IMPREGNATION OF SCOTS PINE WITH COMPOUND MODIFIER AND INDUCTION OF IN-SITU POLYMERIZATION BY HEATING

Xiaoshuai Han

Postgraduate Student
E-mail: hxs141424@gmail.com

Ren Li

Postgraduate Student
E-mail: 1506549401@qq.com

Qinqin Zhang

Postgraduate Student
E-mail: 2219227472@qq.com

Junwen Pu*

Professor
School of Material Science and Technology
Beijing Forestry University
35 Qinghua East Road
Haidian, China 100083
E-mail: jwpu@bjfu.edu.cn

Abstract. Recently, Scots pine wood has received tremendous attention in China because of its high strength weight ratio and aesthetic grain pattern.However, there are some disadvantages for Scots pine such as its low density, inferior mechanical strength, and low dimensional stability. In the present research, Scots pine has been impregnation by pulse dipping at 0.7-0.8 MPa for 150 minutes with urea-formaldehyde prepolymer, 1,3-dimethylol-4,5-dihydroxyethyleneurea and sodium silicate sol, and the sodium silicate sol has been cured within the wood micropores by in situ gel polymerization by kiln drying, so that a Si-O-Si framework can be deposited inside the wood structure. The mechanical properties and dimensional stability of the modified wood were investigated, and the water absorption decreased from 121.13% to 59.13%. The Fouriertransform infrared spectroscopy showed the chemical changes in wood after modification and illustrated the modified mechanism. The thermogravimetric analyzer showed that the thermal stability of modified wood improved. Finally, scanning electron microscopy and energy dispersive analysis of X-rays micrographs proved that the good interfacial adhesion of modifier between wood fiber and polymer.

Keywords: Compound modifier, impregnation, in situ polymerization, Si-O-Si framework, wood modification.

INTRODUCTION

Wood, a kind of natural material of biological origin, has played an important role in human activity since before recorded history because its unique inherent properties, such as high mechanical strength in view of light weight, good formability, heat and sound insulation capabilities, and aesthetic texture (Pettersen 1984; Miao et al 2014). However, some properties of wood are a bane in its utilization; these include dimensional instability with changing moisture, unsatisfying mechanical properties, and low durability (Yano et al 1997; Yano et al 2001). All of these prevent wood from replacing materials that are based on nonrenewable resources (Yano et al 2000).

Chemical modification is an efficient approach aimed at dimensional stability, flammability, moisture sorption, enhanced durability against

* Corresponding author

fungi and insects, fixation during the densification, and ultraviolet stability (Kumar 1992; Donath et al 2004; Nemli et al 2006; Hill et al 2009; Vetter et al 2010; Xiao et al 2012; Li et al 2012). The wood can be regarded as hygroscopic biocomposite, consisting of carbohydrate polymers of cellulose, hemicelluloses, and phenolic polymers of lignin (Devi and Maji 2011). Several studies have reported that these disadvantages are mainly attributed to the existence of abundant hydroxyl groups on wood components (Li et al 2013). For the past so many years, most of the early study areas in wood modification is to reduce the quantity of hydroxyl groups within the wood matrix, including filling wood cell lumen with organic molecules or inorganic molecules, compression and thermal (Saka et al 2001; Yamaguchi 2002; Mai et al 2004; Hansmann et al 2005; Gunduz et al 2009).

Keplinger et al (2014) demonstrated a method to insert methacryl groups into wood cell walls using two different chemistry routes. By using these methacryl groups as the anchor points for grafting, a variety of polymers can be inserted into the wood structure. The polystyrene was grafted as a model compound in the second modification step. They proved that methacryloyl chloride was located mainly at the interface between the cell lumina and the cell wall covering the inner surface of the cells, whereas in case of methacrylic anhydride the polymer was located inside the whole cell wall from the Scanning electron microscopy, Fourier transform infrared (FTIR) spectroscopy and especially Raman spectroscopy.

Yuan et al (2013) pointed out that the sapwood of Populus ussuriensis Kom could be impregnated with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU). Through the DMDHEU modification, it was found that the pores of modified wood became smaller, suggesting partial deposition of pores with DMDHEU. This filling effect of DMDHEU in wood pores contributed to mechanical support to the wood cell wall and it also can compensate for the strength loss resulting from the degradation of wood. The mechanical strength of DMDHEU-modified wood at relatively low temperature (90°C) was better than that at high temperature (120°C). At higher curing temperature (150°C), the mechanical strength properties of DMDHEU-modified wood decreased greatly.

Chen et al (2014) has studied the properties of poplar wood chemically modified with phenolic methylolurea. In their study, they impregnated fast-growing poplar (Populus euramericana) green wood by pulse-pressure at 0.7-0.8 MPa for 50 minutes with phenolic methylolurea, and then the polymerization will be induced in the wood in situ. The swollen cell walls filled with nonleachable polymers enhanced the dimensional stability of wood. Furthermore, the reactions occurred in the amorphous carbohydrates. Wood and the modifier polymerized within the interfibrillar region of the cell wall due to the formation of covalent bonds between methylol group, wood hydroxyl, and acetic acid from hemicelluloses. Meanwhile, in modified wood spectrum, there are some of connection status, such as the phenolic hydroxyl, methylene bridges, and the existence of the phenolic ring. It's indicated that reactions also occurred within the modifier itself, which can be present as a thin layer observed in scanning electron microscopy (SEM) of the cell walls.

The aim of this project is to use the complex structure of wood as a renewable and sustainable material that is by nature a high mechanical strength in view of its light weight and to modify this with a blend of organic and inorganic chemical agents, to prepare a novel functional material. The concept of the present study includes the preparation of a sol by mixing SiO_2 nanoparticles with compound organic modifiers (methylolurea, DMDHEU, and urea). The behavior of wood after the combined treatment with compound organic modifiers and nano-SiO_2 is unknown so far. The dimensional stability, the functional groups, the thermal stability, and the SEM and energy dispersive analysis of X-rays (EDAX) images of modified wood will be evaluated, with a view of developing an effective and environmental means of modifying wood.

Materials

Scots pine (*Pinus sylvestris* var. *mongolica*) was collected in Dalian, China. The timber was processed into wood slices 2600 mm longitudinal (l) × 280 mm tangential (t) × 25 mm radial (r) in size. The air-dried MC of wood slices ranged from 15% to 20% before impregnation.

Synthesis of Compound Modifier

A three-necked flask was charged with urea (41% w/w), formaldehyde (56% w/w), and ammonia (3% w/w). The reaction mixture was stirred and kept at 35°C for 3 hours. At last, the pH was adjusted by sodium hydroxide or hydrochloric acid to be between 5 and 7. At the ambient temperature, 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 (44.25 w/w) were added into this reaction vessel for 10 min with constant mechanical stirring. At last, silica sodium (10% w/w) was added into above organic composite modifier and stirred for 5minutes. The silica sodium (weight ratio, $Na_2O/SiO_2 = 1:3.3$) was obtained from Nanjing High Technology Nano Material Co., Ltd., Nanjing, China.

Pulsedipping and In Situ Polymerization by Kiln Drying

The Scots pine logs were selected approximately 200 mm in diameter and then sawn into 2600 mm in length. First, the fresh Scots pine 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. After soaking, the impregnated logs were sawn into boards about 2600 × 280 × 25 mm (l × t × r) in size for kiln drying. Drying time was approximately 200 hours and the pressure on the timber was 0.2 MPa.

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), method for determination of the swelling of wood (GB/T 1934.2-2009), method for determination of the shrinkage of wood (GB/T 1932-2009), 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 D2240 standard. The specimens for bending strength with a dimension of 300 × 20 × 20 mm (l × t × r), for compression perpendicular to grain of wood with a dimension of 30 × 20 × 20 mm (l × t × r), the others were carried out with 20 × 20 × 20 mm (l × t × r). For this measurement, 20 specimens were tested and the average was recorded.

Antiswelling Efficiency

The antiswelling-efficiency (ASE) index was determined to evaluate the characterization of the dimensional stability of modified wood specimens. All modified samples with a dimension of 20 × 20 × 20 mm (l × t × r) were placed in distilled water. Samples dimensions were measured before exposure at dry state (due to treatment process) and after weight stabilization. Regular weight measurements were made to determine the EMC of samples with time. The

volumetric swelling coefficients were calculated according to Eq. 1. The ASE was calculated from the wet and oven-dried volumes of the natural and modified wood specimens according to Eq. 2.

$$S(\%) = \frac{V_2 - V_1}{V_1} \times 100 \qquad (1)$$

where V_2 stands for the modified sample volume after stabilization in the distilled water, V_1 for the oven-dried sample volume before treatment.

$$\text{ASE}(\%) = \frac{S_c - S_t}{S_c} \times 100 \qquad (2)$$

where S_c stands for the volume swelling coefficient of natural blocks, S_t for the volumetric swelling coefficient of the modified wood blocks.

Water Uptake

To evaluate the hydroscopicity of natural and modified wood, the cubic specimens were prepared 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 hours. 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,

$$\text{WU}(\%) = \frac{m - m_0}{m_0} \times 100 \qquad (3)$$

where m is the final mass and m_0 is the initial mass.

FTIR Spectroscopy

The natural and modified wood samples were ground into a 120-mesh particle size and embedded in potassium bromide 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 Analysis

A thermogravimetric analyzer (TGA) (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-Al_2O_3 was used as the reference material. During testing, the heating unit was flushed with a continuous nitrogen flow at a pressure of 8 KPa.

SEM—EDAX

A US 8020 model SEM attached with an energy dispersive X-ray (EDX) spectrometer was used to observe the natural and modified wood. The specimens were sputtercoated with a layer of gold and mounted on aluminum stubs with conductive adhesive tape. The working conditions were described 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

Table 1 shows the density and mechanical properties of the natural and modified specimens. The modified wood possessed higher density than the natural wood. The air-dried density increased by 52.38% and the oven-dried density by 71.05%. On the one hand, physical filling of organic and inorganic modifiers in the lumen increased the mass of the samples; on the other hand, there were abundant reactions of etherification and esterification between functional modifiers cellulose, hemicelluloses, and lignin, as a result, the polymers embedded in the cell walls increased the density of wood. Meanwhile, the surface hardness

Table 1. Physical and mechanical properties of natural and modified wood.

Properties	Natural	Modified	Improvement (%)
Air-dried density (g·cm^{-1}) (SD)	0.42 (±0.04)	0.64 (±0.01)	52.38
Oven-dried density (g·cm^{-1}) (SD)	0.38 (±0.03)	0.65 (±0.01)	71.05
Bending strength (MPa) (SD)	61.44 (±5.53)	80.25 (±5.24)	30.62
Compressive strength parallel to grain (MPa) (SD)	27.25 (±1.09)	74.69 (±2.35)	174.11
Hardness (shore D) (SD)	38.60 (±2.68)	49.90 (±4.65)	29.25
Antiswelling-efficiency (%) (SD)	—	68.12 (±0.39)	—

of modified wood was 29.25% greater than the natural wood. The increase in surface hardness may have been caused by the formation of bonding between the wood fiber and the modifier. In addition to this, the nano-SiO$_2$ particles may play an important part in it.

The mechanical properties of bending strength and compressive strength parallel to the grain are also shown in Table 1. The modified Scots pine wood revealed an improved bending strength by 30.62%; and the compressive strength parallel to grain were also significantly elevated by 174.11%. These results were in keeping with the expectation that high density and hardness should entail better mechanical properties.

Dimensional Stability

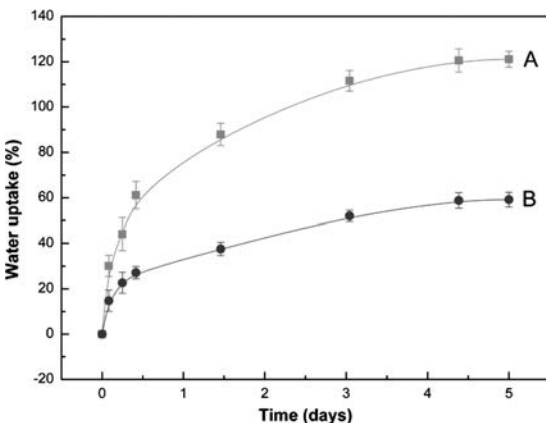The water uptake results of natural and modified wood samples as a function of time at room temperature are shown in Fig 1. As visible, the water absorption rate of modified wood was markedly lower than that of the natural timber after immersion in water for 5 days at atmospheric pressure. The both the natural and modified wood absorb water quickly within the first 12 hours. Then, the curves flatten. The final water uptake of the modified wood decreased from 121.13% to 59.13%.

In addition, the ASE of the modified wood is 68.12%. Differences in the distribution of modifiers in terms of lumen filling and cell wall modification should also be reflected in the dimensional stability of samples, which was determined by a water soaking method (ASE). In natural wood, water soaks the hydrophilic cell wall, leading to a reversible swelling of wood. However, the presence of hydrophobic material in the cell wall reduces the amount of absorbed water, and is therefore expected to limit the swelling of wood. Therefore, the ASE can be interpreted as a value for the improved dimensional stability of the modified wood cubes as a high ASE value reflects a dimensionally stable wood sample.

Figure 1. Water uptake curves of wood: (a) natural wood and (b) modified wood.

FTIR Analysis

The FTIR spectrum of natural Scots pine wood (Fig 2A) is typical for softwood 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 unconjugated ketone, carbonyl, and aliphatic groups (xylan). The absorbance at around 1619and 1511 cm^{-1} arose from
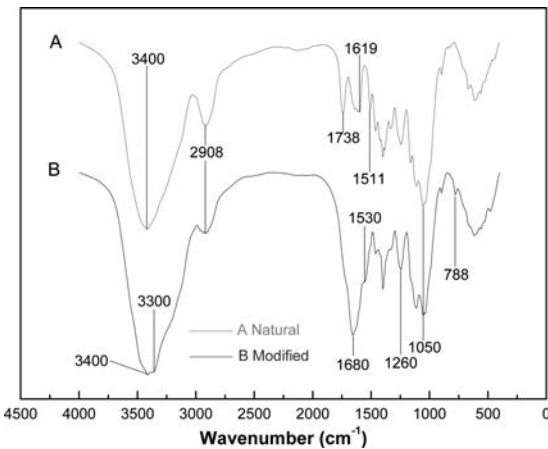
Figure 2. Fourier transform infrared spectrum of natural and modified wood.

O-H bending and aromatic phenyl C=C stretching of lignin respectively (Chen et al 2010). The fingerprint region is dominated by the bands approximately 1050 cm^{-1} due to various polysaccharide vibrations (Horikawa et al 2006; Devi and Maji 2011).

In Fig 2B, it was apparent that obvious that the modified wood samples had typical infrared absorption characteristics of secondary amide spectral bands I (1680 cm^{-1}), secondary amide spectral bands II (1530 cm^{-1}), and secondary amide spectral bands III (1260 cm^{-1}). These absorption bands are attributed to the bond formation between the functional –NHCH$_2$OH groups in methylolurea of the organic modifier and the wood hydroxyl –OH groups. The spectrum of modified wood illustrated the stretching vibration absorption peak from 3400to 3300 cm^{-1} caused by functional groups –OH and –NH, which indicated that there was a great potential for forming intermolecular hydrogen bonds. The intensity also increased, which was ascribed to methylolurea, DMDHEU, and urea; there are an abundance of –OH and –NH groups in these molecules, and they were inserted into the wood microporous structure. The presence of sodium silicate is demonstrated 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 the modifier. Meanwhile, reactions also occurred within the modifier itself.

Thermogravimetric Analysis

The thermogravimetric curves of the natural and modified wood are shown in Fig 3. It was apparent that the TGA and derivative thermogravimetric (DTG) analysis 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 175°C for both samples was due to the evaporation of free water and bound water (Peng and Wu 2010). According to
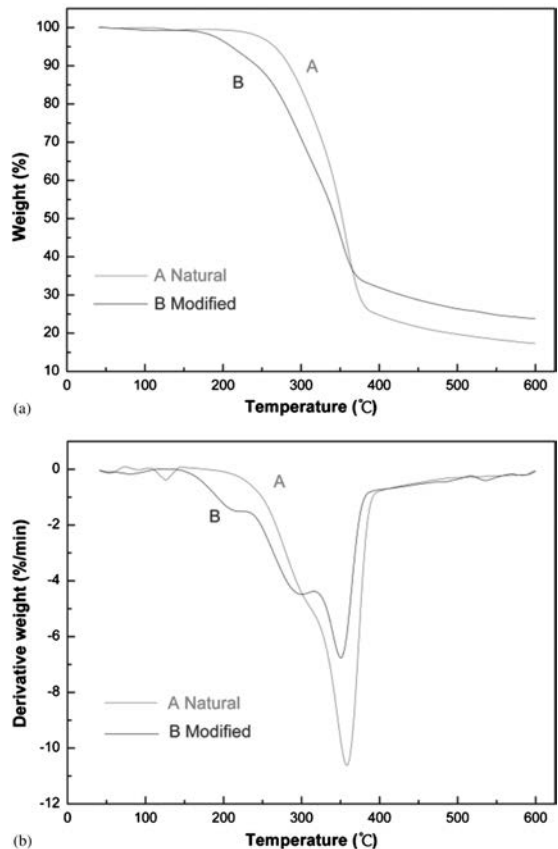

Figure 3. (a) Thermogravimetric analyzer and (b) derivative thermogravimetric curves of natural and modified wood, respectively.

the DTG curve, the thermal decomposition process of natural wood mainly showed two stages as follows: the first stage from 190°C to 310°C was mainly owing to decomposition of hemicelluloses (mass loss ~21%) with an observable shoulder (Shafizadeh and Fu 1973); the second stage from 310°C to 385°C was primarily attributed to the cellulose decomposition (mass loss ~55%) with a strong exothermic peak (~362°C) (Yang et al 2007). Besides, the pyrogenic decomposition of lignin with superior thermal stability was slow and happened under the whole temperature, so there was no an obvious characteristic exothermic peak (Wu et al 2009).
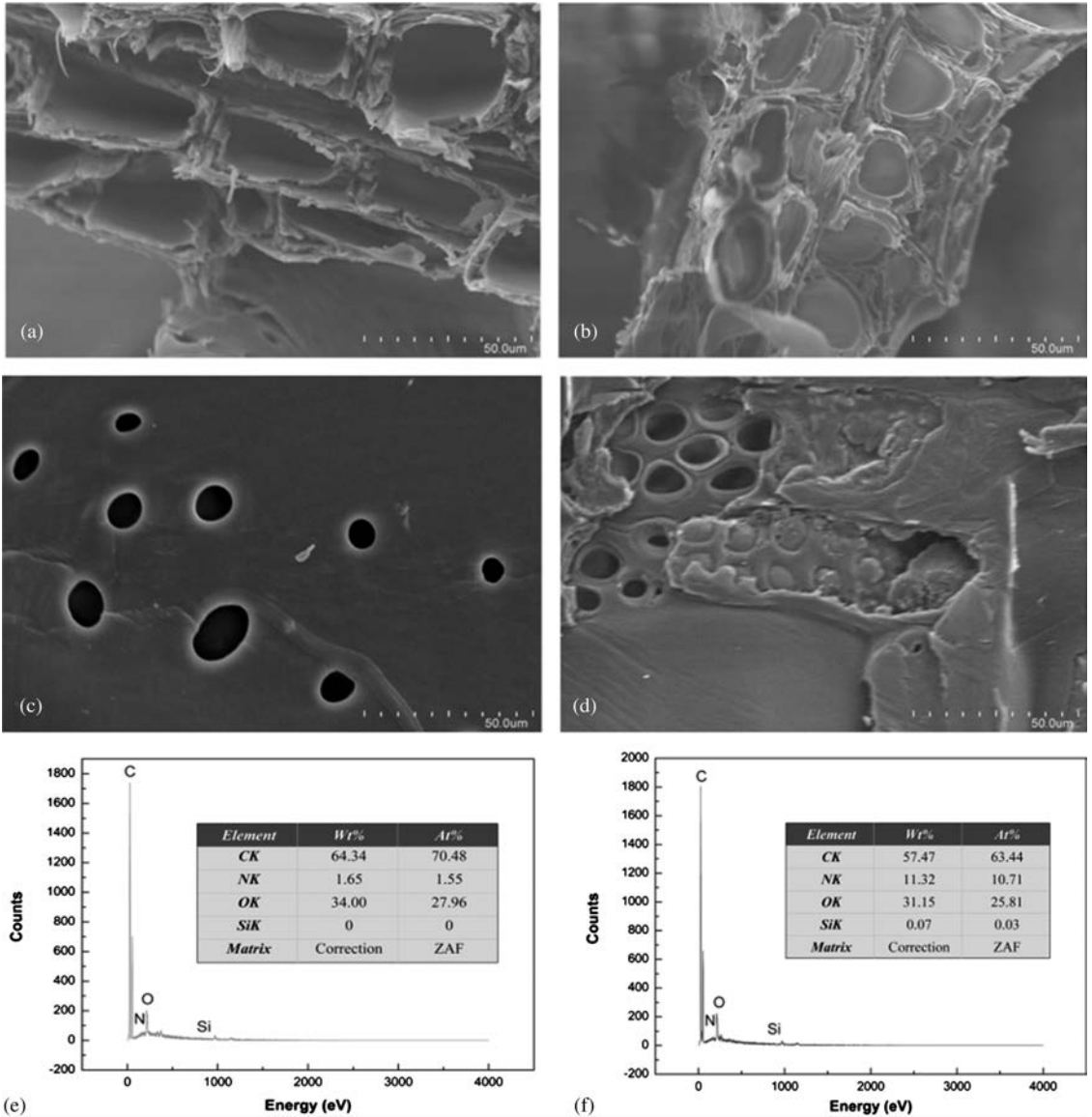

Figure 4.   FESEM image of natural and modified wood: (a) transverse section of natural wood, (b) transverse section of modified wood, (c) radial section of natural wood, and (d) radial section of modified wood; (e) and (f) energy dispersive X-ray spectra of natural and modified wood, and the inserts show the corresponding mass proportions and atomic proportions of C, N, O, and Si elements, respectively.

For the modified wood, it is well known that SiO_2 has superior thermal stability, and the combination of wood matrix with SiO_2 might be conductive for modified wood to obtaining improved heat resistance. Meanwhile, there were a lot of formed intermolecular hydrogen bonds between $-NH_2$ of methylolurea and $-OH$ of holocellulose. And $-OH$ groups of organic modifiers reacted with the hydroxyl groups of the total cellulose to form stable ether linkage. Thus, the thermolysis of hemicelluloses and cellulose will need more energy. So, the wood inserted modifiers possessed a better thermal stability. The lower rate of thermal decomposition rate for modified wood implied that the existence of modifiers on wood matrix significantly enhanced the thermal stability of the composite.

SEM-EDAX Analysis

The microscopic morphologies of natural wood and modified wood were observed by SEM. Fig 4A exhibits that the native wood samples displayed a highly void/hole structure before modification. Whereas, there was an obvious change in wood microstructure that the cell wall and vessels of modified sample were filled by solid wood modifiers. As shown in Fig 4D, compared with the smooth surface of original wood (Fig 4C), the surface of modified wood was coated with dense uninterrupted resin membrane structure. Besides, the natural wood structures of modified wood were also disappeared, and there is 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 4E and Fig 4F), the N mass ratio and atom ratio both dramatically increased after modification from 1.65% to 11.32%, and 1.55% to 25.81%, respectively. Meanwhile, Si element appears on modified 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

1. The compound organic modifiers and nano-SiO_2 had been successfully in situ deposited on the cell wall. The physical and mechanical properties in terms of density, bending strength, compressive strength parallel to grain, and hardness showed a remarkable enhancement compared with the natural sample after modification. Meanwhile, the water uptake of modified wood decreased sharply was due to the reduction of $-OH$ groups via chemical reaction with hydroxyl groups of wood.
2. The FTIR indicated that the wood modifier partly bonded to the cell wall via a cross-linked reaction between the wood modifier and wood fiber. The sodium silicate in the mixture led to a Si-O-Si framework on heat curing.
3. The TGA and DTG showed that the thermal stability of the modified wood was strengthened. The SEM and EDAX analysis indicated that the wood modifier was smoothly distributed in the wood cell lumens. Furthermore, the presence of compound modifier as a cross-linking monomer dramatically improved the comprehensive properties of wood.

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