Improving Bonding Strength of Oven-dried Poplar Veneers Using Atmospheric Cold Plasma Treatment

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Poplar veneers are typically oven-dried at high temperatures to shorten the dying period, and thus reduce energy consumption, which also leads to poor bonding strength. In this study, an atmospheric cold plasma system was self-designed to quickly modify the surface of oven-dried poplar veneers (dried at 120 °C, 200 °C, and 240 °C) to yield high bonding strength samples. The physical and chemical properties of treated samples were investigated with an optical contact angle measuring apparatus, fluorescence microscope (FM), and X-ray photoelectron spectroscopy (XPS). The results showed that surface wettability and adhesive permeability of poplar wood veneer were improved after the atmospheric cold plasma treatment. Moreover, the plasma treatment resulted in the incorporation of oxygen-containing groups onto the surface of the oven-dried poplar veneer. For example, the O-C=O group saw its relative content dramatically increase from 1.37% to 13.57%. These effects synergistically resulted in a high increase (76.2%) in bonding strength when using urea-formaldehyde (UF) resin as the adhesive. The plasma modification system used in this study can be utilized at atmospheric pressure, which is easier to realize industrially as compared to using a radio frequency plasma treatment, which is the currently preferred technique.

Keywords: Poplar veneer; Oven-dried; Atmospheric cold plasma; Bonding strength; Surface modification

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INTRODUCTION

Plywood has the highest mechanical properties in the production of wood-based panels. It has many excellent properties such as high specific strength, natural grain, and ease of processing. As one of the integral components of plywood, veneer has a considerable influence on the quality and production cost of plywood. According to Thant *et al*. (2009), the moisture content of veneer has a direct negative impact on the bonding strength of prepared plywood. Energy consumption accounts for approximately 25% of the processing cost in plywood production, while the energy cost for veneer drying accounts for more than 75% (Wu 2008). To save energy and enhance productivity, a shorter drying time and a high drying temperature are applied on veneer (Han *et al*. 2012). Previous studies have shown that high temperature drying methods can reduce energy consumption, which results in the reduction of production costs. However, the higher temperature has a detrimental effect on veneer surface quality (Wang *et al.* 1998; Han *et al*. 2013).

Recently, plasma technology has been applied to wood materials to quickly modify their surface properties (Chen *et al*. 2016a, 2017). Wood is a polymer material that is mainly composed of cellulose, hemicellulose, and lignin. After plasma treatment, many free radicals are generated on the surface of wood, and the raw chemical bonds in the surface are broken. Simultaneously, depending on the type of plasma treatment selected, target chemical groups can be incorporated into the wood surface with active side chains that result in the improvement of the surface properties of wood materials treated with plasma (Aydin and Demirkir 2010; Zhang *et al*. 2010, 2013). Previous studies have shown that a plasma treatment can lead to considerable improvement in the surface wettability of poplar veneer (Tang *et al*. 2012, 2015).

The surface properties and the adhesive ability of wood can be improved through plasma treatment even under atmospheric pressure (Chen *et al*. 2016a). Surface morphology and chemical properties were simultaneously modified by applying an electric barrier discharge (DBD) plasma treatment, which enhanced the bonding strength of the treated plywood (Chen *et al*. 2016a). It can be expected that a plasma treatment could result in a remarkable improvement in the surface properties of oven-dried poplar veneer. This plasma treatment is conducted under atmospheric pressure, which makes it easier to adapt for industrial use.

In this study, a self-designed cold plasma system was used to modify oven-dried poplar veneer to quickly enhance its surface properties and bond strength under atmospheric pressure. Various characterization methods were used to reveal the change in physical and chemical properties before and after the plasma treatment.

EXPERIMENTAL

Materials

Poplar veneer was purchased from Jinhu Hongda Wood Co., Ltd. (HuaiAn, China). It had a moisture content of approximately 12% to 15% and a thickness of 1.5 mm ± 0.12 mm. The UF resin (viscosity of 86.64 mm^2/s at 25 °C; solids content of 50%) and phenolic resin (PF; viscosity of 109.78 mm^2/s at 25 °C; solid content of 52%) were purchased from a local factory (Dynea Co., Ltd., Nanjing, China).

Methods

Oven-drying process and plasma treatment

The poplar veneer was cut into 300 mm × 300 mm pieces. It was then dried in a hot press at either 120 °C (10 min), 200 °C (3 min), or 240 °C (3 min). A self-designed plasma treatment system was used to quickly modify the oven-dried poplar veneers. The Atmospheric plasma processing power was set to 4.5 kW, and the processing rate was set to 8 m/min. The UF-glued plywood using plasma treatment will increase adhesion strength, improve its properties as surface roughness, chemical properties and high humidity resistant. This study introduces an effective method to enhance the adhesion strength and may be applied in industrial scale (Chen *et al*. 2016a). The untreated oven-dried poplar veneers were denoted as V-120, V-200, and V-240, according to the drying temperature used for each sample, while the plasma-treated oven-dried poplar veneers were similarly denoted as VP-120, VP-200, and VP-240.

Surface wettability of poplar veneer

The contact angles of the treated samples were determined using an optical contact angle measuring apparatus measured in 2-Theta (°) (Biolin Scientific AB, Frölunda, Sweden) to evaluate the wettability of the poplar veneer sample surfaces. The UF and PF (4 mL each) were selected as the testing drops that were dispersed on the wood surface. A camera was used to capture the images of the dispersing process every 50 ms. The initial angle was taken as the angle that the drop formed when it first reached the wood surface, while the equilibrium angle was taken as the angle that formed when the drop shape stopped changing.

FM analysis

Fluorescence microscopy was performed *via* a Fluorolog-3 spectrofluorometer (Jobin-Yvon Horiba, Paris, France). The poplar veneer was tested in a front-facing configuration. Sixteen spectra were collected for each species of poplar veneer. The effective penetration depth (EP) and the average penetration depth (AP) were determined in this study and applied to quantitatively evaluate the permeability of the adhesive.

XPS analysis

X-ray photoelectron spectroscopy is a technique that can determine the bonding state of atoms and the distribution state of electrons in materials by measuring the chemical shifts of the inner electrons of the sample atoms. By referencing the characteristic binding energy and spectra of certain elements, XPS technology can be used to identify all elements except for hydrogen and helium. In this study, XPS was performed using an AXIS Ultra DLD (Shimadzu, Tokyo, Japan). Both the low-resolution spectra with a binding energy of 0 eV to 1200 eV and high-resolution spectra with a binding energy of 277 eV to 296 eV were scanned and recorded. In addition, the C1s spectra were subjected to deconvolution into 4 Gaussian peaks, representing the four carbon-related components detected, using XPSPEAK Software.

Preparation and bonding strength testing of plywood

Three-layered plywood specimens were assembled from the oven-dried poplar veneers that were prepared. When UF was the adhesive used, it was hot-pressed (HD-500, Shenzhen Sans Material Test Instrument Co., Ltd., Shenzhen, China) with a hot-pressing time of 1.0 min/mm, a pressure of 1.0 MPa, a temperature of 110 °C, and a UF adhesive loading level of 240 g/m^2 (using double glue lines).

When PF was the adhesive used, the conditions were a hot-pressing time of 1.3 min/mm, a pressure of 1.1 MPa, a temperature of 135 °C, and a PF adhesive loading level of 280 g/m^2 (using double glue lines). The bonding strength of the prepared plywood was tested using a mechanical testing machine (HD-500, Shenzhen Sans Material Test Instrument Co., Ltd., Shenzhen, China) according to GB/T 9846.3 (2004). Data on the bonding strength of each different preparation process were obtained by averaging the values from the 32 repeated experiments.

RESULTS AND DISCUSSION

Surface Contact Angle Analysis

Presented in Table 1 are the contact angles of the poplar veneer surfaces treated using PF and UF as the testing drops. It can be observed that a high oven-drying temperature led to an increase in both the initial angle and equilibrium angle. The sample V-240 demonstrated the highest equilibrium angle of 70° for UF and 71° for PF, which may result in the poor bonding. The surface carbonization and the transition of non-poplar extracts may have been responsible for the higher angles. All of the samples showed a decrease in both the initial angle and equilibrium angle after plasma treatment, indicating that the plasma treatment can lead to an effective improvement in wettability. V-240 demonstrated the highest decrease in the equilibrium angle, with a 50% decrease after plasma treatment, implying that a high oven-drying temperature favored improvement of the wettability of samples with plasma treatment. Moreover, the samples using PF for the testing drop demonstrated higher contact angles than those with UF as the testing drop. This fact was attributed to the higher viscosity of PF.

Table 1. The Initial and Equilibrium Contact Angles of Poplar Veneer Surfaces Using UF and PF Resins as the Testing Drops at Different Drying Temperatures

Sample		Untreated		Plasma-treated	
		Initial Angle (°)	Equilibrium Angle (°)	Initial Angle (°)	Equilibrium Angle (°)
UF	120 °C	105 ± 2.1	39 ± 3.1	95 ± 6.1	28 ± 4.1
	200 °C	109 ± 4.2	45 ± 2.2	98 ± 4.2	31 ± 4.6
	240 °C	122 ± 3.4	70 ± 2.5	102 ± 5.4	35 ± 3.2
PF	120 °C	107 ± 3.1	42 ± 4.1	101 ± 5.1	35 ± 2.5
	200 °C	112 ± 2.3	48 ± 3.2	104 ± 4.6	37 ± 3.4
	240 °C	131 ± 6.8	71 ± 3.5	109 ± 6.2	42 ± 5.3

Penetrability Analysis

Images of poplar veneer using fluorescence microscopy can be found in Fig. 1, which reveal the permeability of the adhesives used. In addition, the EP and the AP were applied in this study to quantitatively investigate the permeability of the adhesives used. It can be concluded from Fig. 1 that both the EP and AP demonstrated a decreasing trend with increasing oven-drying temperature. This correlated with the results of the contact angle analysis. All of the plasma-treated samples showed an increase in both EP and AP, which indicated that plasma treatment effectively improved the permeability of adhesives in the treated samples. The values of EP and AP of VP-240 increased 75.8% and 89.8%, respectively. This result may be related to the breakdown of the pit membrane in poplar veneer and the etching effect caused by plasma treatment (Chen *et al*. 2017).

XPS Analysis

X-ray photoelectron spectroscopy was applied to study the surface chemistry of the treated samples and to identify and quantify the basic elements and functional groups of poplar veneer (Sun *et al*. 2012). The XPS spectra and results can be found in Fig. 2 and Table 2. It can be observed that the O/C mass ratio decreased as the drying temperature increased. This result may be related to the thermal degradation of raw components, such as cellulose and hemicellulose, in the polar veneer.

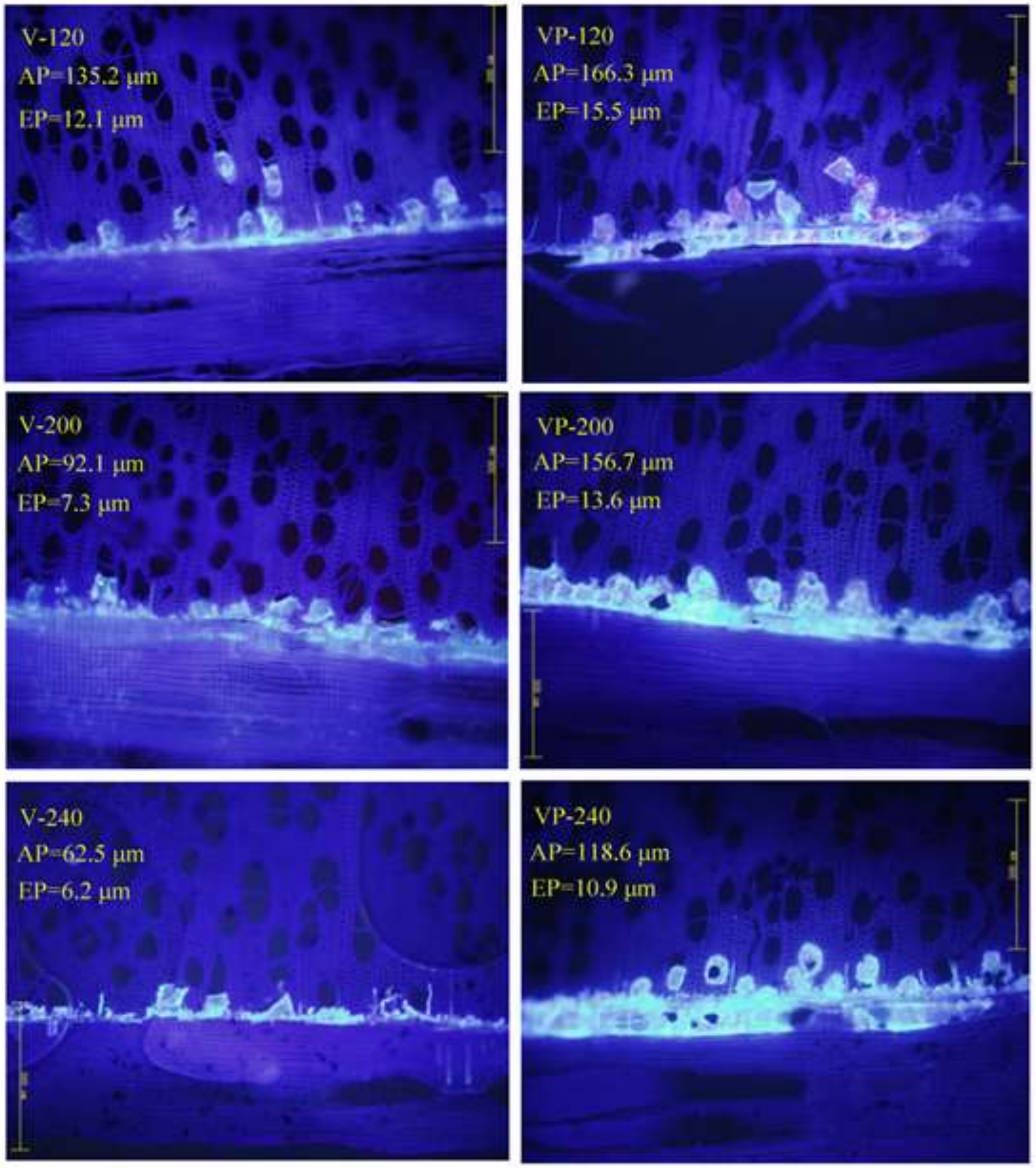

Fig. 1. Images of oven-dried poplar veneer using UF as permeating adhesive treated with plasma using fluorescence microscopy

After plasma treatment, all samples demonstrated an increase in O/C mass ratio, which was indicative of the incorporation of oxygen-containing groups. Plasma treatment can lead to the excitation of oxygen in the air around a sample and thus produce various types of oxygen-containing groups. Based on Chen *et al*. (2016b), it was determined that the C1s spectra of the treated wood were further deconvoluted into four peaks, which correspond to four carbon-related chemical bonds (-C-C- or -C-H-, 284.8 eV; -C-O, 286.4 eV; O-C-O or -C=O, 288.0 eV; O-C=O, 289.0 eV). Table 2 shows that the relative content of -C-C- was reduced after plasma treatment. Ions and atoms in a high-energy state, due to excitement by plasma treatment, would bombard the surface of samples, leading to the rupture of its raw skeleton chemical bonds.

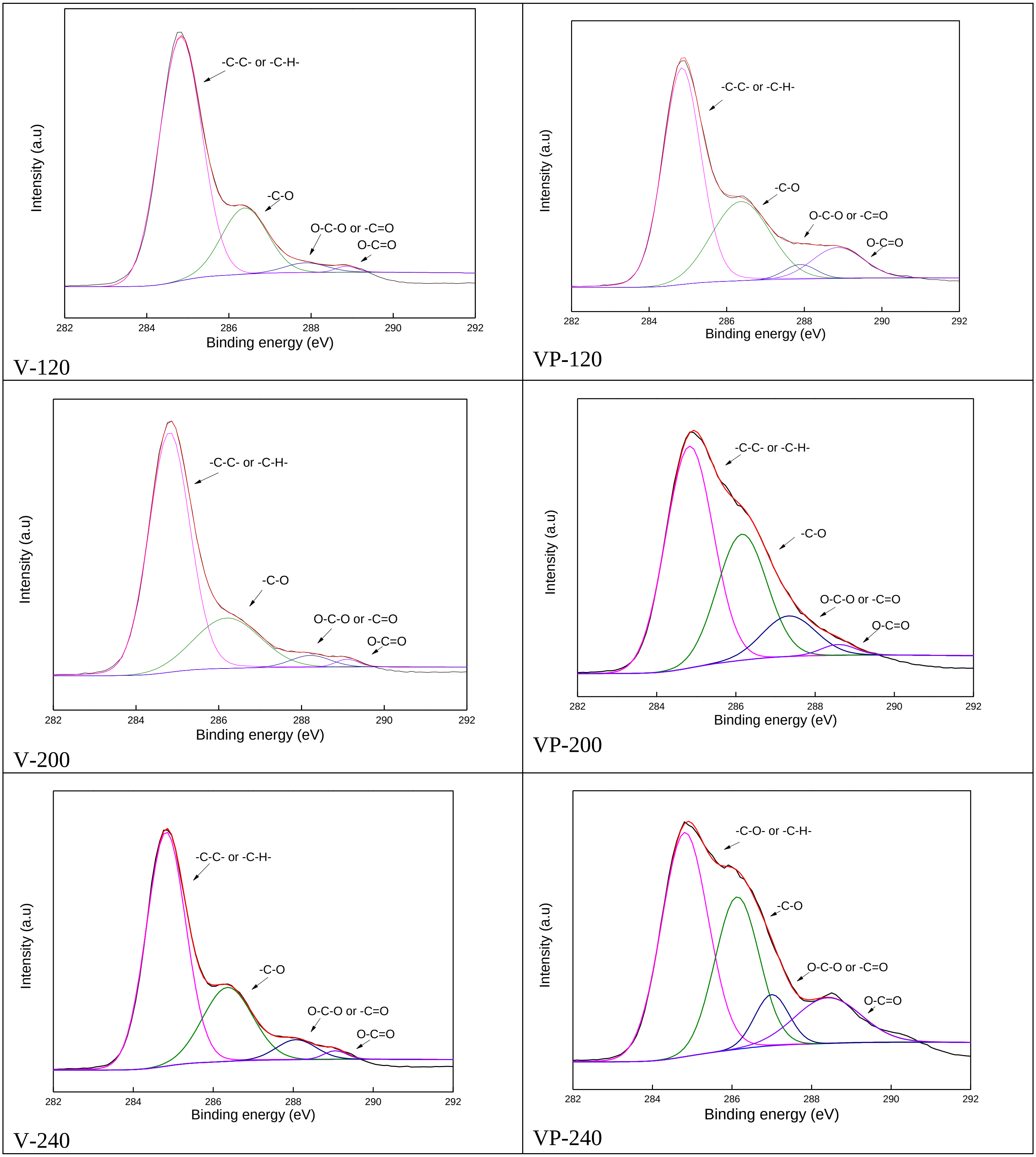

Fig. 2. The C1s spectra of oven-dried poplar veneer samples treated with plasma

In addition, the relative contents of all oxygen-containing groups (-C-O, O-C-O, and O-C=O) increased after plasma treatment. This was related to the incorporation of oxygen-containing groups excited by the plasma and derived from oxygen in the air. Plasma treatment likely led to the generation of free radicals, which can react with active sites on the treated sample surface and thus result in the stable incorporation of oxygen-containing groups. An increase in the relative content of O-C=O was observed (from 1.37% to 13.57%). This improved the surface wettability of oven-dried samples and thus favored the permeation and spread of adhesive onto the sample surface.

Table 2. Atomic Element Composition and C1s Chemical Composition of Poplar Veneer According to Oven-drying Temperature

Atomic Composition (%)	Untreated			Plasma-treated		
	120 °C	200 °C	240 °C	120 °C	200 °C	240 °C
O	17.7	17.12	17.16	20.97	21.17	21.92
N	1.43	1.49	0.94	1.92	1.78	1.34
C	80.87	81.39	81.9	77.11	77.04	76.74
O/C	0.219	0.210	0.209	0.272	0.274	0.286
C1s Composition (%)						
-C-C- or -C-H-	74.47	72.00	66.78	56.43	54.65	48.21
-C-O	21.75	23.48	26.20	30.18	32.26	30.40
O-C-O or -C=O	2.89	3.28	5.65	3.04	7.17	7.82
O-C=O	0.89	1.25	1.37	10.35	5.91	13.57

Bonding Strength Analysis

The bonding strength of poplar plywood samples treated with plasma is shown in Fig. 3. When UF was used as the adhesive, it can be concluded that the plasma treatment led to an increase in the bonding strength of all plywood samples. The sample VP-240 demonstrated the highest increase (76.2%), as compared to the untreated sample. The bonding strength of plywood demonstrated a decreasing trend with an increasing oven-drying temperature, which corresponded with the previous study.

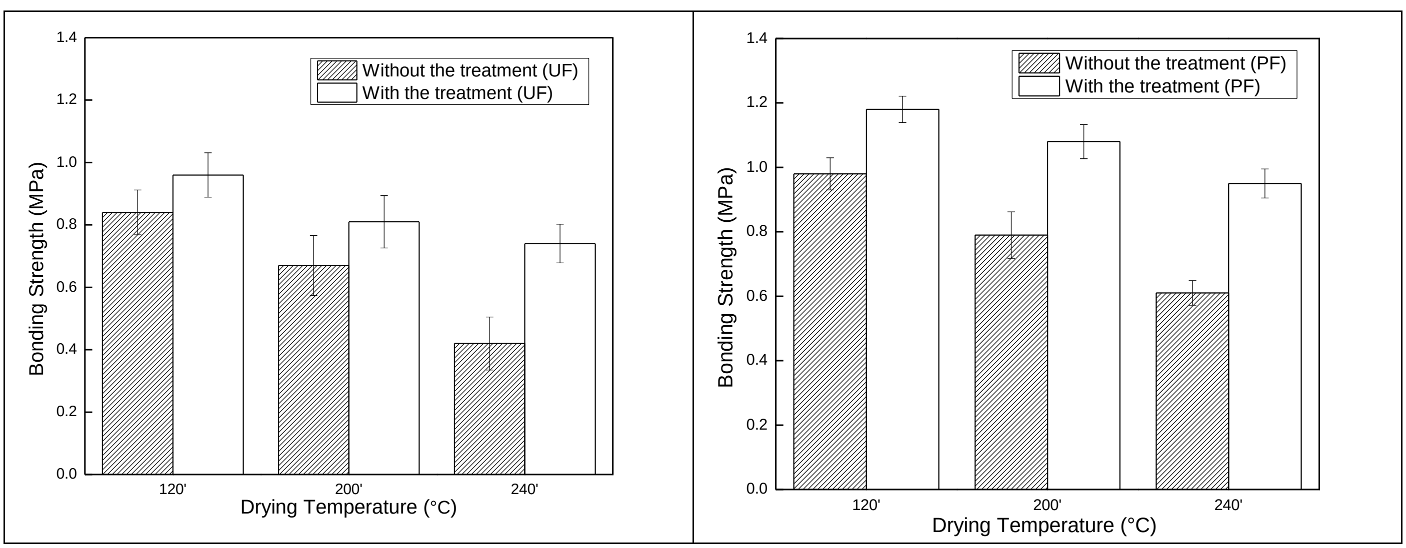

Fig. 3. The bonding strength of poplar plywood using UF and PF adhesives

When PF was used as the adhesive, the bonding strength of plywood samples also exhibited an increase after plasma treatment. In addition, VP-240 showed the highest increase of 55.7%. The improved wettability and adhesive permeability from the plasma treatment may have been responsible for these results. It also can be observed that the bonding strength of plywood using UF adhesive was lower than when PF adhesive was used. This fact was related to the inherent properties of PF, which has a higher viscosity and can form a network cross-linked structure after solidification. It was evident that plasma had a remarkable effect on the bonding strength of plywood.

CONCLUSIONS

1. The surface wettability and adhesive permeability of poplar veneer increased after an atmospheric cold plasma treatment that resulted in a maximal increase of 76.2% in the bonding strength of poplar veneer-based plywood when using UF as the adhesive.
2. Plasma treatment resulted in the incorporation of oxygen-containing groups onto the surface of oven-dried poplar veneer samples. The O-C=O group in particular demonstrated a relative content increase from 1.37% to 13.57%.

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