

GRAFTING ORGANIC-INORGANIC COMPOUND MODIFIER ONTO WOOD CELL WALLS FOR ENHANCED MECHANICAL STRENGTH IN WOOD COMPOSITES

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ABSTRACT

The present study describes the possibility to polymerize functional composite modifier within wood cell walls to obtain functional wood composites (FWCs) with poplar wood acting as the base template. The physical and mechanical properties of the composites, including density, bending strength, compressive strength parallel to grain, surface hardness and water uptake, were evaluated. The FWCs were characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), Scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD). According to the results, the functional composite modifiers were successfully in situ deposited into the wood structure by kiln drying. The chemical treatment not only significantly improved the physical and mechanical properties of wood, but also provided the wood with better hydrophobic properties. The abbreviations for substances used in this study are: N-wood (natural wood), MD-wood (methylolurea/DMDHEU copolymerization treated wood), FCM-wood (functional composite modifier treated wood).

KEYWORDS: Functional composite modifier, pulse-dipping; in situ polymerization, Si-O-Si framework, wood modification.

INTRODUCTION

Natural resources are now to the fore with environmental conservation policies through replacement of fossil based, energy intensive or pollution causing materials (Noël et al. 2015). Wood, a kind of natural organic polymer materials, has played an important role in human

activity since before recorded history because of its remarkable properties such as high mechanical strength in view of its light weight (Pettersen 1984).

Unfortunately, most natural resources, particularly lignocellulosic materials, exhibit properties that do not reach the standard performance of petrochemical based materials in the aspects of decay resistance, rub resistance, and tenacity. Meanwhile, wood is susceptible to many natural degradation processes, such as biological, aqueous, thermal, photochemical, chemical and mechanical degradation (Rowell 2012).

Wood composed of cellulose, hemicelluloses and lignin is hydrophilic and hygroscopic because of a number of hydrophilic OH groups of the wood components (Li et al. 2013). So, wood is prone to absorbing water and moisture; this renders wood vulnerable to fungi and dimensional instability. These vulnerabilities result in numerous harmful effects to wood material, including cracking, mildew, and biological degradation. A variety of traditional wood modification methods have been proposed to reduce the quantity of hydroxyl groups within the wood matrix. To fight hygroscopicity, thermal treatments were developed that resulted in hemicelluloses degradation and associated decrease in moisture sensitivity and wood stability improvement. Wood heat treatment by mild pyrolysis is used to improve wood properties such as its decay resistance and dimensional stability (Rowell et al. 2009, Poncsak et al. 2010). The decay resistance of the treated wood matches to a fully durability (Chaouch et al. 2010), according to the EN 113/A1 (2004). In parallel with improvement of wood durability, mechanical properties were generally significantly weakened (Bengtsson et al. 2002). Mechanical properties were affected due to relative increases in wood crystallinity contributing to decreased impact and bending resistance, which has hindered the thermo-treated wood market development (Beall 1971, Beall 1972).

The wood cell wall can be regarded as a hygroscopic biocomposite, consisting of stiff cellulose fibrils embedded in a lignin and hemicelluloses matrix, which can be altered and functionalized via chemical modifications (Salmén 2009, Paris et al. 2010). It was demonstrated that the components of urea-formaldehyde (UF), ureaformaldehyde, methylolurea, and other adhesives are able to diffuse into wood walls in substantial quantities (Bolton et al. 1988, Cyr et al. 2006, Gierlinger et al. 2005, Kamke et al. 2007, Konnerth et al. 2008; Rapp et al. 1999; Xing et al. 2005). The penetrated and cured adhesives modify certain properties of wood. For example, poplar wood was impregnated by pulse dipping at 0.7-0.8 MPa for 30 min with urea-formaldehyde pre-polymer, and the modifier was cured within the wood micropores by in situ gel polymerization by kiln drying (Chen et al. 2014, Wu et al. 2010). The SEM-energy-dispersive X-ray spectroscopy analysis revealed that the modifier formed layers from various thicknesses ranging from a thin layer on the cell walls up to big amounts filling the lumen. The treatment increased the mechanical strength property, but the dimensional stability of wood was decreased greatly. N-methylol compounds are used as a wrinkle-resistant finish in the textile industry. Modification of wood with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) improves the dimensional stability and induces high resistance against fungi and insects by depositing the chemical into the cell wall (i.e. a bulking effect) and by reacting with the functional groups of wood polymers (e.g., mostly hydroxyl groups of cellulose, hemicelluloses, and lignin) (Militz 1993; Tomazic et al. 2004; Xie et al. 2005; Yuan et al. 2013). Treatment of wood with high loading of wax reduces moisture absorption by wood subjected to accelerated weathering and restricts photo-degradation of wood (Lesar 2011). DMDHEU-modified wood has a higher number of pores smaller than 30 nm and a lower fraction of bound water. This helps to explain why DMDHEU-modified materials exhibits limits water uptake and increases resistance to biological attack (Dieste et al. 2009) DMDHEU treatment of wood strips partially reduces the degradation of lignin and cellulose and stabilizes the wood cell walls during artificial weathering

(Xie et al. 2005). The modification reduces the UV sunlight absorbed by the lignin. Lignin absorbs 80% to 95% of the UV component of sunlight due to its phenolic nature; holocellulose (5% to 20%) and extractives (2%) absorb the remainder (Norrstrom 1969). DMDHEU treatment, however, had a deleterious effect on the bending strength of modified wood (Nicholas and Williams 1987; Ashaari et al. 1990). Wood-based inorganic composites commonly have a highly antibacterial performance by means of sol-gel modification (Furuno et al. 1991; Furuno et al. 1992; Furuno et al. 1993). Furuno et al. impregnated wood with aqueous solutions of sodium silicate followed by treatment with aqueous solutions of aluminum sulfate, barium chloride, or calcium chloride to form nonleachable precipitates. Most of the precipitated material was found in the cell lumens, but there was scanning electron microscopy (SEM)-energy-dispersive X-ray spectroscopy (EDX) analysis evidence of some cell wall penetration. The treatment increased the hygroscopicity and improved the decay resistance and resistance to combustion, but the bending strength was diminished.

The concept of the present study includes the preparation of functional composite modifier by mixing methylol-urea, DMDHEU with sodium silicate. Then, poplar wood was impregnated with the organic-inorganic functional composite modifier by pulse dipping at the pressure of 0.7-0.8 MPa for 30 min, and the sol embedded in the micropores was cured by heating (in situ polymerization). The character of wood combined treatment with functional composite modifier is unknown so far. The expectation is that the properties will be more favorable than those modified wood using a single organic or inorganic modifier. Thus, the FWCs impregnated functional composite modifier will be in focus.

MATERIALS AND METHODS

Materials

Fresh poplar (*Populus euramericana* cv. 'I-214') wood with an average basic density of $0.345 \text{ g}\cdot\text{cm}^{-3}$ (minimum diameter, 0.2 m) was collected in Beijing, China. The tree-ages were about 4-5 years. The initial moisture content of wood ranged from 60 % to 75 % before impregnation.

Synthesis of methylolurea

A three-necked flask was charged with urea (41 % w/w), formaldehyde (56 % w/w), and ammonia (3 % w/w) with a certain molar ratio. The reaction mixture was stirred and kept at 35 °C for 3 h. Then, the pH was adjusted by sodium hydroxide or hydrochloric acid to be between 5 and 7. At last, the reacted mixture was transferred into a container and sealed (Pu et al. 2009a). All the reagents were obtained from KeBaiAo Co., Beijing, China.

Compound of functional composite modifier

The reactive methylolurea (20% w/w) and DMDHEU (15% w/w) were intermixed in the reaction vessel. Meanwhile, carbamide (10% w/w), MgCl_2 (0.75% w/w) and water (45% w/w) were added into this reaction vessel for 10 min with constant mechanical stirring. Then silica sodium (10% w/w) was added into above organic composite modifier and stirred for 5min. The silica sodium ($\text{Na}_2\text{O}/\text{SiO}_2$, 1:3.3 w/w) was obtained from Nanjing High Technology Nano Material Co., Ltd. Nanjing, China.

Pulse-dipping and in situ polymerization by kiln drying.

The Poplar logs were sawn into boards about 2600 (longitudinal) \times 280 (tangential) \times 25 (radial) mm in size for impregnation. Fig. 1 shows the vacuum-pressure impregnation as a schematic diagram.

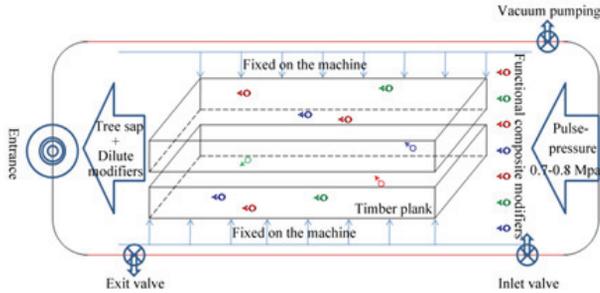


Fig. 1: Diagram of vacuum-pressure impregnation process.

Firstly, the fresh poplar wood was fixed on the pulse-dipping machine (designed by College of Materials Science and Technology, Beijing Forestry University, Beijing, China). Then, the modifier was impregnated from one side of the log by pulse-pressure (0.7–0.8 MPa), which offered by a pneumatic diaphragm pump. The tree sap and low molecular modifier could flow out from the other side of the log because the timber growth orientation was chosen as the pulse-dipping direction. Step by step, the tree sap in the xylem was continually replaced by the original modifier during 30 min (Pu et al. 2009b). After soaking, the impregnated logs were in the air-drying process for 48 hours, and then the air-drying boards were transferred into kiln for drying. Drying time was approximately 200 h and the pressure on the timber was 0.2 MPa (Pu et al. 2009c).

Mechanical properties.

The specimens of the natural and modified wood were analyzed by a universal mechanical testing machine (AG-100KNIMO, Tokyo, Japan). Tests were carried out according to the following Chinese standards: method of testing in bending strength of wood (GB/T 1936.1-2009), method of testing in compression perpendicular to grain of wood (GB/T 1939-2009), and method for determination of the density of wood (GB/T 1933-2009). Surface hardness was measured using a TH210 hardness tester (Beijing TIME High Technology Ltd., China) and indicated as shore D hardness according to ASTM D 2240 standard. Furthermore, the specimens for bending strength with a dimension of 30 \times 2 \times 2 cm (L \times W \times T), for compression perpendicular to grain of wood with a dimension of 30 \times 20 \times 20 mm (L \times W \times T), the others were carried out with 20 \times 20 \times 20 mm (L \times W \times T). Twenty specimens were tested for this measurement and the average was recorded.

Solution uptake (SU), weight percent gain (WPG), and water uptake (WU)

The SU after pulse-pressure impregnation was calculated according to Eq. 1. The WPG of the modified samples was determined by measuring the mass of the modified samples after modification, which was calculated according to Eq. 2. In order to evaluate the hygroscopicity of natural and modified wood, the cubic specimens were made according to the Chinese standard method for determination of the water absorption of wood (GB/T 1934.1-2009). Twelve specimens of natural and modified were analyzed respectively. The specimens were weighted

after drying in an oven at 105 °C until the weight change was less than 0.02 g after 2 h. Then the specimens were immersed in distilled water for 5 days. After immersion, the excess water on the surface was removed by a soft cloth, and the weights of the specimens were immediately taken. The increase in weight was calculated according to Eq. 3,

$$SU(\%) = (S - S_0) / S_0 \times 100 \quad (1)$$

where: S - the wet weight of wood specimens after impregnation,
 S_0 - the oven-dried weight of natural wood specimens.

$$WPG(\%) = (W - W_0) / W_0 \times 100 \quad (2)$$

where: W - the oven-dry weight of wood specimens after impregnation,
 W_0 - the oven-dried weight of natural wood specimens..

$$WU(\%) = (M - M_0) / M_0 \times 100 \quad (3)$$

where: M - the final mass,
 M_0 - the initial mass.

X-ray diffraction (XRD) instrument

X-ray diffraction analysis was carried out using a Shimadzu model XRD 6000 (Kyoto, Japan) (CuK α radiation with graphite monochromator, 30 kV, and 40 mA). The patterns were obtained between 5° and 40° 2 θ with 0.05° steps and scan speed of 2°·min⁻¹. The degree of crystallinity was calculated as the ratio of the intensity differences in the peak positions. The ratio of crystallinity of specimens to the standard amorphous materials was taken as the relative crystallinity. The degree of crystallinity was calculated according to Eq. 4,

$$Cr(\%) = F_c / (F_a + F_c) \times 100 \quad (4)$$

where: F_c - the intensity for the crystalline region,
 F_a - the corresponding quantity for the amorphous region.

Fourier transform infrared (FTIR) spectroscopy

The natural and modified wood samples were ground into a 120-mesh particle size and embedded in potassium bromide (KBr) pellets at a weight ratio of 1:80. Then the pellets were analyzed by FTIR using a Tensor 27 (Bruker, Germany) at a scanning range of 4000 to 400 cm⁻¹ and resolution of 2 cm⁻¹ for 32 scans.

Thermogravimetric analyzer (TGA)

A thermogravimetric analyzer (DTG-60, Shimadzu, Japan) was used to evaluate the thermal properties of natural and modified samples. The specimen pan was placed on a Pt basket in the furnace and continuously heated from room temperature to 600°C at the rate of 10 °C·min⁻¹. α -Al₂O₃ was used as the reference material. During testing, the heating unit was flushed with a continuous nitrogen flow at a pressure of 8 KPa.

Scanning electron microscopy (SEM) – energy dispersive analysis of X-rays (EDAX)

The natural and modified samples were characterized by SEM (SU-8020, Hitachi, Japan). Specimens to be observed under the SEM were mounted on aluminum stubs with conductive adhesive tape. The working conditions were as follows: working distance of 20 mm, accelerating voltage of 1 kV, and illuminating current of 0.7 Na. Besides, the substance on the cell wall of natural and modified wood was analyzed through EDAX.

RESULTS AND DISCUSSION

Mechanical properties

The SU, WPG, density and mechanical properties of the natural and modified wood samples (the data are averages from 12 specimens) are shown in Tab. 1. The SU and WPG of MD-wood samples were 169.41% and 30.94%, respectively. The SU and WPG of FCM-wood were higher than that of MD-wood, mainly as a result of the bonding action of nano-SiO₂ on wood cell walls and cell lumens. The air-dried density was increased by 21.05% and 55.26%, from 0.38 g·cm⁻¹ to 0.46 g·cm⁻¹ and 0.59 g·cm⁻¹. The oven-dried density also was increased by 41.46% and 48.78% from 0.41 g·cm⁻¹ to 0.58 g·cm⁻¹ and 0.61 g·cm⁻¹. The density increased due to the pulse-dipping impregnation of wood modifier. On the one hand, physical filling of modifiers in the lumen increased the mass of the samples; on the other hand, there were abundant reactions of etherification and esterification between modifiers and wood's three major components, as a result, the polymers embedded in the cell walls increased the density of wood. Hardness implies the ability of materials to resist deformation. Compared with the natural wood (46.9 shore), the tangential hardness of MD-wood and FCM-wood increased by 14.92% and 21.11%, respectively. The tangential hardness of the FCM-wood samples was higher than that of MD-wood, mainly owing to the grafting of inorganic nano-SiO₂.

Tab. 1: Mechanical properties of natural and modified wood samples.

Properties	N-wood	MD-wood	FCM-wood	Improvement, respectively (%)
Air-dried density (g·cm ⁻¹)	0.38 ± 0.05	0.46 ± 0.06	0.59 ± 0.08	21.05, 55.26
Oven-dried density (g·cm ⁻¹)	0.41 ± 0.08	0.58 ± 0.04	0.61 ± 0.05	41.46, 48.78
Bending strength (MPa)	96.29 ± 9.78	118.04 ± 10.69	131.24 ± 11.58	22.59, 36.30
Compressive strength parallel to grain (MPa)	29.47 ± 1.76	69.66 ± 1.28	74.75 ± 1.56	136.38, 153.65
Hardness (shore D)	46.90 ± 2.69	53.90 ± 4.67	56.80 ± 3.77	14.92, 21.11
SU (%)	-	169.41 ± 10.58	184.13 ± 12.46	-
WPG (%)	-	30.94 ± 1.52	41.78 ± 1.68	-

Meanwhile, the modification caused an obvious enhancement of bending strength and compressive strength parallel to grain. The MD-wood exhibits an improved bending strength by 22.59% and a better compressive strength parallel to grain by 36.30%. At the same time, the bending strength and compressive strength parallel to grain of FCM-wood increased by 136.38% and 153.65%, respectively. These results could be explained by that the adhesion and

compatibility between wood fibers and the polymer were enhanced by the reaction between functional composite modifier and wood cell. The methylolurea, DMDHEU and nano-SiO₂ had participated in the *in situ* polymerized reaction to form complicated large molecules, which increased the mechanical properties of wood. These results are also in agreement with the expectation that higher densities should entail better mechanical properties. The mechanical properties were tested under the same external conditions. The wood modification mechanism is schematically illustrated in Fig. 2.

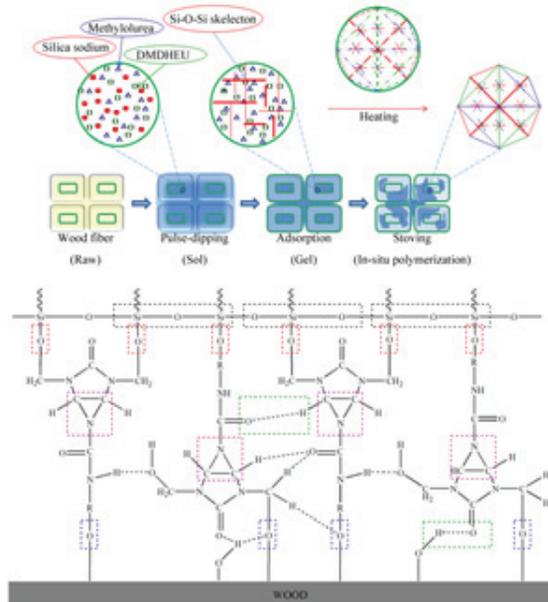


Fig. 2: Illustration of chemical reaction between functional composite modifier and hydroxyl of wood.

Water uptake

The water uptake results of natural and modified wood samples as a function of time at room temperature are shown in Fig.3.

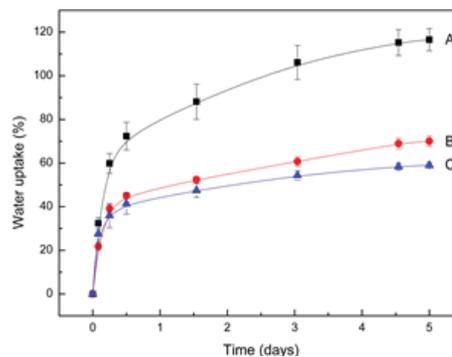


Fig. 3: Water uptake curves of wood: (A) N-wood, (B) MD-wood and (C) FCM-wood.

As visible, the water absorption rate of modified wood was markedly lower than that of the natural wood after immersion in water for 5 days at atmospheric pressure. The both the natural and modified wood absorb water quickly within the first 12 h. Then, the curves flatten. The final water uptake of the MD-wood decreased from 116.55% to 70.06% at 30.94% weight percent gain (Table 1). It was reasonable to infer that methylolurea and DMDHEU can polymerize with the wood fiber, which would decrease the amount of hydroxyl groups (-OH) of wood. The organic modifier not only covalently linked with hydroxyl groups but also interacted with the wood fiber through *in situ* polymerization, masking of some of the hydroxyl groups. Theoretically, the FCM-wood samples should absorb less water than MD-wood, because of the hydrophobic nature of inorganic materials. From the water uptake figure, we can see that the hygroscopicity of FCM-wood was 59.01% at 41.78% weight percent gain (Tab. 1). This result was also in keeping with previous theory.

FTIR analysis

FTIR spectra of the natural and modified wood samples are shown in Fig. 4. The FTIR spectrum of natural poplar wood (Fig. 4A) is typical for hardwood spectra in general. The adsorption at around 3400 cm^{-1} was assigned as the O-H stretching in hydroxyl groups and the broad band at around 2908 cm^{-1} was originated from the C-H asymmetric stretching in methylene groups. Besides, the adsorption at around 1738 cm^{-1} was assigned as the C=O stretching in un-conjugated ketone, carbonyl and aliphatic groups (xylan).

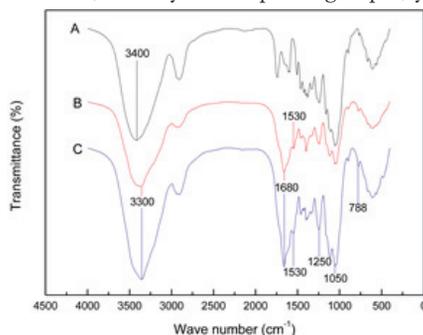


Fig. 4: FTIR spectra of N-wood (A), MD-wood (B) and FCM-wood (C), respectively.

The absorbance at around 1619 cm^{-1} and 1511 cm^{-1} arose from O-H bending and aromatic phenyl C=C stretching of lignin respectively (Yuan et al. 2013). In Fig. 4B and 4C, the influence of impregnation is evidenced by strong absorptions at 1680 cm^{-1} (secondary amide spectral band I), 1530 cm^{-1} (secondary amide spectral band II) and 1260 cm^{-1} (secondary amide spectral band III), which are characteristic for the functional $-\text{NHCH}_2\text{OH}$ groups in methylolurea and the wood hydroxyl-OH groups. The spectrum of modified wood illustrated the stretching vibration absorption peak from 3400 cm^{-1} to 3300 cm^{-1} caused by functional groups -OH and -NH, which indicated that there was a great potential for forming intermolecular hydrogen bonds. The presence of sodium silicate is manifest at 1250 cm^{-1} (Si-O-C), 1050 cm^{-1} (Si-O-Si stretching), and 788 cm^{-1} (Si-O symmetric stretching) (Inari et al. 2007; Gwon et al. 2010; Yu et al. 2011). With the increase of temperature in the drying process, chemical bonding accelerated between wood and functional composite modifier. Meanwhile, there were many reactions within the modifier itself.

XRD analysis

XRD was used to identify the intercalated structure of wood. Fig. 5 presents the curves of the natural and modified samples.

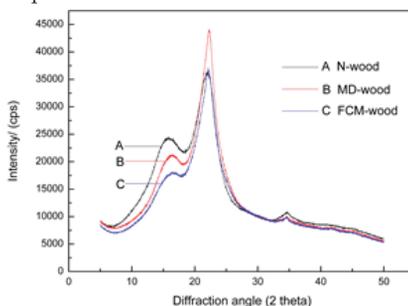


Fig. 5: XRD patterns of natural and modified wood.

The natural wood shows a maximum at $16.1^\circ 2\theta$ (cellulose crystal diffraction, 101), and the pattern extended to a minimum at $18^\circ 2\theta$, a region that is characteristic of the amorphous cellulose. The most significant diffraction peak (002) of the cellulose crystal is near $22.5^\circ 2\theta$, whereas a small diffraction peak (040) occurs near $35^\circ 2\theta$ (Cave et al. 1997). According to the results of experimentation, the crystallinity of the natural wood was 22.4%, while the results for MD-wood and FCM-wood were 27.7% and 24.2%, respectively. Comparing the three curves, the position of the peaks did not change, which indicated that the structure of cellulose was steady. The higher crystallinity of the modified wood can be explained that the quasi-crystalline form occurred between groups of the functional composite modifier and hydroxyl groups of the wood. Furthermore, methylolurea, DMDHEU and carbamide are polar molecules, which can be inserted into the amorphous region of the wood cellulose cell wall; hence, a crystalline region can be formed by rearranging the cellulose molecule chains.

Thermogravimetric analysis (TGA)

The thermogravimetric curves of the natural and modified wood are shown in Fig. 6. It was apparent that the TGA and DTG curves of modified wood had slower rate of heat release compared with those of natural wood, which revealed the more superior thermal stability of modified wood. The slight weight loss before 177°C for both samples was due to the evaporation of free water and bound water.

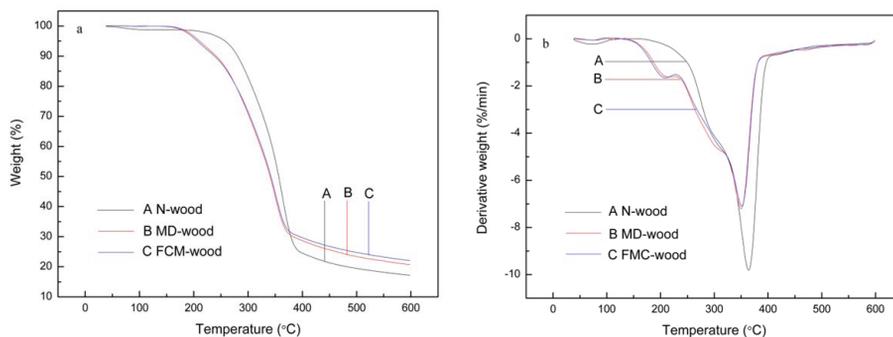


Fig. 6: (a) TG and (b) DTG curves of natural and modified wood, respectively.

According to the DTG curve, the thermal decomposition process of natural wood mainly showed two stages as follows: the first stage from 180°C to 300°C was mainly owing to decomposition of hemicelluloses (mass loss ~17%) with an observable shoulder; the second stage from 300°C to 380°C was primarily attributed to the cellulose decomposition (mass loss ~56%) with a strong exothermic peak (~365 °C). Besides, lignin exhibits high structural diversity, and degradation is slow and happens from 200°C to 900°C, there was no an obvious characteristic exothermic peak. From the TGA-DTG curves of natural and modified wood, we can see that the modified wood samples have superior thermal stability. After copolymerization, the hydrophilicity and moisture content of the MD-wood and FCM-wood samples further decreased, resulting in less mass loss in the temperature range of 38°C-600°C. Meanwhile, the treated wood not only had a much lower volatile extractive content, but also had much stronger cross-linking tendency between the modifier and the wood groups (Chen et al. 2012). These two phenomena would lead to an enhancement in the thermal stability of modified wood. It is well known that nano-SiO₂ is an inorganic nonmetal material, and the combination of wood matrix with nano-SiO₂ might be conducive for FCM-wood to obtaining improved heat resistance. So, the FCM-wood had a better thermal stability than MD-wood in the temperature range of thermal decomposition for modified wood implied that the existence of modifiers on wood matrix significantly enhanced the thermal stability of the wood polymer composite.

SEM-EDAX analysis

The microscopic morphologies of natural wood and modified wood were observed by SEM. Fig. 7a exhibited that the native wood samples displayed a highly void/hole structure before modification.

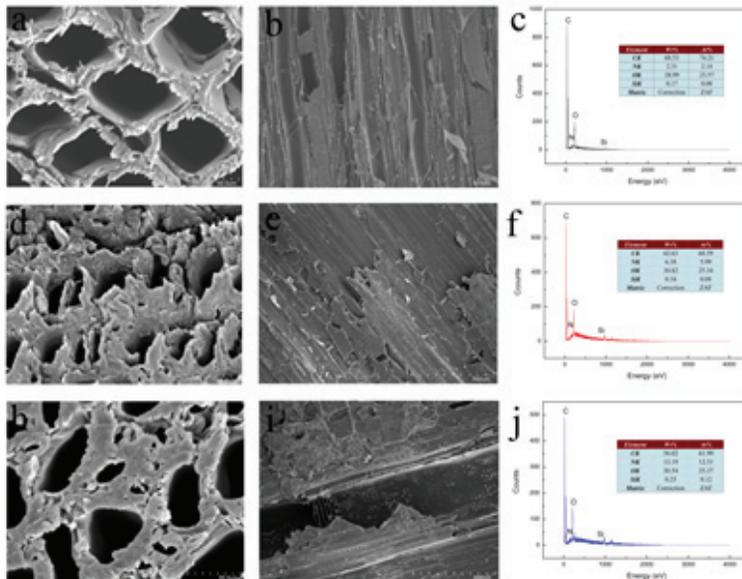


Fig. 7: FESEM image of natural and modified wood: (a) transverse section of N-wood, (d) transverse section of MD-wood, (g) transverse section of FMD-wood, (b) radial section of N-wood, (e) radial section of MD-wood and (h) radial section of FMD-wood; (c), (f) and (j) spectra of N-wood, MD-wood and FMD-wood, and the inserts show the corresponding mass proportions and atomic proportions of C, N, O, and Si elements, respectively.

Whereas, there was an obvious change in wood microstructure that the cell wall and vessels of modified samples were filled by solid wood modifiers. As shown in Fig. 7e and Fig. 7i, the surface of modified wood was coated with dense uninterrupted resin membrane structure compared with the smooth surface of original wood (Fig. 7b). There was no doubt that these close-knit accumulated modifiers would play a key role in protecting the wood from various damages. Furthermore, according to the results of EDX spectra (Fig. 7c, Fig. 7f and

Fig. 7j), the N mass ratio dramatically increased after modification from 2.31% to 6.38% and 13.19%. The atom ratio of N element also increased from 2.14% to 5.99% and 12.51%, respectively. Meanwhile, Si element had a slightly increase in FCM-wood. These results further revealed the presence of organic and inorganic modifiers on the modified wood structure.

Consequently, the SEM and EDAX micrographs proved that the wood modifiers were found to be present in the cell lumen and in the cell wall.

CONCLUSIONS

On the basis of the characterization and analysis of functional wood composites, we drew the following conclusions. The mechanical properties of functional wood composites, including density, bending strength, compressive strength parallel to grain, and hardness, were remarkable enhanced compared to the natural wood. Meanwhile, the water uptake of modified wood decreased sharply due to the reduction of $-OH$ groups via chemical reaction with hydroxyl groups of wood. The in situ polymerization was shown to have significant contribution on the dimensional stability of the functional wood composite. Wood and the modifier polymerized within the interfibrillar region of the cell wall due to the formation of covalent bonds between the methylolurea, DMDHEU, nano- SiO_2 , the wood hydroxyl, and acetic acid from hemicelluloses (esterification and etherification). Thus, the polymers tightly contacted the wood cell walls which resulted in a high property. In general, the performance of natural wood was significantly improved by in situ polymerization with the organic-inorganic functional composite modifier. This novel modifier will provided a higher value-added wood-based material in the industry.

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