

EFFECT OF UREA-FORMALDEHYDE PREPOLYMER ON FAST-GROWING WOOD

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ABSTRACT

The objective of this study was to investigate the effects of functional wood modifier (urea-formaldehyde prepolymer) on fast-growing wood. The physical and mechanical properties and mainly chemical components were tested. Thermo-gravimetric analysis resulted in thermal stability improvement of the modified composites. The durability against fungus was examined and weight loss reached 6.16 % after modification. The FTIR spectroscopy showed the chemical changes in wood after modification and illustrated the modified mechanism. Finally, SEM and EDXA micrographs presented the distribution of wood modifier in cell wall.

KEYWORDS: Wood modifier, physical and mechanical properties, mechanism.

INTRODUCTION

Fast-growing woods are widely planted in China and possess some inferior characteristics, which are expected to be used as an alternative raw material for furniture and construct production. Due to the factor of short growing cultivation, the fast growing woods, may also have some undesirable properties regarding the low bond strength, poor mechanical properties and dimensional stability (swelling and shrinking), which limit their application in modern life.

In the past few years, the chemical wood modification has been accelerated considerably due to the increasing demand for the high quality wood raw material. This has led the research toward the fast-growing woods for their low price and high quality. Generally, wood is a natural complex porous materials consisting mainly of celluloses, hemicelluloses, and lignin. Special structure is the vital factor for the properties of wood in terms of physical and mechanical property, thermal stability and so on (Wang and Cooper 2005).

The chemical wood modification can be defined as a chemical reaction between some reactive part of wood and a simple chemical reagent, with or without catalyst, to form a covalent bond between the two (Rowell 1980). Chemical modification is an effective way to enhance wood properties. Recently, considerable work has been done on the wood modification by impregnation with a variety of wood modifier such as phenol formaldehyde, methyl methacrylate, glycidyl

methacrylate, and maleic anhydride to overcome the disadvantageous characteristics of fast-growing woods.

Wood modification with chitosan acetate solutions significantly improved the physical properties (Basturk and Guntenkin 2009). Phenol formaldehyde resin treatment was widely used for better dimensional stability and mechanical strength in different woods (Furuno et al. 2004). Papadopoulos displayed the effect of wood modified with isopropyl glycidyl ether on the sorption of water vapour. The results confirmed the reduction in hygroscopicity was lower than that of esterification with acetic anhydride (Papadopoulos 2008).

The aim of this study was to assess the improvement of fast-growing wood on the physical and mechanical properties, thermo-stability and durability against wood decay by a multi-functional wood modifier. Meanwhile, the major chemical compositions were analyzed to investigate the group changes after chemical modification. Furthermore, Fourier Transformed Infrared Spectroscopy (FTIR) analysis was performed to confirm the chemical reaction between the modifier and wood. Finally, the distribution of the modifier was characterized by Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Analysis (EDXA).

MATERIAL AND METHODS

Raw materials

The fast-growing wood (*Populus x euramericana* cl. Zhonglin 46) sample originated from Shandong province, China. Each felled stem was cross-cut into 1 meter-long logs, which was sawn into 100×20×20 cm (L×W×T) boards for impregnating. The moisture content of samples was about 60 %.

Synthesis of wood modifier and heat treatment

A functional wood modifier was composed of urea-formaldehyde prepolymer (Pu et al. 2009b) synthesized in a laboratory with the following conditions: inorganic salt (2 % w/w), solidifying agent (10 % w/w), and stabilizing agent (4 % w/w) (Pu et al. 2009a). The solid content of wood modifier was 40±3 % and the viscosity was about 6 mPa.s.

The heat treatment was performed on board 100×10×3 cm (L×W×T) in a dry kiln. The hot-press procedure took about 110 hrs under 0.5-0.7 MPa.

Physical and mechanical properties

The samples were prepared for evaluating physical and mechanical properties according to the Chinese standard GB/T 1936.1-2009 : Method of testing in bending strength of wood, GB/T 1939-2009 : Method of testing in compression perpendicular to grain of wood, GB/T 1934.2-2009 : Method for determination of the swelling of wood, GB/T 1934.1-2009 : Method for determination of the water absorption of wood, GB/T : Method for determination of the shrinkage of wood and GB/T 1933-2009 : Method for determination of the density of wood. Furthermore, the specimens for bending strength with a dimension of 30×2×2 cm (L×W×T), for compression perpendicular to grain of wood with a dimension of 3×2×2 cm (L×W×T), the others were carried out with 2×2×2 cm (L×W×T). The average data of ten specimens for each kind of measurements are recorded.

Wood chemical composition analysis

Both unmodified and modified wood samples were ground into sawdust (40-60 mesh). The tests were carried out according to GB/T 2677.4-93 : Method for content of hot-water extract, GB/T 2667.6-94 : Method for content of alcohol-benzene extract, GB/T 2667.8-94 : Method for content of lignin extract, and GB/T 2667.2-93 : Method for content of holocellulose extract.

TG analysis

Thermal stability experiments were performed with an apparatus (Shimadzu DTG-60, Japan). The temperature was raised from 10 to 600°C at a rate of 20°C.min⁻¹ in a nitrogen atmosphere. The samples (5-10 mg) were placed in alumina crucibles.

FTIR analysis

FTIR analysis was carried out using a Tensor 27 (Bruker, Germany). The spectra consisted of an average of 32 scans recorded in the wave number range of 4.000 to 400.cm⁻¹ with a spectral resolution of 2.cm⁻¹. The samples were mixed with the dried KBr (80:1 in weight) and pressed into discs.

Fungal decay analysis

Unmodified and modified wood blocks were cut into specimens of 2×2×1 cm (L×W×T) for fungal durability evaluations and were dried at 103±2°C to constant weight before the decay experiment. The experiments were conducted in Petri dishes with maize flour, malt agar and inject with a piece of mycelium of a freshly grown brown rot fungus *Coriolus versicolor*. The Petri dishes were placed at 28°C and 75 % relative humidity (RH) until the surface of medium was full of colonization by the mycelium. Samples degraded by brown rot fungus *Coriolus versicolor* for 12 weeks. Then, the mycelia and impurity were removed from the Petri dish. The samples were dried at 103°C until mass stabilization and weighed the samples to analyze the change caused by the fungal decay.

$$\text{Mass loss} = (m_0 - m_1) / m_0 \quad (\%)$$

where: m_0 - the initial drying mass of the sample before exposure,
 m_1 - the mass of the sample after fungal attack.

Scanning electron microscope analysis

The unmodified and modified samples were characterized by a JSM 5900 model electron microscope and a thin gold-palladium was deposited on the exposed surface of samples to reduce the charging effect. The experiments were operated at 15 kV.

EDXA analysis

A JSM 5900 energy-dispersive X-ray analyzer were conducted to investigate the distribution and of C, N, O, Si element in the microstructure of the samples. The samples were sputtered-coated with a thin layer of gold and the experiment was tested at 20 kV.

RESULTS AND DISCUSSION

Physical and mechanical properties

To explore the fundamental changes in physical and mechanical properties after modification, samples were analyzed via a series of tests. Tab. 1 displays that the modified sample exhibited higher density than the unmodified sample. The air-dry density was increased by 54.76 % compared with the unmodified ones. The basic density and over-dry density were increased by 52.77 and 58.97 %, respectively. Meanwhile, the bending strength and compressive strength parallel to grain were increased by 34.92 and 40.54 %, respectively. The properties of water uptake and moisture absorption of modified wood were improved significantly in comparison to the unmodified wood.

Tab. 1: Physical and mechanical properties of unmodified and modified sample.

| Sample | Air-dry density | Basic density | Over-dry density | Bending strength (MPa) | Water uptake (72 h) (%) |
|----------------|-----------------------|---------------|------------------|------------------------|-------------------------|
| | (g.cm ⁻³) | | | | |
| Unmodified | 0.42 | 0.36 | 0.39 | 63 | 104 |
| Modified | 0.65 | 0.55 | 0.62 | 85 | 87 |
| Additional (%) | 54.76 | 52.77 | 58.97 | 34.92 | -19.54 |

| Sample | Compressive strength parallel to grain (MPa) | Moisture absorption (volume) | Moisture absorption (radial) | Moisture absorption (tangential) |
|----------------|--|------------------------------|------------------------------|----------------------------------|
| | | (%) | | |
| Unmodified | 37 | 3.74 | 4.12 | 9.72 |
| Modified | 52 | 3.14 | 3.91 | 7.03 |
| Additional (%) | 40.54 | -16.04 | -5.10 | -27.67 |

The increased density can be interpreted that the impregnated wood modifier formed a chemical bond between the wood modifier and wood fiber. Moreover, the deposition of hemicelluloses in the hot-press drying enhanced the bending strength and compressive strength parallel to grain, which also supported analyses of major composition and thermo-stability. Hydroxyl groups were mainly responsible for water uptake and moisture absorption of wood (Popper et al. 2005). The wood modifier reduced -OH groups in wood due to a chemical reaction, which mitigated the susceptibility of wood fiber to water.

Wood chemical composition analysis

Wood is a natural polymeric material, made up mainly of cellulose, hemicelluloses, and lignin, as well as small amounts of extract. These components are significantly responsible factors for the physical, mechanical, and thermal properties of wood (Winandy and Rowell 2005). For better understanding of the mechanism of modified reaction which takes place after wood modification, data about the major chemical composition of the unmodified and modified

samples was analyzed. Fig. 1 presented that the content of hot-water extract and benzene alcohol extract increased to 16.82 and 9.04 %, respectively, compared with the unmodified sample (5.79, 2.81 %). While, the content of lignin and holocellulose decreased to 16.41, 60.26 %, respectively, compared with the unmodified sample.

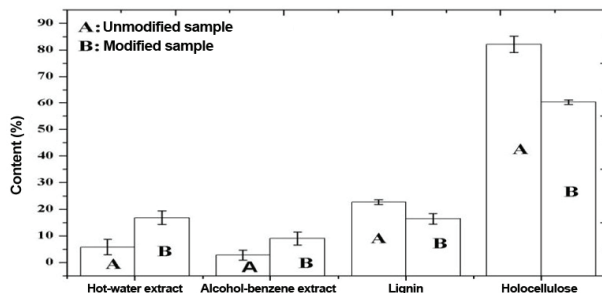


Fig. 1: Content of major chemical composition.

The increasing content of hot-water extract and alcohol-benzene extract demonstrated that the wood modifier distributed among intercellular space of wood. Although extract constitutes less than other components, they had a major contribution to the physical and mechanical properties of wood. The increment of hot-water extract and alcohol-benzene extract explained the enhancement of physical and mechanical properties. While, the decrease of acid-insoluble lignin and holocellulose can attribute that the wood modifier impregnated into the inner structure of wood and reacted with the major components of wood. The change of wood major chemical component confirmed the chemical reaction between the wood modifier and composition of wood.

TG analysis

The DTA curve of unmodified samples shows four stages of degradation. The first stage corresponded to the loss of water (up to 120°C) with a 3 % mass loss. The second stage referred to decomposition of hemicelluloses and unstable cellulose (180 to 220°C) with a 14 % mass loss. The third stage was associated with the combustion and degradation of cellulose (270 to 370°C) with a 55 % mass loss. The last stage was relevant to the degradation of lignin. After chemical modification the DTA curve of modified sample showed a sharp change. The first stage was similar to the unmodified sample. The second stage, there was an obvious much slower mass loss (10 %) than the unmodified samples. The reason can be summarized that the reaction between wood modifier and wood enhanced the stability of the hemicelluloses and cellulose. Meanwhile, in the second stage, the mass loss involved the decomposition of some inactive fragmentation from wood modifier. However, the third stage appeared a severe mass loss which can be ascribed to the react between the wood modifier and wood. The weaker bond reaction was easily broken under the high temperature. It was approximately the same behavior for the fourth step in comparison with the unmodified samples.

The DTG curves confirmed the enhancement of wood stability. The first absorption peak in 50°C was involved in the absorbance of heat due to water evaporation. The second absorption peak occurred at the 205°C due to the absorbance of heat due to pyrolysis of hemicelluloses. While, the deposition of lignin and cellulose caused a strong exothermic peak which occurred at the 510°C due to the deposition of lignin and cellulose. After wood modification, the absorption

peak at the 205°C appeared to be weakened, which confirmed the conspicuous increased stability of hemicelluloses.

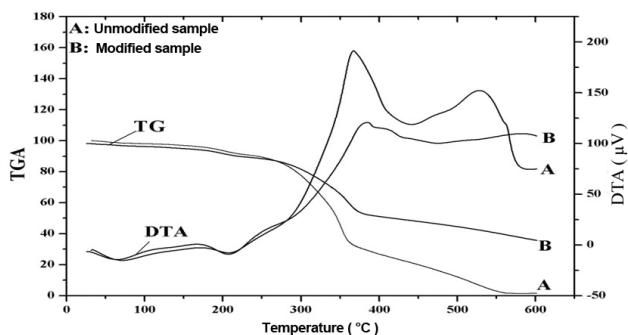


Fig. 2: TGA and DTA curves of modified and unmodified sample.

FTIR analysis

Fig. 3 presents the FTIR spectrum of unmodified and modified samples. The region 400 to 4000. cm^{-1} was studied to demonstrate a chemical reaction of wood modification. Compared with -OH absorbance at 3435. cm^{-1} of unmodified wood, the corresponding band of modified shifted to 3351. cm^{-1} and the intensity is diminished, which was attributed to the cross-linked reaction between wood modifier material and the hydroxyl groups of fiber. Meanwhile, a sharply decreased intensity at the 1.000–640. cm^{-1} (out of plane C–H bending vibration) manifested the shrinkage of -OH groups. A decrease in carbonyl stretching vibration (C=O) at 1750. cm^{-1} after modification was associated with degradation of xylan from hemicelluloses. Moreover, a chemical reaction occurred in the group of hemicelluloses. Additional, the change at 1250. cm^{-1} and 1020. cm^{-1} (C–O stretching) and the absorption peak at 1670. cm^{-1} confirmed the N–C=O group from the modified sample which generated from wood modifier and wood carboxyl C=O.

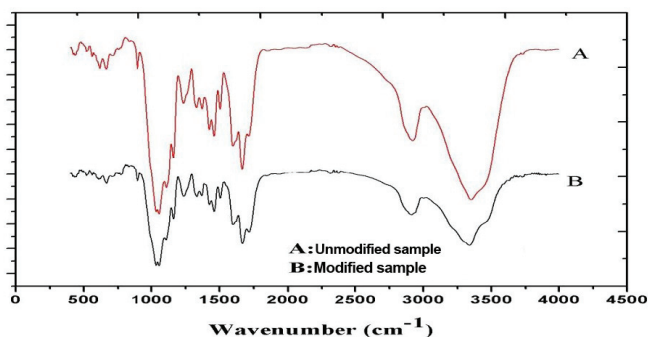


Fig. 3: FTIR spectrum of unmodified and modified sample.

Wood decay fungi analysis

The results showed an obvious improvement on durability of the chemical wood modification against the brown rot fungus *Coriolus versicolors*. The average decrease in weight loss of unmodified samples achieved 59.39 %, however, the average decrease in weight loss reached

6.16 % after modification, which can be considered as very durable (Class 1) according to the classification of natural durability against wood-destructive fungi (Fig. 4). The low weight loss occurred after modification which due to the following reasons. On one hand, the empty cell walls were covered with the wood modifier and react with the fiber, which reduced the low moisture content of modified wood and stopped the fungus from initiating the breakdown of hemicelluloses as an energy source (Hakkou et al. 2006). On the other hand, the resistance to fungal attack was probably related to the diminished contents of hemicelluloses and lignin after chemical modification and hot-press.

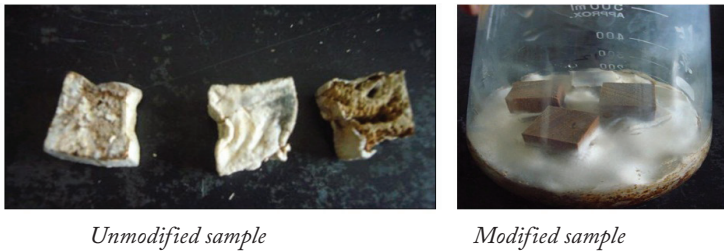
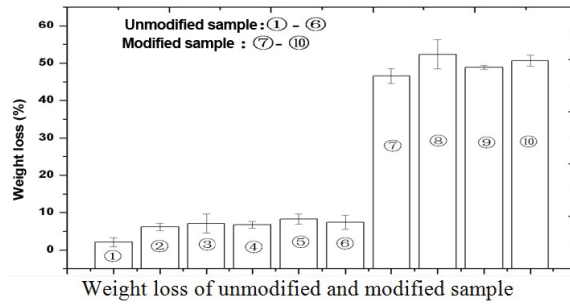


Fig. 4: The results of wood decay text.

Scanning electron microscope

Fig. 5 depicts the comparison SEM micrographs of transaction of unmodified (Fig. 5a) and modified sample (Fig. 5b). Wood displayed the empty cell wall, pit and parenchyma before modification. Whereas, there was an obvious change in wood microstructure that the cell wall and vessels of modified sample were covered by a considerable amount of solid wood modifier in comparison to the unmodified sample.

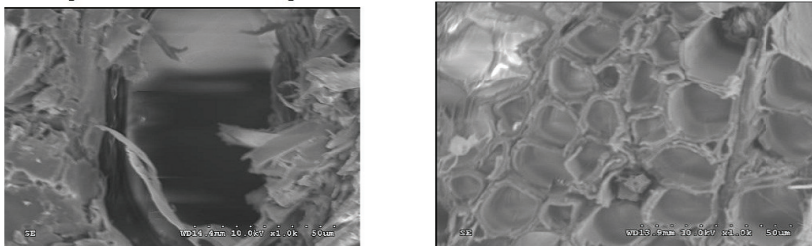


Fig. 5: SEM of unmodified and modified sample: a) Transaction of unmodified sample, b) Transaction of modified sample.

The empty spaces were occupied by the impregnated materials confirmed the enhancement of physical and mechanical properties was due to the wood modifier strongly adhered to the fiber. Meanwhile, the cell wall was full of wood modifier which blocked the passageway of water outside of wood that improved the properties of water uptake and moisture absorption (Stevanic and Salmén 2009).

EDXA analysis

The Fig. 6 presents the major elements distribution of modified wood samples. The EDXA micrographs presented that nitrogen was evenly distributed in the cell wall and intercellular space. Moreover, the wood cell contour was shown in the Fig. 6. Accordingly, it was obvious that the wood modifier materials impregnated into the cell wall and reacted with the active groups. The statistics manifested that the carbon content was 59.87 % (mole percent), the content of nitrogen was 11.50 %, and the content of oxygen was 28.43 %.

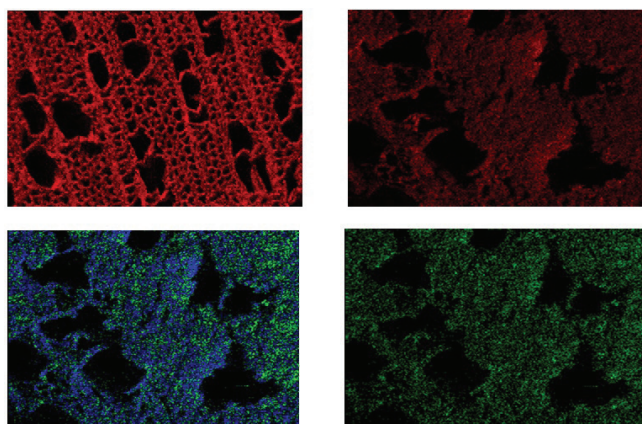


Fig. 6: EDXA analysis about element distribution of unmodified and modified sample: a) Distribution of C (unmodified \times 200), b) Distribution of C (modified \times 200), c) Distribution of N (modified \times 200), d) Distribution of O and N (modified \times 200).

Consequently, the SEM and EDXA micrographs manifested that the wood modified materials were found to be present either in the cell lumen or in the cell wall.

CONCLUSIONS

Modification with the functional wood modifier proved that the modifier effectively improved the properties of fast growing wood all-round. The main conclusions can be drawn as follows:

The physical and mechanical properties in terms of density, bending strength, compressive strength parallel to grain showed an obvious enhancement compared to the unmodified sample after modification. Meanwhile, moisture absorption and water uptake of modified wood decreased sharply was due to the reduction of $-OH$ groups via chemical reaction with hydroxyl groups of wood.

The changes of major chemical components revealed that the diminishment of acid-insoluble

lignin and holocellulose confirming the enhancement of dimensional stability and thermal stability. Moreover, the contents of hot-water and alcohol-benzene extract were found to increase to 16.82 and 9.04 %, respectively, which supported the evenly impregnation of wood modifier. Improvement of decay resistance and thermal stability associated with the multi-function wood modifier were proofed the functional modifier improved the property all-round.

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 results from SEM and EDXA micrographs showed the wood modifier was evenly distributed in the wood cell wall. Furthermore, the presence of functional-modifier as a cross-linking monomer significantly improved the properties of wood.

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