CHARACTERIZATION OF CHEMICAL WOOD MODIFICATION WITH MELAMINE–UREA–FORMALDEHYDE PREPOLYMER ON FAST-GROWING WOOD

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Abstract. To improve their overall performance, fast-growing poplar logs were modified by impregnation with a melamine–urea–formaldehyde (MUF) prepolymer. The results showed that density, dimensional stability, and mechanical properties of fast-growing poplar were markedly improved. The vertical density profile curves confirmed the even distribution of wood modifier in wood cells after impregnation. The water uptake for 72 h improved from 118.5 to 77.2%. Meanwhile, swelling of the modified wood in cross-section, radial section, and volume was decreased to 2.6, 3.1, and 4.8%, respectively. Significant improvements occurred in wood mechanical properties such as bending strength, compressive strength parallel to grain, modulus of elasticity in static bending, and hardness. The mechanism of modification was characterized by X-ray diffraction (XRD), Fourier transform IR spectroscopy (FTIR), and scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDXA). Dynamic mechanical analysis showed that the storage modulus value of wood samples increased from 6.4 to 7.48 GPa. XRD showed that crystallinity of wood increased and formed a quasi-crystalline. FTIR analysis demonstrated that a chemical crosslinking reaction existed between the function groups of --NHCH2OH from the MUF prepolymer and the wood carboxyl C=O. Finally, SEM-EDXA indicated good dispersion of the modifier in wood fiber and other vertical cells.

Keywords: Chemical modification, impregnation, fast-growing wood.

INTRODUCTION

Both growing awareness of the decreasing amount of natural wood resources and increasing pressure on the environment have led to a deeper interest in wood modification. Wood is a natural renewable polymeric and porous material made up of chemical components: cellulose, hemicelluloses, lignin, and extractives. These constituents are responsible for the physical–chemical properties of wood. Wood contains largely reactive sites. Hydroxyl groups are the most important reactive sites and abundantly exist in the three major chemical components of wood.

The chemical modification of wood can be defined as a chemical reaction between some reactive part of wood and a simple single chemical reagent, with or without a catalyst, to form a covalent bond between the two parts. The aim
of chemical modification is to improve decay resistance or dimensional stability, decrease water absorption, and modify weathering performance, among other things.

Many methods have been used to modify the properties of wood by treatment with various chemical agents. Chemical modification of cell wall polymers is one of the most effective methods to improve dimensional stability, biodegradation properties, mechanical properties, and UV resistance of wood. Pandey et al (2010) proposed a method in which the alkylene epoxides were used to modify Scots pine (Amy et al 2005). Etherified wood exhibited an improvement in dimensional stability, but the efficacy dropped with successive water soaking and oven-drying cycles, indicating a loss of modifying chemical. Devi et al (2003) investigated chemical modification of rubber wood by impregnation with styrene and glycidyl methacrylate. Polymerization and crosslinked reactions were carried out by catalyst thermal treatment (Cavallaro et al 2013). The antishrink efficiency and dimensional stability were found to improve after modification. Fabiyia et al (2011) investigated the surface properties of fast-growing poplar clones and their methyl methacrylate-hardened wood related to potential end uses. The incorporation of the polymer increased density and hardness. The modified wood also exhibited superior abrasion resistance compared with the controls. Rocha et al (2013) presented a modified method with different poly(vinyl chloride)-based block copolymers containing poly(hydroxypropyl acrylate) segments (Deka and Saikia 2000). The adhesion and the mechanical performances of blocks were improved. The waterlogged archaeological woods were impregnated with poly(ethylene) glycol (PEG) mixtures by using aqueous mixtures of PEG 4000 and PEG 400 as well as mixtures of these polymers in their melted state. Cavallaro et al (2013) showed that the thermal stability of wood was enhanced after modification (Gindla and Gupta 2002).

Fast-growing wood has a lot of advantages in terms of its rapid growth and short cultivation time. However, fast-growing wood also suffers from low density, dimensional instability, and poor resistance to degradation, which limits its development in the wood processing industry. The most common and inexpensive method to modify fast-growing wood is impregnating a polymeric monomer or prepolymer, followed by chemical reaction of the monomer or curing the prepolymer to form a solid. The essential condition of chemical wood modification is that the reacting chemicals can impregnate the wood cell wall and react with the available hydroxyl groups of the cell wall polymer, preferably in neutral or mild alkaline conditions at certain temperatures (Kumar 1994).

Melamine–urea–formaldehyde (MUF) resin is widely used in the manufacture of water-resistant particleboards, papers, and laminates (Pandey et al 2010). MUF is a typical thermosetting resin, and its potential for improving solid wood properties, such as water absorption, hardness, and modulus of elasticity (MOE), good thermo-stability, and low flammability. It has the potential to improve the properties of fast-growing wood (Devi et al 2003; Cai et al 2008; Rocha et al 2013). Wood modification by resin treatment is targeted to modify the wood cell wall. Compressive strength properties and moisture-related shrinking and swelling behaviors of wood were improved with resin treatment (Kumar 1994).

One of the main distinguishing characteristics of MUF is its much better water resistance compared with urea–formaldehyde (UF) resins. The water-soluble MUF resin is hydrophilic before curing and becomes hydrophobic after curing.

This study was carried out to investigate the effect of modification with MUF prepolymer on the mechanical properties, dimensional stability, and vertical density profile of fast-growing wood. Also, the wood samples were characterized by X-ray diffraction (XRD), Fourier transform IR spectroscopy (FTIR), and scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDXA) to clarify changes
in the modified mechanism, crystallinity, and microstructure during the modification.

MATERIALS AND METHODS

**Wood Materials and Chemicals**

Eight-yr-old, fast-growing green logs (Populus euramericana [Dode] Guiner CL. ‘zhonglin-46’) were collected from Shandong province, China. The diameter of the logs was about 300 mm. The logs were cut into samples about 250 mm × 250 mm × 1 m (tangential [T] × radial [R] × longitudinal [L]) and dried to 20% MC.

**Synthesis of Melamine–Urea–Formaldehyde Prepolymer**

The synthesis process involved two stages. First, urea (60% w/w), formaldehyde (25% w/w), and ammonia (15% w/w) were added to a reaction vessel used for synthesis of UF prepolymer. The reaction mixture was stirred and heated to 35°C for 4 h. Subsequently, 12% melamine (amount of UF prepolymer) was added to the formaldehyde prepolymer and heated at 55-60°C for 2 h while stirring. The pH was adjusted to 7-8 with sodium hydroxide or hydrochloric acid and maintained for 3 h. After this, the MUF prepolymer was removed to a container. The solid content of wood modifier was 55 ± 3%, and the viscosity was about 12 mPa·s. The purity grade of the chemicals was 99%.

**Impregnation and Thermal Treatment**

The wood modifier was composed of MUF prepolymer (20% w/w), urea (15% w/w), ammonium phosphate (3% w/w), and water (62% w/w). The dimensions of the wood samples for impregnation were 250 mm in diameter and 1 m long. The samples were immersed in the modifier using a pulse-dipping machine under pressure of 1.0 MPa for 1.5 h. The weight percent gains (WPG) of modified wood samples were 30%. Then, the impregnated samples were cut into blocks with dimensions of 50 mm × 100 mm × 1 m (T × R × L) for drying. Drying was performed under atmospheric conditions in a kiln at 90°C for 99 h. Kiln temperature was increased from room temperature to 90°C following the experimental drying schedule (Table 1). After 99 h of thermal treatment, wood samples with 10 ± 2% MC were removed from the drying kiln.

**Vertical Density Profile**

The vertical density profile of natural and modified wood was measured using GreCon’s X-ray densitometer. Samples were sawn into dimensions of 50 × 50 × 30 mm (L × T × R) for the test. The sampling position on the wood was heartwood. Five samples were prepared for the test.

**Mechanical Properties Measurements**

The mechanical properties were evaluated according to Xiuqin et al (2009a, 2009d, 2009e, 2009f), which involve a three-point bending test at a crosshead rate of 1 mm/min. Sample size was 20 × 20 × 30 mm (T × R × L) for test of the compressive strength parallel to grain, 20 × 20 × 350 mm (T × R × L) for test of bending strength, 70 × 50 × 50 mm (T × R × L) for test of hardness and MOE in static bending with the dimensions of 20 × 20 × 300 mm

<table>
<thead>
<tr>
<th>Moisture content (%)</th>
<th>Dry bulb temperature (°C)</th>
<th>Wet bulb temperature contrast (°C)</th>
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<tbody>
<tr>
<td>&gt;70%</td>
<td>68</td>
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<td>&gt;70%</td>
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<td>30-35%</td>
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<td>Steam treatment</td>
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<td>25-30%</td>
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<td>15-20%</td>
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<tr>
<td>MC &lt; 15%</td>
<td>84</td>
<td>10</td>
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<tr>
<td>Steam treatment</td>
<td>90</td>
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</table>
At least 10 samples were tested for each combination.

**Dimensional Stability Measurements**

The dimensional stabilities were carried out according to the procedure described in Xiuqin et al (2009b, 2009c). Samples for water uptake with dimensions of 20 × 20 × 20 mm (T × R × L) were completely immersed into water at 20 ± 2°C for 72 h. Water uptake was calculated based on the WPG after 6, 24, 48, and 72 h and thereafter at 72-h intervals with removing excess water on the surface. The swelling rates were calculated based on the midspan changes every 6 h until the weight of wood samples was unchanged. At least 10 samples were tested for each combination.

The WPG of the plywood during the test was calculated using the following equation:

\[
WPG = \left(\frac{M_m - M_u}{M_u}\right) \times 100(%) \quad (1)
\]

where \(M_m\) is the oven-dry mass of the modified samples at the end of every cycle, and \(M_u\) is the oven-dry mass of the unmodified samples (Hill 2006).

**Dynamic Mechanical Properties**

Dynamic mechanical analysis (DMA) was carried out on a DMA242 analyzer at ambient air atmosphere. The dimensions of the test specimens were 50 × 10 × 5 mm (L × T × R) with 10% compression ratio. All samples were characterized in a three-point flexure test at a heating rate of 2°C/min from 30-180°C with the initial static force being 100 g. Experimental conditions were as follows: frequency sweeps, 1 to 2 Hz; static stress, 0 N; deformation amplitude, 50 μm; load, 4 N; and scale factor, 1.3. Five samples were prepared for the test. Each experiment was repeated three times.

**X-Ray Diffraction Analysis**

XRD experiments were conducted using a Shimadzu (Kyoto, Japan) diffractometer, model XRD 6000, with a Cu Kα (λ = 0.154 nm) radiation source at 30-kV voltage and 40-mA electric current. The patterns were obtained within a 10-50°, 2 angular interval with a 0.05° step and scan rate of 2°/min. All wood samples were first ground to pass an 80-mesh sieve and extracted before analysis. Five samples were prepared for the test.

**Fourier Transform IR Characterization**

The FTIR spectra of samples were characterized using a Tensor 27 (Bruker, Germany) spectrometer at a resolution of 64 scans in the wave number range of 4000-400 cm⁻¹. The modified and natural samples were ground to 200 grit, mixed with KBr (100:1 in weight), and then pressed into disks. Three samples were prepared for the test.

**Scanning Electron Microscopy with Energy-dispersive X-Ray Analysis**

The morphologies of the modified and natural wood samples were observed using a Hitachi (Tokyo) 3400-N scanning electron microscope at an acceleration voltage of 15 kV and a current of 10 nA. A 2-nm-thick gold palladium layer was sputtered on the samples. A Jeol Ltd. (Tokyo) JSM 5900 energy-dispersive X-ray analyzer was used to investigate the distribution of C, N, and O in the microstructure of the wood samples. The samples were sputtercoated with a thin layer of gold, and the experiment was conducted at 15 kV. Twelve samples were prepared for the test.

**RESULTS AND DISCUSSION**

**Vertical Density Profile Analysis**

The density of a material has a great impact on its performance. Figure 1 displays the density profiles of natural and modified wood. It is evident that the density of modified wood significantly increased after impregnating with the wood modifier. In particular, the mean density
of wood increased from 401.96 to 494.45 kg/m³. Also, it is obvious that the curve of the density profile is much more uniform than the natural one, which indicates that a great amount of wood modifier was evenly impregnated into the wood and homogeneously dispersed in the wood cell walls. The wood modifier existed both in the cell wall and in the vessels after thermal curing. The reason could be that MUF prepolymer not only filled existing pores, but also crosslinked with the cell wall polymers. Accordingly, density of the wood increased, and the distribution of the wood modifier was uniform.

Mechanical Properties

Figure 2 gives the average mechanical property values of the natural and modified wood samples. It is evident that mechanical properties of the wood were improved after impregnating the MUF prepolymer modifier. The hardness changes for the end, tangential, and radial sections of modified wood samples increased to 3968, 2581, and 2315 N from 3153, 1468, and 1288 N, respectively. Bending strength and compressive strength parallel to grain showed a similar tendency. There was a 55.17% increase in bending strength (from 73.4 to 113.4 MPa), a 55.05% increase in compressive strength parallel to grain (from 43.6 to 67.8 MPa), and a 50.06% increase in MOE in static bending (from 6.88 to 11.02 GPa). This is because wood is a porous material. Anatomically, the porosity of both cell cavities (cell lumen) and micropores in the cell walls exists (Schneider 1994). Wood modifier entered the cell wall and cell cavity of the wood, potentially forming hydrogen bonds, which added bulk to the cell wall (Singha and Thakur 2009). Also, MUF prepolymer may react with the hydroxyl groups of the wood components, enhancing the mechanical properties of the wood.

Dimensional Stability

After modification, the WPG of wood increased to 28.59%. On average, water absorption values of modified wood were superior to those of natural wood. Water uptake for 72 h decreased from 118.5 to 77.2%. Meanwhile, the swelling of modified wood in transection, radial section, and longitudinal section decreased to 2.5, 3.2, and 0.25%, respectively, compared with swelling of the natural ones (3.3, 3.8, and 0.3%) (Fig 3). Improved dimensional stability
has been ascribed to the entrance of MUF prepolymer into the tracheids and wood cell cavities. The MUF prepolymer shielded the wood surfaces and remained in the cell wall and lumen, leading to less water penetration into the wood cell. Numerous hydroxyl groups in wood components and various cavities exist in wood, which are major paths for moisture movement. The MUF prepolymer not only filled existing pores, but also crosslinked with the cell wall polymers, which decreased the amount of hydroxyl groups. The stable chemical combinations between the wood cell wall and MUF prepolymer strengthened the cell cavities and tracheids. Hence, the dimensional stability of wood was improved.
Dynamic Mechanical Properties

The storage modulus (\(E'\)) is closely related to the load-bearing capacity of a material. A graph of the storage modulus of natural and modified wood is shown in Fig 4. This dropping trend in modulus is typical of the viscoelastic behavior of wood in general (Morlat et al 1999; Pothan et al 2003). Observing the effect of wood modifier content on the \(E'\) values of the wood, it was evident that the \(E'\) of all the samples increased after modification from 30°C to about 180°C. Comparing the natural wood sample (6.4 GPa), the \(E'\) value of modified wood was 7.48 GPa. Also, the glass transition of the modified wood sample occurred at about 75°C and the modulus value remained unchanged after that. These results also indicated that the modified wood modifier molecules crosslinked the growing linear chains during the curing process, which tightened the structure of wood and thereby restricted the molecular motions more in wood. In addition, the hydroxyl groups of MUF prepolymer molecules increased hydrogen bond formation and restricted molecular rotations at lower temperatures. It also can be deduced that there is a better interface interaction between MUF prepolymer and wood fiber, which allowed greater stress transfer at the interphase (Cai et al 2008; Islam et al 2012).

X-Ray Diffraction

XRD patterns of natural and modified wood samples are presented in Fig 5. For natural wood, the maximum peak of the cellulose crystal diffraction (100) occurred near 17° and an obvious trough was observed near 19.4°, which is characteristic of the amorphous wood region. The most significant diffraction peak (002) of the cellulose crystal surface was near 22.5°, whereas a small diffraction peak (040) occurred near 37° (Singha and Thakur 2009). Compared with natural wood, the unchanged diffraction pattern for the modified wood implies that the regularity of the crystallites of cellulose was not disrupted by modification. However, the crystallinity of modified wood increased to 42.18% from 37.91%, indicating that the MUF prepolymer can penetrate into the wood cell wall and the amorphous region of cellulose fibrils (Yu et al 2011). The chemical crosslinking reaction occurred in the amorphous region of the cellulose because
the reagent cannot diffuse into the crystalline region. Also, the reaction between MUF pre-polymer and the hydroxyl groups of wood opened some of the hydrogen-bonded cellulose chains, producing some new amorphous cellulose during the thermal treatment. Rearranging the cellulose molecule chains may contribute to an increase in crystallinity and form a quasi-crystalline.

Fourier Transform IR Analysis

Figure 6 displays the FTIR spectra of natural and modified wood ranging from 4000 to 400 cm\(^{-1}\).
The two spectra exhibit obvious differences. The 3300-3050 cm\(^{-1}\) absorption peak present in the modified wood demonstrates a decreased intensity and an enhanced broadness, mainly because of the decreased amount of hydroxyl groups. It can be inferred that the MUF prepolymer can easily penetrate the wood substrate to reach the hydroxyl groups of the cellulose chains and form a chemical bond between the MUF prepolymer and hydroxyl groups of the wood cell. In addition, the modified wood showed peak changes at 3590-3300, 2950-2840, 2986, 1610, and 1160-1052 cm\(^{-1}\), assigned as NH\(_2\) stretching vibration, aliphatic CH\(_2\) stretching vibration, C-NH\(_2\) stretching vibration, NH bending vibration, and NH bending vibration, respectively. This is because of the stronger bonding between triazine carbons of MUF prepolymer and wood cells. Also, the increased absorption peak intensity close to the ether bond at 1545-1480 and 1073-1312 cm\(^{-1}\) indicates that the impregnated MUF prepolymer gained a large number of N-O asymmetric stretch (nitrogen and oxygen compounds) and ether bonds (Singha and Thakur 2009). Simultaneously, the absorbance caused by the increasing N-C=O stretching at 1740 cm\(^{-1}\) suggests a chemical crosslinking reaction between the function groups of –NHCH\(_2\)OH from the MUF prepolymer and the wood carboxyl C=O. In conclusion, the MUF prepolymer cannot only fill the wood cell walls, but also can form bonds with the groups of wood cells because of the abundantly active groups in the MUF prepolymer. The hygroscopicity of wood significantly decreased with the decrease in hydroxyl groups, which is in agreement with the dimensional stability. Meanwhile, the crosslinking reaction between the MUF prepolymer and wood fiber enhanced the mechanical properties of wood.

Figure 7. Scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDXA) micrographs of wood: (a) SEM of cross-section of natural wood, (b) SEM of cross-section of modified wood, (c) SEM of radial section of natural wood, (d) SEM of radial section of modified wood, (e) SEM photograph (×200) (modified wood), (f) EDXA micrograph distribution of C (modified wood), (g) EDXA micrograph distribution of O (modified wood), and (h) EDXA micrograph distribution of N (modified wood).
Scanning Electron Microscopy with Energy-Dispersive X-Ray Analysis

Figure 7 illustrates morphologies of the natural and modified wood samples in cross-section and a radial section. For natural wood, empty cell walls, the pit, and parenchyma can easily be seen, whereas for the modified wood, these empty places have been occupied by the wood modifier. Also, it is clear that the prepolymer was homogeneously dispersed in both the cell wall and vessels, and good adhesion of the prepolymer to the cell wall can be observed for the modified wood.

Further work has been done through X-ray elemental analysis of natural and modified wood samples. Elements such as C, O, and N, which are mainly from prepolymer and urea, were detected. The statistics demonstrate that the content of carbon decreased to 56.87% (mole percent) from 59.79% (natural wood), the content of nitrogen increased to 12.48% from 10.70% (natural wood), and the content of oxygen increased to 30.62% in the modified wood samples (natural wood 28.83%). The dispersion of the MUF prepolymer in the wood fiber and other vertical cells can be attributed to the chemical bonds from the numerous active groups in the MUF prepolymer and the hydroxyl groups of the wood cell. This not only results in enhanced mechanical properties of the wood, but also contributes to decreased water absorption and increased dimensional stability of the modified wood as well.

CONCLUSIONS

On the basis of the characterization and analysis of natural and modified wood samples, we drew the following conclusions:

It could be clearly demonstrated that the mechanical properties and dimensional stability of fast-growing wood can be improved to a highly significant degree after chemical modification. Dynamic mechanical analysis showed that the $E'$ value of wood samples increased from 6.40 to 7.48 GPa, which indicated better plasticity of wood after chemical modification. XRD analysis demonstrated that the crystallinity of wood increased after modification with MUF prepolymer. Although the location of the peaks was unchanged, there was indication that the ordered structure of the crystalline region of cellulose was not disrupted and that a quasi-crystalline form was formed by rearranging the cellulose molecule chains. FTIR analysis confirmed that the MUF prepolymer cannot only fill the wood cell walls, but can also form bonds with the groups of wood cells because of the abundant active groups in the MUF prepolymer. A chemical crosslinking reaction occurred during the wood modification, which led to significant improvement in the mechanical properties and dimensional stability of fast-growing wood. SEM-EDXA studies provided evidence that the wood modifier dispersed in wood fiber and other vertical cells evenly.

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