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Improvements in dimensional stability and lightfastness of wood by butyrylation using microwave heating

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Abstract Microwave heating was used as the heat source for butyrylation of wood with the aim of reducing the reaction time. The photostability and dimensional stability of butyrylated wood were also investigated in this study. Chemical changes of wood were confirmed by cross polarization/magic angle spin ¹³C-nuclear magnetic resonance and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) after butyrylation by microwave heating. Results from DRIFT with the Si-Carb sampling technique revealed that, using microwave heating, a higher degree of butyrylation of maple wood occurred in the middle of the specimen than on the outer surface. The increase in yellowness index of butyrylated wood treated with microwave heating was much less than that of untreated wood after the lightfastness test, indicating that photoyellowing of wood is effectively inhibited by butyrylation using microwave heating. The dimensional stability of wood was also improved after modification.

Key words Wood · Butyrylation · Microwave · Lightfastness · Dimensional stability

Introduction

Conventional heating of wood is a prolonged method by which heat conduction moves from the outside toward the interior. The temperature of the outer layers is usually higher than that of the inner layers. The microwave is an electromagnetic wave whose frequency ranges from about 300 MHz to 300 GHz. The process of microwave heating is opposite to that of conductive heating: Microwave energy is transferred into the material immediately and is absorbed by molecules, causing the molecules to vibrate, converting the electrical energy to heat. The temperature rise of micro-

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wave-heated specimens results from the friction of molecules.^{1,2} Microwave heating is one of the electromagnetic heating methods.

In the past, several studies have been reported on the microwave drying of lignocellulosic materials.^{3,4} The main advantage of microwave drying is the sharp reduction in drying time. Maximal drying rates of wood were at 0.20%–0.45% moisture content per minute when drying was carried out above the fiber saturation point (FSP); below the FSP, the feasible drying rates ranged from 0.1%–0.2% moisture content per minute.⁵ The properties of wood are readily impaired if the output power of the microwave oven is too high (above 800 W).⁶

Instead of conventional heating, microwave heating has also been applied to the chemical modification of wood.⁷⁻⁹ Chemical modifications efficiently protect wood from environmental degradation, such as photodegradation and fungal decay.¹⁰⁻¹² They also improve the dimensional instability induced by changes in environmental humidity.^{13,14} The procedures and reactions associated with chemical modifications have been reported.^{15,16} Some modifications require a longer heating time to obtain a certain reaction, which may have a negative effect on the quality of the final product. Using microwaves as the heating source significantly reduces the reaction time. In one study antioxidantbearing isocyanate groups were grafted on wood by microwave activation without the need for a catalyst.⁷ The penetration depth of the microwave at 2450MHz is about 10 cm.⁸ Acetylation of wood using microwave heating did not cause any adverse effects when the output power was about 500 W.⁹

In contrast to acetylation, the effects of butyrylation on the properties of wood have not been studied extensively.^{16,17} Using conventional heating for 12h, butyrylated wood exhibited better stability against photodegradation than acetylated wood, as noted in a previous paper.¹⁸ To shorten the reaction time, therefore, we attempted to achieve butyrylation by means of microwave heating. The study was performed in four parts. We determined (1) the influence of the dipping time and microwave heating time on the weight gains of treated specimens; (2) the depth

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profile of butyrylated specimens using microwave heating by infrared spectra with the Si-Carb sampling technique; (3) the color variations of butyrylated specimens using microwave heating after the lightfastness test; and (4) the dimensional stability of butyrylated wood.

Experimental

Wood specimens

China fir (*Cunninghamia lanceolata* var. *lanceolata*) and maple (*Acer* sp.) specimens, measuring $3 \times 3 \times 1$ cm (longitudinal × radial × tangential), were extracted in a Soxhlet apparatus with alcohol/toluene (1:2, v/v) for 24h, followed by leaching in running water for 12h. They were then oven-dried at 105°C for 24h.

Butyryaltion of wood by microwave heating

Extractive-free wood blocks were immersed in neat butyric anhydride liquid for 10, 20, and 30 min with vacuum treatment (at 10 mmHg). After the immersion treatment, the wood blocks were transferred to a microwave-use case and placed in the microwave oven (SM1210; Sunpentown). The frequency of the microwave oven was 2450 MHz, and its output power was 250 W during the treatment. The specimens were heated for 3 and 6 min, respectively. After the microwave treatment, the specimens were subjected to Soxhlet extraction with alcohol/toluene (1 : 2, v/v) for 24 h to remove unreacted anhydride and then oven-dried.

CP/MAS ¹³C-NMR analysis

Solid-state cross polarization/magic angle spin (CP/MAS) ¹³C-nuclear magnetic resonance (¹³-NMR) spectra were obtained by the Bruker DMX-300 Fourier transform (FT)-NMR spectrometer at a frequency of 75.47 MHz. The acquisition time was 0.035 s, the relaxation delay 7 s, and the spectral width 22.7 kHz. Chemical shifts were calculated relative to tetramethylsilane (TMS) for spectrometer control.

FTIR analysis

Fourier-transform infrared (FTIR) spectra were obtained using a Bio-rad spectrometer (FTS-40) incorporating a Spectra Tech diffuse reflectance accessory unit. Depth profiles of treated specimens were analyzed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy with the Si-Carb sampling technique. The sampling method used Si-Carb abraders to obtain samplings from various areas of the specimens.¹⁹ The sampling areas of a specimen are shown in Fig. 1. Wood meals at the various points of treated specimens were scraped using the Si-Carb abraders. The spectral resolution was 4 cm⁻¹ and the scanning range 400–4000 cm⁻¹.



Fig. 1. Sampling areas of the specimen for depth profiling of butyrylated wood. *Small filled circles* in the specimens indicate the sampling position

Ultraviolet light irradiation

The accelerated lightfastness test of specimens was conducted in a QUV lightfastness tester (Q-Panel Co.) equipped with UVA-351 fluorescent lamps. The UVA-351 fluorescent lamp is recommended for simulating sunlight filtered through window glass. It operates over a range of 315–400 nm with a peak emission at 351 nm. The temperature of the black panel was $60^{\circ} \pm 2^{\circ}$ C.

Color measurement

The surface color changes of specimens were measured using a Jasco model 550 UV-VIS spectrophotometer equipped with an integrating sphere. Tristimulus values X, Y, and Z of all the specimens were derived from the spectral reflectance curves. Using the CIE L*a*b* system (Commission Internationale de l'Eclairage, 1976), the yellowness index (YI) and yellowness index difference (ΔYI) of the specimens were calculated with the following formulas. Results were mean values from two replicate specimens.

$$YI = 100(1.28X - 1.06Z)/Y$$

 $\Delta YI = YI_{.} - YI_{0}$

When YI_t is the yellowness index of irradiated specimen; and YI_0 is the yellowness index of nonirradiated specimens.

Bulking coefficient

The bulking coefficient (BC) was calculated using Eq. (1).

$$BC(\%) = \left| \left(V_{\rm t} - V_{\rm u} \right) / V_{\rm u} \right| \times 100 \tag{1}$$

where V_t and V_u are the oven-dried volumes of wood after and before modification, respectively. Results were mean values from three replicate specimens.

Antiswelling efficiency

The antiswelling efficiency (ASE) was measured by the water-soaked method reported by Rowell and Tillman.¹³ The volumetric swelling coefficient (S) and the ASE were



Fig. 2. Weight gains of butyrylated China fir wood with various dipping times and microwave times. *Open bars*, after 3 min of microwave heating; *Striped bars*, after 6 min of microwave heating

calculated according to Eqs. (2) and (3). Triplicate specimens were run, and the values were averaged.

$$S(\%) = \{(V_{\rm w} - V_{\rm o})/V_{\rm o}\} \times 100$$
 (2)

where $V_{\rm w}$ is the volume of water-saturated wood; and V_0 is the volume of oven-dried wood.

$$ASE(\%) = \{(S_{c} - S_{t})/S_{c}\} \times 100$$
 (3)

where S_c and S_t are the volumetric swelling coefficients of untreated and modified wood, respectively, after the water-soaking test.

Results and discussion

Influence of dipping time and microwave time on the weight gain of butyryated wood

Weight gains of butyrylated China fir wood when treated with various dipping times and microwave heating times are shown in Fig. 2. After 10 and 30 min of dipping treatment followed with 3 min of microwave heating, weight gains of China fir wood were 10.6% and 18.6%, respectively. The weight gain of specimens increased with the increase in dipping time. The weight gains of specimens are also increased with the microwave heating time. The weight gains of specimens treated with 6 min of microwave heating are slightly higher than those treated with 3 min of microwave heating with the same dipping time. Butyrylation of wood by the conventional heating requires several hours to attain a certain degree of weight gain.^{12,18} Microwave heating can greatly reduce the reaction time of butyrylation. Further investigations are required to determine the influence of the output power of the microwave oven and the temperature on the butyrylation of wood using microwave heating.



Fig. 3. Cross polarization/magic angle spin ¹³C-nuclear magnetic resonance spectra of butyrylated China fir wood

Chemical changes and depth profiling of butyrylated wood by microwave heating

Figure 3 shows the solid-state CP/MAS ¹³C-NMR spectrum of butyrylated China fir wood [weight gain (WG) 21.5%]. The relative intensity of the 61.2 ppm band, which is the absorption of the C-6 position in the amorphous cellulose component,²⁰ decreased after the wood was treated with butyric anhydride. In addition to the amorphous C-6 position, the decreased intensity of the 73.4 ppm band indicated that a small reaction also occurred at C-2 positions of holocelluloses. The appearance of the 12.8ppm of treated specimen arises from the methyl group (CH_3) . The appearances of the 17.6 and 35.1 ppm bands of the treated specimen arise from the methylene group (CH_2) and the methylene group adjacent to the carbonyl group ($\underline{C}H_2C=O$), respectively. The intensity of the 171.2 ppm (C=O) band was also increased. Data from the spectrum revealed clearly the reaction sites in the holocelluloses and the formation of the butyryl groups after treatment.

Weight gains of butyrylated China fir and maple wood specimens, treated with 30min of dipping and 6min of microwave heating, were 21.5% and 10.6%, respectively. The depth profile of the reaction of butyrylated wood using microwave heating was analyzed by DRIFT spectroscopy with the Si-Carb sampling technique. Figure 4 shows the IR spectra at various depths along the tangential direction of butyrylated China fir wood treated with microwave heating. Relative to the untreated specimen (Fig. 4, curve d), the intensities of carbonyl absorption peak bands (1740 cm^{-1}) and C-O absorption bands (1170 and 1270 cm⁻¹) were increased in curves a, b, and c of Fig. 4. The intensities of the CH₂ bands (1460, 2877, and 2937 cm⁻¹) and CH₃ absorption bands (1373, 2910, and 2966 cm⁻¹) in the spectra of treated specimens were also enhanced, and the decreased intensity of the O-H absorption band (3430 cm⁻¹) revealed that the hydroxyl group content is reduced. These results confirmed further that parts of the hydroxyl groups of wood were replaced by the butyryl groups after butyrylation using microwave heating.

The intensity of the aromatic skeletal vibration at 1510 cm^{-1} remains relatively unchanged (Fig. 4) and is therefore used as an internal standard for calculating the relative intensity ratios of the carbonyl absorption peak

 (1740 cm^{-1}) . The relative intensity of the carbonyl group at various locations of treated wood can be used to judge the degree of butyrylation in this study. The relative intensity ratio at 1740 cm⁻¹ to 1510 cm⁻¹ for untreated China fir wood was only 0.24 (Table 1). For the three layers along the tangential direction of butyrylated China fir wood, the relative intensity ratios at 1740 cm⁻¹ to 1510 cm⁻¹ were 2.41 (surface layer), 2.55 (quarter layer), and 2.77 (middle layer), respectively. It is clear that the relative intensity of the carbonyl group of treated specimens increased with the depth from the outer surface toward the middle. With microwave heating, the reaction that occurred in the middle of the specimen had the highest degree of butyrylation among all three layers along the tangential direction. The higher butyryl group content presumably results from the higher temperature in the inner portion of wood during



Fig. 4. Infrared spectra at various depths of butyrylated China fir wood treated with microwave heating along the tangential direction. a, middle layer of treated specimen; b, quarter layer of treated specimen; c, surface layer of treated specimen; d, untreated specimen

the process of microwave heating. The result is consistent with that of acetylation of wood using microwave heating.⁹

The intensity of the carbonyl group of treated maple wood increased with the increase in depth from the outer surface toward the middle. The relative intensity ratios at 1740 cm^{-1} to 1510 cm^{-1} of butyrylated maple wood were 2.93 (surface layer), 3.29 (quarter layer) and 3.97 (middle layer), respectively (Table 1). In the tangential direction, the higher degree of butyrylation of maple wood using microwave heating also occurred in the middle of the specimens.

To examine the depth profiles of butyrylated wood along the longitudinal direction, the relative intensities of the carbonyl groups at various longitudinal depths of treated specimens were calculated, as shown in Table 1. For the butyrylated China fir wood, the relative intensity ratios (I_{1740}/I_{1510}) of the end, quarter, and middle positions were 2.04, 2.24, and 2.77, respectively. Similar to the results obtained in the tangential direction, a higher relative intensity for the carbonyl group was observed in the middle position of the specimens along the longitudinal direction.

Lightfastness of butyrylated wood

As a consequence of absorbing light, wood is definitely degraded by ultraviolet (UV) light. After further photochemical reactions of the components in wood, the aesthetic characteristics and the physical and chemical properties of wood changed significantly.²¹ Acetylation has proven to be effective protection against photodegradation,^{10,22} but the effectiveness of reducing wood photoyellowing by butyrylation was superior to that achieved by acetylation.¹⁸

Figure 5 shows the yellowness indices (YI) of control and butyrylated wood treated with microwave heating after 24 days of irradiation. Without any proper protection, photoyellowing occurred readily on the surface of the wood. After 24 days of irradiation, the yellowness index (YI) of untreated China fir wood changed from 47.6 to 98.0. After subtracting the YI of nonirradiated China fir wood from the YI of 24-day irradiated wood, the value for the YI difference (Δ YI) was 50.4 units. After butyrylation via microwave heating, the Δ YI of treated China fir wood (WG 21.5%) was significantly reduced to 6.9 units after 24 days of irradiation. The values for the Δ YI of untreated and butyrylated (WG 10.6%) maple woods were 33.5 and 3.7 units, respectively. These results demonstrated that photoyellowing of wood is markedly reduced by

Table 1. I_{1740}/I_{1510} values of different depths of butyrylated wood along the tangential and longitudinal directions

Species	Control	Along the tangential direction of treated wood			Along the longitudinal direction of treated wood		
		Surface	Quarter ^a	Middle	Surface	Quarter ^b	Middle
China fir Maple	0.24 1.89	2.41 2.93	2.55 3.29	2.77 3.97	2.04 3.43	2.24 3.63	2.77 3.97

^a At 0.25 cm from the outer surface toward the middle in the tangential direction

^bAt 0.75 cm from the end surface toward the middle in the longitudinal direction



Fig. 5. Yellowness indices of butyrylated wood treated with microwave heating after 24 days of irradiation. *Open bars*, nonirradiated; *Striped bars*, irradiated

butyrylation, consistent with the results reported in our previous study.¹⁸ With a shorter reaction time (6 min) of microwave heating, the commendable stability of butyrylated wood to light can be obtained, similar to specimens treated with conductive heating with a longer reaction time (12 h). The sharply reduced reaction time using microwave heating makes butyrylation of wood feasible for industrial applications.

Dimensional stability of butyrylated wood

The volume of the specimen increased after the reaction. It was reported that the volume increase was due to the volume occupied by the reagent and a void volume created within the wood matrix.^{14,17} The dimensional stability of butyrylated wood was evaluated by the water-soaked method, and the antiswelling efficiencies of specimens are shown in Table 2. After butyrylation the volumetric swelling coefficient of treated wood was greatly reduced owing to the decrease in the reversible swelling of wood during the water-soaked test. The antiswelling efficiency increased with the WG of treated wood; the antiswelling efficiency of specimens with higher WGs (21.6%) was 76.8%. The dimensional stability of wood was greatly improved by the butyrylation treatment.

Conclusions

Butyrylation of wood is efficiently carried out in a short reaction time using microwave heating. With the appropriate microwave treatment, modification of the wood does not cause any adverse effects. Based on analyses using the DRIFT with Si-Carb sampling technique, the degree of butyrylation in the inner part of a specimen is higher than that on the surface. The dimensional stability of wood was greatly improved by butyrylation. Meanwhile, photoyellowing of wood was significantly inhibited by butyrylation using microwave heating, similar to that achieved with conventional heating.

Table 2. Bulking effect, volumetric swelling coefficients, and antiswelling efficiencies of butyrylated China fir wood

Treatments	WG (%)	BC (%)	Water-soaked test		
			S (%) ^a	ASE (%)	
Control Butyrylation Butyrylation	- 14.65 21.64	- 11.45 11.58	$\begin{array}{c} 14.11 \pm 0.35 \\ 4.76 \pm 0.06 \\ 3.28 \pm 0.10 \end{array}$	- 66.27 76.77	

^aResults are means \pm SD

BC, bulking coefficient; *S*, swelling coefficient; ASE, antiswelling efficiency; WG, weight gain

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