Dynamic Wettability of Different Adhesives on Wheat Straw Surface Modified by Cold Oxygen Plasma Treatment

Xuehui Yang, Rong Zhang, Lijuan Tang, Minzhi Chen, Yang Li, and Xiaoyan Zhou*

The effects of cold oxygen plasma treatment on the exterior and interior surfaces and wettability of wheat straw were investigated. The wheat straw was treated with oxygen plasma for 150 s, and the radio-frequency power was set at 100 W. The surface wettability was evaluated by measuring the contact angles and the K values of urea-formaldehyde, phenol-formaldehyde, and methylene diphenyl diisocyanate resins. Specimens with different gluing surfaces were bonded together with urea-formaldehyde and phenol-formaldehyde and then hot-pressed to assess bonding strength. Results indicate that the dynamic wettability and the shear strength of wheat straw were remarkably improved after it was exposed to the cold oxygen plasma. Additionally, the adhesive type and the wheat straw surface characteristics had significant effects on the dynamic wettability and bonding strength of both untreated and plasma-treated wheat straw.

Keywords: Wettability; Contact angle; Cold oxygen plasma treatment; Wheat straw; Shear strength

*Contact information: College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China; *Corresponding author: xyzhou@aliyun.com*

INTRODUCTION

Wettability is the property of a solid that describes what will happen when a drop of liquid (such as water, adhesive, solvent, and so on) is placed on the surface of a solid (Zhao *et al.* 2009; Shen *et al.* 2011). It is well known that wettability is a crucial property of lignocellulosic composite materials. It has a direct influence on interfacial bonding strength and mechanical properties.

Poor bondability remains a major problem with the production of wheat straw based composites (Liu *et al.* 2004; Xu 2011). The exterior surface of the wheat straw contains amounts of cutin, wax, silica, and some non-polar extracts, which prevents adhesives from wetting, spreading, and penetrating the surface (Lian *et al.* 2005; Liu *et al.* 2004; Shen *et al.* 2011). Therefore, the wheat straw-based composites bonded with traditional adhesives, such as phenol-formaldehyde (PF) resin and urea-formaldehyde (UF) resin, are barely strong enough to meet the standard for straw-based composites. Though methylene diphenyl diisocyanate (MDI) could improve the interface bonding strength between the wheat straw, it has a higher cost and can stick to the press platen (Mo *et al.* 2003; Wang and Zhang 2005; Zhou 2009). Several treatment methods have been investigated to improve the surface wettability of wheat straw (Yang *et al.* 2013). These treatments include mechanical modification (Zhou *et al.* 2008; Gadhe *et al*. 2006), thermal treatment (Lawther *et al.* 1996; Sun *et al.* 2005; Munawar *et al.* 2008; Han *et al.* 2010; Kaparaju and Felby 2010; Li *et al.* 2011), chemical modification (Kalia *et al.* 2009; Li *et al.* 2010), and enzymatic pretreatment (Zhang 2003; Zhang *et al.* 2008). These treatment methods have some potential problems such as weakening the natural strength of the wheat straw and producing liquids toxic to the environment.

The treatment employed in the present work involved a promising alternative technique – cold oxygen plasma treatment – to modify the surface of wheat straw. Plasma is an excited gas consisting of atoms, molecules, ions, free electrons and metastable species (Jamali and Evans 2011). Plasma treatments have been widely used to modify the surface of materials, including lignocellulosic materials. Some research has shown that the chemical composition on the surface of wood and poplar veneer surface was changed effectively (Zhang *et al.* 2013; Tang *et al.* 2012) and wood cell walls were etched differentially (Jamali and Evans 2011). The wettability and adhesive properties were improved accordingly. Additionally, plasma makes it possible to improve the surface wettability and bonding strength without destroying the bulk properties of the straw, polluting the environment, or spending large amounts of money (Acda *et al.* 2012). The aim of this study was to determine the effects of modifying the wheat straw surface with cold oxygen plasma on the dynamic wettability and bonding strength with different adhesives, and to lay the foundation for future industrial production.

EXPERIMENTAL

Materials

Wheat straw was harvested in an agricultural field of the northern Jiangsu Province in China. After harvesting, the straw was air-dried for several months. It was cleaned of impurities with distilled water and then cut into 10-cm long pieces. Before plasma treatment, the straw samples were flattened and dried in a vacuum drying oven at 60 °C to a moisture content of 2%.

Urea-formaldehyde (UF) resin was prepared in the laboratory of Nanjing Forestry University. Phenol-formaldehyde (PF) resin was purchased from Shanghai Taier Chemical Industry Co. Ltd. The methylene diphenyl diisocyanate (MDI) was acquired from Huntsman Chemical Industry Co. Ltd. They were used to evaluate dynamic wettability and shear strength. Table 1 shows the properties of UF, PF, and MDI resins.

Table 1. Specifications of UF, PF, and MDI Resin

Specification	UF	PF	MDI
Color	Opalescent to maroon	Pale red-brown	Dark brown to black
Solid Content (%)/2h,120℃	60.39	46.81	100
pH Value at 20℃	7.76	11.74	6.37
Viscosity (mPa*s) at 20℃	40.70	77.00	275.00
Surface tension* (mJ/m^2)	135.30	114.37	56.78
* Surface tension was tested by the pendant drop method using JC2000D.			

Cold Oxygen Plasma Treatment

Plasma treatments of wheat straw specimens were performed using a radio frequency (RF) glow discharge produced from a plasma reactor (HD-1B, made in Changzhou P.R. China). The specifications of the reactor were described by Tang *et al.* (2012).

The flattened wheat straw specimens were placed inside the reactor. Before RF glow discharge, the system was depressurized to 3 Pa and oxygen was injected into the chamber at a flow rate of 15 to 20 mL/min for about 3 min. The chamber was then depressurized to 3 Pa again. This procedure operation was repeated three times in order to remove any gaseous impurities. The steady-state oxygen flow rate was controlled and plasma treatments were carried out at 15 Pa. The RF power input was set at 100 watts, and the treatment time was 150 seconds. At the end of the reaction, the chamber was pressurized, and the samples were removed and stored under dry conditions for later analysis.

Contact Angle Measurement

Drops of UF, PF, and MDI were dispersed on the interior and exterior surfaces of the plasma-treated and untreated wheat straw specimens (5 mm x 100 mm in size) using a 1-mL syringe. Ten replicates were made to measure the contact angle and the surface free energy of wetting. The tests were carried out using a JC2000D Contact Angle Measuring Apparatus (CAA, made in Shanghai, P.R. China). The images of the drop shape on the specimens were captured by a camera connected to the computer and saved every 40 milliseconds. As time elapsed, the drop shape tended to stabilize, reaching an equilibrium contact angle. The contact angles of UF, PF, and MDI resins were measured by the imaging software package (JC2000-USB) at 0, 50, 100, 200, 400, 600, 800, and 1000 seconds after they were placed on the surfaces of specimens. The spreading and penetrating abilities of resins were quantified with the wetting model developed by Shi and Gardner (2001). The model is described by the following equation:

$$\theta = \frac{\theta_i \theta_e}{\theta_i + (\theta_e - \theta_i)\exp\left[K\left(\frac{\theta_e}{\theta_e - \theta_i}\right)t\right]} \tag{1}$$

In this model, the contact angle θ changes as a function of time t. θ_i and θ_e represent the instantaneous contact angle and the equilibrium contact angle, respectively, and K is the spreading/penetrating constant, the change rate constant of the contact angle. The higher K is, the better the wettability is (Shen *et al.* 2011).

Shear Strength Evaluation

Before evaluating shear strength, two pieces of untreated and plasma-treated wheat straw specimens were coated with UF, PF, and MDI, then heated and pressed in the hot-press (X16, made in Qingdao P.R. China). The experimental conditions were as follows:

Specimen dimensions: 5 mm ×100 mm
Gluing section: 5mm ×15mm
Gluing surface: interior-to-interior, interior-to-exterior, and exterior-to-exterior
Resin content: 200 g/m^2
Resin type: UF, PF, MDI
Hot-pressing pressure: 1.5 MPa
Hot-pressing temperature: 110 F
Hot-pressing time: 90 seconds

The shear strength was measured using a paper tension meter (WZL-300, made in Hangzhou, China) referred to the method of the tensile strength of paper (ISO1924/2-1985), after the prepared specimens cooled for more than 24 h. Twenty replicates were made for each sample. The procedure for preparing and measuring the specimens for one of three types of gluing surface is illustrated in Fig. 1.

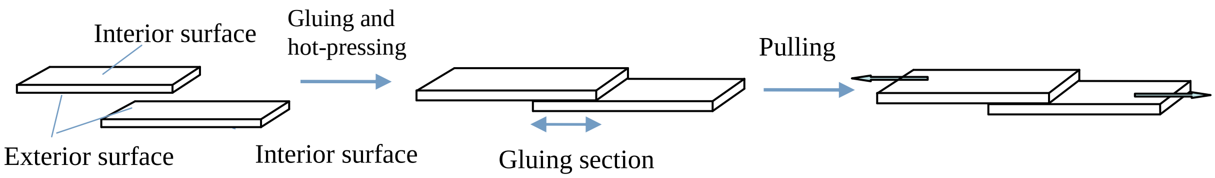


Fig. 1. Method of measurement of shear strength of specimens glued with UF, PF, and MDI

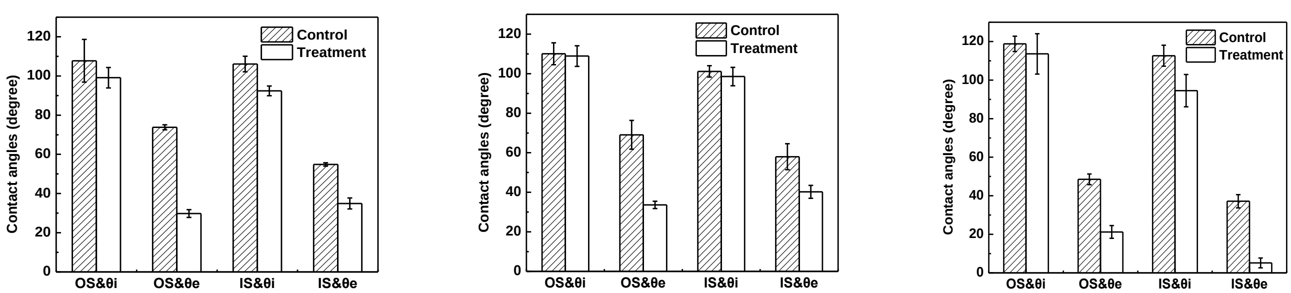
RESULTS AND DISCUSSION

Effect of Cold Oxygen Plasma Treatment on Dynamic Wettability of Different Adhesives on Wheat Straw Surface

The wettability of solid materials is largely dependent on the contact angle (Aydin 2004). At the same time, the coefficient of spreading and penetrating, *K*, is also used to compare interior and exterior wheat straw surface wettability for each adhesive. In this study, the dynamic wettability of different adhesives (UF, PF, and MDI) on different surfaces of untreated (control) and plasma-treated (treatment) wheat straw was analyzed using the contact angle and *K* value.

Contact Angle: Instantaneous Contact Angle *vs*. Equilibrium Contact Angle

As can be seen in Fig. 2 and Table 2, for the UF resin, the instantaneous and equilibrium contact angles of the plasma treated wheat straw (99.10° and 29.8° on the exterior surface, 92.38° and 34.94° on the interior surface) were much lower than those of untreated specimens (107.75° and 73.8° on the exterior surface, 106.10° and 54.85° on the interior surface).



a b c

Fig. 2. The instantaneous and equilibrium contact angles of the three adhesives on surfaces of untreated and treated wheat straw (a - UF, b - PF, c - MDI; OS - the exterior surface, IS - the interior surface, θ_i - the instantaneous angle, θ_e - the equilibrium angle)

The percent decrease from instantaneous contact angle to equilibrium contact angle of the plasma-treated wheat straw (67.61 to 81.29% on the exterior surface, 59.16 to 94.50% on the interior surface) was much greater than that of the untreated specimen (31.51 to 59.15% on the exterior surface, 42.66 to 69.71% on the interior). The trends for the PF and MDI were consistent with that of UF. Hence, it is clear that the cold oxygen treatment improved the spreading and penetrating ability of the three resins on both the interior or exterior surfaces of the wheat straw.

Wheat Straw Surface: Exterior vs. Interior

From the comparison columns plotted in Fig. 2, it is apparent that the cold oxygen plasma had a significant effect on the equilibrium contact angles of the specimens. Additionally, there was a significant difference between the contact angles on the interior and exterior surfaces of the wheat straw. As seen in Fig. 2 and Table 2, the equilibrium contact angle of the interior surface was lower than that of the exterior surface for the same resin on the untreated wheat straw (control). This indicates that the wettability of the interior was greater than that of the exterior. This is because the structure of the exterior and interior surface of wheat straw is different. The exterior surface contains plenitudinous cuticle, composed mostly of cutin and wax, which prevent the resin from spreading and penetrating the surface (Liu *et al.* 2004). However, for the plasma-treated wheat straw, the equilibrium contact angle of the interior surface was higher than that of the exterior surface for UF and PF resins, while MDI had a lower contact angle on the interior compared to the exterior surface. All contact angles of treated specimens were lower than that of control sample. The wettability of the two surfaces was improved after they were treated with the cold oxygen plasma.

Table 2. Instantaneous and Equilibrium Contact Angles of the Three Adhesives on Surfaces of Untreated and Treated Wheat Straw

Surface	Condition	Contact Angle(degree)					
		UF		PF		MDI	
		θ_i	θ_e	θ_i	θ_e	θ_i	θ_e
OS	control	107.75	73.80	110.06	69.06	118.81	48.53
	treatment	99.10	29.80	103.90	33.65	113.60	21.25
IS	control	106.10	54.85	101.15	58.00	122.65	37.15
	treatment	92.38	34.94	98.55	40.25	94.50	5.20

In order to determine whether the conclusion above was legitimate, the coefficient of spreading and penetrating (*K*) was calculated. Figure 3 shows the contact angle values as a function of wetting time for the different surfaces of the untreated and treated wheat straw. The wetting data were well fit by curves and the R^2 values were over 0.93 for all samples. Comparing the results obtained for the different conditions, it was found that the *K* value of the three resins on the exterior and interior surfaces of the plasma-treated wheat straw was 1.55 to 17.14 times greater than that of the untreated samples. This indicates that the spreading and penetrating ability of the plasma treated surface for the three resins was substantially improved. This may have been because the weak boundary surface layer of wheat straw was destroyed by the plasma, and some oxygen containing groups, such as hydroxyl and carbonyl groups, were introduced to the surface (Yang *et al.* 2012).

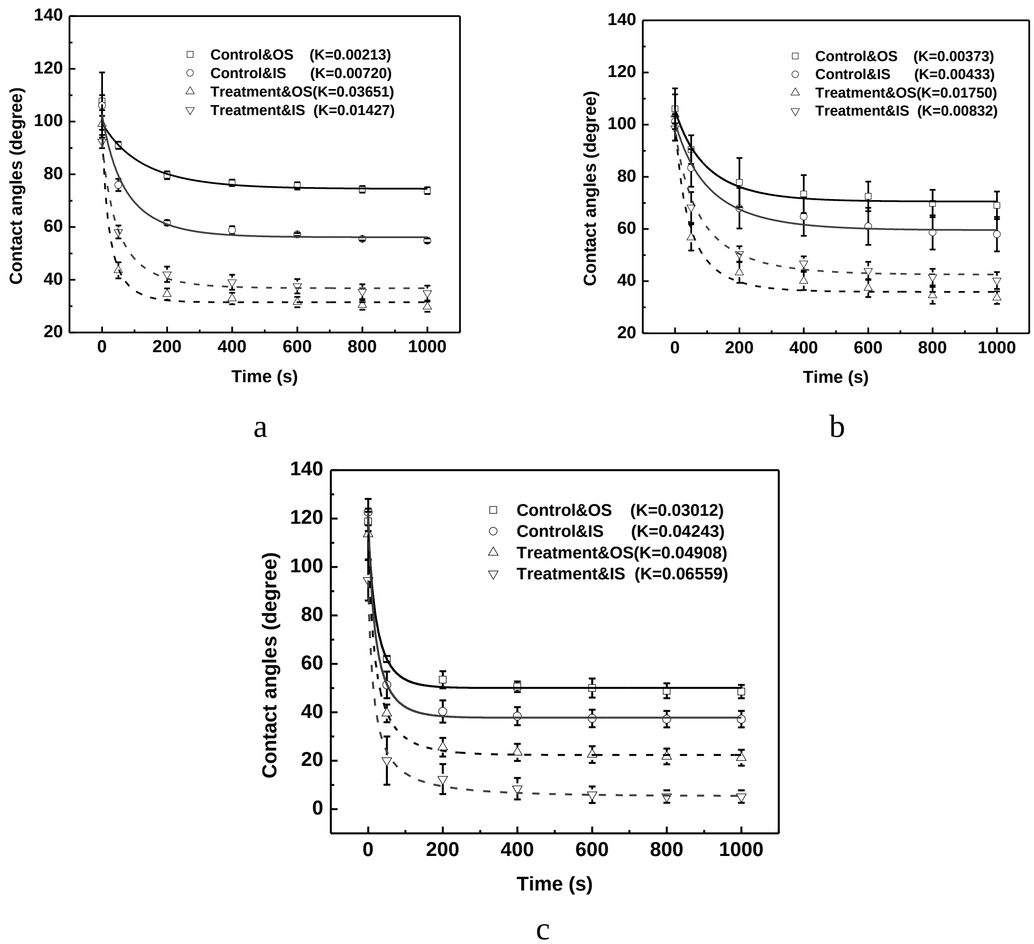


Fig. 3. The contact angles of UF, PF, and MDI change as a function of wetting time for untreated and treated wheat straw (a - UF; b - PF; c - MDI)

The *K*-value of the interior surface of the untreated wheat straw was approximately two times higher than that of the exterior surface for the same resin. However, the *K*-values of the exterior surfaces for UF and PF resins were 0.03651 and 0.01750, respectively, values almost 2.5 times greater than those of the interior surface. Plasma-treated wheat straw treated with MDI resin had a higher *K*-value on the interior surface compared to its exterior surface. The spreading and penetrating ability of the interior surface is undoubtedly greater than that of the exterior surface for the untreated wheat straw. The cold oxygen plasma treatment resulted in greater improvement of hydrophilicity and wettability of the exterior surface than that of the interior surface.

Adhesive Type: UF, PF, and MDI

As was shown in Figs. 2 and 3, the adhesive type (UF, PF, or MDI) had a significant effect on the wettability of both the untreated and the treated wheat straw. The untreated wheat straw with MDI resin had lower equilibrium contact angles and higher *K* values than those with the UF and PF resins. The equilibrium contact angle of the MDI (48.53°) was 34.24% lower than that of UF (73.80°) and 29.73% lower than that of PF (69.06°) on the exterior surface, while the *K* value of the MDI (0.03012) was 14.14 times greater than that of UF (0.00213) and was 8.1 times greater than that of PF (0.00373).

The trends regarding the interior surface were similar to those of the exterior surface. The isocyanate groups of MDI effectively produced cross-linked polyureas, providing mechanical bonding by reacting with the wheat straw. Consequently, the chemical bonding through the hydrogen bonds and polyurethane covalent bonds was enhanced, and the wettability on the surfaces of the wheat straw was improved by using the MDI resin (Mo *et al.* 2003). Conversely, the UF and PF were hardly bonded to the hydroxy groups in the wheat straw because of the substantial amounts of cutin, wax, and silica on the surface of the straw (Liu *et al.* 2004). The higher solid surface energy and the lower liquid surface tension also show the better wettability at the interface of the solid and liquid (Liu *et al.* 2007). In this experiment, the surface tension of MDI was 56.78 mJ/m^2, which was lower than that of the UF (135.30 mJ/m^2) and the PF (114.37 mJ/m^2). Therefore, of the three resins, MDI exhibited the best wettability on the surface of the wheat straw.

Table 3. Factorial Analysis of Variance for the Contact Angles of Exterior Surface of Untreated Wheat Straw on UF, PF, and MDI

	SS	df	MS	F	P-value	F(crit)
MSG	1804.31	2	902.15	55.22	0.000001	3.885
MSW	196.06	12	16.34			
SUM	2000.37	14				

A factorial analysis of variance for the contact angles of exterior surface of untreated wheat straw on UF, PF, and MDI was conducted. As shown in Table 3, it was evident that the value of F (55.22) was much greater than the value of F(crit) (3.885). And the P-value (0.000001) was far lower than 0.01. Consequently, the contact angles of wheat straw had great difference on different resins.

Effect of Cold Oxygen Plasma Treatment on Shear Strength of Wheat Straw with Different Adhesives

As can be seen in Fig. 4, it was evident that the shear strength of the specimens with exterior-to-exterior surfaces, exterior-to-interior surfaces, and interior-to-

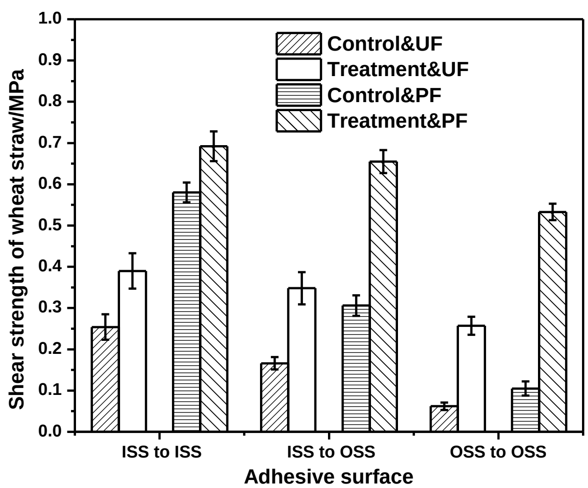


Fig. 4. The shear strength of the untreated and plasma-treated wheat straw on different adhesive surfaces of UF and PF

interior surfaces of wheat straw were dramatically improved after it was exposed to the cold oxygen plasma treatment. This is true for both UF and PF resin. Looking specifically at UF resin, the shear strength of treated wheat straw increased by 53.54%, 109.64%, and 314.52% at the interior-to-interior surface, interior-to-exterior surface, and exterior-to-exterior, respectively. For PF resin, the shear strength of treated samples was 19.31%, 114.05%, and 407.62% greater than that of control samples, respectively. The plasma treatment can improve the surface wettability effectively, which directly influences the bonding property. Additionally, the shear strength with PF resin was slightly higher than that with UF resin

The shear strength of surfaces bonded with MDI resin could not be tested because the specific strength of that wheat straw is much lower than its shear strength.

CONCLUSIONS

1. The interior surface of the wheat straw had higher wettability than that of the treated wheat straw for the three resins.
2. Of the three resins, MDI yielded the highest wettability on the surface of the wheat straw.
3. The cold oxygen plasma treatment was an effective method to improve the surface dynamic wettability of the wheat straw, especially for the exterior surface.
4. The surface wettability had a direct effect on the bonding property. The shear strength in three cases (interior-to-interior, interior-to-exterior, and exterior-to-exterior) with the UF and PF resins was remarkably improved after the wheat straw was treated with the cold oxygen plasma, particularly in the case of the exterior-to-exterior surface.

ACKNOWLEDGMENTS

The authors are grateful for support from the National Natural Science Foundation of China (Grant No. 31270606), Program for New Century Excellent Talents in University (Grant No. NCET-10-0177), Program for 333 High-level Talents in Jiangsu Province (Grant No. BRA2011166) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). Sincere thanks go to Jiangsu Engineering Research Center of Fast-growing Trees and Agri-fiber Materials for providing equipment for this study.

REFERENCES CITED

Acda, M. N., Devera, E. E., Cabangon, R. J., and Ramos, H. J. (2012). "Effects of plasma modification on adhesion properties of wood," *Int. J. Adhes. Adhes.* 32(1), 70-75.

Aydin, I. (2004). "Activation of wood surfaces for glue bonds by mechanical pre-treatment and its effects on some properties of veneer surfaces and plywood panels," *Appl. Surf. Sci*. 233(1-4), 268-274.

Gadhe, J. B., Gupta, R. B., and Elder, T. (2006). "Surface modification of lignocellulosic fibers using high-frequency ultrasound," *Cellulose* 13(1), 9-22.
Han, G., Deng, J., Zhang, S., Bicho, P., and Wu, Q. (2010). "Effect of steam explosion treatment on characteristics of wheat straw," *Ind. Crops Prod.* 31(1), 28-33.
Jamali, A., and Evans, P. D. (2011). "Etching of wood surfaces by glow discharge plasma," *Wood Sci. Tech.* 45(1), 169-182.
Kalia, S., Kaith, B. S., and Kaur, I. (2009). "Pretreatments of natural fibers and their application as reinforcing material in polymer composites-A review," *Polym. Eng. Sci.* 49(7), 1253-1272.
Kaparaju, P., and Felby, C. (2010). "Characterization of lignin during oxidative and hydrothermal pre-treatment processes of wheat straw and corn stover," *Bioresour. Technol.* 101(9), 3175-3181.
Lawther, J. M., Sun, R., and Banks, W. B. (1996). "Effect of steam treatment on the chemical composition of wheat straw," *Holzforschung* 50(4), 365-371.
Li, X. J., Cai, Z. Y., Winandy, J. E., and Basta, A. H. (2011). "Effect of oxalic acid and steam pretreatment on the primary properties of UF-bonded rice straw particleboards," *Ind. Crops Prod.* 33(3), 665-669.
Li, X. L., Zhang, F. Q., and He, N. Y. (2010). "Effects of different pretreatment methods on performance of rice straw fiber," *Pack. Eng.* 31(1), 7-9.
Lian, H. L., Zhou, D. G., and You, J. X. (2005). "Studies on layer composites of wheat stalk and their adhesion properties," *Chem. Ind. For. Prod.* 25(1), 69-72.
Liu, Z. M., Wang, F. H., and Wang, X. M. (2004). "Surface structure and dynamic adhesive wettability of wheat straw," *Wood Fiber Sci.* 36(2), 239-249.
Liu, Z. M., Wang, F. H., and Wang, X. M. (2007). "Spectroscopic analysis of the interface for wheat straw specimen glued with PMDI," *Wood Fiber Sci.* 39(1), 109-119.
Mo, X., Cheng, E., Wang, D., and Sun, X. S. (2003). "Physical properties of medium-density wheat straw particleboard using different adhesives," *Ind. Crops Prod.* 18(1), 47-53.
Munawar, S. S., Umemura, K., and Kawai, S. (2008). "Manufacture of oriented board using mild steam treatment of plant fiber bundles," *J. Wood Sci.* 54(5), 369-376.
Shen, J. H., Liu, Z. M., Li, J., and Niu, J. (2011). "Wettability changes of wheat straw treated with chemicals and enzymes," *J. For. Res.* 22(1), 107-110.
Shi, S. Q., and Gardner, D. J. (2001). "Dynamic adhesive wettability of wood," *Wood Fiber Sci*. 33(1), 58-68.
Sun, X. F., Xu, F., Sun, R. C., Geng, Z. C., Fowler, P., and Baird, M. S. (2005). "Characteristics of degraded hemicellulosic polymers obtained from steam exploded wheat straw," *Carb. Polym.* 60(1), 15-26.
Tang, L. J., Zhang, R., Zhou, X. Y., Pan, M. Z., Chen, M. Z., Yang, X. H., Zhou, P., and Chen, Z. (2012). "Dynamic adhesive wettability of poplar veneer with cold oxygen plasma treatment," *BioResources* 7(3), 3327-3339.
Wang, L. J., and Zhang, S. B. (2005). "Present situation and problem of wheat-straw board in China," *Wood Proc. Mach.* 2005(1), 39-41.
Yang, X. H., T, L. J., Zhang, R., and Zhou, X. Y. (2013). "Review on progress of crop straws surface modification," *J. Nanjing For. Univ. (Nat. Sci. Ed.)* 37(3), 157-162.
Xu, F. R. (2011) "Problems in wheat straw board production and relevant proposals," *China For. Prod. Ind.* 38(1), 9-11.

Zhang, R., Tang, L. J., Zhou, X. Y., and Yang, X. H. (2013). "Effect of gluing process on atmospheric pressure cold plasma treatment for improving bonding strength of poplar veneer," *China For. Prod. Ind.* 40(4), 24-39.

Zhang, Y. (2003). "Influence of enzyme preparation on character of wheat straw," *Acta Agric. Bor.-Occ. Sinica* 12(1), 146-149.

Zhang, Y., Jiang, H., and Zhou, Z. B. (2008). "Influence of enzyme pretreatment on surface bonding properties of wheat straw," *China Wood Ind.* 22(1), 15-18.

Zhao, M., Huang, H., and Miao, A. (2009). "Study on the wettability of surface veneer of five kinds of engineered solid wood flooring," *China For. Sci. Tech.* 23(6), 29-33.

Zhou, D. G. (2009). "The development of straw-based panel," *Eng. Sci.* 11(10), 115-121.

Zhou, D.G., Lian, H. L., and Zhou, X. Y. (2008). "Interface characteristics of mechanically ground rice/wheat straws," *Chem. Ind. For. Prod.* 28(1), 16-22.

Article submitted: November 2, 2013; Peer review completed: December 26, 2013; Revised version received and accepted: January 10, 2014; Published: February 3, 2014.