

Thermal Treatment of Poplar Hemicelluloses at 180 to 220 °C under Nitrogen Atmosphere

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Hemicelluloses were separated from poplar wood and exposed to thermal treatment. Changes in chemical content were investigated from 180 °C to 220 °C in a nitrogen atmosphere. Fourier transform infrared spectroscopy, X-ray diffraction, and differential thermal gravimetric analysis were used to characterize the hemicellulose before and after the thermal treatment. The effects of temperature on hygroscopicity and color were measured. The results showed that hemicelluloses were sensitive to temperature. β -glucosidic bonds and side chains in hemicelluloses were cleaved around 180 °C, and the increased temperature promoted the breaking process. Esterification reactions happened during the treatment. When the treatment temperature reached 220 °C, all side chains broke down, and partial carbonization occurred. Therefore, the color became darker, and the hydrophobicity increased. This study could help to explain the changes in wood that occur during thermal treatment.

Keywords: Poplar hemicelluloses; Thermal treatment; Characterization; Color; Hydrophobicity

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INTRODUCTION

Wood is a complex polymeric material that consists of cellulose, hemicellulose, lignin, and other components such as extractives and minerals (Pasangulapati *et al.* 2012). The dimensional stability of wood becomes worse in wet conditions, which results in swelling of the wood and increases the risk for degradation by wood decay fungi. Thermal treatment, usually controls wood constituents without the use of oxygen (to avoid oxidation) and is carried out in the range 200 to 260 °C; this treatment gives the wood new physical, chemical, and mechanical properties (Turner *et al.* 2010), and is an effective method to reduce hygroscopicity, improve dimensional stability, and resist fungal decay (González-Peña *et al.* 2009; Šušteršič *et al.* 2010). This treatment provides potential for the outdoor application of wood. In the thermal treatment process, complicated chemical changes occur for wood components, such as carbohydrate degradation, lignin degradation, and condensation. Hemicellulose is the most sensitive component of wood during heat treatment. Hemicellulose is a branched polymer composed of sugar monomers, such as glucose, xylose, mannose, arabinose, galactose, and uronic acid (Cheng *et al.* 2010; Gírio *et al.* 2010). Research on hemicellulose has focused on the extraction, separation, chemical derivation, hydrothermal treatment, or carbonization for energy-related applications (Schlesinger *et al.* 2006; Brienzo *et al.* 2009; Egüés *et al.* 2011; Kang *et al.* 2012; Liu *et al.* 2013). The chemical changes have been reported for hemicelluloses in terms of mass loss (Bremer *et al.* 2013). To date, there has been no report on the structure change during heat treatment.

In this work, hemicelluloses were extracted from poplar wood powder and heat-treated at 180 °C, 200 °C, or 220 °C for 4 h in a nitrogen atmosphere. The thermally treated hemicelluloses were analyzed by using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and differential thermal gravimetric (DTG) analysis. The hygroscopicity and chroma of the treated wood were also investigated.

EXPERIMENTAL

Holocellulose Preparation Procedure

Populus tomentosa Carrière flour (40 to 60 mesh) was extracted by water and a benzene/ethanol mixture according to standards GB/T 2677.4 (1993) and GB/T 2677.6 (1994). Holocellulose was prepared according to GB/T 2677.10 (1995) for the further preparation of hemicellulose.

Hemicelluloses Preparation Procedure

Hemicelluloses were prepared according to the following process: 2 g of holocellulose was added to 30 mL of 10% KOH and stirred for 20 min at 25 °C. The mixture was filtered with G2 sintered discs, washed with 20 mL of 10% KOH, and filtered again. The sample was treated in 45 mL of 18% NaOH and stirred for 20 min at 25 °C. After being filtered, the sample was washed with 20 mL of 18% NaOH. The pH value of the filtrate was adjusted to 5.0 with glacial acetic acid, and a double volume of 95% ethanol solution was added. Hemicelluloses were obtained after the solution was centrifuged and washed twice sequentially by 80% ethanol solution, 100% ethanol, and 100% ether. Finally, the obtained hemicelluloses were dried in a vacuum drying oven (Ren *et al.* 2008).

Thermal Treatment

The hemicelluloses were treated at 180 °C, 200 °C, and 220 °C for 4 h in a nitrogen atmosphere. Hemicelluloses were first heated at 60 °C for 1 h to balance the temperature. The temperature was raised to 100 °C at the rate of 2 °C/min, and nitrogen was flowed in at the rate of 200 L/h. The temperature was raised to the required temperature at the rate of 2 °C/min and maintained for 4 h. Finally, the heating power was shut off, and the samples were removed when the temperature in the treatment device decreased to 80 °C.

Characterization and Measurements

To analyze the color changes of the samples, chroma values were tested before and after treatment by a colorimeter (Model CM-2600d, Konica Minolta, Tokyo, Japan). The changes in functional groups were characterized by ATR-FTIR (model MAGNA-IR560, Thermo Nicolet, Waltham, MA, USA) from 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 0.1 cm⁻¹. The crystal structures of the samples were analyzed by XRD (model D/MAX-3B, Rigaku, Tokyo, Japan). The thermal stability of all the samples was measured on a TGA-Q5000 instrument (TA Instruments, New Castle, DE, USA) at the rate of 10 °C/min from 30 °C to 600 °C. The equilibrium moisture content was measured gravimetrically after conditioning for 2 h at 25 °C in 75% relative humidity and each sample was tested for 5 replicates to obtain the average value.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectrum of the pristine hemicelluloses obtained in this study is shown in Fig. 1(a). The bands at 3300 to 3400 cm^{-1} and 2930 to 2850 cm^{-1} are attributable to $-\text{OH}$ stretching and the $-\text{CH}$ bond deformation of $-\text{CH}_2$ groups, respectively. The band at around 1408 cm^{-1} is due to the $-\text{CH}$ and $-\text{OH}$ groups bending (Sun *et al.* 2000). The presence of xylans was found at 1034 to 1040 cm^{-1} (Egüés *et al.* 2013). The band at 895 cm^{-1} is due to β -glucosidic linkage between monosaccharides (Lv and Wu 2012). The characteristic band of uronic acid occurred at 1598 cm^{-1} (Sun *et al.* 2014). After thermal treatment, some changes can be found in the FTIR spectra, as shown in Fig. 1(b, c, d). The bands of $-\text{OH}$ stretching, $-\text{CH}$ bond deformation, and characteristic peaks of xylans, β -glucosidic linkage, and uronic acid became weaker by increasing the treatment temperature. On the contrary, a new band at around 1722 cm^{-1} (ester bond) appeared and became stronger with treatment temperature increasing from 180 $^{\circ}\text{C}$ to 220 $^{\circ}\text{C}$. Those results indicate β -glucosidic bonds and side chains in hemicelluloses cleaved. Higher temperatures accelerated the breaking process. Simultaneously, esterification reactions occurred between uronic acid and $-\text{OH}$ groups.

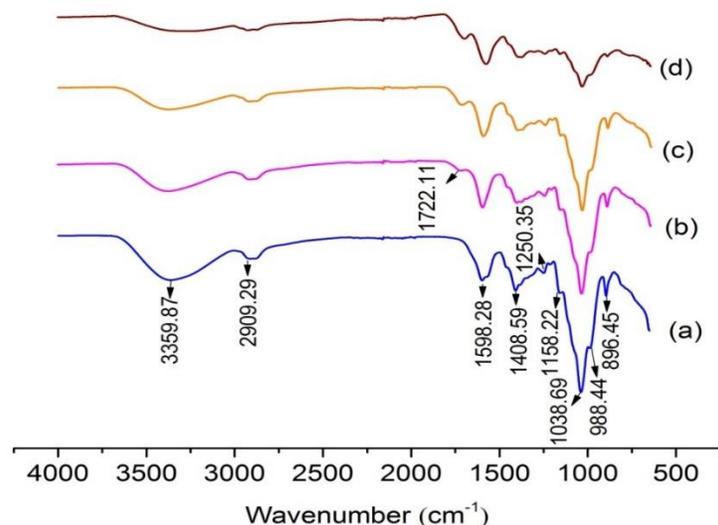


Fig. 1. FTIR spectra of pristine hemicelluloses (a), treated hemicelluloses in 180 $^{\circ}\text{C}$ (b), 200 $^{\circ}\text{C}$ (c), and 220 $^{\circ}\text{C}$ (d) for 4 h

XRD Analysis

The XRD patterns of the hemicelluloses before and after thermal treatment are shown in Fig. 2. Hemicelluloses are a group of polysaccharides consisting of different monosaccharides. More side chains hinder the hemicellulose molecules from adopting a regular arrangement. Figure 2 shows a wide peak at $2\theta = 18.9^{\circ}$, which indicated the amorphous structure of hemicelluloses. After thermal treatment at 180 $^{\circ}\text{C}$ or 200 $^{\circ}\text{C}$, the resultant products had similar XRD patterns as the pristine hemicelluloses. In Fig. 2(d), the peak shifted to $2\theta = 20.4^{\circ}$, and the strength weakened obviously, which corresponded to the carbon structure. Based on these findings, partial carbonization occurred after treatment at 220 $^{\circ}\text{C}$ for 4 h.

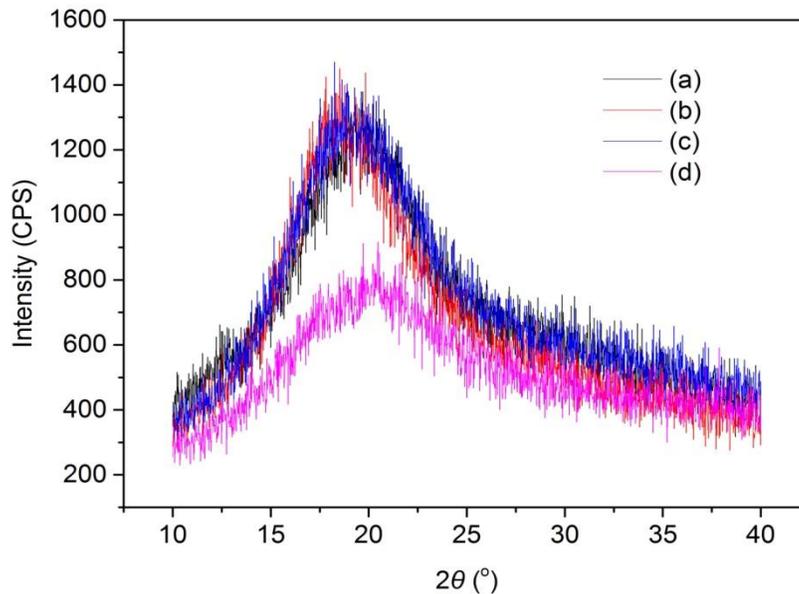


Fig. 2. XRD spectra of pristine hemicelluloses (a), hemicelluloses treated at 180 °C (b), 200 °C (c), and 220 °C (d) for 4 h

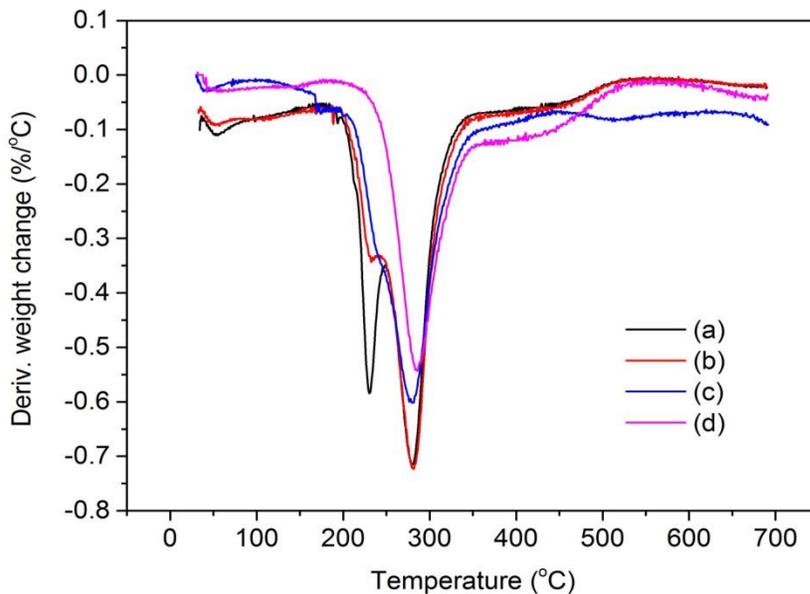


Fig. 3. DTG curves of hemicelluloses (a), hemicelluloses treated at 180 °C (b), 200 °C (c), and 220 °C (d) for 4 h

DTG Analysis

Figure 3 shows the weight loss curves in the form of DTG curves from hemicelluloses before and after treatment for 4 h at 180 °C, 200 °C, and 220 °C. These curves reflect the decomposition of hemicelluloses during thermal treatment. The weight loss of hemicelluloses mainly occurred from 178 to 248 °C and from 248 to 348 °C, which indicated that hemicelluloses began to degrade around 180 °C (Garcia-Maraver *et al.* 2013). However, the DTG curves of the thermally treated hemicelluloses obviously

changed. The peak at 178 to 248 °C noticeably decreased for hemicelluloses treated at 180 °C and disappeared at 200 °C and 220 °C. The peak at 248 to 348 °C decreased and became thinner. This result suggested that some of the side chains of hemicelluloses were cleaved at 180 °C, while most were broken at 200 °C. When the treatment temperature reached 220 °C, all side chains broke down, and some carbonization occurred. The results supported the conclusions based on the FTIR and XRD analyses.

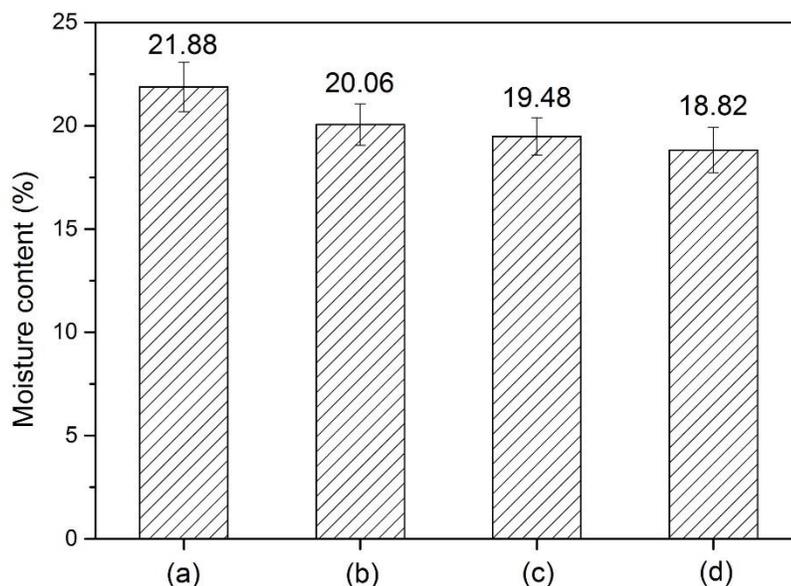


Fig. 4. Moisture contents of untreated hemicelluloses (a), hemicelluloses treated at 180 °C (b), 200 °C (c), and 220 °C (d) for 4 h

Hygroscopicity Analysis

As shown in Fig. 4, the moisture content of pristine hemicelluloses was 21.88%. After thermal treatment, the moisture content decreased from 20.06% to 18.82% with the treatment temperature increasing from 180 °C to 220 °C. The result corresponded to the decreased content of hydrophilic groups such as –OH and –COOH, and ester bond occurred and increased, which was shown through FTIR analysis. The moisture absorption test further indicates that the increased hydrophobicity of thermally treated wood was not only a result of a simple removal of hemicelluloses by their degradation and formation into volatile compounds emitted, but also further facilitated by chemical changes of the ester reactions between the remaining hemicellulose polymers.

Chroma Analysis

The chroma value and color of hemicelluloses before and after thermal treatment are shown in Table 1. The pristine hemicelluloses were yellowish-white with a high brightness of 91.69. However, the a^* value was close to 0. After the treatment at 180 °C for 4 h, the brightness value decreased by one-third compared with the pristine hemicelluloses. In addition, the a^* and b^* values increased. After further increasing the temperature to 200 °C, the a^* and b^* values slightly decreased. When the treatment temperature reached 220 °C, the brightness value remarkably decreased, and the sample changed to dark brown. The color further indicated that partial carbonization occurred.

Table 1. Chroma Values of Pristine and Treated Hemicelluloses

Treatment	L^*	a^*	b^*	ΔE	Picture
None (pristine hemicellulose)	91.69	0.77	5.75	0	
180 °C, 4 h	66.79	5.37	14.16	26.68	
200 °C, 4 h	53.62	5.26	11.54	38.77	
220 °C, 4 h	34.2	2.23	1.12	57.69	

Note:

$$\Delta E = ((L_{\text{sample}} - L_{\text{pristine hemicelluloses}})^2 + (a^*_{\text{sample}} - a^*_{\text{pristine hemicelluloses}})^2 + (b^*_{\text{sample}} - b^*_{\text{pristine hemicelluloses}})^2)^{1/2}$$

CONCLUSIONS

1. FTIR results showed that β -glucosidic bonds and side chains in hemicelluloses were cleaved at 180 °C. Higher temperatures accelerated the breaking process. Some esterification reactions simultaneously occurred between uronic acid and -OH groups during the thermal treatment.
2. DTG analysis indicated that some side chains of hemicelluloses cleaved at 180 °C, but most were degraded at 200 °C. All side chains broke down, and some carbonization occurred when the treatment temperature reached 220 °C.
3. Thermal treatment improved the hydrophobicity and the darkness of hemicelluloses.
4. This study showed that changes in hemicelluloses play important roles in the thermal treatment of wood.

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