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REDUCING THE FORMALDEHYDE EMISSION OF COMPOSITE WOOD PRODUCTS BY COLD PLASMA TREATMENT

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ABSTRACT

Free formaldehyde which releases from composite wood products in the indoor environment causes tremendous harm to the human health. Researchers from the entire world have made unremitting endeavor to reduce the formaldehyde emission of composite wood panels. This study evaluates the formaldehyde emission of plasma pretreated plywood and MDF panels. The desiccator test method was used to evaluate the formaldehyde emission. The results show that cold ammonia plasma treatment can reduce the formaldehyde emission of plywood panels by 35 to 40 % and cold air plasma treatment by 9 to 17 %. Formaldehyde emission of coated medium density fiberboard panels can also be reduced by cold air and ammonia plasma treatment by 21 and 31 %, respectively. It is exciting to find that cold plasma treatment as an efficient and ecosystem friendly method, which is completely different from traditional formaldehyde reducing methods, can reduce the formaldehyde emission greatly and increase material stability without decreasing and even increasing the wet bonding strength of the UF resin.

KEYWORDS: Formaldehyde emission; cold plasma treatment; the bonding strength; surface coating; composite wood products.

INTRODUCTION

Composite wood products are widely used in furniture making, interior decoration and fitting in recent years. Because most of the panel products used indoor are bonded with urea-formaldehyde resin (UF), free formaldehyde will be released more or less which will lead to consumer dissatisfaction and health related complaints (Wang et al. 2004, Petinarakis and Kavvouras 2006, Blondel and Plaisance 2011, Salem et al. 2011). These emission have caused various symptoms, the most common of which are irritation in the eyes and the upper respiratory tract and prolonged exposure to formaldehyde in high dose can lead to chronic toxicity and even cancer (Aydin et al. 2006, Que et al. 2007, Uchlyama et al. 2007, Kim 2009, 2010). So the legal limits concerning the formaldehyde emission of composite wood products have been developing very quickly (Roffael 2006, Ruffing et al. 2010).

Formaldehyde emission research and there to related topics have been raising great interest in the wood industry during the last few years. Improving the adhesives and technical processors and the use of scavenger are the main methods to control the free formaldehyde emission nowadays (Que et al. 2007). A new method of cold plasma technology to reduce the formaldehyde emission of composite wood products was proposed in this paper.

Over the past decade, the technology of cold plasma has been explored and commercialized rapidly because it can improve surface properties without changing their bulk properties and is relatively inexpensive and more ecosystem friendly compared to direct chemical treatment (Sahin 2009, Wolkenhauer et al. 2009, Aydin and Demirkir 2010, Acda et al. 2012). In addition to being extensively used in the metal, textile and plastic industries, this technology has gain acceptance for modifying wood's surface properties to improve wettability and thus increase coating adhesion (Rehn et al. 2003, Wolkenhauer et al. 2008, Blanchard et al. 2009) and to decrease wettability and thus make the surface waterproof for extra protection (Magalhaes and de Souza 2002, Bente et al. 2004). There are few open literatures about cold plasma treatment applied to reduce formaldehyde emission of composite wood products which are widely used in indoor environment.

The main purpose of this study was to explore the feasibility of cold plasma used to reduce formaldehyde emission of composite wood products. In this study, cold air and ammonia plasma were used to pretreat the poplar veneer sheets and then plywood panels were manufactured with these veneer sheets and different formaldehyde to urea (F/U) molar ratio UF resins. Desiccator test method was used to test the formaldehyde emission and both wet and dry bond strength were also tested to evaluate the pros and cons of this approach. Medium density fiberboard (MDF) panels were also pretreated with cold plasma and then coated with melamine-impregnated papers to study the effect of cold plasma treatment on formaldehyde emission of coated MDF.

MATERIAL AND METHODS

Preparation of different F/U molar ratio UF resins

All UF resins used for this study were prepared in the laboratory by the traditional "alkaline-acid-alkaline" three-step reaction. Formaldehyde (37 wt %) was placed in the reactor and heated to 30°C, and then the reaction pH was adjusted to 7.5 with sodium hydroxide (30 wt %). Subsequently, the first urea was added to control the F/U molar ratio to be 2.2 and the mixture was heated to 90°C for just 1 h. Then, the reaction pH was adjusted to 4.5 with formic acid (20 wt %) for the condensation. After the mixture reacted for 45 min, the reaction pH was again adjusted to 7.5 and the second urea was added. After constant temperature reaction lasted for 30 min, the reaction mixture should be cooled and the third urea should be added. After 30 min stirring and automatic cooling, the resin was prepared and the final pH was adjusted to 8.0. Different amounts of the final urea were added for the synthesis to obtain F/U ratios of 0.9, 1.0, 1.1 and 1.2. Properties of different F/U molar ratio UF resin are shown in Tab. 1.

Tab. 1: Properties of UF resins produced with different F/U molar ratio.

F/U molar ratio	Nonvolatile solid content (%)	Viscosity (mPa.s)	Free HCHO (%)	pH
0.9	57	120	0.12	8.0
1.0	56	132	0.15	8.0
1.1	56	125	0.20	8.0
1.2	55	134	0.32	8.0

Cold plasma treatment and specimens manufacturing

Rotary cut veneer sheets with dimension of 300×300×2 mm were manufactured from a 5-year-old freshly cut hybrid poplar (*Populus italica*) log with diameter of 32 cm acquired from a plywood mill in Jiangsu, P.R. China. After manufacturing, the veneer sheets were air dried and then conditioned in a climate chamber to 12 % moisture content. MDF panels with 8 mm thickness, 0.7 g.cm^{-3} and 10 % moisture content and melamine-impregnated papers which were used for the coating of the MDF surfaces were bought from the market and sawed into the same dimension of the veneer sheets.

A HD-1B cold plasma system as shown in Fig. 1 with a radio frequency of 13.56 MHz was used to treat poplar veneer sheets and MDF. The maximum treatment width was about 30 cm. Both air and ammonia were used to produce cold plasma to treat the veneer sheets and MDF panels in this study. The purity of the liquid ammonia as the process gas was 99.6 % and the air was drawn from the atmosphere.

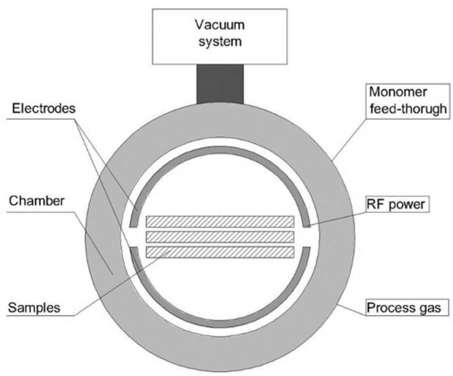

Fig. 1: The schematic diagram of RF plasma system.

The specimens were placed in the vacuum chamber between the electrodes to carry out the treatment. The system was evacuated to 20-40 Pa and then the treatment gas was fed into the chamber. Such a cycle was repeated five times to remove volatile contaminants. A pressure of 160-200 Pa and a steady-state flow rate were maintained by the gas feeding system. A radio frequency magnetron sputtering unit was used to produce cold plasma. The input power was set to 200 W and last for 3 min which were the optimized process parameters from our previous studies. After the end of the reaction, the chamber was pressurized and the specimens were taken out for the next step.

After the veneer sheets were treated with cold air and ammonia plasma, plywood panels with three plies and 6 mm thickness were immediately manufactured from these poplar veneer sheets by using UF resins with different F/U molar ratio. The plywood panels manufactured with untreated veneer sheets and different UF resins were used as the control groups. Approximately 150 $g.m^{-2}$ adhesive mixture was spread on single surface of veneer sheets by a gluing tool. In the manufacturing of plywood panels, hot press time, pressure, and temperature were 5 min, 0.8 MPa and 110°C, respectively. In the surface coating of MDF panels processes, hot press time, pressure, and temperature were 60 s, 2.5 MPa and 180°C. Ten replicate panels were manufactured for each condition.

Before the tests, all the panels were conditioned at a relative humidity of 50± 2 % and at a temperature of 23±1°C until the panels reached equilibrium as indicated by no progressive changes in weight. The equilibrium moisture content of the panels was about 10 to 12 %.

Test methods

Formaldehyde emission contents of plywood and MDF panels were determined according to desiccator test method described in ASTM D 5582 2006. Forty specimens were prepared in each group, so five results of the formaldehyde emission degree of each condition could be gained. Wet and dry shear strength tests of plywood panels were performed to evaluate bonding strength according to ASTM D 906 2011. Wet bonding strength was tested after the specimens had been immersed in water of 63°C for 3 h according to test method of the second grade plywood panels of China in G/B T 17657. Forty specimens of each group for different bonding strength tests were prepared. SPSS statistical software was used to analysis the results of the experiment by ANOVA.

RESULTS AND DISCUSSION

Formaldehyde emission from panels is caused by residual formaldehyde present in the UF bond boards trapped as gas in the structure as well as dissolved in the water in the boards. Hydrolysis of weakly bound formaldehyde from N-methylol groups, acetals and hemiacetals and hydrolysis of methylene etner bridges in more severe cases, also increase the content of volatilizable formaldehyde (Aydin et al. 2006). Two conditions must be met for the free formaldehyde releasing from the panel products: one is the channel for the external release and the other is that the formaldehyde gas pressure must be greater than the partial pressure of the outside.

Effect of cold plasma treatment on the formaldehyde emission

Average values of formaldehyde emission by the desiccator test method of plywood panels based on veneer sheets pretreatment methods and F/U molar ratio of the UF resins are given in Fig. 2, respectively. Using SPSS statistical software, the ANOVA results in Tab. 2 showed that both plasma treatment and U/F molar ratio have significant effect at the 0.05 level on the formaldehyde emission of the poplar plywood panels.

As shown in Fig. 2, both plywood panels manufactured with cold-air and ammonia plasma released less formaldehyde than that made with untreated veneer sheets bonded with different molar ratio UF resins ranged from 0.9 to 1.2. The results demonstrated that the cold plasma is effective for reducing formaldehyde emission of plywood panels no matter what kind of working gas to be chosen. This could result from some etching effect and a large number of free radicals generated after the cold plasma treatment which could improve the wetting and interfacial contact between the UF resin and the veneer sheets (Rehn et al. 2003, Wolkenhauer et al. 2008, Blanchard et al. 2009). The improvement of the wetting and contact increased the bond strength and blocked the channels for the formaldehyde to release.

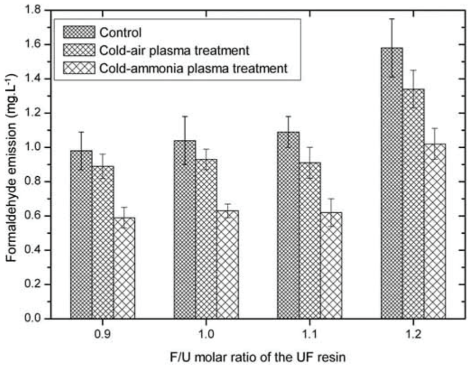

Fig. 2: Average values of formaldehyde emission by desiccator test method of plywood panels based on veneer sheets treatment method and F/U molar ratio of the UF resin.

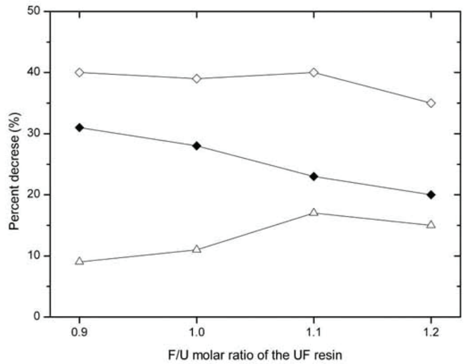

Fig. 3: Percent decrease of formaldehyde emission of the plywood panels. (Δ: ◇ercent decrease of air (%)=(air–control)/control; : Percent decr◆e of ammonia (%)=(ammonia–control)/control; : Percent decrease (%)= percent decrease of ammonia (%)- percent decrease of air (%).).

Tab. 2: ANOVA table for formaldehyde emission of plywood panels.

Source of variation	Sum of squares	D.F.	Mean square	F ratio	P-value	F crit
Treatment	2.13	2	1.07	111.42	0.00	3.19*
U/F	2.40	3	0.80	83.67	0.00	2.80*
Treatment×U/F	0.05	6	0.01	0.94	0.47	2.29
Error	0.46	48	0.01			
Total	5.05	59				

*Significant at 0.05 level

Formaldehyde emission of plywood panels manufactured with cold-ammonia plasma pretreated veneer sheets were lower than that manufactured with cold-air plasma pretreated veneer sheets. As shown in Fig. 3, formaldehyde emission of plywood panels manufactured with cold-air plasma pretreated veneer sheets decreased by 9 to 17 % compared with that manufactured with untreated veneer sheets and that manufactured with cold-ammonia treated veneer sheets decreased by 35 to 40 %. Meanwhile cold-ammonia plasma treatment could decrease the formaldehyde emission by 20 to 31 % compared to cold-air plasma treatment and the percent decrease lowered with the F/U molar ratio of UF resins increasing. The difference between cold-air and ammonia plasma treatment was that only cold-ammonia plasma treatment could produce N-H functional groups on the surface of the veneer sheets which help to reduce the formaldehyde emission (Schroder et al. 2001, Wen et al. 2006).

The poplar plywood panels manufactured with 1.2 U/F molar ratio UF resin without cold-plasma treatment did not belong to the E1-class boards according to the Chinese regulations

(≤1.5 mg.L[-1]), but it can been solved by cold-plasma pretreatment of the veneer sheets.

Effect of cold plasma treatment on the wet and dry bonding strength of plywood

Fig. 4 shows the results of the average of wet shear bonding strength and percentage wood failure of plywood panels manufactured with different F/U molar ratio UF resins and pretreated veneer sheets.

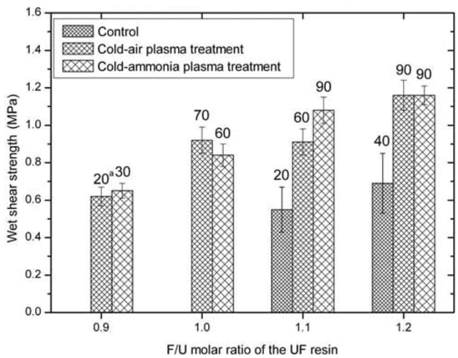

Fig. 4: The wet bond strength of plywood panels manufactured with different F/U molar ratio UF resin and treated veneer sheets (The specimens were immersed in water of 63°C for 3 h before test).

[a] indicates the average percentage wood failure.

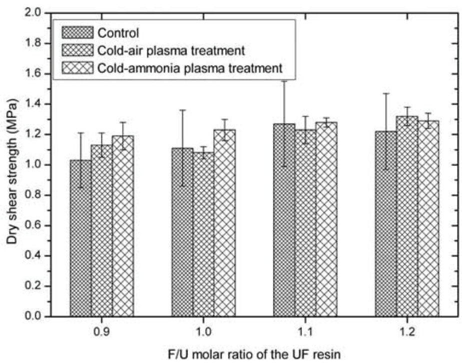

Fig. 5: The dry bond strength of plywood manufactured with different F/U molar ratio UF resin and treated veneer sheets (All the average percentage wood failure were more than 80 %, which indicated the good dry bonding strength).

The plywood panels bonded with 0.9 and 1.0 F/U molar ratio UF resin had low water resistance. From Fig. 4, we clearly saw that both cold-air and ammonia treatment could greatly improve the water resistance of the shear bonding strength of plywood panels bonded with different F/U molar ratio UF resins ranged from 0.9 to 1.2. The same results could be draw from the average percentage wood failure. This was also attributed to the etching effect and a large number of free radicals developed on the surface of the cold-plasma pretreated veneer sheets (Rehn et al. 2003, Wolkenhauer et al. 2008, Blanchard et al. 2009) which had great positive influence on the water resistance of the shear bonding strength.

As shown in Fig. 5, the entire dry shear bonding strength of different kind plywood panels was very high. There was no significant difference between the dry bonding strength of the different test groups indicated by ANOVA analysis using SPSS. The destruction of the specimen in dry bonding strength test is all caused by wood damage not caused by split of the bond line. In this situation, the test results reflected the strength of the wood not the shear bonding strength of the plywood. From the standard deviation of the dry bonding strength shown in Fig. 5, cold plasma treatment could greatly reduce the variability of the bonding strength and increase the stability of the properties of the plywood panels.

As we have known that the emission of formaldehyde from composite wood products bonded with UF resin decreased as the molar ratio falls, but unfortunately, the other physical and mechanical properties were influenced negatively at the same time (Que et al. 2007, Boran et al. 2011). But from this study we found that we could decrease the formaldehyde emission of the plywood panels meanwhile the wet and dry bonding strength, which affect the other physical and mechanical properties positively, could be increased.

Effect of cold plasma treatment on the formaldehyde emission of coated MDF

Surface coating of composite wood products has a lot of advantages and is widely used in the wood industry. In addition to play a decorative role, it can also suppress the absorption of water and humidity, increase the mechanical properties and decrease the thickness swelling and formaldehyde emission (Nemli and Colakoglu 2005, Barry and Corneau 2006). In this study, we focused on the effect of cold plasma treatment on the formaldehyde emission of coated MDF panels.

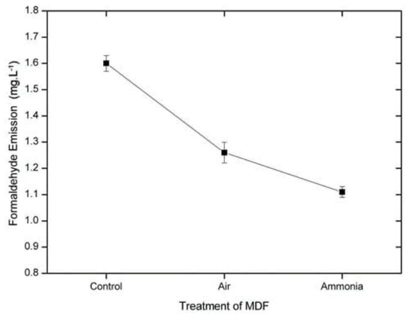

Fig. 6: Different average formaldehyde emission of cold plasma treated MDF coated by melamine-impregnated paper.

Tab. 3: ANOVA table for formaldehyde emission of MDF panels.

Source of variation	Sum of squares	D.F.	Mean square	F ratio	P-value	F crit
Between groups	0.64	2	0.32	269	0.00	3.88*
Within groups	0.02	12	0.00			
Total	0.65	14				

*Significant at 0.05 level

Fig. 6 depicts the average formaldehyde emission of coated MDF panels with different cold plasma pretreatment of the substrates. The ANOVA results in Tab. 3 also showed that treatments have significant effect at the 0.05 level on the formaldehyde emission of the MDF panels. Cold air plasma treatment can decrease the formaldehyde emission by 21 % and cold-ammonia by 31 %. It is owing to the same reasons related in section 3.1. Some etching effect and a large number of free radicals generated on the surfaces of MDF panels after the cold plasma treatment increased the laminated strength and blocked the channels for the formaldehyde to release. N-H functional groups generated on the surfaces of MDF panels on the cold ammonia plasma treatment help to explain why the cold ammonia plasma treatment had better results compared to cold air plasma treatment. Besides these, the vacuum in the plasma treatment chamber could also reduce the formaldehyde emission, because the presure difference between inside and outside MDF panels generated by cold plasma treatment extracted the formaldehyde which was already in the MDF panels or produced by the cold plasma.

CONCLUSIONS

Cold plasma treatment of veneer sheets can reduce the formaldehyde emission of the plywood panels; on the contrary it can improve the wet bonding strength of the plywood bonded with different F/U molar ratio UF resins ranged from 0.9 to 1.2. Formaldehyde emission of coated MDF can also be reduced by cold plasma treatment of the substrates. It is different from the traditional formaldehyde emission decreasing methods which negatively affect the other physical and mechanical properties of the panels. Besides that, the variability of the shear bonding strength of the plywood panels can also be improved by the cold plasma pretreatment. Cold ammonia plasma pretreatment decreases more formaldehyde emission compared to cold air plasma pretreatment. So cold ammonia plasma pretreatment has a hugh potential to be used to reduce the formaldehyde emission of the composite wood panels.

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