

Guanben DU, Zhaobin SUN, Linrong HUANG

Effects of surface performance on bamboo by microwave plasma treatment

© Higher Education Press and Springer-Verlag 2008

Abstract Surface treatment of bamboo was carried out by microwave plasma (MWP), surface contact angle of the sample was measured using glycerin and urea-formaldehyde resin (UFR) liquid, and the effects on the surface performance of the bamboo sample was evaluated. The results show that the surface contact angle of the sample presented a generally decreasing trend when prolonging the MWP treatment time and shortening the distance between the sample and the resonance cavity. The surface contact angle of the sample decreased by 49%–59% under the following conditions: MWP treatment for 30 s, the distance between the sample and resonance cavity at 40 mm, and measurement at 15 s after dripping with glycerin. The surface contact angle of the sample measured with the glycerin was lower than that with UFR. No matter whether we used glycerin or UFR, the contact angle of the sample at 15 s after dripping was lower than that at 5 s after dripping. The grinding treatment had little effect on the surface contact angle of the sample after MWP treatment, and the modification effect of MWP treatment after grinding was better than that of sole MWP treatment.

Keywords microwave plasma, bamboo, surface treatment, contact angle

1 Introduction

In recent years, with serious shortages in forest resources across the world, a broad range of non-wood resources

have been widely used, such as bamboo, cotton stalk and so on. Exploiting bamboo resources following an idea of “substituting wood with bamboo” and the opinion “bamboo surpasses wood” has been proposed (Zhang et al., 2001; Jiang et al., 2002). Processing and utilization of bamboo resources in China are in a leading position in the world, and the utilization proportion of bamboo also increases year by year. In this situation, in order to make up for the shortage of wood resources, high-efficiency processing and utilization of bamboo is becoming more and more important.

The modification of bamboo can increase its utilization efficiency and improve bamboo-based panel quality. There have been some reports about the surface modification of wood and other materials using microwave plasma (MWP) treatment (Du et al., 1999; Wang et al., 2001; Mei et al., 2004). Some researchers have carried out surface modification studies for different materials using microwave plasma treatment, such as rubber (Liao et al., 2003), the properties of urea-formaldehyde resin (Sun et al., 2007), and wood surface modification (Du et al., 1998, 1999).

Various treatments for surface modification of bamboo have been implemented (Zhang et al., 1990; Chen et al., 1992; Yu et al., 2002). However, few reports (Huang et al., 2006) were found with respect to surface treatment of bamboo with microwave plasma. This paper investigated the effect of MWP for bamboo surface performance produced by microwave plasma treatment.

2 Materials and methods

2.1 Materials

2.1.1 Bamboo

Three-year-old fresh bamboo (*Dendrocalamus brandisi*) from the Jinghong County of Yunnan Province was collected, with dimensions of 20 m height, 15 cm diameter at breast height, and 15–40 mm wall thickness. The

Translated from *Journal of Nanjing Forestry University (Natural Sciences Edition)*, 2007, 31(4): 33–36 [译自: 南京林业大学学报(自然科学版)]

Guanben DU (✉), Linrong HUANG
Faculty of Wood Science and Interior Decoration, Southwest Forestry College, Kunming 650224, China
E-mail: gongben9@hotmail.com

Zhaobin SUN
Faculty of Forestry, Agricultural University of Hebei, Baoding 071000, China

segment of bamboo timber for experiment was about 1–2.5 m high from bamboo root. All the samples were soaked in water for use. Samples taken out from water were air-dried in a room for one week, and their moisture content was kept lower than 15%. Bamboo nodes were removed. The sample dimension was 25 mm × 16 mm × 8 mm. The sample surface treated by MWP was planed. The tangential surface near the outer surface of the bamboo was set as the experimental surface.

2.1.2 Chemical reagents

Distilled water, glycerin, methylene iodide and urea-formaldehyde resin adhesive (UFR) were used. Before measuring the contact angle, powdered UF was mixed with distilled water with the volume ratio of UF to water at 10:6. No other additive was added and the aimed viscosity was about 57 s measured by a TU-4 cup viscometer. It was used for measuring the surface contact angle right after mixing.

2.2 Methods

The surface treatment of bamboo specimens with MWP treatment was carried out within three days after they were planed; the static surface contact angle was measured within three days after MWP treatment. The bamboo was treated with MWP at a distance of 40 and 80 mm (the distance from the specimen to the reaction chamber), and then the surface contact angle was measured with the instrument. Water and methane diiodide are the most used liquid media for measuring of the contact angle. However, when considering that both of them had very small wetting angles on the surface of the bamboo and the angle between the interface of solid and liquid was too difficult to observe, glycerol and urea-formaldehyde resin adhesive were instead used in this paper. The capillary of the bamboo surface at different sizes absorbed the measuring liquid, and it caused changes in the wetting angle, therefore the surface contact angle became dynamic, even while using a

higher viscosity liquid such as the glycerol and urea-formaldehyde resin adhesive. The surface contact angle was measured at 5 and 15 s after dripping the liquid onto the bamboo surface.

For evaluating the effect of grinding treatment on surface performance, a group of grinded specimens was chosen and their contact angles were measured and then compared with that of specimens treated by MWP alone.

2.3 Experimental equipment

The following equipment were used in the experiment: a set including a microwave plasma generator (self-made), a vacuum pump, a high-pressure nitrogen apparatus, blast ovens, an electronic balance, and a JC2000A infusion contact angle/interfacial tension measuring instrument.

3 Results and discussion

3.1 Effects of reaction distance on the surface contact angle

The results showing the contact angles of bamboo with grinding and MWP treatments at 40 and 80 mm (the distance from the specimen to the reaction chamber) are presented in Table 1.

As seen from Table 1, the closer the distance between the bamboo sample and the resonance cavity was, the bigger the declination range of the bamboo contact angle was in a short time under the same treatment conditions; also, the overall treatment effect was better. Compared with the average contact angle of the sample between 120–330 s, the surface contact angle dripped with UFR at 80 mm was 14.86% (5 s) and 23.42% (15 s) higher than the grinding and MWP treatments done at 40 mm, respectively, and it was 57.25% (5 s) and 12.51% (15 s) higher than that when dripped with glycerin. The contact angles of the bamboo samples significantly decreased after MWP treatment, and the effect

Table 1 Comparison of contact angle of bamboo with different treatments

distance/mm	item	contact angle/°			
		glycerin (5 s)	glycerin (15 s)	UFR (5 s)	UFR (15 s)
40	contact angle of sample by grinding and MWP treatment	72.67	69.25	74.92	55.25
	contact angle of sample treated by MWP after 30 s	59.40	51.60	46.80	26.25
	average contact angle of sample treated by MWP within 120–330 s	52.69	43.24	25.01	11.67
	minimum contact angle of sample	42.20	31.33	14.50	3.00
	contact angle of unground sample	72.67	61.00	100.17	83.67
	contact angle of sample treated by MWP after 30 s	58.33	48.00	51.33	34.50
80	average contact angle of sample treated by MWP within 120–330 s	52.49	44.26	34.82	17.17
	minimum. contact angle of sample	47.00	40.33	32.33	8.50
	contact angle of sample treated by MWP after 30 s	68.86	61.83	48.83	26.83
	average contact angle of sample treated by MWP within 120–330 s	60.52	53.37	39.33	13.13
	minimum contact angle of sample	54.57	45.75	32.33	6.80

was also prominent even though the MWP treatment time was very short.

When MWP was evaluated for point power sources, only if enough energy of the plasma and active particles was accumulated on the sample surface would the modification function of MWP take place. The energy density of the MWP source is inversely proportional to the square of the distance. When the reaction distance is longer, the energy flow density would be smaller, and a longer reaction time would be needed to achieve the same treatment results. It has a close relationship with reducing the reaction distance and increasing the reaction time. The modification effect of MWP treatment is mainly due to the large number of plasma free radicals and active groups. The treatment of grinding samples can increase their surface roughness; however, the effect of grinding is weaker than that of the free radicals and active groups generated from MWP.

3.2 Effects of liquid types and MWP treatment time on the surface contact angle

The type of test liquid influences the measurement results of the contact angle to some degree. As can be seen from the measured contact angle data, the sample surface contact angle was reduced by 49%–59% with glycerol treatment compared with the untreated sample, and it just decreased by 20%–21% with UFR treatment when the treatment time was 30 s.

MWP treatment time had significant effects on the measurement results. As can be seen from Table 1, the surface contact angle of the sample presented a generally decreasing trend with the MWP treatment time at two reaction distances, and the trend was even obvious when measured with UFR liquid. Compared with the untreated sample, the surface contact angle dropped by 78% at most.

As can be seen from the measurement results in Table 1, the time to reach the smallest contact angle at the two distances (40 mm, 80 mm) was 330 s and 210 s, respectively, under the same treatment conditions. The time needed to achieve the best treatment effect with MWP became longer when the distance was closer. When the contact angle was reduced sharply in a very short time, the contact angle changed little even if the treatment time was continually prolonged; however it showed a generally decreasing trend.

When the MWP point power sources produced large numbers of active functional groups and free radical agglomerates on the bamboo surface in a very short time, the rapid accumulation of energy and particles caused the contact angle to decrease sharply; then, despite fluctuations, the surface contact angle of the bamboo presented a generally decreasing trend until it reached a minimum value.

The active functional groups and free radical agglomerates on the bamboo surface became gradually saturated over time, so the surface contact angle descended slowly. When the sample was continuously radiated with the plasma, the active functional groups and free radical agglomerates that were accumulated previously began to be consumed, and the sample contact angle ascended instead of decreasing.

The experiment results showed that a longer time was needed to achieve better treatment effects when the distance was closer, which is unreasonable. The reason was possibly the instability of the microwave plasma device. When the specimen was removed in and out frequently in the quartz reaction chamber, it was difficult to maintain vacuum stability. In addition, the purple light produced by the plasma flashed in this state, which also showed that the plasma was very unstable, i.e. the state of the plasma device was not exactly the same during the sample treatment at the two reaction distances, hence, the results had errors. This case could be validated by further experiments.

During the experimental process, we also observed that the color of the sample became gradually dim at the beginning of treatment at 300 s. The color of the specimen changed from black to black light (360 s) with the more prolonged time, and a burnt smell appeared after treating for 450 s. The contact angle measured with glycerol or with urea-formaldehyde glue had a slightly more ascending trend compared to the previous results at the same instant. The reason was probably that the high-temperature produced by plasma made the surface structure of the bamboo acutely change (the high heat severely damaged the surface structure), so the contact angle had an increasing trend instead of a decreasing trend. The value of the surface contact angle of the sample treated by MWP was at a low ebb after 270 s at the 40 mm distance, and it reached minimum value at 330 s. We can thus presume that the suitable MWP treating time was during 270–360 s.

3.3 Effect of grinding treatment on the surface contact angle of bamboo wood

Comparing the average contact angle with the minimum contact angle during the treatment time of 120–330 s, the modification effect by grinding, followed by the MWP treatment was on the whole better than that of a direct treatment with MWP. The grinding treatment had little effect on the surface contact angle of the samples after MWP treatment.

As can be observed from Table 1, when the distance between the samples and the resonance cavities was 40 mm, using glycerin and UFR liquids for measuring the contact angle, the drop in the value of the contact angle was 5% and 26%, respectively, after grinding without MWP treatment; 17% and 54%, respectively, after grinding

followed by MWP treatment; and, 16% for both controls, and 17% and 51%, respectively, after direct MWP treatment. When the distance between the samples and the resonance cavities was 80 mm, the drop in value of the contact angle was 12% and 60% with glycerin and UFR, respectively, measured after grinding and MWP treatment.

Given our results, the grinding treatment seemed to have had some effect on the surface performance, but less than for samples treated with MWP after grinding. Although the grinding treatment can increase the surface roughness of bamboo, it had less effect on the chemical properties of the surface. The effect of the modification on surface performance was not clear after MWP treatment.

The functional improvement due to MWP treatment, which produced large amounts of active functional groups and free radicals accumulated on the surface of the bamboo, was greater than the effect of the functional improvement due to an increase in roughness. The surface contact angle of samples without grinding was similar to that of the ground samples over a short time period. When the modification effect of grinding on the samples became gradually weaker with an increase in the MWP treatment time, the effect of modification due to the MWP treatment on the samples became gradually stronger.

3.4 Effect of time on the surface contact angle of bamboo wood

As seen from Table 1, the surface contact angle of the samples show, on the whole, a decreasing trend over time under the same treatment liquid. When the distance between the samples and the resonance cavities was 40 mm, the contact angle of the samples decreased on the average by 17.62° measured after 15 s with glycerin liquid, compared with the UFR liquid treatment measured after 5 s, which decreased, on the average, by 9.12° at 15 s under the same conditions.

When the distance between the samples and the resonance cavities was 80 mm, the contact angle of the samples treated with UFR and measured after 15 s decreased, on average, by 12% and 60% compared with the glycerin treatment. The longer the treatment liquid stayed on the samples, the faster the decline of the surface contact angle of the sample. The reason is that the capillaries on the sample surface would absorb the treatment liquids, which would gradually disappear over time, hence the wetting angle of the sample changed. It was the MWP treatment which caused improvement of the liquid absorption capacity of the capillaries.

4 Conclusions

1) The length of time of MWP treatment had a significant effect on the surface contact angle of the samples. The

surface contact angle of the samples showed, on the whole, a decreasing trend with prolonged exposure to the MWP treatment at two reactions distances, 40 and 80 mm. In particular, it clearly decreased when treated with UFR liquid. Compared with untreated samples, the maximum drop in value was as high as 78%. The most suitable length of MWP treatment was between 270–360 s.

2) The distance between the samples and resonance cavities had a significant effect on the surface contact angle of the samples. The closer the distance between the bamboo samples and the resonance cavities, the larger the decline in the range of bamboo contact angles in the short treatment time under similar treatment conditions. The overall treatment effect was also better. Compared with the average contact angle of the samples between 120–330 s, the surface contact angle decreased with UFR liquid treatment at 80 mm, and was 14.86% higher at 5 s and 23.42% at 15 s than the treatments at 40 mm, and it was 57.25% higher at 5 s and 12.51% at 15 s when dripped with glycerin.

3) The grinding pretreatment can improve surface performance of bamboo wood. The effect of modification by grinding followed by MWP treatment was, on the whole, better than that of treatment by MWP directly. The grinding treatment had little effect on the surface contact angle of the samples after MWP treatment.

4) The length of time of measurement of the contact angle had a significant effect on the surface contact angle of the samples, which showed, on the whole, a decreasing trend when the time of measurement was prolonged using the same liquid.

5) To a certain degree, the type of liquid used when measuring the result of the contact angles has an effect. The type of liquid also has, to some extent, an effect on the result of the contact angle measurements. The sample surface contact angle was reduced by 49%–59% with glycerol, and it decreased only by 20%–21% with UFR when the treatment time was 30 s.

Acknowledgements This project was financially supported by the National Natural Science Foundation of China (Grant No. 39970696) and the Natural Science Foundation of Yunnan Province (No. 1999-C0060M).

References

- Chen G Q, Hua Y K (1992). Study on surface wettability of bamboo. *J Nanjing For Univ*, 16(3): 77–81 (in Chinese)
- Du G B, Hua Y K (1999). Prospect of microwave plasma and its application on wood science and technology. In: *Wood Industry Brands Symposium of Chinese Forestry Society*. Shanghai: Chinese Forestry Society, 10: 60–63 (in Chinese)
- Du G B, Hua Y K, Wang Z (1998). Surface performance of Chinese fir wood treated by microwave plasma. *J China Wood Ind*, 12(6): 17–20 (in Chinese)
- Du G B, Hua Y K, Wang Z (1999). Surface treatment on wood by microwave plasma. In: *Wood Industry Brands Symposium of*

- Chinese Forestry Society. Shanghai: Chinese Forestry Society, 10: 81–92 (in Chinese)
- Du G B, Hua Y K, Wang Z (1999). Wood surface ablation under microwave plasma. *Sci Silv Sin*, 35(2): 95–99 (in Chinese)
- Huang H L, Lu X N, Xue L D (2006). Bonding performance of bamboo plywood improved by O₂ plasma treatment. *J Zhejiang For Coll*, 23(5): 486–490 (in Chinese)
- Huang H L, Xue L D, Lu X N (2006). Effects of low temperature plasma treating on bonding strength of bamboo strip surface. *J Nanjing For Univ (Nat Sci Ed)*, 30(6): 23–26 (in Chinese)
- Jiang Z H, Wang G, Fei B H (2002) The research and development on bamboo/wood composite materials. *J For Res*, 15(6): 712–718 (in Chinese)
- Li J (1999). *Wood Protection*. Harbin: Northeast Forestry University Press
- Liao B, An T Y, Wang Y S, Zhu S Z (2003). A study of rubber surface modification using microwave plasma. *J East China Norm Univ (Nat Sci)*, 2: 40–45 (in Chinese)
- Liao B, An T Y, Wang Y S (2003). Study on improving rubber surface wettability using microwave plasma. *Surface Tech*, 32(06): 22–24 (in Chinese)
- Mei Y X, Tang X L (2006). The application of low-temperature plasma in surface modification of materials. *Modern Phys*, 16(3): 40–43 (in Chinese)
- Song H J, Dong H S, Hao Y (2000). Theoretic foundation of youngood- girifalco- fowkes equation use for solid surface energy calculation. *J Adhes*, 5: 1–5 (in Chinese)
- Sun F W, Wang Y, He L (2007). Influence of microwave plasma processing on the properties of UF resin. *J Jiangxi For Sci Tech*, 5: 56–57 (in Chinese)
- Wang F H, Liu Z M (2001) Research advance of the interface for wood-based material. *J Northeast For Univ*, 29(5): 84–87 (in Chinese)
- Yang J, Wang J H (2006). Study on surface properties of cold-plasma modified aluminum alloys. *J Mater Sci Tech*, 14(2): 113–115 (in Chinese)
- Yu W J, Jian Z H, Ye K L (2002). Characteristics research of bamboo and its development. *J For Res*, 15(2): 712–718 (in Chinese)
- Zhang Q S (2001). Playing great attention on bamboo chemical processing and exploiting bamboo charcoal applying technique. *J Bamboo Res*, 20(3): 34–35 (in Chinese)
- Zhang Q S, Yang P (1990). Improvement of bamboo bonding performance. *China For Prod Ind*, 1: 1–4 (in Chinese)