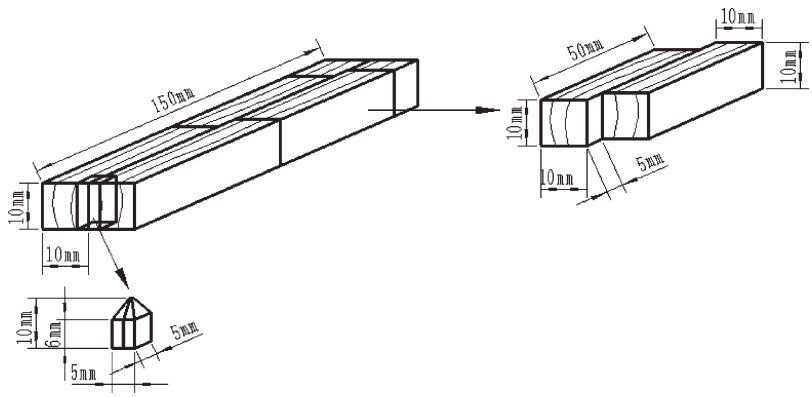

Figure 2. Sample preparation for nanoindentation (left) and shear testing (right).

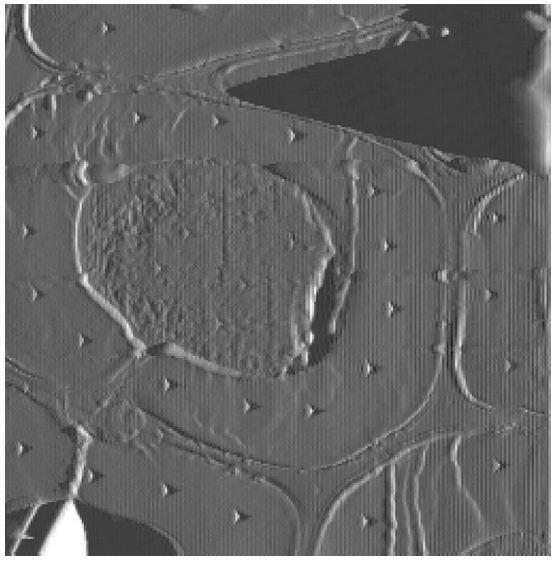

Figure 3. Postindentation image—SPM.

selected as valid data. Any indentations performed at the border of the cell walls were expunged.

The hardness and reduced elastic modulus were calculated from the valid data following the methods of Oliver and Pharr (1992) and Wu et al (2009). On the basis of nanoindentation theory, the reduced modulus E_γ (the composite modulus for indenter and sample combination), can be evaluated from the nanoindentation measurements by using the following equation (Oliver and Pharr 1992):

$$E_\gamma = \frac{\sqrt{\pi}\left(\frac{dP}{dh}\right)_{\text{unloading}}}{2\sqrt{A_{\text{hc}}}} \quad (1)$$

where P is the indentation load; h and hc are the penetration and contact depths, respectively; and A_{hc} is the projected contact area, which is a function of the contact depth. The Meyer hardness (H) can be obtained from the following equation:

$$H = \frac{P_{\max}}{A_{\text{hc}}} \quad (2)$$

Testing the Nano-SiO_2 Content of the Cell Wall in the Interface

The Si content of the cell wall at the interface of wood and UF resin with nano-SiO_2 can be tested by scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) instrument. Twenty points were tested in different positions of the interface by SEM (FEI Quanta200, Hillsboro, Oregon) with EDS (Oxford INCA 250, Oxfordshire, UK) as may be seen in Fig 4. The test voltage was 20 kV.

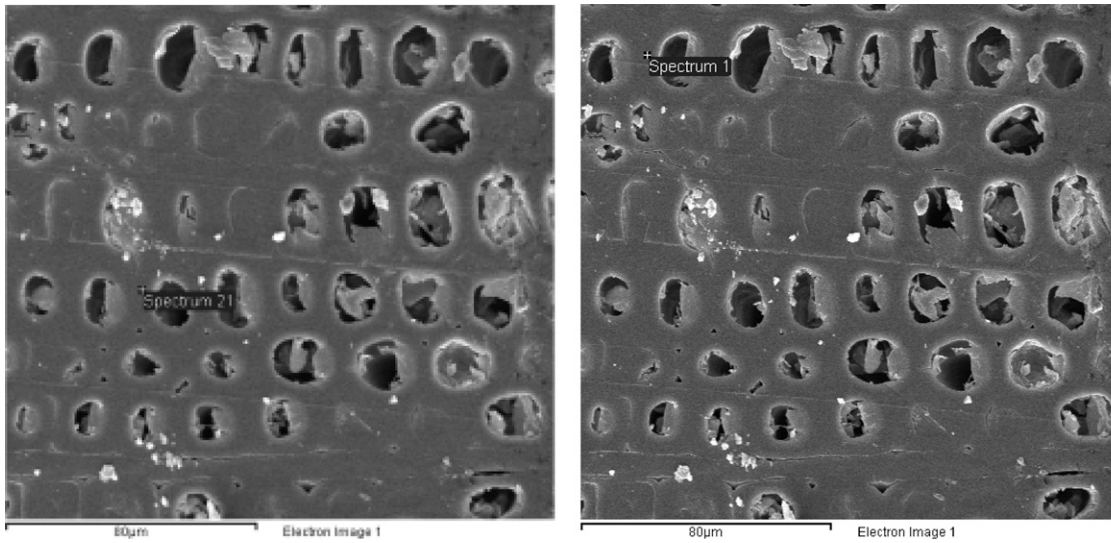

Figure 4. The test point as seen by SEM (FEI Quanta200) with EDS (Oxford INCA 250).

Method for Testing Glue-line Shear Strength

Glue-line shear strength can be calculated as follows:

$$F = \frac{Q}{A} \quad (3)$$

where F is the glue-line shear strength (MPa), Q is the break load (N), and A is the sheared area (mm^2).

RESULTS AND DISCUSSION

The Influence of Nanocellulose on the Mechanical Properties of the Cell Wall in the Bond Interface

From Fig 4, it can be seen that UF resin is able to enter the cell lumen through pits under certain pressure. The shape of the cell in the bond interface changes a little because of the effect of hot pressure (as shown in Fig 5). The CNF's average length was in the range of 400-600 μm, and the average diameter was in the range of 10-50 nm. But the pore in the wood cell wall is usually just a few nanometers. So it is possible that, through the pits, the nanofibrillated cellulose (NFC) particles penetrated the wood microstructure, such as lumen, but not the cell walls. Though the shape of the NFC particles makes it difficult for them to penetrate the internal cell wall microstructure, the UF itself is able to permeate into the lumen to influence the mechanical properties of the cell wall in the bond interface.

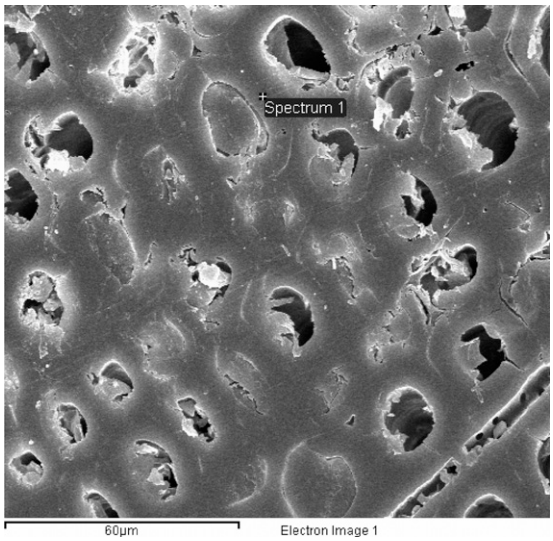

Figure 5. The cell at the bond interface.

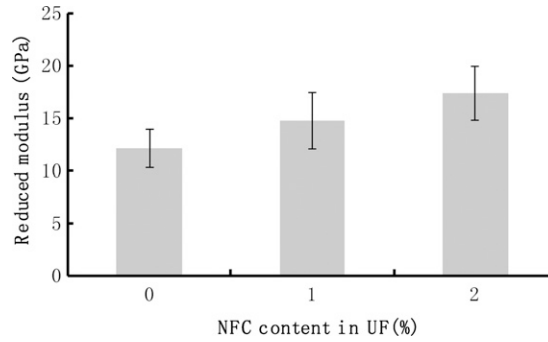

Figure 6. Reduced modulus of the cell wall at the interface of wood and UF resin with nanocellulose. Hot-pressing conditions: 120°C temperature, 1.5 MPa pressure, with 10-min pressing time.

Figure 6 shows that the reduced modulus of the cell walls in the wood-adhesive interface is clearly dependent on the percentage of nanocellulose in the UF. One percent and 2% (wt/wt) NFC in the UF increased the reduced modulus values of the cell wall at the interface from 12.1 GPa up to 14.8 and 17.4 GPa, respectively; in addition, the hardness reached 0.49 and 0.59 GPa, respectively, from 0.42 GPa. This improvement of the modulus and hardness suggests that the reinforcement of UF resin with NFC can improve the strength of the cell wall. The efficient load transfer to the nanocrystal network may enable more uniform stress distribution and minimization of the stress concentration area (Khan et al 2012). The effect is more clear when the pressing pressure is larger (as shown in Fig 7). If the pressure is set at 2.0 MP and 1% and 2% (wt/wt) NFC in UF is added, the reduced modulus value in the cell wall at the interface of wood and UF resin with nanocellulose goes up to 16.2 and 18.4 GPa, respectively from 13.7 GPa. The reason is that the greater the pressing pressure, the

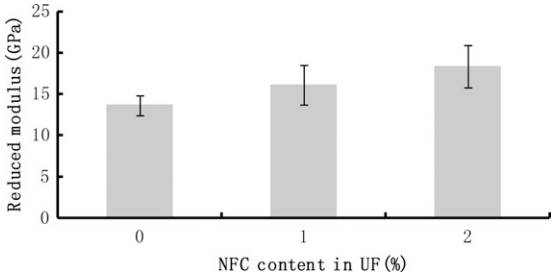

Figure 7. Reduced modulus of the cell wall at the interface of wood and UF resin with nanocellulose. Hot-pressing conditions: 120°C temperature, 2.0 MPa pressure, and pressing time 10 min.

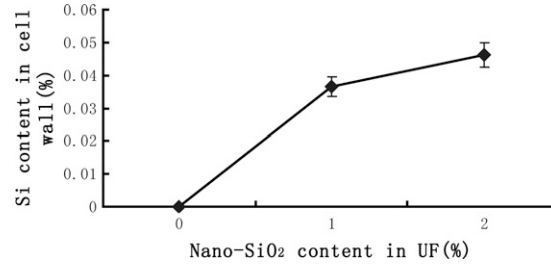

Figure 9. Si content of the cell wall at the interface of wood and UF resin with nano-SiO_2. Hot-pressing conditions: 120°C temperature, 2.0 MPa pressure, and pressing time 10 min.

more UF resin with NFC enters the cell wall at the interface.

The Influence of Nano-SiO_2 on the Mechanical Properties of the Cell Wall at the Bond Interface

As shown in Fig 1, SiO_2 was in the range of dozens of nanometers. So it is possible that, through the pits, the SiO_2 particles penetrated the wood microstructure but not the cell walls. UF resin with SiO_2 is able to permeate into the lumen to influence the mechanical properties of the cell wall in the bond interface.

Figure 8 shows the result of the influence of UF resin with nano-SiO_2 (nano-SiO_2) on the mechanical properties of the cell wall at the bond interface. If the amount of nano-SiO_2 is changed from 0% to 1% and 2% (wt/wt), the reduced modulus value of the cell wall at the interface of wood and UF resin with nano-SiO_2 increases from 13.7 to 15.9 GPa and 21.1 GPa. The main reason for the greatly improved reduced modulus in the cell wall is that the nano-SiO_2 particles can enter the cell wall with UF resin under conditions of hot pressure, as shown in Fig 9 (tested by SEM [FEI Quanta 200] with EDS [Oxford INCA 250]). From this figure it can be seen that the Si content of the cell walls at the interface of wood increased from 0% to 0.036% and 0.046% with an increase of 0-1% and 2% (wt/wt) nano-SiO_2 in UF. It has been previously proven that nano-SiO_2 particles have a remarkably heterogeneous nucleation effect in the matrix, and that the free–OH of nano-SiO_2 is useful in forming bonds (Yao et al 2011). Moreover, nano-SiO_2 may influence the structure of composites' crystalline regions and fibrils, strengthening the interfacial interaction of the composites (Zhang et al 2010).

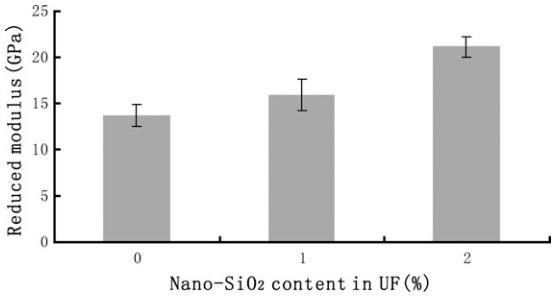

Figure 8. Reduced modulus of the cell wall at the interface of wood and UF resin with nano-SiO_2. Hot-pressing conditions: 120°C temperature, 2.0 MPa pressure, and pressing time 10 min.

The Mechanical Properties of the Cell Walls at the Wood-adhesive Interface and the Bonding Strength

Gluing shear strength is a frequently used reference parameter for the evaluation of adhesive bond strength between wood and adhesive (Pizzo et al 2003). The shear strength of UF resin glued to wood was tested to compare the mechanical properties of the cell walls in the wood-adhesive interface with their gluing strength (Figs 10 and 11). The gluing shear strength of UF resin with NFC or nano-SiO_2 bonded to wood was found to increase gradually when these two kinds of

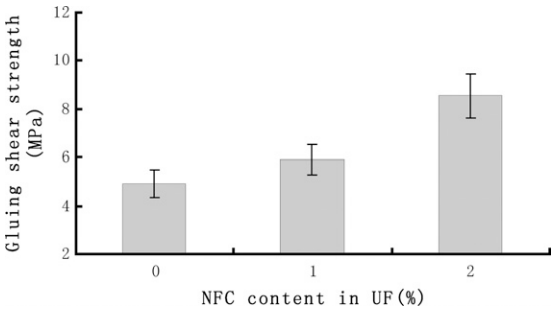

Figure 10. The shear strength of UF resin with NFC bonded to wood (hot-pressing conditions: 120°C temperature, 2.0 MPa pressure, and pressing time 10 min).

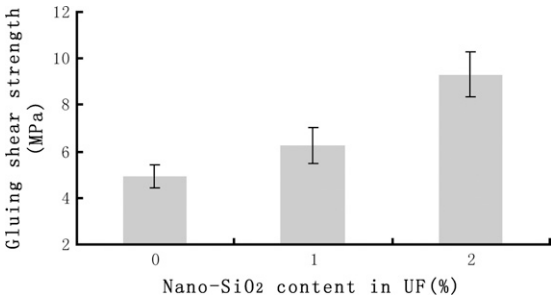

Figure 11. The shear strength of UF resin with nano-SiO_2 bonded to wood (hot-pressing conditions: 120°C temperature, 2.0 MPa pressure, and pressing time 10 min).

nanomaterials were added at percentages from 0% to 2%.

CONCLUSION

A small amount of UF with NFC or SiO_2 under pressing pressure was able to permeate into cells to influence the mechanical properties of the cell wall at the bond interface. There was a close relationship between the mechanical properties of the cell walls at the wood-adhesive interface and the percentage of nanocellulose or SiO_2 in the UF. The shear strength of UF resin with NFC or nano-SiO_2 in bonded wood also gradually increased when the content of these two kinds of nanomaterials was increased from 0% to 2%.

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REFERENCES

Dunky M, Pizzi A (2002) Wood adhesives. Pages 1039–1104 *in* Adhesion Science and Engineering—2. Surfaces, Chemistry and Applications, Chaudhury M and Pocius AV, eds. Amsterdam, The Netherlands.

Gindl W, Gupta HS (2002) Cell-wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation. Compos Part A: Appl Sci Manuf 33(8): 1141-1145.

Gindl W, Gupta HS, Schöberl T, Lichtenegger HC, Fratzl P (2004a) Mechanical properties of spruce wood cell walls by nanoindentation. Appl Phys A Mater Sci Process 79(8):2069-2073.

Gindl W, Schoberl T, Jeronimidis G (2004b) The interface in phenol-formaldehyde and polymeric methylene diphenyl-di-isocyanate glue lines in wood. Int J Adhes Adhes 24(4):279-286.

Kaboorani A, Riedl B, Blanchet P, Fellin M, Hosseinaei O, Wang S (2012) Nanocrystalline cellulose (NCC): A renewable nano-material for polyvinyl acetate (PVA) adhesive. Eur Polym J 48(11):1829-1837.

Khan A, Khan RA, Salmieri S, Le Tien C, Riedl B, Bouchard J, Chauve G, Tan V, Kamal MR, Lacroix M (2012) Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films. Carbohydr Polym 90(4):1601-1608.

Lam E, Male KB, Chong JH, Leung ACW, Luong JHT (2012) Applications of functionalized and nanoparticle-modified nanocrystalline cellulose. Trends Biotechnol 30(5):283-290.

Liu C, Zhang Y, Wang S, Meng Y, Hosseinaei O (2014) Micromechanical properties of the interphase in cellulose nanofiber-reinforced phenol formaldehyde bondlines. BioResources 9(3):5529-5541.

Liu CK, Lee S, Sung LP, Nguyen T (2006) Load-displacement relations for nanoindentation of viscoelastic materials. J Appl Physics 100(3):033503.

Oliver WC, Pharr GM (1992) An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J Mater Res 7(6):1564-1583.

Pandey JK, Lee S, Kim HJ, Takagi H, Lee CS, Ahn SH (2012) Preparation and properties of cellulose-based nano composites of clay and polypropylene. J Appl Polym Sci 125(1):E651-E660.

Peng B, Dhar N, Liu HL, Tam KC (2011) Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective. Can J Chem Eng 89(5):1191-1206.

Pikulev V, Loginova S, Gurtov V (2012) Luminescence properties of silicon-cellulose nanocomposite. Nanoscale Res Lett 7(1):426.

Pizzo B, Lavisci P, Misani C, Triboulot P, Macchioni N (2003) Measuring the shear strength ratio of glued joints within the same specimen. Holz Roh - Werkst 61(4):273-280.

Stöckel F, Konnerth J, Kantner W, Moser J, Gindl W (2010) Tensile shear strength of UF-and MUF-bonded veneer related to data of adhesives and cell walls measured by nanoindentation. Holzforschung 64(3):337-342.

Stöckel F, Konnerth J, Moser J, Kantner W, Gindl-Altmutter W (2012) Micromechanical properties of the interface in pMDI and UF bond lines. Wood Sci Technol 46(4):611-620.

Tang HL, Xiong HG, Tang SW, Zou P (2009) A starch-based biodegradable film modified by nano silicon dioxide. J Appl Polym Sci 113(1):34-40.

Wang S, Xing C (2010) Wood adhesives containing reinforced additives for structural engineering products. U.S. Patent Application No. 20100285295. (https://www.google.com/patents/US20100285295).

Wu Y, Wang S, Zhou D, Xing C, Zhang Y, Pharr GM (2009) Use of nanoindentation and Silviscan to determine the mechanical properties of 10 hardwood species. Wood Fiber Sci 41(1):64-73.

Xiong HG, Tang SW, Tang HL, Zou P (2008) The structure and properties of a starch-based biodegradable film. Carbohydr Polym 71(2):263-268.

Yao KH, Cai J, Liu M, Yu Y, Xiong HG, Tang SW, Ding SY (2011) Structure and properties of starch/PVA/nano-SiO_2 hybrid films. Carbohydr Polym 86(4):1784-1789.

Zhang Y, Yu JR, Zhou CJ, Chen L, Hu ZM (2010) Preparation, morphology, and adhesive and mechanical properties of ultrahigh-molecular-weight polyethylene/SiO_2 nanocomposite fibers. Polym Compos 31(4):684-690.