Surface Characterization of Plasma-modified Poplar Veneer: Dynamic Wettability

Lijuan Tang, a,b Xuehui Yang, Minzhi Chen, Xiangming Wang, and Xiaoyan Zhou a,*

The dynamic wettability of plasma-modified poplar veneer was investigated with sessile adhesive droplets using a wetting model. Dynamic contact angle, instantaneous and equilibrium contact angles, and their rates of change (K-value) were used to illustrate the dynamic wetting process. The experiment consisted of selecting treatment parameters (type of gas, power) that would lead to the increased wettability of wood. Three resin systems, urea-formaldehyde (UF), phenol-formaldehyde (PF), and diphenylmethylene diisocyanate (MDI), were evaluated. Based on the wetting model, the K-value was used to interpret the kinetics of wetting. The higher the K-value, the faster the contact angle reaches equilibrium, and the faster the liquid penetrates and spreads. Therefore, the model was helpful for characterizing the dynamic wettability of wood surfaces modified with different plasma treatments. The K-values of plasma-treated veneer surfaces at different plasma power levels and with different gases (such as O2, N2, Ar, air, and NH₃) were 458% to 653% and 332% to 528% higher than those of untreated veneer surfaces, respectively. In addition, the K-values of the three resins on the oxygen plasma-treated veneer surfaces were 38% to 1204% higher than those on the untreated veneer surfaces. Therefore, this method was helpful for characterizing the dynamic wettability of veneer surfaces modified with plasma treatment.

Keywords: Plasma treatment; Poplar veneer; Dynamic wettability; K-value

Contact information: a: College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China; b: FPInnovations, 319 rue Franquet, Québec (Québec) G1P 4R4, Canada; *Corresponding author: zhouxiaoyan@njfu.edu.cn

INTRODUCTION

It is well known that bonding is a complex process involving both physical and chemical technology. Bonding is related to the flow, wetting, curing, and deforming of adhesives. Of all these factors, wetting appears to be more important than resin curing.

Wetting has been defined by Berg (1993) as macroscopic manifestations of the molecular interactions between liquids and solids in direct contact at the interface between them, including contact angle formation, spreading, and penetration. For nonporous materials, no liquid penetration occurs. Wood is a lignocellulosic and porous material. When a liquid drop is placed on a wood surface, a contact angle at the liquid/solid surface is formed. Then, liquid penetration along with liquid spreading occurs. At the initial stage of the wetting process, the contact angle decreases quickly. As time elapses, the contact angle decreases more slowly and finally attains relative equilibrium (Shi and Gardner 2001). In most of the previous studies on the wettability of wood, instantaneous or equilibrium contact angles or surface free energy were used (Nylund *et al.* 1998; Meijer *et al.* 2000; Gindl *et al.* 2001; Esteves and Pereira 2009, Jarusombuti *et*

al. 2010; Büyüksarı et al. 2011). However, these studies neglect adhesive penetration and the spreading process.

It is clear that liquid wetting on wood surfaces is a complex process influenced by many factors, including surface roughness, porosity, liquid viscosity, and the reorientation of functional groups at the wood-liquid interface. Several models have been proposed for describing the dynamic wetting process (Liptáková and Kúdela 1994; Liu *et al.* 1995; Shi and Gardner 2001). Among these models, the wetting model proposed by Shi and Gardner is more applicable for studying the dynamic wettability of wood. The rate of constant angle change is related to the rate of the liquid penetration and spreading on the solid surface. The *K*-value in the wetting model is a constant that can be referred to as the penetration and spreading constant. The physical meaning of the *K*-value represents how fast the liquid spreads and penetrates into the solid. With the wetting model, the spreading and penetration abilities of a liquid/solid system can be quantified. This is more useful and eaier to for the comparison of adhesive wettability.

A number of studies on the dynamic wetting process for wood adhesion have been published (Scheikl and Dunky 1998, Follrich et al. 2006, Lu and Wu 2006, Blantocas et al. 2007; Huang et al. 2012). Blantocas et al. (2007) applied a low-energy hydrogen ion shower (LEHIS) to an inactive wood surface. The change rate constant (K) of the wetting model equation was used to evaluate the moisture absorbency of Narra wood. The surface became more inactive as the K-value decreased. Lu and Wu (2006) used the wetting slop and K-value to illustrate the dynamic wetting process of chemically-modified yellow-poplar veneer. Huang et al. (2012) used the K-value of three probe liquids on heat-treated jack pine surfaces prepared with three types of machining. However, there have been few reports on the dynamic wettability for wood surfaces with different plasma treatments. In our previous work, oxygen plasma was applied to activate poplar veneer surface to improve its wettability (Tang et al. 2012). The plasma treatment times were varied from 1 to 9 min. The power was set to 200 W and the pressure to 15 Pa. The wettability of veneers was assessed using contact angle, surface free energy, and K-value analysis. The results suggest that longer treatment times lead to better dynamic wettability. In the cased work, this trend was found to stabilize after a treatment time of 7 min. However, only the effect of plasma treatment time on veneer surface was investigated in that publication.

The objective of this study was to evaluate the dynamic wettability of poplar veneer surfaces modified by different plasma treatments. The experiment involved selecting treatment parameters (type of gas, power) that would lead to the better wettability of wood. All the experiments were carried out with a treatment time of 7 min in this study. Three common types of adhesive were used: urea-formaldehyde (UF), phenol-formaldehyde (PF), and diphenylmethylene diisocyanate (MDI). In this study, a wetting model developed by Shi and Gardner (2001) was used to describe the dynamic wettability in which a parameter (K) was used to quantify adhesive penetration and spreading during the adhesive wetting process.

EXPERIMENTAL

Materials

Poplar (*Populus* spp.) was selected for all following experiments, since it is a fast-growing species and commonly used because of its low cost. Sheets of commercial

poplar veneer (1200 mm \times 800 mm) were purchased from Anhui Tiankang Wood Co., Ltd. The thickness of the poplar veneer was 1.50 ± 0.074 mm. Each veneer specimen (without defects or impurities) was cut to a 100-mm length (along the grain) and a 20-mm width from the veneer sheets.

All contact angle measurements were conducted on the tight surface of the veneer specimens. The tight surface was lightly sanded with 150-grit paper before plasma measurement. After sanding, the veneer surface was blasted by an air stream to remove the attached dust. Before plasma treatment, all specimens were dried to a moisture content of approximately 2% in a vacuum-drying oven at 60 °C and then kept in a desiccator for at least two weeks to balance the moisture content.

Three adhesive resins commonly used in the wood composite industry were evaluated in the wetting experiments: urea-formaldehyde (UF), phenol-formaldehyde (PF), and diphenylmethylene diisocyanate (MDI). The UF resin was obtained from Santai Wood Co., Ltd. The PF resin and MDI resin were provided by Dynea (Shanghai) Co., Ltd. The typical physical and chemical properties of the three resins are listed in Table 1.

Specification	UF	PF	MDI	
Color	Opalescent to Maroon	Pale Red-brown to Black	Dark Brown	
Solid Content (%)	49.70	53.70	100.00	
pH Value	7.20	7.90	6.80	
Viscosity (cps)/20 °C	195.00	202.00	245.00	
Density (g·cm³)	1.18	1.15	1.21	
Surface Tension* (mJ/m²)	54.63	52.39	44.81	

Table 1. Typical Physical and Chemical Properties of the UF, PF, and MDI

Plasma Treatment

Surface treatments of poplar veneer were performed using a plasma unit (HD-1B, Changzhou Zhongke ChangTsi Plasma Processing Apparatus Plasma Technology Co., Ltd., China), as described in our previous work (Tang *et al.* 2012). The plasma was produced inside a cylindrical stainless-steel vacuum chamber (volume 870 cm³) by 13.56-MHz radio frequency (RF) generators. The specimens were perpendicularly placed between the electrodes. Before operating the discharge, the device was evacuated up to a residual pressure of 1 to 5 Pa using a roots vacuum pump (ZJ-70, produced by Xingye Vacuum Pump Co., Ltd., Shanghai, China). The system was then put through repressurizing cycles with gas injected through a micrometer valve at a flow rate of approximately 15 to 20 mL/min to remove any volatile contaminants. After five repressurizing cycles and after reaching the desired initial pressure of 15 Pa, the plasma was generated using different gases: argon (Ar), nitrogen (N₂), oxygen (O₂), air, and ammonia (NH₃).

The plasma power input varied from 100 to 500 W, and the samples were exposed to the plasma for 7 min. The temperature was in a range of 20 to 50 °C inside the chamber during plasma treatment. After each treatment, argon was fed into the chamber for 10 min to remove any traces of extractives inside the chamber. At the end of the

^{*} Surface tension of resins was measured using the suspending drop method with a Contact Angle Measuring Apparatus (JC2000D, produced at Zhongchen Co., Ltd., Shanghai, China).

reaction the chamber was pressurized, and the specimens were removed and stored in a desiccator to dry for later analysis. Contact angle measurements were completed within 5 min after plasma treatment.

Contact Angle Measurements

When a droplet is placed on a flat solid surface, the contact angle is defined as the angle between the tangent to the liquid surface and the liquid/solid surface at the point of liquid/solid contact (Gindl *et al.* 2004). Droplets (droplet volume $V=5~\mu L$) were placed on the tight side of the popular veneer using the sessile drop method and were determined using a Contact Angle Measuring Apparatus (JC2000D, produced at Zhongchen Co., Ltd., Shanghai, China). For all specimens, the measurements were conducted at a temperature of $20\pm1~^{\circ}C$ and a relative humidity (RH) of 50%. Images of the liquid drop shape on the veneer surface along the grain direction were captured by a camera and saved every $0.04~\rm s$.

The contact angles were measured directly from the images using an imaging software package (JC2000-USB, Zhongchen Co., Ltd., Shanghai, China). Three resins were tested: UF, PF, and MDI resins. The contact angles at both ends of the measured drop were averaged. The contact angles from the images were measured at 0, 5, 10, 20, 40, 60, 80, and 100 s after initial contact with each veneer surface. Twenty contact angle measurements were taken per liquid for each poplar veneer specimen. To minimize possible aging of the treated surfaces, contact angle measurements were made within 5 min after the plasma treatment.

Dynamic Wettability Model

When a liquid drop is placed on a porous surface, a contact angle can be evaluated at the liquid/solid surface. As time elapses, liquid penetration and spreading may occur.

In this study, a dynamic wetting model developed by Shi and Gardner (2001) was applied. This model is easier and more useful for describing wettability on porous wood surfaces. The final expression of the wetting model, in which the contact angle (θ) changes as a function of time (t), is,

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

where θ_i and θ_e represent the instantaneous contact angle and the equilibrium contact angle, respectively, and K is the contact angle change rate constant. The K-value represents how quickly the liquid penetrates and spreads into the porous structure of wood. The higher the K-value, the faster the contact angle reaches equilibrium, and the faster the liquid penetrates and spreads.

The contact angles were obtained at 0, 5, 10, 20, 40, 60, 80, and 100 s after initial contact with veneer surface. The wetting model (Eq. 1) was applied to these experimental data.

The statistical analysis software (OriginPro 8.0) was used to obtain the penetration and spreading constant (K-value) that provides the best fit between the equation and the data.

RESULTS AND DISCUSSION

The Effect of Plasma Treatment Power on the Dynamic Wettability of Poplar Veneer Surfaces

Oxygen plasma was applied to poplar veneer surfaces with a power from 100 to 500 W. The treatment time was 7 min, and the pressure was 15 Pa. UF resin was used as the liquid for contact angle determination. As shown in Table 2 and Fig. 1, the instantaneous and equilibrium UF resin contact angles of plasma-treated veneer surfaces were smaller than those of untreated samples. A smaller contact angle on a plasma-treated veneer surface indicates that it had more intimate contact on the plasma-treated poplar veneer surface than it did on the untreated samples. As the plasma power increased from 100 W to 500 W, the instantaneous contact angles showed little change, while the equilibrium contact angles changed slightly from 16.4 to 23.1 degrees.

It can also be seen in Table 2 and Fig. 1 that the contact angle decreased as a function of wetting time. In the initial 10 s of the wetting process, the contact angle decreased quickly. After approximately 20 s, it changed more gradually and finally attained relative equilibrium. It can also be seen that the wetting model provided an excellent fit for the experimental data. The R² values of the wetting model were close to 0.99 for all plasma-treated samples. The K-value increased dramatically after the oxygen plasma treatment; it was approximately 7 times greater than that of the untreated control sample. This shows that the spreading and penetration of UF resin on the plasma-treated veneer surface were significantly improved. The K-value increased from 0.480 (1/s) to 0.648 (1/s) with a plasma power level of 100 W to 200 W. However, it was slightly smaller when the plasma treatment power increased from 300 W to 500 W. Molecules in the plasma reactor were activated by collisions with electrons, and highly excited atomic, molecular, ionic, and radical species were generated (Bhat and Upadhyay 2002). The species of highly excited atomic, molecular, ionic, and radial species subsequently attacked the poplar wood surface. When oxygen was used as a plasma gas, oxygen radicals created by oxygen plasma formed oxygen-containing functional groups near the veneer surface (Chu et al. 2002). However, when the plasma power was too high, the newly formed oxygen-containing functional groups could decompose as a result of the species of highly excited atomic, molecular, ionic, and radial species continuously attacking because of high plasma energy (Andreozzi et al. 2005; Tang et al. 2012).

Table 2. Contact Angles and *K*-Values of UF resin on Poplar Veneer Surfaces Treated with Oxygen Plasma at Different Power Levels

Dloomo	Contact Angles			<i>K</i> -values			
Plasma Power Levels	$ heta_{i}$	$ heta_e$	Percent Decrease (%)	Value (1/s)	SE ^a (1/s)	CV ^b (%)	R ^{2c}
Control	128.7(7.2*)	60.3(3.3)	53.1	0.086(0.014)	0.010	11.6	0.977
100 W	117.5(6.1)	18.5(2.5)	84.3	0.480(0.078)	0.027	5.6	0.999
200 W	114.6(5.7)	16.4(2.7)	85.7	0.648(0.116)	0.031	4.8	0.998
300 W	116.2(8.5)	23.1(3.3)	80.1	0.536(0.100)	0.049	9.1	0.999
400 W	117.2(3.4)	19.8(2.5)	83.1	0.546(0.104)	0.034	6.2	0.998
500 W	117.0(5.6)	18.5(3.6)	84.2	0.553(0.100)	0.032	5.8	0.999

^{*} Values in the brackets are the standard deviation; ^a SE: Asymptotic standard errors; ^b CV: Coefficient of variation; ^c R²: coefficients of correlation.

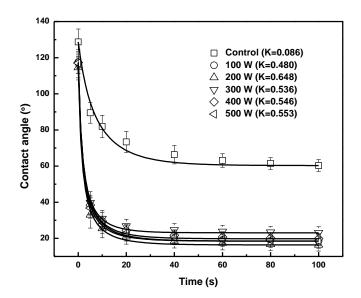


Fig. 1. Changes in contact angle as a function of time on poplar veneer surface treated with oxygen plasma at different power levels using UF resin

Effect of Different Plasma Gases on the Dynamic Wettability of Poplar Veneer Surfaces

Different gas plasmas were applied to poplar veneer surfaces. The power was set to 200 W, the treatment time to 5 min, and the pressure to 15 Pa. UF resin was used as the liquid for contact angle determination. As shown in Table 3 and Fig. 2, the effects of different plasma treatment gases (O₂, N₂, Ar, air, and NH₃) on the dynamic wettability of poplar veneer surfaces were characterized by contact angle and *K*-value. The instantaneous and equilibrium UF resin contact angles of different gas plasma treatments on poplar veneer surfaces were 9% to 15% and 65% to 79% smaller than those of untreated samples, respectively. Also, the contact angles changed rapidly after different gas plasma treatments.

Table 3 and Fig. 2 show that the contact angle decreased as a function of wetting time. It can also be seen that the wetting model provided an excellent fit for the experimental data. The R² values of the wetting model were over 0.97 for all samples. The K-value increased dramatically after different gas plasma treatments. The extent of increase was approximately 6 times relative to the untreated control sample. This means that the spreading and penetration of UF resin on the plasma-treated veneer surface were both significantly improved. The K-value increased from 0.428 1/s to 0.622 1/s with different gas plasma treatments, compared with 0.099 1/s for untreated samples. The results suggest that the surface wettability of veneers is 3 to 5 times improved by treatment with different gas plasmas. The K-values showed significant differences between gas treatments. The plasmas were gaseous mixtures of electrons, radicals, ions, and excited molecular states. Plasma treatment introduced some polar groups to material surfaces (chemical process) and enhanced surface roughness (physical process). (Bhat and Upadhyay 2002; Chen et al. 2008). The high-energy particles and photons of the plasmas interact with the polymer surface by both chemical and physical processes. Polar groups could contribute more than the plasma etching effects for the improvement of surface wettability of the plasma-treated veneer surface (Chen *et al.* 2008). When O₂, N₂, or air was used as the gas plasma, O₂ appeared to be the most successful at forming oxygenated functional groups on the veneer surface. It has been reported that cold oxygen plasma can react with wood to produce a variety of oxygen functional groups such as C-O, C=O, O-C=O, C-O-O, and CO₃ at the surface (Belgacem *et al.* 1995; Yuan *et al.* 2004; Klarhofer *et al.* 2010). The *K*-value obtained with NH₃ plasma was 6% to 31% higher than other gas treatments. This indicates that, in addition to the former two processes, absorption occurred when the sample was exposed to NH₃ plasma. NH₃, as a volatile gas with an offensive smell, may volatilize from veneer as time elapses. The fact that the lowest *K*-value was obtained with Ar plasma can be explained by its inertness, which makes negligible any secondary reaction of surface activation (chemical etching) with respect to the physical etching (Klarhoefe *et al.* 2010).

Table 3. Contact Angles and *K*-Values of UF resin on Poplar Veneer Surfaces Treated at 200W with Different Gas Plasmas

Plasma _ Gas Type	Contact Angles			<i>K</i> -values				
	$ heta_i$	$ heta_e$	Percent Decrease (%)	Value (1/s)	SE (1/s)	CV (%)	R ²	
Control	127.1(4.9)	56.3(5.6)	55.7	0.099(0.020)	0.012	12.1	0.979	
O ₂	110.2(6.0)	14.6(2.3)	86.8	0.584(0.090)	0.045	7.7	0.986	
N ₂	108.1(3.6)	15.1(1.6)	86.0	0.572(0.104)	0.036	6.3	0.996	
Air	115.7(3.3)	11.9(1.6)	89.7	0.543(0.088)	0.026	4.8	0.998	
Ar	109.6(4.6)	19.7(2.0)	82.0	0.428(0.051)	0.025	5.8	0.992	
NH ₃	108.6(6.5)	15.7(1.5)	85.5	0.622(0.092)	0.052	8.4	0.982	

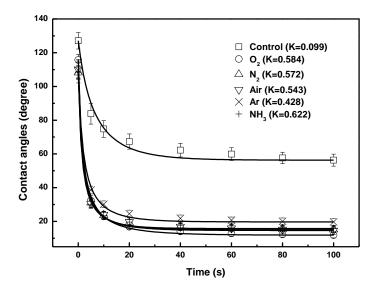


Fig. 2. Changes in contact angle as a function of time on poplar veneer surface treated with different plasma gases at 200 W using UF resin

Effect of Resin Type on the Dynamic Wettability of Plasma-treated Poplar Veneer Surfaces

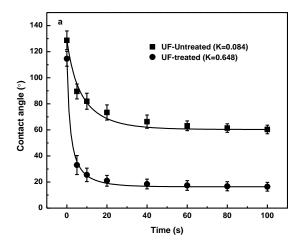
Oxygen plasma was applied to poplar veneer surfaces. The power was set to 200 W, the treatment time to 5 min, and the pressure to 15 Pa. UF, PF, and MDI resins were used as the liquids for contact angle determination. It can be seen in Table 5 that resin type had a significant effect on the dynamic wetting process. It can be seen from Table 4 and Fig. 3 that the instantaneous contact angles of untreated veneer surfaces with three resins were almost the same. The instantaneous contact angles of plasma-treated veneer surfaces with UF and PF resins were lower than those of untreated samples, whereas the instantaneous contact angle of MDI resin exhibited little effect on plasma-treated and untreated veneer surfaces. The equilibrium contact angles of plasma-treated and untreated veneer surfaces with MDI resin were much lower than those of UF and PF resins. Lower contact angles for the MDI resin were expected, given the fact that MDI is 100% organic, while the UF or PF resin is an aqueous alkaline mixture. MDI had a lower surface tension (44.81 mJ/m²) than that of the UF (54.23 mJ/m²) and PF (52.39 mJ/m²) resins, as shown in Table 1. According to Young's equation for the classical case of the three-phase line of solid, liquid, and vapor, the relationship between contact angle and surface tension is,

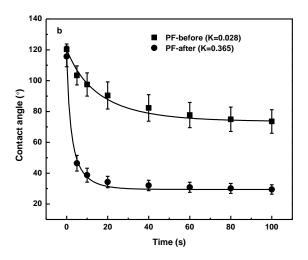
$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{2}$$

in which γ_{SV} , γ_{LV} , and γ_{SL} are the interfacial free energies of liquid-vapor, solid-vapor, and solid-liquid interfaces, respectively. From Eq. (2), a higher solid surface tension or a lower liquid surface tension will form a lower contact angle in the solid/liquid system (Liu *et al.* 2004). In this experiment, MDI resin had a lower surface tension and had a lower equilibrium contact angle than UF and PF resins. The lower equilibrium contact angle of the MDI resin on poplar veneer surface indicates that the MDI resin has a greater wettability than the UF and PF resins.

The equilibrium contact angles of plasma-treated veneer surfaces with three resins were 73% (UF), 60% (PF), and 91% (MDI) lower than those of untreated samples. This indicates that higher solid surface energy were obtained after plasma treatment. It has been shown by many researchers that solid surface energy can be improved using plasma treatment (Manolache *et al.* 2008, Blanchard *et al.* 2009; Wolkenhauer *et al.* 2009; Huang *et al.* 2011).

MDI resin exhibited greater *K*-values than UF and PF resins for both plasmatreated and untreated veneer surfaces, as shown in Table 4 and Fig. 3. The *K*-values of MDI on untreated veneer surface (0.762 1/s) was 786% and 2621% greater than those of UF (0.086 1/s) and PF (0.028 1/s) resins, respectively, while the *K*-value of MDI on plasma-treated veneer surface (1.055 1/s) was 63% and 189% greater than that of UF (0.648 1/s) and PF (0.365 1/s) resins, respectively. The greater *K*-values of MDI resin indicate that its penetration and spreading on the veneer surfaces was much faster than that of the UF and PF resins. It can also be seen in Table 4 that compared with the UF and PF resins, MDI resin had a larger percentage of decrease in contact angle from initial to equilibrium both on plasma-treated and untreated veneer surfaces. This trend indicates that MDI exhibited better spreading and penetration behavior than that of UF and PF resins.





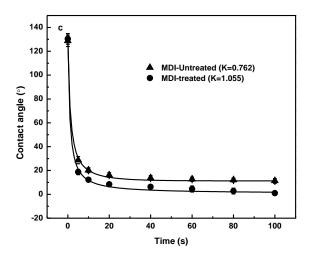


Fig. 3. Changes in contact angle as a function of time on oxygen plasma-treated at 200 W and untreated poplar veneer surfaces with (a) UF resin, (b) PF resin, and (c) MDI resin

The K-values of PF, UF, and MDI resins on plasma-treated veneer surfaces were 1204%, 653%, and 38% greater than that of untreated samples, respectively. This indicates that resins formed more intimate contact with the plasma-treated veneer surface. The spreading and penetration of resins on plasma-treated veneer surfaces was faster than that of untreated samples. The improved spreading and penetration of resins on wood surface is beneficial for the adhesive wettability of wood and thus, the bonding strength of wood composites can be improved.

Previous publications have shown that wood composites treated with plasma generally exhibit better physical and mechanical properties than those of untreated (Moghadamzadeh *et al.* 2011; Abbasipour 2012; Acda *et al.* 2012). This is attributed to surface roughness and chemical modification of the substrates. It is indicated that roughness parameters and chemical indices of surfaces are changed with plasma treatment. The properties of wood composites bonded with MDI are better than those bonded with UF or PF resin (Shi and Gardner 2001; Liu *et al.* 2004). The bonding strength of wood composites is highly depended on adhesive wettability of wood. Better adhesive wettability results in higher bonding strength of wood composites. The results of this study partially explain this phenomenon.

Table 4. Contact Angles and *K*-Values of Oxygen Plasma-treated at 200 W and Untreated Poplar Veneer Surfaces with Different Resin Systems

	Contact Angles			<i>K</i> -values			
Resin Type	$ heta_i$	$ heta_e$	Percent Decrease (%)	Value (1/s)	SE (1/s)	CV (%)	R ²
UF-untreated	128.7(7.2)	60.3(3.3)	53.1	0.086(0.014)	0.010	11.6	0.977
UF-treated	114.6(5.7)	16.4(2.7)	85.7	0.648(0.116)	0.031	4.8	0.998
PF-untreated	120.3(3.5)	73.5(7.7)	38.9	0.028(0.004)	0.002	7.1	0.991
PF-treated	115.7(6.7)	29.5(3.1)	74.5	0.365(0.076)	0.035	9.6	0.989
MDI-untreated	128.8(4.8)	11.3(2.0)	91.2	0.762(0.111)	0.056	7.3	0.995
MDI-treated	130.4(4.5)	1.0(1.8)	99.2	1.055(0.168)	0.090	8.5	0.993

CONCLUSIONS

- 1. The influence of plasma gas type (O₂, N₂, Ar, air, and NH₃) and treatment power (100 W to 500 W) on the dynamic wettability of poplar veneer was investigated. The dynamic wettability of plasma-modified poplar veneer was evaluated using a wetting model. The constant (K-value) in the model could be used to quantify the spreading and penetration rate of the adhesive/poplar veneer system. UF, PF, and MDI resins were used to evaluate the dynamic wettability.
- 2. Both instantaneous and equilibrium contact angles of plasma-treated veneer surface at the plasma power level from 100 W to 500 W were 11% and 73% lower than those of untreated samples, respectively. The *K*-value increased as the plasma power level increased to 200 W, and then decreased slightly when the plasma power continued increasing. That can be explained that when the plasma power was too high, the newly formed oxygen-containing functional groups could decompose because of high plasma energy.

- 3. After different gas plasma treatments, the instantaneous and equilibrium contact angles were 15% and 79% lower than those of untreated samples, and the *K*-value was approximately 6 times greater than that of the untreated control sample. However, the *K*-value of the Ar-plasma-treated veneer surface was lower than that of other gasplasma-treated samples. And the *K*-value of the NH₃-plasma-treated veneer surface was the highest among the five different gas plasma treatments. Part of NH₃ absorption occurred when the sample was exposed to NH₃ plasma. NH₃, as a volatile gas with an offensive smell, may volatilize from veneer as time elapses. Therefore, O₂ plasma is more appropriate for poplar veneer surface modification.
- 4. The instantaneous contact angles of untreated veneer surfaces with PF, UF, and MDI resins were almost the same. The equilibrium contact angles of plasma-treated veneer surfaces with three resins were much lower than those of the untreated samples. The *K*-values of the three resins on plasma-treated veneer surfaces were 1204%, 653%, and 38% greater than those of the untreated samples, respectively.

ACKNOWLEDGMENTS

The authors are indebted to the following organizations for their financial support: the National Department Public Benefit Research Foundation of China (Grant No. 2013-04507), the National Natural Science Foundation of China (Grant No. 31270606), the National Science and Technology Special Action Project of Fumin Qiangxian (BN2012132), the Doctorate Fellowship Foundation of Nanjing Forestry University, Jiangsu Province Ordinary University Students' Scientific Research Innovation Project (Grant No. CXLX12_0533), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). This paper was also sponsored by the Qing Lan Project. Sincere thanks go to the Jiangsu Engineering Research Center of Fast-growing Trees and Agri-fiber Materials for providing equipment for this study.

REFERENCES CITED

- Abbasipour, M. (2012). "The effect of low-pressure air plasma treatment on the wettability and surface energy of polyvinyl chloride films," *Radiat. Eff. Defect. S.* 167(10), 752-757. DOI: 10.1080/10420150.2011.595412
- 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, 70-75. DOI: 10.1016/j.ijadhadh.2011.10.003
- Andreozzi, L., Castelvetro, V., Ciardelli, G., Corsi, L., Faetti, M., Fatarella E., and Zulli, F. (2005). "Free radical generation upon plasma treatment of cotton fibers and their initiation efficiency in surface-graft polymerization," *J. Colloid In. Sci.* 289(2), 455-465. DOI: 10.1016/j.jcis.2005.03.058
- Belgacem, M. N., Czeremuszkin, G., Sapieha, S., and Gandini, A. (1995). "Surface characterizatiom of cellulose fibers by XPS and inverse gas chromatography," *Cellulose* 2, 145-157.
- Berg, J. C. (1993). "Role of acid-base interactions in wetting and related phenomena," in: *Wettability*, J. C. Berg (ed.), Marcel Dekker, New York.

- Bhat, N., and Upadhyay, D. (2002). "Plasma induced surface modification and adhesion enhancement of polypropylene surface," *J. Appl. Polym. Sci.* 86(4), 925-936. DOI: 10.1002/app.11024
- Blanchard, V., Blanchet, P., and Riedl, B. (2009). "Surface energy modification by radiofrequency inductive and capacitive plasmas at low pressures on sugar maple: An exploratory study," *Wood Fiber Sci.* 41(3), 245-254.
- Blantocas, G. Q., Mateum, P. E. R., Orille, R. W. M., Ramos, R. J. U., Monasterial, J. L. C., Ramos, H. J., and Bo-ot, L. M. T. (2007). "Inhibited flammability and surface inactivation of wood irradiated by low energy hydrogen ion showers (LEHIS)," *Nucl. Instrum. Meth. B.* 259(2), 875-883. DOI: 10.1016/j.nimb.2007.03.009
- Büyüksarı, Ü., Akbulut, T., Guler, C., and As, N. (2011). "Wettability and surface roughness of natural and plantation-grown narrow-leaved ash (*Fraxinus angustifolia Vahl.*) wood," *BioResources* 6(4), 4721-4730. DOI: 10.15376/biores.6.4.4721-4730
- Chen, P., Zhang, C. S., Zhang, X. Y., Wang., B. C., Li, W., and Lei, Q.Q. (2008). "Effects of oxygen plasma treatment power on surface properties of poly (*p*-phenylene benzobisoxazole) fibers," *Appl. Surf. Sci.* 255(5), 3153-3158.
- Chu, P. K., Chen, J., Wang, L., and Huang, N. (2002). "Plasma-surface modification of biomaterials," *Mat. Sci. Eng. R.* 36(5–6), 143-206. DOI: 10.1016/S0927-796X(02)00004-9
- Esteves, B. M., and Pereira, H. M. (2009). "Wood modification by heat treatment: A review," *Bioresources* 4(1), 370-404. DOI: 10.15376/biores.4.1.370-404
- Follrich, J., Mueller, U., and Gindl, W. (2006). "Effects of thermal modification on the adhesion between spruce wood (*Picea abies* Karst.) and a thermoplastic polymer," *Holz Roh. Werkst.* 64(5), 373-376. DOI: 10.1007/s00107-006-0107-y
- Gindl, M., Sinn, G., Reiterer, A., and Tschegg, S. (2001). "Wood surface energy and time dependence of wettability: A comparison of different wood surfaces using an acid-base approach," *Holzforschung* 55(4), 433-440. DOI: 10.1515/HF.2001.071
- Gindl, M., Reiterer, A., Sinn, G., and Stanzl-Tschegg, S. E. (2004). "Effects of surface aging on wettability, surface chemistry, and adhesion of wood," *Holz Roh. Werkst*. 62(4), 273-280. DOI: 10.1007/s00107-004-0471-4
- Huang, H., Wang, B. J., Dong, L., and Zhao, M. (2011). "Wettability of hybrid poplar veneers with cold plasma treatments in relation to drying conditions," *Dry. Technol.* 29(3), 323-330. DOI: 10.1080/07373937.2010.496133
- Huang, X., Kocaefe, D., Boluk, Y., Kocaefe, Y., and Pichette, A. (2012). "Effect of surface preparation on the wettability of heat-treated jack pine wood surface by different liquids," *Eur. J. Wood Prod.* 70(5), 711-717. DOI: 10.1007/s00107-012-0605-z
- Jarusombuti, S., N., Ayrilmis, P., Bauchongkol, and Fueangvivat, V. (2010). "Surface characteristics and overlaying properties of MDF panels made from thermally treated rubber wood fibers," *BioResources* 5(2), 968-978. DOI: 10.15376/biores.5.2.968-978
- Klarhofer, L., Vioel, W., and Maus-Friedrichs, W. (2010). "Electron spectroscopy on plasma treated lignin and cellulose," *Holzforschung* 64(3), 331-336. DOI: 10.1515/HF.2010.048
- Liptáková, E., and Kúdela, J. (1994). "Analysis of the wood-wetting process," *Holzforschung* 48(2), 139-144. DOI: 10.1515/hfsg.1994.48.2.139
- Liu, F. P., Gardner, D. J., and Wolcott, M. P. (1995). "A model for the description of polymer surface dynamic behavior 1: Contact angle *vs.* polymer surface properties," *Langmuir* 11(7), 2674-2681. DOI: 10.1021/la00007a056

- 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.
- Lu, J. Z., and Wu, Q. (2006). "Surface characterization of chemically modified wood: Dynamic wettability," *Wood Fiber Sci.* 38(3), 497-511.
- Manolache, S., Jiang, H., Rowell, R. M., and Denes, F. S. (2008). "Hydrophobic wood surfaces generated by non-equilibrium, atmospheric pressure (NEAPP) plasmaenhanced coating," *Mol. Cryst. Liq. Cryst.* 483, 348-351. DOI: 10.1080/15421400801917486
- Meijer, M., Haemers, S., Cobben, W., and Militz, H. (2000). "Surface energy determinations of wood: Comparison of methods and wood species," *Langmuir* 16(24), 9352-9359. DOI: 10.1021/la001080n
- Moghadamzadeh, H., Rahimi, H., Asadollahzadeh, M., and Hemmati, A. R. (2011). "Surface treatment of wood polymer composites for adhesive bonding," *Int. J. Adhes. Adhes.* 31(8), 816-821. DOI: 10.1016/j.ijadhadh.2011.08.001
- Nylund, J., Sundberg, K., Shen, Q., and Rosenholm, J. B. (1998). "Determination of surface energy and wettability of wood resins," *Colloid. Surface. A* 133(3), 261-268. DOI: 10.1016/S0927-7757(97)00209-4
- Scheikl, M., and Dunky, M. (1998). "Measurement of dynamic and staue contact angles on wood for the determination of its surface tension and the penetration of liquids into the wood surface," *Holzforschung* 52(1), 89-94. DOI: 10.1515/hfsg.1998.52.1.89
- Shi, S. Q., and Gardner, D. J. (2001). "Dynamic adhesive wettability of wood," *Wood Fiber Sci.* 33(1), 58-68.
- 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. DOI: 10.15376/biores.7.3.3327-3339
- Wolkenhauer, A., Avramidis, G., Hauswald, E., Militz, H., and Vioel, W. (2009). "Sanding *vs.* plasma treatment of aged wood: A comparison with respect to surface energy," *Int. J. Adhes. Adhes.* 29(1), 18-22. DOI: 10.1016/j.ijadhadh.2007.11.001
- Yuan, X., Jayaraman, K., and Bhattacharyya, D. (2004). "Effect of plasma treatment in enhancing the performance of woodfibre-polypropylene composites," *Composites Part A*. 35(12), 1363-1374.

Article submitted: July 11, 2014; Peer review completed: September 28, 2014; Revised version received and accepted: November 12, 2014; Published: November 20, 2014.