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RESEARCH ARTICLE

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Effect of microwave plasma treatment on surface wettability of common teak wood

Abstract The improvement of wood surface wettability can clearly improve bonding properties, as well as enhance physical and mechanical properties of wood composites. In our investigation, the microwave plasma (MWP) technique was adopted to treat the surface of common teak. The treatment effect was evaluated by measuring the contact angles of liquids and calculating the free surface energy. The results show that the modification effect improved when the sample was located 120 mm from the resonance cavity, rather than at 80 mm. A MWP treatment over a short span of time is useful to lower the contact angles and improve the surface wettability considerably. The range of decreasing contact angles, tested by water, could reach 74% at a distance of 120 mm.

Keywords microwave plasma treatment, common teak, surface contact angle, surface wettability

1 Introduction

Wood modifications can increase the efficiency of its utilization and improve the quality of wood-based composites. Research related to surface modification of wood and other material have been carried out and important achievements were made. For instance, several publications reported progress in the research on the wettability of wood and veneer surfaces (Zhang et al., 1997; Sheldon and Douglas, 2001; Cheng and Gu, 2002), while others focused on new techniques of wood modification (Li et al., 1995; Luo and Chao, 1998; Wang and Liu, 2001).

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Among the techniques for modifying wood surfaces, plasma treatment is a particularly eye-catching novelty. As the fourth existing state of natural substances (the other three being solid, liquid and gas), plasma contains a large number of active particles which can promote chemical reactions and have sufficient energy to break typical chemical bonds on the surface of wood. Short-term plasma irradiation can produce a lot of free radicals on wood surfaces. Therefore, graft copolymerization of vinyl monomers onto wood surfaces can be realized. Hence, the performance of wood surfaces is improved by establishing a chemical bonding-based interface, which is fundamental for improving the overall quality of wood-based composites.

It is reported that microwave plasma treatment (MWP) has been adopted widely to modify the surface properties of different kinds of material (Du et al., 1998; Mei and Tang, 2006). For example, MWP was introduced to modify rubber surfaces (Liao et al., 2003a, 2003b), urea-formaldehyde resins, bamboo timber surfaces (Huang et al., 2006a, 2006b), as well as wood surfaces (Du et al., 1998, 1999a). In order to enhance our understanding of MWP, the treatment effects on surface properties have been evaluated in terms of free surface energy, ablation (Du et al., 1998, 1999b), X-ray photoelectron spectroscopy (XPS) (Du et al., 1999a) and ESR (Du, 2002).

The main purpose of our study was to investigate the effects of microwave plasma treatment on the surface wettability of common teak wood. We searched for a feasible method to obtain chemical activity on the surface of common teak (Cheng, 1985) in order to enhance its surface bonding properties.

2 Materials and methods

2.1 Materials

Common teak wood (*Tectona grandis* L.) with a moisture content of around 11% to 12% was purchased from the local market and cut into samples with dimensions of

25 mm × 15 mm × 6 mm. The sample surfaces were planed to smoothness before MWP treatment. In our study, we used distilled water, glycerol and the methylene iodide as testing liquids to measure the contact angles.

2.2 Methods

The effect of MWP treatment on wood surface wettability was evaluated by measuring the change in the contact angle of the sample surfaces before and after treatment. The time of treatment and the distance from the resonator chamber to the samples were selected as two independent variables. The microwave plasma equipment was preheated for 30 min and vacuumed to 700 Pa before starting the treatment, which caused the plasma equipment to maintain a certain pressure and microwave output power. The wood samples were placed in the resonator cavity at a certain distance from the resonator chamber and then the plasma was exploded by a low-pressure gas after vacuuming to 700 Pa. The samples was taken out after being treated by MWP for a specified period of time and rapidly sealed with nitrogen gas and stored in the dark at room temperature. The contact angles of the treated samples were measured within the next three days and the free surface energy was calculated.

2.3 Equipment

The following pieces of equipment were used in this study: a set of microwave plasma generators (self-made), a vacuum pump, a high-pressure nitrogen instrument, blast ovens, an electronic balance and a JC2000A infusion contact angle / interfacial tension measuring instrument.

2.4 Calculation of free surface energy

There are many methods to test the free thermodynamic surface energy of liquids (γ_L) (i.e., surface tension). The free surface energy of solids (γ_S) is calculated by measuring the contact angle of a particular liquid on the solid surface. For low-surface energy solids (where the free surface energy is < 100 MJ/m^2 or the contact angle is $> 10°$), the surface free energy is commonly calculated by combining geometric equations, harmonic equations or the Young-Good-Girifalco-Fowkes equation (YGGF equation) with the measured values of the contact angle (θ). In our investigation, the following geometric equations were used:

$$\gamma_L(1+\cos\theta) = 2\left(\sqrt{\gamma_S^d\gamma_L^d}+\sqrt{\gamma_S^P\gamma_L^P}\right) \quad (1)$$

$$\gamma_S = \gamma_S^d + \gamma_S^P \quad (2)$$

where γ_S^d is chromatic dispersion energy, γ_S^P chromatic non-dispersion energy, γ_L^d and γ_L^P are testing liquids for chromatic dispersion energy and chromatic non-dispersion energy.

According to these equations, the free surface energy of solid wood can be calculated and obtained with two kinds of testing liquids.

Dripping the two kinds of testing liquids on the same wood surface, two contact angles (θ_1 and θ_2) would be measured. Because γ_L^d and γ_L^P values of the two testing liquids are known, Eqs. (3) and (4) can be derived by substituting them in Eq. (1):

$$\gamma_{L1}(1+\cos\theta_1) = 2\left(\sqrt{\gamma_S^d\gamma_{L1}^d}+\sqrt{\gamma_S^P\gamma_{L1}^P}\right) \quad (3)$$

$$\gamma_{L2}(1+\cos\theta_2) = 2\left(\sqrt{\gamma_S^d\gamma_{L2}^d}+\sqrt{\gamma_S^P\gamma_{L2}^P}\right) \quad (4)$$

There are a number of specifications for testing liquids when geometric equations are used. First, the testing liquids should not quickly dissolve the testing solids. Second, the viscosity and volatility of the liquids should not be too high. Furthermore, the liquids should have relatively high γ_L values so that the measured contact angles can be kept higher than 10°. In addition, the two testing liquids should present different polarities.

3 Results and discussion

3.1 Surface contact angles of common teak treated by MWP

Figure 1 shows the measured surface contact angles of the wood samples after they were treated at a distance of 80 mm from the reaction chamber. The corresponding data of calculated free surface energy of wood is shown in Table 1.

It is clear from Fig. 1 that significant changes in surface contact angles of our samples were primarily observed from the angles measured with water. It was difficult to observe the treatment effects from the data of surface contact angles of samples measured with glycerin and methylene iodide.

Large changes in both contact angles and free surface energy were observed from the samples which were treated at a distance of 80 mm from the reaction chamber, although a clear, stable trend did not emerge. Particularly, the surface contact angles measured with glycerin decreased about 36%, while those measured with methylene iodide were clearly 22% higher (at 120 s) than those of untreated samples. Ablation and other exceptional phenomena were not observed during the time of treatment. The best MWP treatment effects were obtained when the time of plasma treatment was 210 s and 300 s. Starting after 270 s of treatment, the surface of treated common teak wood became darker with the increase in the length of time of treatment. The color of the samples became black when the treatment time was prolonged to 450 s. This may be caused

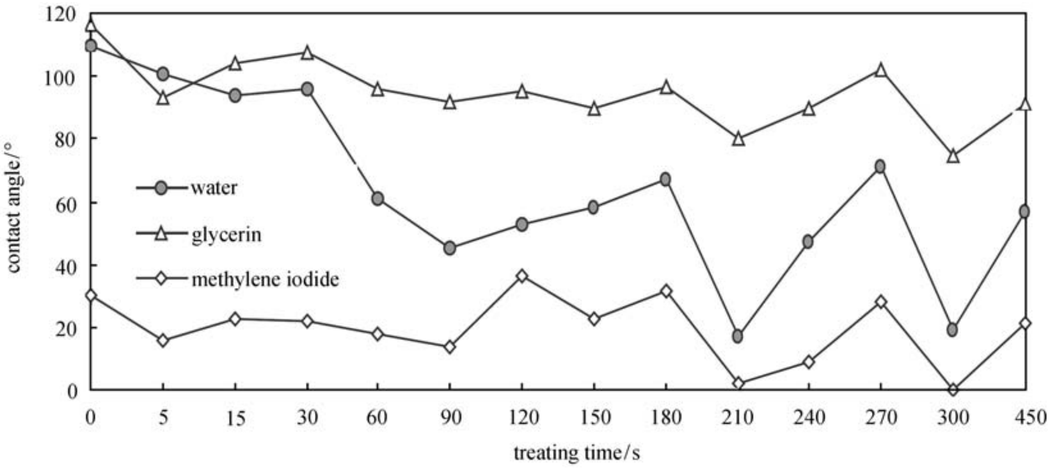

Fig. 1 Effect of time of treatment by MWP on contact angles of common teak at 80 mm distance

Table 1 Effect of MWP treatment on surface wettability of common teak

treating time/s	free surface energy/(MJ·m^{-2})	
	at 80 mm distance	at 120 mm distance
0	51.708	51.708
5	53.465	52.124
15	48.783	47.95
30	49.584	47.033
60	52.218	46.584
90	59.851	48.669
120	51.765	48.087
150	52.481	47.329
180	46.549	56.486
210	–	59.461
240	–	67.143
270	46.592	55.968
300	–	47.536
450	53.006	37.343

by the high temperature of the plasma when the samples were kept at a short treatment distance from the reaction chamber for a longer treatment period.

As can be seen from Table 1, the free surface energy of common teak wood has been calculated for most periods. From the changes in free surface energy, it is clear that this free surface energy did not increase much after being treated for certain periods of time at a distance of 80 mm, but it did decrease considerably at 120 mm distance. From this point of view, it is appropriate to suggest that the improvement of surface wettability of common teak with MWP treatment is a complicated issue. It is very important to select both a proper distance and time of treatment in order to improve the wood surface properties as was expected.

Figure 2 presents the measured surface contact angles of the wood samples after they were treated at a distance of 120 mm from the reaction chamber. The corresponding data of free surface energy of wood is shown in Table 1. It can be seen from Fig. 2 that the modifying effect of MWP treatment at a distance of 120 mm was better than that at 80 mm. The fluctuations of the curves were less and the maximum decrease in contact angles was up to 28% during the first 30 s.

It is clear from Table1 that the amount of free surface energy of treated wood fluctuated with the increase in length of the MWP treatment at a response distance of 120 mm. The free surface energy of the samples being treated for 15 s to 150 s decreased rather than improved. The maximum amount of 67.143 MJ/m^2 was observed on the sample being treated for 240 s. Given our previous research experience with the surface performance of MWP-treated Chinese fir, we extrapolate and suggest that this unconventional phenomenon may have resulted from the intrinsic surface characteristics of common teak.

3.2 Factors affecting wood surface properties

The decreasing trend of contact angles is not obvious for wood surfaces treated only for a short time with MWP. With an increase in the length of time of treatment, only the contact angle measured with water presented a better treatment effect while no clear improvements were observed from the contact angles measured with the other two testing liquids. When the processing time was longer than 300 s, the contact angle measured with methylene iodide was double of that of the untreated sample. It is very difficult to improve surface properties of teak wood significantly with microwave plasma in a short time. In order to achieve enhanced improvement of surface properties by MWP treatment, a longer processing time is required. Simultaneously, the total processing time should be controlled precisely, for the surface performance of

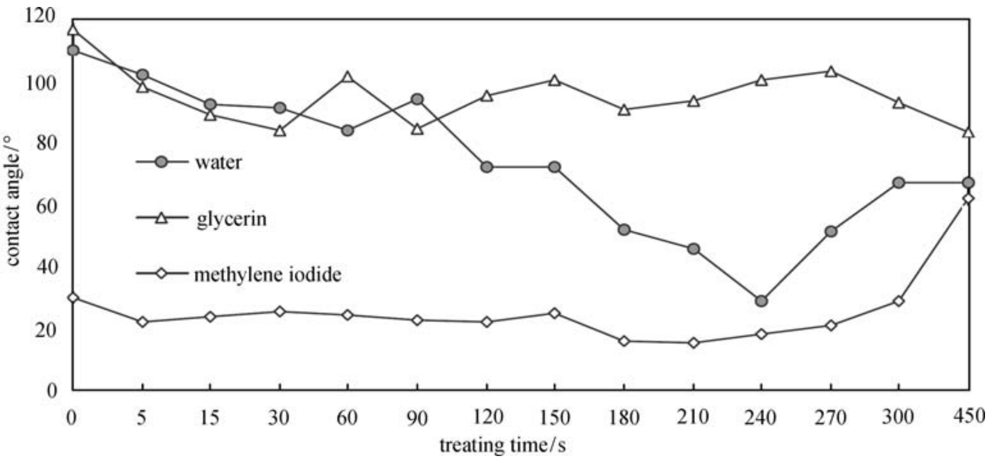

Fig. 2 Effect of time of treatment by MWP on contact angles of common teak at 120 mm distance

wood is likely to be seriously changed if the time cannot be calibrated and controlled within tens of the time required. The contact angles of MWP-treated common teak wood show greater fluctuation at the lower end of the time scale. The etch degree on the wood surface can be seen from its color change after being treated longer than 360 s. At this point, the contact angle of the treated samples was increasing instead of decreasing and the value of the angles may be increased to be double of those of the untreated samples.

3.2.1 Effect of response distance on surface performance of teak wood

Table 2 presents the average of the contact angles of wood with the MWP treatment for 60–300 s at two responding distances (the distance from the specimen to the reaction chamber), as well as the angles of the untreated samples.

As can be seen from Table 2, the longer the reaction distance between the wood samples and resonance cavity, the larger the range of declination of the contact angle of teak wood and the better modification effect achieved. To gain the same treatment effect in a short period of time at a longer reaction distance, a longer response time is required. According to the fluctuation curves of the contact angles, the shorter the reaction distance, the more serious the fluctuation, which may be the result from the consumption of energy and particles in the resonance cavity. During plasma radiation, a part of the plasma energy would have been consumed before the plasma reached the samples if the distance between the samples and the reaction chambers was too long. Therefore, the active functional groups and free radicals were reduced and the contact angles of the treated samples were increased instead of being decreased.

Only when the MWP was seen as a power source and the sample surfaces accumulated enough energy from the plasma and active particles could modification improvement by MWP take place. The energy density of MWP as a power source is inversely proportional to the square of the distance. When the response distance became longer and the energy flow density smaller, a longer response time was required to achieve the same treatment effect. There is an intrinsic relation between reducing the reaction distance and increasing the reaction time. The modification effect of MWP treatment is mainly due to the large number of free radicals and the active groups produced by plasma.

This plasma treatment effect reflected by common teak wood, i.e., the longer response distance that resulted in a better modification effect, was not likely caused by the plasma environment. It was probably caused by the natural properties of the teak wood itself. The methods to improve surface performance of teak wood should be carefully chosen. If the MWP treatment was used, the more appropriate reaction distance and reaction time should be selected, based on repeated experiments.

Table 2 Comparison of average contact angles of teak wood treated and untreated by MWP for 60–300 s

response distance/mm	MWP-treated samples			untreated samples		
	water	glycerin	methylene iodide	water	glycerin	methylene iodide
80	62.94 (43%)	95.86 (18%)	21.29 (29%)	109.64	30.00	116.38
120	48.74 (56%)	90.92 (22%)	17.91 (40%)			

Note: percentage decrease (r) of the angles (in bracks). $r = \frac{a-b}{a} \times 100\%$, where a is the average contact angle of untreated samples and b the average contact angle of MWP-treated samples.

3.2.2 Effect of types of measuring liquid on contact angles of teak wood

Comparing the surface wettability of MWP-treated teak wood measured with the three types of measuring liquids, it is apparent that the contact angles measured with water presented a better modification effect than the angles measured with the other two liquids. The decrease in value of the contact angle measured with glycerol was small and barely changed with the increase of response time. The angles of samples treated with methylene iodide were even higher than those of the untreated samples. A possible explanation is that the plasma particles had an etching reaction with the wood surface, which not only made the wood surface rough but also produced some reactive substances on the wood surface. Those substances could promote water wetting for wood surfaces, but hampered glycerol and methylene iodide wetting of wood surfaces. Thus, the surface contact angles measured with glycerol and methylene iodide increased rather than decreased.

3.2.3 Effect of time of MWP treatment on contact angles of teak wood

The change of contact angles at the two different reaction distances can be seen in Fig. 1. With the increase of reaction time, the value of contact angles became gradually smaller. After reaching a minimum level at a certain moment, the values fluctuated but gradually increased. But on the whole, the trend was decreasing. The reasons for this phenomenon may have something to do with the action of plasma on the surface of the teak wood. At the very beginning when the switch was turned on to produce plasma, the state of the plasma device fluctuated but later became stable. Stable plasma transfers large amounts of energy and exports all kinds of active particles to the surface of wood being treated. In a very short period of time, the fast accumulation of active, functional groups and free radicals on the wood surface sharply decreased the contact angles of the liquid to the wood surface until they reached minimum values. After that, the active functional groups and free radicals produced on the wood surface became gradually saturated over time, so the surface contact angles decreased slowly. When samples continued to be radiated with plasma, the previously accumulated active functional groups and free radicals began to be consumed, which caused the contact angles of the samples to increase instead of to decrease.

4 Conclusions

Based on the results from our investigation, the following conclusions can be drawn: The length of time of the MWP treatment had a significant effect on the surface contact angle of our samples. The contact angles of the treated samples sharply decreased, until they reached a minimum value in a very short period of time, after which they barely changed with an increase in the length of treatment. But, on the whole, the surface contact angles of treated wood decreased when the time of treatment was extended, despite the fluctuations observed (angles measured with methylene iodide provided an exception).

The distance between the sample and resonance cavity had a significant effect on the surface contact angle of samples. The longer the reaction distance between the wood samples and the resonance cavity is, the better the hydrophobic modification effect on wood. The longer the reaction distance is, the longer the response time required for achieving the same treatment effect. MWP treatment can improve wood wettability and decrease its contact angle as the decreasing range of contact angles tested by water could reach 74% at a distance of 120 mm.

The measuring liquids had, to some degree, an effect on the measurement results of contact angles. When the contact angles were measured with water, they presented a better modifying effect than that of measuring with glycerol and methylene iodide.

The improvement of wood surface performance, treated with MWP, was a comprehensive result caused by many factors, such as the intrinsic surface characteristic of the teak wood, the interaction between the wood and plasma, the etching action and the accumulated action of plasma, etc., factors which should be explored in further studies.

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