Effects of Dielectric Barrier Discharge Plasma Treatments on the Performance of Poplar Plywood Produced with UF Resins of Different Molar Ratios

Hui Wang,[a,b] Zhigang Duan,[a] Feng Wang,[a] Hongyan Wang,[c,]* and Guanben Du [a,]*

Poplar veneers were treated with dielectric barrier discharge (DBD) plasma at atmospheric pressure, and the effects on the veneer surface feature were explored. The bonding strength of poplar plywood glued with different urea-formaldehyde resins of varying molar ratios was also investigated. The wettability and resin penetration of the veneer treated with DBD plasma were dramatically improved, especially for the UF resin with a higher formaldehyde to urea (F/U) molar ratio. The apparent contact angle of the veneer-treated plywood decreased and the resin penetration content increased as well. The bonding strength of the plywood increased in different degrees, and the wet bonding strength in particular sharply increased; when the F/U molar ratio was 1.3, the strength was improved by 138.2%. However, when the F/U molar ratio increased, the wet bonding strength improvement declined. The veneer surface image before and after the DBD treatment was invested *via* scanning electron microscopy, the surface was rougher and looser, which was beneficial for resin penetration. These all indicated that the balance between the characteristics of the resin and the penetration of the veneer surface is critical for an improvement in the bonding strength of plywood.

Keywords: Plasma treatment; UF resins; Poplar plywood; Penetration behaviors

*Contact information: a: Southwest Forestry University, Yunnan Key Laboratory of Wood Adhesives and Glued Products, Kunming, Yunnan, P. R. China; b: Key Laboratory of Bio-based Material Science & Technology (Northeast Forestry University); c: Zhejiang Academy of Forestry, Hangzhou, Zhejiang, P. R. China; *Corresponding authors: swfudgb@163.com; why2007236@126.com*

INTRODUCTION

Based on its recyclable and biodegradable characteristics, wood is considered as an environmentally friendly material and is used extensively for producing wood-based products, such as furniture, artificial panels, and wood-plastic composites. However, due to the lack of wood resources and the fact that its physical properties are easily changed, wood often is modified with physical or chemical methods to achieve greater value and utilization rate in recent years (Prakash and Mahadevan 2008; Lande *et al.* 2008; Gregorova *et al.* 2009; Korkut *et al.* 2009). To some extent, both physical and chemical treatments will cause some negative effects on the environment or people's health. Plasma is known as the fourth state of matter, composed of a large number of electrons, ions, atoms, molecules, free radicals, and other particles; plasma has sufficient energy to break the chemical bonds of substrates (Denes *et al.* 1999; Ma *et al.* 2018). Thus, plasma treatment has been studied in wood research because it is a simple, highly efficient, and non-pollutant process, and has a wide application range.

According to treatment temperature, the plasma treatment can be divided into hot and cold plasma. A cold plasma has relatively stable discharge and does not require vacuum conditions; thus, it has more widespread applications. According to the literature (Custodio *et al.* 2008; Li *et al.* 2010; Blajan *et al.* 2013; Ma *et al.* 2018), it has been used to modify the surface of wood, metals, plastics, and glass to enhance the deposition or improve the adhesion of glues.

Cold plasma treatment has been considered as a way to improve wood bonding strength, especially for plywood. It has been shown that the bonding strength could be improved by 10% to 30% after cold plasma treatment (Acda *et al.* 2012; Zhang *et al.* 2015; Chen *et al.* 2015). The cited authors also considered plasma treatment to be a promising method for wood modification. Although the effects of cold plasma modification of wood substrates were reported in each case, there is uncertainty about the mechanism of modification owing to the complex system of the plasma and wood bonding process. Some researchers believed that the bonding strength improvement of wood products after cold plasma treatment was due to the wettability and penetration increase of adhesive on wood surface (Podgorski *et al.* 2000; Custodio *et al.* 2008; Chen *et al.* 2015; Tang *et al.* 2015), whereas others considered that cold plasma could effectively improve the bonding strength owing to some new functional groups reacting with the adhesive on the wood surface. (Wolkenhauer *et al.* 2007; Totolin *et al.* 2008; Acda *et al.* 2012). Hence, the further detailed investigation related to the mechanism of cold plasma on wood bonding strength is necessary.

Bonding is a very complex system involving many factors, such as the adhesive type, wetting, curing, hot pressing parameters, and the surface appearance of the substrate. Among these factors, the selection of adhesive is important to obtain the bonding strength. In some reports (Scholz *et al*. 2010; Tang *et al.* 2015; Zhang *et al.* 2015), different types of adhesives were used to produce plywood to explore the mechanisms of plasma modification; however, different kinds of adhesive including various functional groups, and the itself gluing mechanism is quite different, so, it cannot convincingly explain the mechanism of cold plasma treatment. In fact, the adhesive was not considered as a major factor of impacting the bonding strength of wood treated with cold plasma.

In order to eliminate the effects of adhesive type, therefore, considering the importance of adhesives for improving the bonding strength of plywood, various molar ratio urea-formaldehyde (UF) resins and poplar plywood with DBD plasma modified veneer were prepared in the laboratory. In this work, the relationship among UF resins, DBD plasma treatments, and the bonding strength of plywood were be explored in an effort provide a fundamental basis for the mechanism of bonding strength improvement *via* DBD plasma treatment.

EXPERIMENTAL

Materials

Wood specimens

Poplar (*Populus* spp.) veneer with a 1.5-mm thickness and a moisture content of 8% to 10% was purchased from the Zhi Wei Veneer Factory in the Hebei province (China). Each veneer specimen selected was defect free and cut into 40 mm × 40 mm sections.

Resin preparation

In this work, all chemicals were reagent grade and supplied by the chemical reagent operation department of Danchi Trading Co., Ltd. (Kunming, China). The UF resin was synthesized in the authors' laboratory following the procedures reported in Wang *et al.* (2017). By changing the urea dosage, three UF resins with a formaldehyde to urea (F/U) molar ratio of 1.0, 1.3, and 1.5 were obtained. The properties of these UF resins are listed in Table 1.

Table 1. The Basic Performance of UF Resins with Different F/U Molar Ratio

F/U Molar Ratio	Solid Content (%)	Viscosity (s) / 20 °C	Appearance
1.0	50	20	Milky white liquid
1.3	49	17	Milky white liquid
1.5	47	18	Milky white liquid

Plasma treatment

Dielectric barrier discharge plasma (ZD-1000C; Nanjing Suman Electronics Co., Ltd., Nanjing, China) equipment with a transmission platform, electronic control systems, and plasma transformer was employed. The veneer (40 mm × 40 mm), was uniformly treated *via* passage between two electrodes on a roller conveyor, one-by-one, at atmospheric pressure and ambient air. The processing power was 5 kW, and the plasma processing rate was 12 m/min, and the veneers were treated 3 times by passing through the gap between two electrodes.

Methods

Contact angle and resin penetration behavior measurements

The contact angle was measured on a contact angle measuring apparatus (JC2000A; Zhongchen Co., Ltd., Shanghai, China). The contact angles between the control or treated poplar veneer and the different molar ratio UF resins was measured at 0 s, 10 s, and 60 s. The contact angle measurements were made within 5 min after the plasma treatment. To further analyze the effects of plasma treatment on wood veneers, the resin penetration amount was measured as follows: the control wood veneer was measured firstly, and the mass was designated as M_1. Then after being treated with DBD cold plasma and immersed in the UF resins immediately, then 10 s, 30 s, 60 s, 3 min, and 5 min later, the samples were taken out and the surface was wiped with filter paper, and the mass was designated as M_2. The resin penetration amount was equal to the (M_2-M_1) value.

Scanning Electron Microscopy (SEM) Analysis

The surface structure of the poplar veneer before and after plasma treatment was analyzed with a scanning electron microscope (TM3030; Hitachi Limited, Tokyo, Japan) at an operating voltage of 5 kV to 15 kV under vacuum. The variable-pressure mode was selected because the veneer samples are insulators.

Plywood Preparation and Properties

The three-layer plywood was produced with plasma-treated poplar veneer and non-treated poplar veneer as the control. The various UF resin loading was 180 g/m^2 (single side), the hot pressing time was 3 min, the pressure was set at 1 MPa, and the temperature was 140 °C. The bonding strength was evaluated with a universal testing machine (HD-

500; Shenzhen Sans Material Test Instrument Co., Ltd., Shenzhen, China) in accordance with the procedure described by Chinese National Standard GB/T 17657 (2013). In this work, 6 to 8 specimens of each type were tested, and the average (effective value) was used as the final result.

RESULTS AND DISCUSSION

Bonding Strength of Plywood

In the present study, three pieces of poplar veneer, formed into one group, were treated with DBD plasma at atmospheric pressure and ambient air conditions. Then the three-layer plywood was manufactured under the conditions mentioned above, while the control plywood was produced with untreated veneer. The dry and wet bonding strengths of the plywood were tested, and the results are shown in Fig. 1.

The bonding strength of the plywood after DBD plasma treatment was much higher than that of the untreated plywood; meanwhile, the standard deviation is smaller. It means the adhesive distributed uniformly on the wood surface after plasma treatment, the bonding strength is more even. For the dry bonding strength, when the F/U ratio was 1.0, the increase in strength was the most obvious. When the F/U ratio was 1.3, the increase in strength was slightly decreased, and the trend continued with an increase of the F/U molar ratio. These findings imply that lowering of the UF resin molar ratio gave a higher increase of plywood bonding strength after DBD plasma treatment.

At the same time, after treatment with cold water, the wet strength of the plywood with a F/U ratio of 1.0 vanished entirely due to the poor water resistance of the UF resin. However, the DBD plasma treatment was very beneficial to the wet strength of plywood with an F/U ratio of 1.3 or 1.5, with a variation trend similar to the dry strength. The wet bonding strength of plywood after DBD plasma treatment far surpassed that of the non-treatment, which means that DBD plasma treatment had a positive effect on the excellent bonding strength.

From the results shown in Fig. 1, an F/U of 1.3 is the best. As the authors have shown, the F/U final ratio was higher and the hydroxymethyl (-CH_2OH) content was also much higher (Liang *et al.* 2018), and the bonding strength of the plywood was relatively better. Therefore, the results of the F/U of 1.3 exceeded that of the F/U of 1.0, but if there were too many groups, such as hydroxymethyl (-CH_2OH) in the UF resin, it decreased the bonding strength durability due to its hydrophilic character. Meanwhile, after DBD plasma treatment, because lots of active groups (such as -NH_2) are formed on the veneer surface, at a higher F/U molar ratio the bonding strength increase was more obvious. Apparently, the present results are not in agreement with the above speculation. So, the formation of active groups cannot be the exclusive reason for bonding strength increase. Because the veneer face was treated with DBD plasma, both the surface polarity and the penetration changed drastically in accordance with reported literature (Podgorski *et al.* 2000; Rehn and Viol 2003; Avramidis *et al*. 2009; Chen *et al.* 2016). Hence, to explore the factors of bonding strength improvement, the wettability and resin penetration behaviors of veneer were investigated as well.

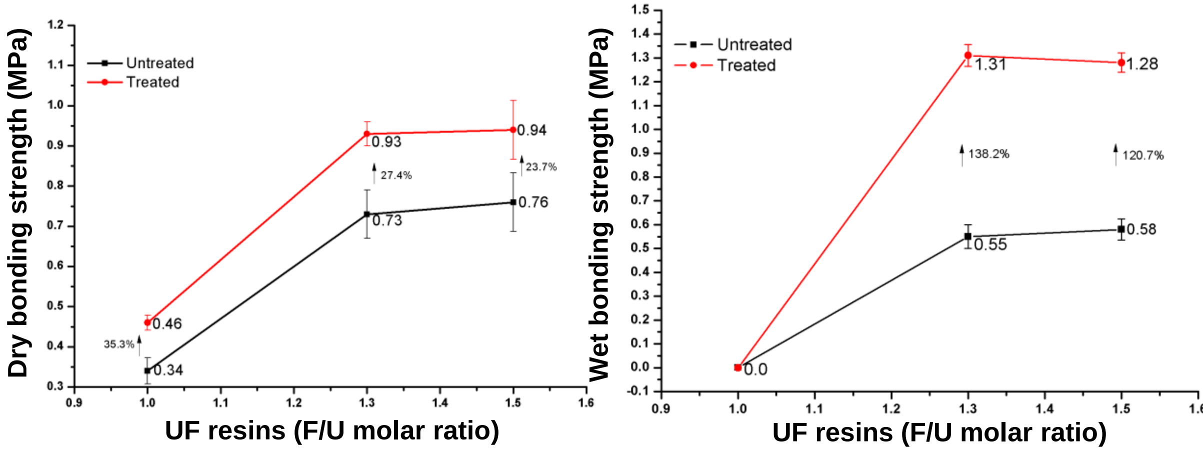


Fig. 1. Bonding strength of plywood with various UF resins and uniform DBD plasma treatment

Wettability and Resin Penetration Behavior

Wettability is usually represented as the apparent contact angle (CA), and the UF resin contact angle was tested and presented in Table 2. It can be confirmed that treated poplar veneer surfaces had a good wettability, with the highest CA decrement of an F/U ratio of 1.5 at 57.7% (from 71° to 30°), in addition to an F/U ratio of 1.3 at 50.6% (from 83° to 41°), and a F/U ratio of 1.0 at 33.3% (from 70° to 46.7°). These findings demonstrated that a higher F/U ratio resulted in a better UF resin wettability of the poplar veneer after treatment with DBD plasma. Because the UF resin included multiple polar groups, the DBD plasma treatments caused a stronger surface polarity on the poplar veneer according to the similarity description principle. Moreover, after 30 s, the CA of the control sample was far higher than the treated samples, which showed that the DBD plasma treatment was beneficial to the UF resin absorption. It was also interesting that when the glue deposition time reached 30 s, the CA of the control sample surface showed no obvious difference between the F/U ratios of 1.0, 1.3, and 1.5, so the control plywood bonding strength mainly depended on the type of the applied resin, which was an improvement in surface wettability, but not the main reason that resulted in a bonding strength change. Nevertheless, plasma-treated samples are very special, and the penetration speed of an F/U ratio of 1.0 was the fastest, an F/U ratio of 1.5 was second, and an F/U ratio of 1.3 was the slowest.

Table 2. The Initial Contact Angles of Poplar Veneer Surfaces Using UF Resins as the Testing Drops at Different Deposition Time

Sample	Initial Angle (°)			
	Control		Plasma-treated	
	0 s	30 s	0 s	30 s
UF 1.0	70.0(0.216*)	36.5(0.171)	46.7(0.238)	13.5(0.222)
UF 1.3	83.0(0.208)	36.0(0.129)	41.0(0.330)	27.6(0.265)
UF 1.5	71.0(0.222)	34.8(0.183)	30.0(0.299)	19.3(0.206)

* Values in the brackets are the standard deviation

As is well known, there is a close relationship between resin penetration and bonding strength. Generally, a deeper resin penetration results in a stronger bonding strength of the plywood. However, if the resin penetration is too deep, the bonding strength will be weaker due to the lack of glue on the surface of the veneer. Therefore, to investigate the effects of DBD plasma treatment on resin penetration, some experiments were also conducted, and the results are shown in Table 3.

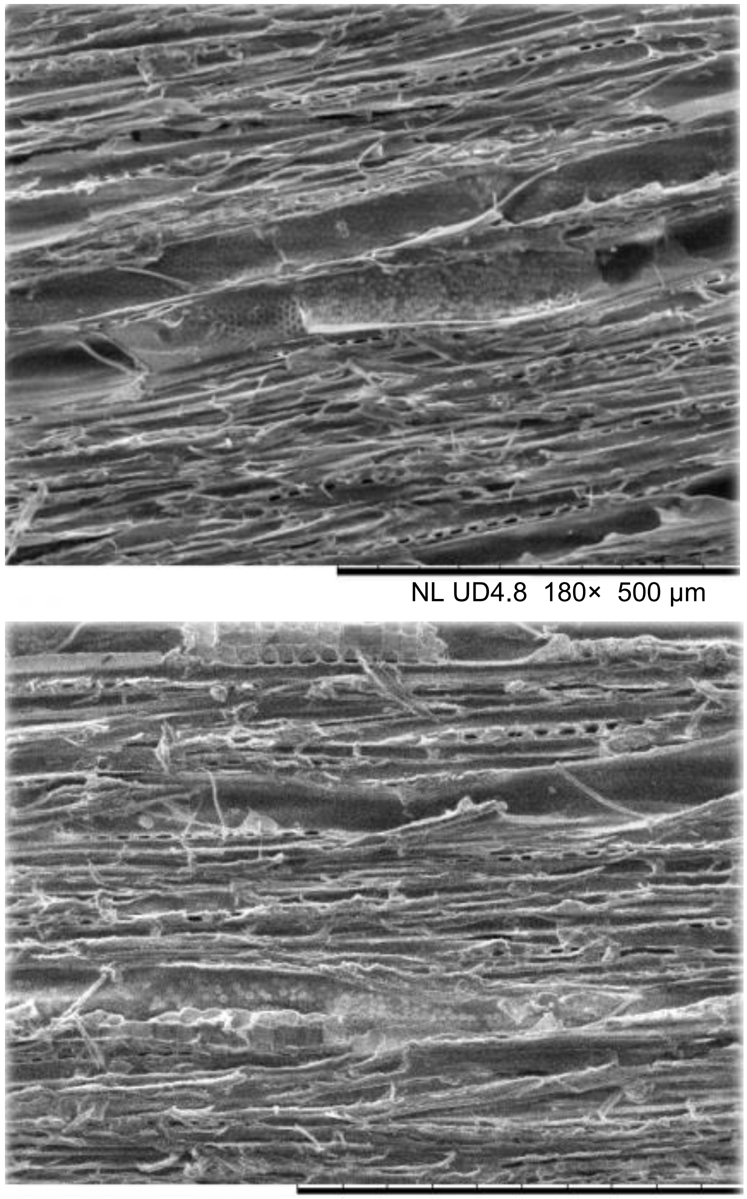
Table 3. The Glue Absorption of Poplar Veneer Treated with DBD Plasma

F/U Molar Ratio	Resin Penetration at Different Immersion Times(g)					
		10 s/g	30 s/g	60 s/g	180 s/g	300 s/g
1.0	Control	0.09(0.005*)	0.10(0.050)	0.13(0.036)	0.16(0.016)	0.18(0.009)
	Treated	0.16(0.013)	0.19(0.003)	0.19(0.012)	0.21(0.008)	0.21(0.006)
1.3	Control	0.14(0.004)	0.15(0.075)	0.17(0.023)	0.17(0.011)	0.17(0.008)
	Treated	0.16(0.007)	0.19(0.002)	0.24(0.003)	0.24(0.003)	0.25(0.004)
1.5	Control	0.16(0.083)	0.16(0.080)	0.20(0.087)	0.20(0.085)	0.20(0.094)
	Treated	0.18(0.015)	0.20(0.010)	0.21(0.009)	0.22(0.008)	0.23(0.011)
* Values in the brackets are the standard deviation						

Plasma-treated samples absorbed more resin than a non-treated veneer under the same time condition, which is in accordance with the reported results (Wascher *et al*. 2017). To some extent, this contributed to the improvement of bonding strength. In particular, UF resins with an F/U ratio of 1.0 had the most obvious penetration differences before and after plasma treatment. When the immersion time was 180 s, the resin absorption nearly reached a level of full stability, which told the authors that the assembly time of a plywood mat would be most suitable at 3 min. However, with an F/U ratio of 1.3 or 1.5, the change in the resin penetration trend was nearly the same. Thus, there should be no difference between the bonding strength of plywood with an F/U ratio of 1.3 or 1.5. Samples with an F/U ratio of 1.0, 1.3, or 1.5 had better penetration behavior than the control, with an F/U ratio of 1.5 performing optimally. It was possible that this was the main component responsible for the bonding strength improvement.

Surface Characteristics of Poplar Veneer

The poplar veneer surface before and after the atmospheric-pressure plasma treatment was observed under 180× magnification, as shown in Fig. 2. The veneer surface after the plasma treatment showed morphological changes when compared to the control sample surface image. The untreated veneer had a relatively smooth surface, while the surface treated with DBD plasma was rougher and looser. These phenomena were ascribed to the plasma etching effect. The highly energetic plasma species bombarded the surface layer of the veneer, destroyed the original surface structure, and then caused the plasma etching and produced a new surface characteristic. The changes in morphology induced by the plasma treatment were beneficial for resin absorption and penetration and generated excellent interface bonding strength. According to the literature (Asandulesa *et al.* 2010; Tang *et al.* 2015; Zhang *et al.* 2015), the main element contents, such as carbon, oxygen, hydrogen, and nitrogen, will be changed after a DBD treatment, especially an increase in the hydrogen and nitrogen content. Therefore, after a DBD plasma treatment, the bond strength of plywood formed with an UF resin with a higher F/U molar ratio could be higher than the control. To some extent, the improvement in chemical bonding was also beneficial to the bond strength of plywood.



(a) Control sample

(b) Treated sample

Fig. 2. SEM images of poplar veneer surface: (a) the control sample (untreated) and (b) the treated sample (5 KW, 3 times)

CONCLUSIONS

1. Three kinds of UF resin with different F/U molar ratios were used to produce the sample plywood, and the improvement in the bonding strength of plywood was various due to UF resins with different F/U molar ratios. Moreover, a higher F/U molar ratio resulted in a greater wet bonding strength of the plywood after the plasma treatment.

However, when the F/U molar ratio was increased from 1.3 to 1.5, the improvement in bond strength was minimal, or it potentially decreased the bond strength. This indicated that the effects of the DBD plasma treatment on the bond strength of the plywood not only depended on the veneer surface active groups formation.

2. After a DBD plasma treatment, the wettability and resin permeability of the poplar veneer increased to varying degrees, and the SEM results showed that the veneer surface was rougher and looser than the untreated surface. This was all beneficial for the absorption and penetration of UF resin into the veneer. For the lower molar ratio UF resin, it was the main reason of the bonding strength of plywood. But for the UF resin with high molar ratio, the active groups may be the main reasons for bonding strength improvement. Therefore, the balance between the characteristics of used resin and the DBD treatment is very critical to obtain proper bonding strength.

ACKNOWLEDGMENTS

The authors are grateful for the support from the Key Laboratory of Bio-based Material Science & Technology (Northeast Forestry University) and the Ministry of Education.

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," *International Journal of Adhesion and Adhesives* 32, 70-75. DOI: 10.1016/j.ijadhadh.2011.10.003

Asandulesa, M., Topala, I., and Dumitrascu, N. (2010). "Effect of helium DBD plasma treatment on the surface of wood samples," *Holzforschung* 64(2), 223-227. DOI: 10.1515/hf.2010.025

Avramidis, G., Hauswald, E., Lyapin, A., Militz, H., Viöl, W., and Wolkenhauer, A. (2009). "Plasma treatment of wood and wood-based materials to generate hydrophilic or hydrophobic surface characteristics," *Wood Material Science & Engineering* 4(1-2), 52-60. DOI:10.1080/17480270903281642

Blajan, M., Umeda, A., and Shimizu, K. (2013). "Surface treatment of glass by microplasma," *IEEE Transactions on Industry Application* 49(2), 714-720. DOI:10.1109/TIA.2013.2244543

Chen, M., Zhang, R., Tang, L., Zhou, X., Li, Y., and Yang, X. (2015). "Effect of plasma processing rate on poplar veneer surface and its application in plywood," *BioResources* 11(1), 1571-1584. DOI: 10.15376/biores.11.1.1571-1584

Chen, M., Zhang, R., Tang, L., Zhou, X., Li, Y., Yang, X. (2016). "Development of an industrial applicable dielectric barrier discharge (DBD) plasma treatment for improving bondability of poplar veneer," *Holzforschung: International Journal of the Biology, Chemistry, Physics, & Technology of Wood* 70(7), 683-690. DOI:10.1515/hf-2015-0122

Custodio, J., Broughton, J., Cruz, H., and Hutchinson, A. (2008). "A review of adhesion promotion techniques for solid timber substrates," *Journal of Adhesion* 84(6), 502-529. DOI: 10.1080/00218460802161558

Denes, A. R, Tshabalala, M. A., Rowell, R., Denes, F., and Young, R. A. (1999). "Reduction of weathering degradation of wood through plasma polymer coating," *Holz-forschung* 53(6), 318-326. DOI:10.1515/HF.1999.104

Gregorova, A., Wimmer, R., Hrabalova, M., Koller, M., Ters, T., Mundigler, N. (2009). "Effect of surface modification of beech wood flour on mechanical and thermal properties of poly (3-hydroxybutyrate) / wood flour composites," *Holzforschung* 63(5), 565-570. DOI:10.1515/HF.2009.110

GB/T 17657 (2013). "Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels," Chinese National Standardization Management Committee, China.

Korkut, S., and Budakci, M. (2009). "Effect of high-temperature treatment on the mechanical properties of rowan (*Sorbus aucuparia* L.) wood," *Drying Technology* 27(11), 1240-1247. DOI:10.1080/07373930903267161

Li, J., Chen, Q., and Yang, L. (2010). "The characterizations of the film modified with DBD plasma and chemosynthesis," *Surface and Coatings Technology* 205(1), 431-434. DOI:10.1016/j.surfcoat.2010.08.135

Lande, S., Westin M., Schneider M. (2008). "Development of modified wood products based on furan chemistry," *Molecular Crystals and Liquid Crystals* 484, 367-378. DOI:10.1080/15421400801901456

Liang, J., Li, T., Cao, M., and Du, G. (2018). "Urea-formaldehyde resin structure formation under alkaline condition: A quantitative ^{13}C-NMR study," *Journal of Adhesion Science and Technology* 32(4), 439-447. DOI: 10.1080/01694243.2017.1361127

Ma, L., Hu, S., Li, P., Wang Q., Ma, H., and Li, W. (2018). "In situ synthesis of sulfur doped carbon nitride with enhanced photocatalytic performance using DBD plasma treatment under H_2S atomosphere," *Journal of Physics and Chemistry of Solids* 118, 166-171. DOI:10.1016/j.jpcs.2018.03.017

Podgorski, L., Chevet, B., Onic, L., and Merlin, A. (2000). "Modification of wood wettability by plasma and corona treatments," *International Journal of Adhesion and Adhesives* 20(2), 103-111. DOI: 10.1016/S0143-7496(99)00043-3

Prakash, G. K., and Mahadevan, K. M. (2008). "Enhancing the properties of wood through chemical modification with palmitoyl chloride," *Applied Surface Science* 254(6), 1751-1756. DOI:10.1016/j.apsusc.2007.07.137

Rehn, P., and Viol, W. (2003). "Dielectric barrier discharge treatments at atmospheric pressure for wood surface modification," *Holz als Roh- und Werkstoff* 61(2), 145-150. DOI: 10.1007/s00107-003-0369-6

Scholz, G., Nothnick, E., Avramidis, G., Krause, A., Militz, H., Viol, W., and Wolkenhauer, A. (2010). "Adhesion of wax impregnated solid beech wood with different glues and by plasma treatment," *European Journal of Wood and Wood Products* 68(3), 315-321. DOI:10.1007/s00107-010-0466-2

Tang, L., Yang, X., Chen, M., Wang, X., and Zhou, X. (2015). "Surface characterization of plasma-modified poplar veneer: Dynamic wettability," *BioResources* 10(1), 369-381. DOI: 10.15376/biores.10.1.369-381

Totolin, V., Manolache, S., Rowell, R. M., and Denes, F. S. (2008). "Application of cold plasma to improve properties of phenolic-bonded aspen fiberboard," *Journal of Natural Fibers* 5(2), 170-192. DOI:10.1080/15440470801929671

Wascher, R., Avramidis, G., Kühn, C., Militz, H., and Viöl, W. (2017). "Plywood made from plasma-treated veneers: Shear strength after shrinkage-swelling stress," *International Journal of Adhesion and Adhesives* 78, 212-215. DOI:10.1016/j.ijadhadh.2017.07.003

Wolkenhauer, A., Avramidis, G., Cai, Y., and Viöl, W. (2007). "Investigation of wood and timber surface modification by dielectric barrier discharge at atmospheric pressure," *Plasma Processes and Polymers* 4, 470-474. DOI:10.1002/ppap.200731209

Zhang, J., Pizzi, A., Lagel, M. C., Du, G., Zhou, X., and Wang, H. (2015). "Dielectric barrier discharge plasma at atmospheric pressure to enhance pine wood surfaces hydrophilic character and adhesion properties," *Wood Research* 60(5), 773-782.

Article submitted: September 26, 2018; Peer review completed: November 18, 2018; Revised version received: December 9, 2018; Accepted: December 15, 2018; Published: December 21, 2018.
DOI: 10.15376/biores.14.1.1279-1288