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Modification of the properties of wood via combination of treatments: Freeze treatment and silicone oil heat treatment - Part 2

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Abstract

The effects of freeze-silicone oil heat treatment (combination of treatments) on the chemical properties of wood were investigated using fourier transform infrared (FTIR), X-ray diffractometer (XRD) and thermogravimetric analysis (TGA). Results obtained showed that the impact of combine treatments on the wood was positive. FTIR results showed apparent changes in the chemical composition of the treated wood, XRD results indicated relative increase in the crystallinity index of the treated wood compared to the untreated and TGA showed reduction in the weight loss of the treated as compared with the untreated wood samples.

Keywords crystallinity index, freeze treatment, silicone oil heat treatment, x-ray diffraction, wood

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Introduction

In part 1 of this paper, we reported effects of combination of treatments on the physical properties of the wood. It was indicated that chemical changes in the biopolymer components of the cell wall could fully account for the changes observed in the hygroscopicity of the wood material [1]. A literature review indicated that thermal modification of wood was not adequate enough to ensure resistance against different biodegrading agents [2]. It is expected that additional treatment by combination of treatments would improve wood performance.

The influence and mechanisms of thermal degradation process and rearrangement of biomolecules under combined treatments condition, with regard to changes in the chemical structure have not been fully characterized and understood. However, several works have reported that changes in the chemical composition and wood structure in thermal processes are caused by the degradation of hemicelluloses, cellulose and lignin which directly influences the physical and chemical properties of the wood [3-7]. In this paper fourier transform infrared (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were utilized to track the variations in chemical structures under freeze treatment combined with silicone oil heat treatment.

These results will promote the understanding of the effects and mechanism of thermal degradation combined with freezing condition and also provide a scientific basis for the development of environmentally friendly wood products that may have the potential to substitute the wide use of toxic chemical preservatives for wood. No previous studies have used freeze treatment in combination with silicone oil heat treatment to modify *Firmiana simplex* wood. This study provide information on combined

effects of freeze– silicone oil heat treatment in the chemical structure of F. simplex wood.

Methodology

Materials

Plantation grown Chinese parasol (*Firmiana simplex* L.) trees were obtained from Fuzhou, People's Republic of China (26°04'34"N119°18'23"E). Five trees were selected in accordance with the American Society for Testing and Materials Standard [8]. Silicone oil was purchased from Chemicals Reagent Beijing Company Limited, Beijing - People's Republic of China. The dimension of the wood samples obtained from the sapwood were 60 × 60 × 80 mm (Radial × Tangential × Longitudinal). Prior to treatments, samples were conditioned in a climate chamber at 65±5% relative humidity (RH) and temperature of 20±2°C to stabilize the moisture and other were immersed in water to avoid water loss prior to freeze treatment.

Methods

Freeze-silicone oil heat treatment

Freeze-silicone oil heat treatments were performed as shown in Table 1. Ten samples were frozen from room temperature (21.5°C) to -22°C with an average cooling rate of 0.07°C. min^{-1}. The freezing rate ranged from the temperature of freezing water (~3°C) to the final freezing temperature (~22°C). The treatment time was 50h and measured after temperature was stabilized at -22 °C. All freeze treated samples were allowed to defrost, then oven-dried at 60°C to ~12% moisture content.

Silicone oil heat treatment was carried out in a closed chamber using oil bath. Silicone oil served as a medium of heat transfer. Samples were immersed in a pre-heated oil bath at 150, 180 and 210 °C. The heat treatment started immediately after the desired high-temperature was reached and samples were thermally treated for 4 h. After the treatment process, all the samples were wiped, cooled in a silica gel desiccator and kept in a climatic chamber (20 °C and 65% RH).

Table 1. Freeze - silicone oil heat treatment parameters

	Freeze treatment			Silicone oil heat treatment		
Treatment	**Condition**	**Temperature (°C)**	**Time (h)**	**Condition**	**Temperature (°C)**	**Time (h)**
Untreated	-	-	-	-	-	-
FT	Wet	-22	50	-	-	-
FSOH150	Wet	-22	50	Climate chamber (20°C and 65%)	150	4
FSOH180	Wet	-22	50	Climate chamber (20°C and 65%)	180	4
FSOH210	Wet	-22	50	Climate chamber (20°C and 65%)	210	4
SOH150	-	-	-	Climate chamber (20°C and 65%)	150	4
SOH180	-	-	-	Climate chamber (20°C and 65%)	180	4
SOH210	-	-	-	Climate chamber (20°C and 65%)	210	4

T: Freeze treatment, FSOH: Freeze-silicone oil heat treatment, SOH: silicone oil heat treatment

Determination of chemical properties

Fourier transform infrared (FTIR) analysis

The untreated and freeze-silicone oil heat treated samples were ground into powder for chemical composition analysis. Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 380 FTIR spectrophotometer (Thermo Electron Instruments Co., Ltd., USA). The spectra were measured in transmittance for 32 scans at resolution of 4 cm^{-1} in the range of 4000-500 cm^{-1}. The background spectra were corrected before the tests.

X-ray diffraction (XRD) analysis

The crystalline structures were analyzed using Rigaku Ultima IV X-ray diffractometer (XRD) to determine the amorphous and crystalline peaks of the untreated and freeze-silicone oil heat treated samples. Measurement was taken at 2θ range from 5-45^{o} in reflection mode with a scanning rate of 2^{o} min^{-1} at 40kV and electric current 40 mA, using a computer-controlled wide angle goniometer coupled to a sealed-tube source of nickel filtered CuKα radiation. The relative degree of crystallinity (C_rI) was calculated according to equation (1) [9].

$$C_rI = (I_{200} - I_{non-cry})/I_{200} * 100 \quad \ldots\ldots\ldots\ldots 1$$

Thermogravimetric analysis (TGA)

The thermogravimetric properties of the untreated and freeze-silicone oil heat treated samples were investigated using the NETZSCH 44 thermogravimetry machine. The thermo grams were recorded between the temperatures 25℃ and 700℃ at the heating rate of 5^{o}C/min in a nitrogen environment using 20 ml/min flow rate. The statistical program used for these analyses was Origin Pro 8.

Results and Discussion

Fourier transform infrared spectroscopy (FITR) of the untreated and freeze-silicone oil heat-treated wood samples are presented in Figure 1. The treated wood showed apparent changes in the chemical composition of the cell wall and the peak at 3400 cm-1 represents – OH bond that affects the dimensional stability of the wood. The peak at 2958 cm^{-1} denotes the aliphatic C-H vibration peak which is the characteristic peak of cellulose [10]. The wavelength 1723 cm^{-1} referred to non-conjugated ketone C=O in hemicelluloses. The wavelengths 1622 cm^{-1} and 1532 cm^{-1} are related to the characteristic peak in lignin [11-12]. The wavelength at 1266 cm^{-1} is ascribed to C − O group in lignin, which suggest the loss of acetyl groups and has linkages with cellulose and hemicelluloses [13]. The band at 784 cm^{-1} is assigned to C-H linkages present in β-glycosides. Table 2 shows the typical bands found in the wood after subjection to combined treatments. FTIR spectroscopy shows that cellulose, hemicellulose and lignin components of the wood were affected due to freeze- silicone oil heat treatments applied in this study. X-ray diffraction (XRD) diffraction patterns of the treated and freeze-silicone oil heat treated wood is shown in Figure 2. The crystal structure of cellulose in the treated wood is similar and corresponded to the typical cellulose I pattern because both the diffraction peaks at 2θ=16.02 ^{o}C and 22.32 ^{o}C could be observed in all three diffraction profiles [14]. This indicates that the freeze-silicone oil heat treatment applied in this study did not change the crystal structure of the wood. Though the relative crystallinity of treatments may differ from each other. The intensity of diffraction peak at 34.62 ^{o}C was stable and may be interpreted as the glucan chains of cellulose that are largely unaffected [15]. Crystallinity is the major factor that influences the mechanical and dimensional properties of wood-based materials [16]. The influence of combined treatments on the components of the wood and on the crystallization behaviour of cellulose could be reflected through calculating the crystallinity index of the wood (Table 3).

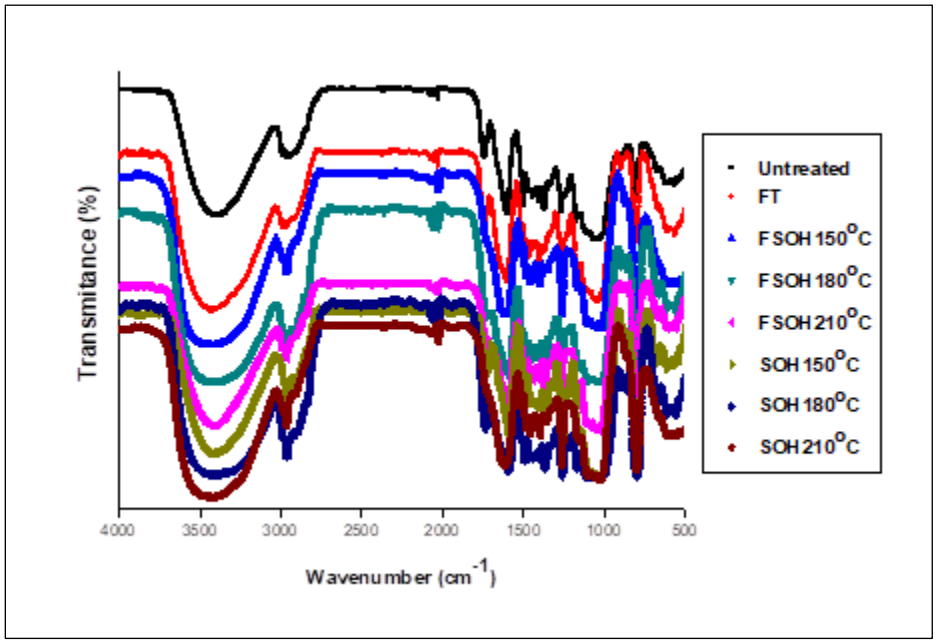

Figure 1. ATR-IR spectra of untreated and freeze-silicone oil heat treated wood

Table 2. Typical bands assignment of FTIR of untreated and freeze-silicone oil heat treated *Firmiana simplex*

Wave Number (cm^{-1})	Functional Group	Chemical Composition
3400	O-H Stretching Vibration	Cellulose
2958	C-H Stretching Vibration	Cellulose
1723	C=O Stretching Vibration	Hemicellulose
1622	Aromatic Carbon Stretching Vibration	Lignin
1532	Aromatic Carbon Stretching Vibration	Lignin
1266	G-Ring and Acyloxy C-O Stretching Vibration	Lignin
784	C-H Stretching Vibration	Cellulose

On comparison with the untreated samples, freeze-silicone oil heat treated samples showed slightly increased crystallinity (Table 3). The degradation of hemicelluloses, lignin and extractives resulted in a relative increase in cellulose content, which could contribute to the relative increase in crystallinity [16]. It should be noted that both the hemicellulose and lignin has amorphous; while cellulose has both amorphous and crystalline regions.

Figure 3 shows the representative thermogravimetry of the untreated and freeze-silicone oil heat treated wood. Figure 3a presents three major weight losses that occurred at 110, 350 and 600 ℃. The weight loss at 110 ℃ for the untreated samples was attributed to moisture content and other volatiles in the samples, whereas in case of the freeze-silicone oil heat treated samples lesser mass loss was observed. This implies that the moisture content and other volatiles of the treated samples were reduced by the combination of treatments.

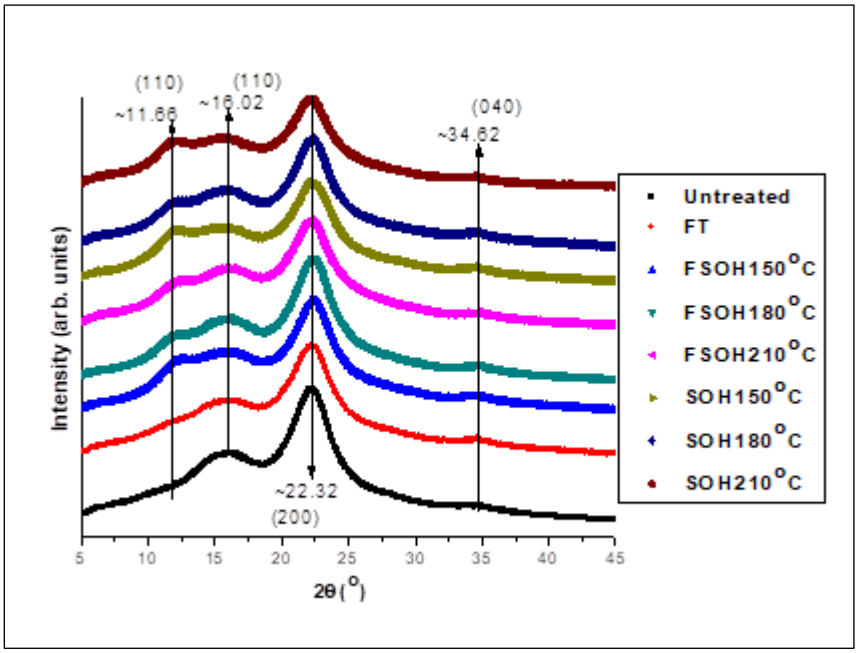

Figure 2. X-ray diffractogram of untreated and freeze-silicone oil heat treated wood

Table 3. Crystallinity index of untreated and freeze-silicone oil heat treated wood

Treatment	I_{am} (2θ =18.50)	I_{200} (2θ = 22.32)	C_rI (%)
Untreated	165642	287375	42.36
FT	153850	270697	43.17
FSOH150 °C	153317	276475	44.55
FSOH180 °C	147367	291883	49.51
FSOH210 °C	152450	277058	44.98
SOH150 °C	138833	255733	45.71
SOH180 °C	140642	267800	47.48
SOH210 °C	138975	249592	44.32

The second mass loss occurred at 350 °C and was 40% for the untreated samples and much higher in the treated samples at various treatments. This reveals that the combination of treatments have affected the thermogravimetry properties of the wood. High mass loss obtained in the untreated samples with regards to the freeze-silicone oil heat treated samples could be attributed to the differences in thermal degradation of the cellulose crystal present in the wood. Figure 3b shows the rate of mass losses in both the untreated and freeze-silicone oil heat treated samples.

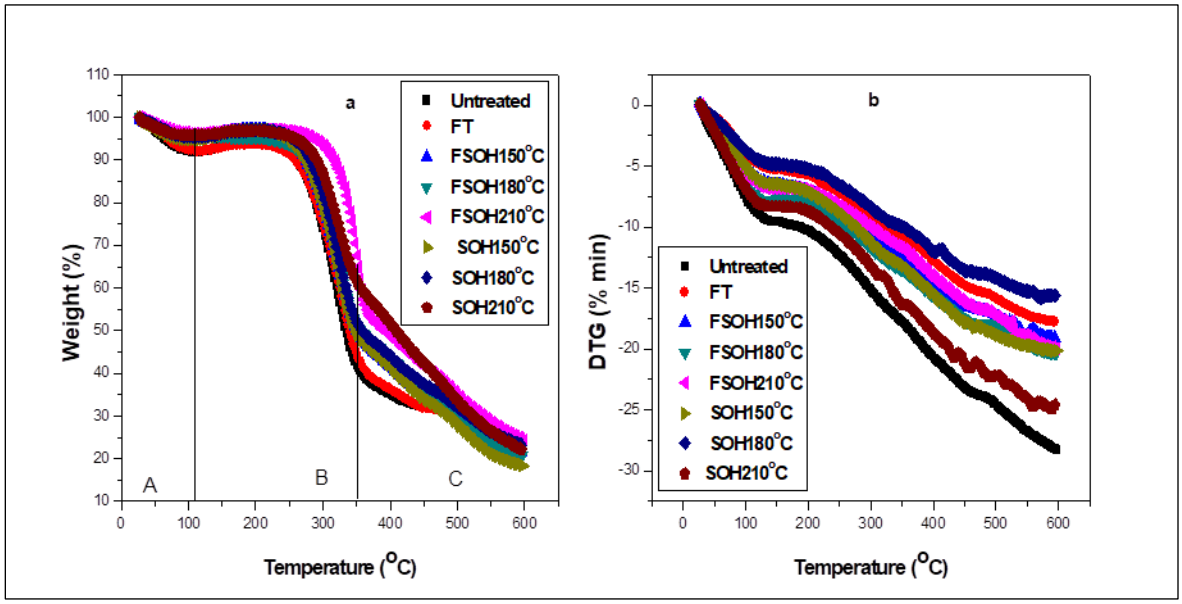

Figure 3. (a) Thermogravimetric (TG) (b) derivative thermogravimetric (DTG) curves of untreated and freeze-silicone oil heat treated wood

Conclusion

The work highlights the effects of combination of treatments i.e. freeze – silicone oil heat treatment on some chemical properties of *Firmiana simplex* wood and the following conclusions were drawn.
1. The combined treatment modified the chemical composition of the wood as evident by the Fourier Transform Infrared (FITR) spectra.
2. The combined treatments modified the microstructural properties of the wood as evident by the crystallinity indexes obtained.
3. The combined treatments modified the thermogravimetry properties of the wood by reducing the weight losses and rate of thermal degradation.

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