WOOD RESEARCH
60 (5): 2015
773-782

DIELECTRIC BARRIER DISCHARGE PLASMA AT ATMOSPHERIC PRESSURE TO ENHANCE PINE WOOD SURFACES HYDROPHILIC CHARACTER AND ADHESION PROPERTIES

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(Received February 2015)

ABSTRACT

In this paper, the effects of dielectric barrier discharge plasma treatment at atmospheric pressure on wettability, aging behavior and adhesion properties on a Yunnan pine wood surface were investigated. Contact angle, X-ray Photoelectron Spectroscopy and Fourier Transform Infrared Spectroscopy measurements were used to study the changes of surface energy and chemical elements in the wood surface due to dielectric barrier discharge plasma treatments. An increase in the surface energy, in the proportion of -OH, -CO and -COOH functional groups and in the shear bond strength of wood bonded with Urea-formaldehyde, Melamine-formaldehyde and Melamine-Urea- formaldehyde adhesives after plasma treatment were observed. The results indicated that the wood surface hydrophilic character, wettability and adhesion properties were improved. However, the results of aging behavior indicated that wood surface modification of plasma treatment had a limit of time. With the time increased, the modification effects were eventually disappeared.

KEYWORDS: Contact angle, bond strength, dielectric barrier discharge plasma, surface energy.

INTRODUCTION

Modification of material surfaces with different discharge plasma such as Radio Frequency (RF), Microwave and Corona discharge are well known and have been used for a long time to increase surface free energy, wetting behavior, adhesion properties or maintaining and protecting material surface properties (Lukowsky and Hora 2002, Deng et al. 2012, Sokolowska et al. 2009, Qu et al. 2013). However, the discharge RF and microwave processes need greater power to be maintained, vacuum and batch systems must be used to reduce pressure, which makes continuous industrial application difficult and its costs high (Favia et al. 1996, Chintala et al. 2006). Corona discharges easy to implement, but the discharge region is small. It is difficult to obtain a large volume of plasma and it has a low power density (Rosocha et al. 2004). However, the process of dielectric barrier discharge plasma (DBD) takes advantage of the high reactivity of the derived reactive species at regular atmospheric pressure which gets rid of the limit of the vacuum system and it has large areas of the discharge area in a continuous process (Borcia et al. 2003). Meanwhile, the discharge process is easily controlled. It has high energy efficiency and wide operating pressures and voltages. Nowadays, some DBD applications for wood surface produce a shallow buried layer to improve water and fire repellent characteristics (Bente et al. 2004, Avramidis et al. 2009). However, DBD treatment is also useful for surface modification of wood to increase hydrophilic character to enhance their adhesion properties. Meanwhile, Urea-formaldehyde (UF) resin is inexpensive and is easy to manufacture. Melamine-formaldehyde (MF) and Melamine-Urea- formaldehyde (MUF) resins have high bonding strength, and good resistance to boiling water. Thus, they are widely applied in the wood industry. This study mainly investigated the potential of DBD at atmospheric pressure and ambient air to improve the adhesion properties of Yunnan pine with the UF, MF, MUF resins to determine the effect of DBD on the hydrophilic character and aging behavior. The measurement of the contact angle has been found to be the best method to estimating wood surface modification.

MATERIAL AND METHODS

Materials

Yunnan pine (*P. yunnanensis*) veneer with a length of 1500 mm, width of 100 mm and thickness of 0.8 mm (RH is 9-12 %) was supplied by Kunming building market. The UF, MF and MUF resins were purchased from the plywood plant of Xin Fei Lin. Distilled water and diiodomethane were purchased from Aladdin reagent online shopping.

Contact angle measurement

The water contact angles were measured by Data physics (JC2000A) equipment after plasma treatment. Each measurement size of droplet was 2μL and the values of the six different places of each sample were averaged. Surface energy was determined by using the Owens-Wendt approach on the basis of Young's equation (Martins and Knaebe 1992). The distilled water (γ^P =51 mN•m^{-1}, γ^P =21.8 mN•m^{-1}) and diiodomethane (γ^P = 0 mN•m^{-1}, γ^D =50.8 mN•m^{-1}) were used.

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \quad (1)$$

where: γ_S - the surface energy of the solid in mN•m^{-1},
γ_{SL} - the interfacial energy between solid and liquid,
γ_L - the surface tension of the liquid and θ is the contact angle.

This approach divides the total surface energy (γ^{tot}) into a polar component (γ^P) and a disperse component (γ^D).

$$\gamma^{tot} = \gamma^D + \gamma^P \quad (2)$$

Plasma treatments

The dielectric barrier discharge plasma (ZD-1000C) modified equipment was mainly composed of transmission platform, electronic control systems, the host of PG-6000F power and plasma transformer. Wood veneers were placed in the transmission platform and then were taken into the reactor chamber to treatment with ambient air at atmospheric pressure. The speed of conveyor was 10 m.min.$^{-1}$ The range of DBD power is 1000-6000 W and in order to solve the problem of efficiency and safety, power range of 2000-5000 W was selected. The combinations of the DBD power levels and treatment times used are shown in Tab. 1.

Tab. 1: The power levers and treatment times used in the air plasma treatment for veneer.

Power level (W)	Treatment time (s)							
2000	0	20	60	100	140	180	220	260
3000	0	20	60	100	140	180	220	260
4000	0	20	60	100	140	180	220	260
5000	0	20	60	100	140	180	220	260

Adhesion preparation and shear bond strength test

The properties parameters of MUF, UF and MF were shown in Tab. 2.

Tab. 2: The properties parameters of MF, MUF and UF.

Resin	Molar ratio	Solids content (%)	Viscosity (s)
MF	F / M = 2.7	52.78 %	17 s (25°C)
MUF	F / (M + U) = 1.7	56.53 %	21 s (25°C)
UF	F / U = 1.04	50.00 %	18 s (25°C)

The veneers (200 × 100 × 0.8 mm) were composed of three layers of plywood with different adhesion (The glue content is 200 g.mm^{-2}) under the pressure of 1 MPa, pressing time of 5 min. The pressing temperature: MF and MUF were 1°C, UF was 120°C. The shear bonding strength tests were conducted according to the ASTM D905_08 (2013), samples were selected in each test to obtain the average value. The shear bond strength tests were conducted with the mechanical testing machine (AG-10 TA).

X-ray Photoelectron Spectroscopy (XPS) and Fourier transform infrared Spectroscopy (FTIR) analysis

XPS analysis was performed using a PHI 5000 Versa Probe spectrometer (Physical Electronics) equipment. The degree of vacuum is 2 × 10^{-9} Torr; the operating voltage is 15 kV, 20 mA. To analyze the C1 s spectra of the wood surface, the carbon atoms were usually divided into C1, C2, C3 and C4 (Dorris and Gray 1978). C1 is that carbon atom bonded to other carbon

atoms or a hydrogen atom (C-C, C-H), the binding energy approximately is 285 eV. C2 is that carbon atom bonded to non-carbonyl oxygen (C-O); the electron binding energy approximately is 286.5 eV. C3 is that carbon atom bonded to two non-carbonyl oxygen or a carbonyl oxygen (O-C-O, C=O), the electron binding capacity approximately is 288 eV. C4 is that carbon atom bonded to a carbonyl oxygen and a non-carbonyl oxygen (O-C=O), the binding energy approximately is 289 eV.

The Varian1000 Infrared spectrometer was used to test the samples. The ZnSe crystal was adopted to be the ATR and the test range of the wave number was 700-4000 cm^{-1}. In infrared absorption spectrum, the peak of 3350 cm^{-1} can be attributed to the O-H peaks, 1635-1740 cm^{-1} were the absorption peak of the C=O peaks, the absorption peaks of 1050-1230 cm^{-1} were the characteristic peaks of the C-O.

RESULTS AND DISCUSSION

Contact angle measurements

The water contact angles of different treatment times and at different powers are presented in Fig. 1. The results show that the contact angle decreased gradually with the increase of treatment time and reached the lowest value of all at 140 s. Especially in the 4000 W power, it decreased with the lowest value being 43°. However, it appears that the contact angle has slightly increased with the increase of treatment time from 140 to 260 s. The energy levels (approximate 10 eV) of active particles in the plasma were close to the typical bond energies level of wood surfaces, such as C-H (4.3 eV), C-C (3.4 eV), C-O (3.4 eV), O-H (4.4 eV). This suggests that the chemical bonds in the wood surface were easy to be broken or to form small molecules which were separated from the wood. Besides, by extending the treatment time, the new chemical bonds were formed by crosslinking. This might explain the increase of contact angles from 140 to 240 s.

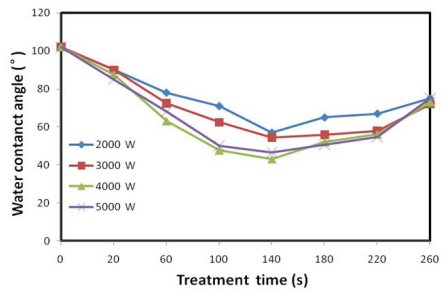


Fig. 1: Changes of water contact angle on the veneer surface at different treating time and different power settings.

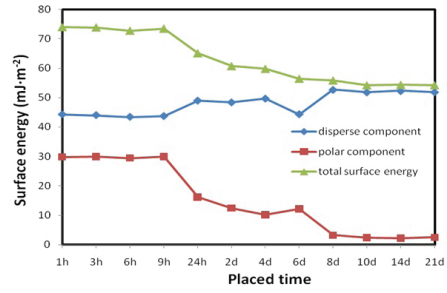


Fig. 2: The free energy change rule after wood surface treated by DBDP (4000 W, 140 s).

The total surface energy of veneers for the 2000-5000 W power level with the treatment time in the 20 to 260 s range are shown in Tab. 3 suggesting that the total energy surface increased gradually during the 20-140 s treatment time compared with untreated veneer surfaces. Especially from the value 51.220 $mJ \cdot m^{-2}$ to the highest value 74.736 $mJ \cdot m^{-2}$ at 4000 W, 140 s. The results also revealed that the surface energy decreased with the treatment time extending from 140 to 260 s. This was consistent with the result of the contact angle test. It indicated that

the Air DBD treatment at atmospheric pressure positively affected the wettability of veneer. When the treatment power was 4000 W and the treatment time was 140 s, the effect of water contact angle and the total surface energy were optimized.

Tab. 3: Changes of wood surface energy as a function of treating time under different power settings.

Power/w	Surface energy ($mJ•m^{-2}$)							
	0 s	20 s	60 s	100 s	140 s	180 s	220 s	260 s
2000	51.220	56.739	60.963	65.214	68.489	69.791	61.508	60.109
3000	51.220	58.339	62.641	64.699	70.537	67.518	61.867	62.165
4000	51.220	58.909	65.806	70.618	74.736	70.204	63.543	62.179
5000	51.220	56.713	64.231	71.618	72.523	71.704	61.136	63.105

To investigate the aging behavior after the plasma treatment, the power of 4000 W and treatment time of 140 s were selected. The result shown in Fig. 2 indicated that the total surface energy decreased gradually with the extension of time after the DBD treatment. Changes were obvious after 9 hours. When the time was 8 days, the total surface energy decreased to 52.68 $mJ•m^{-2}$ which was close to the untreated value (51.22 $mJ•m^{-2}$). Besides, it had a significant change in the polar component of surface energy compared to the change of dispersion component, which also indicates that the change of total surface energy were caused by the polar component (Mahlberg et al. 1998). The results suggested that wood surface modification of DBD treatment had a limit of time. Indeed with the time increase, the modification effects were eventually disappeared.

This aging behavior was caused by the result of some unstable polymer chains on the wood surface which were oxidized by extending the treatment time. Thus, the aging mechanism is complicated as it depends on many factors such as the surface structure of the wood, the parameters of the plasma process and the environment.

XPS analysis

The content of each element on the wood surface after plasma treatment at a power of 4000 W for a treatment time of 140 s is shown in Tab. 4. Nitrogen was thus introduced in the treated wood surface compared with the elemental composition of the untreated veneer surface. This implies that it exists as amino groups (-NH_2) in the wood surface. Moreover, it can also be seen in Tab. 4 that the oxygen concentration at the wood surface increased from 18.2 to 21.9 % and that the O / C ratio significantly increased. It indicated that the functional groups which contain oxygen increased in the wood surface and were present as hydroxyls groups (-OH). The introduction of-NH_2 and the increase in –OH at the wood surface can promote the wetting properties of the wood surface.

Tab. 4: Binding energy, C1 s peak area ratio of wood untreated/treated by DBDP.

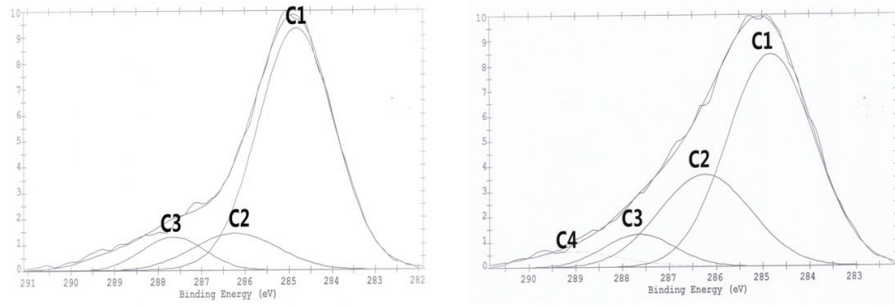
Wood sample	Concentration (atom %)			
	C1 s	O1 s	N1 s	O/C
Untreated	81.80	18.20	0	0.22
Treated	74.63	21.90	3.47	0.29

The area ratio and peak of C1 s spectra of untreated and treated wood surfaces are shown in Tab. 5 and Fig, 3. The untreated wood surface is composed mainly of three different peaks which

were respectively attributed to the C1, C2 and C3 according to the binding energy, these being respectively 75.30, 14.46 and 10.24 % for C1, C2 and C3. After DBD treatment the C1 peak was significantly reduced, C2 and C3 increased, while the C4 peak appeared and its area accounts for 5.15 %. The increasing of the C2 peak area indicates that the number of hydroxyl groups (-OH) increased. This is beneficial for the wetting properties of the wood surface. The producing of carbonyl compounds during the plasma treatment leads to an increase in the peak area of C3. C4 indicates that the wood surface was deeply oxidized. Thus, the wood surface resulted in a large number of oxygen-containing functional groups during the treatment with DBD.

Tab. 5: Binding energy, C1 s peak area ratio of wood untreated/treated by DBDP (4000 W, 140 s).

	Untreated		Treated	
	Binding energy (eV)	**Peak area (%)**	**Binding energy (eV)**	**Peak area (%)**
C_1	284. 83	75.3	284.83	52.99
C_2	286. 23	14.46	286.24	24.31
C_3	287. 65	10.24	287.64	17.55
C_4	—	—	289.01	5.15



a) b)

Fig. 3: C1 s XPS spectra of untreated and air-DBD-treated wood at 4000 W and 140 s.
Fig. 3 a) shows the spectrum of untreated wood. Fig. 3 b) shows the air-DBD-treated wood.

FTIR analysis

It can be seen in Fig. 4 that the absorption rate of the O-H peaks at 3350 cm^{-1} was about 0.015, and for the C-O peaks at 1050-1230 cm^{-1} was about 0.065 for the untreated veneer surface. However, after plasma treatment, the absorption rate of the O-H peaks at 3350 cm^{-1} was over 0.02 and the absorption rate of C-O at the characteristic peaks of 1050-1230 cm^{-1} were also greater than 0.1. The absorption peaks of O-H and C-O increased. The results further confirmed that the wood surface had acquired a large number of -OH, -CO and -COOH functional groups and these groups can significantly improve the wettability of wood surface.

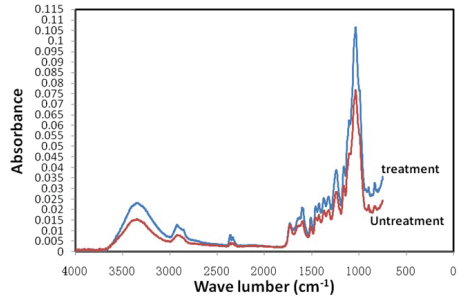


Fig. 4: The FTIR spectra of wood surface-treated/untreated by DBDP at 4000 W, 140 s.

Adhesion measurement

Tab. 6 presents the results of the shear strength tests. The samples which were stored for 0.5 hour after the plasma treatment showed a distinct increase in shear bond strength. The shear bond strength of wood-UF increased from 0.90 to 1.05 MPa. Furthermore, the wood-MF increased from 1.49 to 1.97 MPa and the wood–MUF increased from 1.76 to 2.18 MPa. It exhibited astonishingly high shear bond strength. But the shear bond strength of the samples which were stored 8 days after the plasma treatment did not show the difference in the untreated wood. A slight increase in the wood failure values might be related to the drop in the bonding strength.

Tab. 6: Shear bond strengths of untreated and plasma treated UF, MF and MUF adhesives.

Specimen	Shear bond strength (MPa)		Wood failure (%)
	Mean	Rate of increase (%)	Mean
Untreated wood Surface +UF	0.90	0	52
Wood surface for 0.5 h +UF	1.05	16.6	55
Wood surface for 8d +UF	0.86	-4.4	55
Untreated wood Surface +MF	1.49	0	60
Wood surface for 0.5 h +MF	1.97	32.2	72
Wood surface for 8d +MF	1.52	2.0	66
Untreated wood Surface +MUF	1.76	0	59
Wood surface for 0.5 h +MUF	2.18	23.8	65
Wood surface for 8d +MUF	1.82	3.4	63

CONCLUSIONS

The test of contact angle and total surface energy of the surface indicated that DBD treatment at atmospheric pressure positively affected the wettability of wood surface. When the processing power was 4 000 W and processing times was 140 s, the effect was optimized.

The test of aging behavior revealed that the modification was limited by the time after the treatment. The total surface energy began to decrease gradually after 9 h, with increase of time, the effect of modification were eventually disappeared.

The shear bond strength tests on an untreated and plasma treated wood demonstrated the

effectiveness of plasma treatment to increase their adhesion property. The shear bond strength tests on UF, MUF and MF adhesive-bonded wood samples showed a difference increase in bond strength.

ACKNOWLEDGMENT

The authors would like to thank the Yunnan province international cooperation project of China (2014IA017) and Program of the Ministry of Science and Technology of China (2012BAD24B03) for the support.

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