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EFFECT OF WOOD MODIFIERS ON THE PHYSICAL PROPERTIES OF FAST- GROWING POPLAR WOOD

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ABSTRACT

Investigate the wood modifilers effect on the physical properties of fast-growing poplar wood. Wood modifier was applied to impregnation drying operation on fast-growing poplar, and the characteristics of poplar wood before and after modification were observed with X-ray diffractometer (XRD), scanning electron microscope (SEM), energy-dispersive spectrometer and Fourier transform infrared (FTIR) spectrophotometer to analyze the physical properties of the wood. The modification could significantly improve physical properties of the poplar wood. XRD data illustrated that wood modifier could reduce crystallinity of wood from 39.65% to 36.89%. The findings of energy-dispersive spectrometer indicated that nitrogen (N), oxygen (O) and carbon (C) were evenly distributed in the wood. SEM spectrum analyzed the distribution of wood modifier in the wood pores. The FTIR spectra proved that there was cross-linking reaction between the modifier and the internal parts of the wood, and the amount of hydroxyl decreased sharply.

KEYWORDS: Wood science, fast-growing wood; wood modifier; chemical modification.

INTRODUCTION

Wood and wooden materials were the important social and economic construction material, not only widely used in all areas of daily life, but also widely applied in transportation, construction, aerospace and other industrial fields (Wang and Guan 2000). With the growing worldwide shortage of forest resources, especially precious wood. A large number of fast-growing species were widely cultivated in order to meet the global timber supply. Therefore, fast-growing wood with physical or chemical modification not only increased the added value of fast-growing wood, but also played a role on the protection of precious tree species resources. In recent years, China has strongly advocated planting fast-growing tree speciese. compared to the native trees, fast growing species had shorter growing year, and caused material differences, looser materials, poorer mechanical properties, thus narrowed the fast-growing wood application in everyday life (Tu et al. 2004). Because wood is a natural polymer material with porosity and stagger connected with different size, shape and different tubular unit of different connectivity (Wang and Guan 2000) having a fluid permeability, and its unique porous structure provided the condition for wood modification. Wood modification were the application of physical, chemical and mechanical methods to process wood logs(Chen et al. 2013, Fernandez et al. 2014), so that the physical and mechanical properties of wood, such as density, hardness, strength and dimensional stability were given a good improvement. In the paper, the hexamethylenetetramine formaldehyde and ammonia synthesed the intermediates carbamoyl urea with highly reactive. the pulsed pressure impregnation were compressed into wood. Then, the modified wood were performed press drying. The physical mechanical strength of wood before and after modification. through and X-ray diffraction, scanning electron microscopy, Fourier transform infrared and spectrum analyzer (FTIR) were employed to characterize the wood before and after modification.

MATERIALS AND METHODS

Materials

Test materials: poplar 107 (*Populus × euramericana* '74/76'); Origin: Beijing; average age: 6 years; average height: 18 m; average diameter: 25 cm; experiments specifications: 25 cm of diameter, 100 cm of length. about 65% moisture content.

Main reagent

Industrial grade carbamide were from Sinopec Ningxia Petrochemical company; analytically purified carbamide were from Beijing Chemical Works; analytically purified hexamethylenetetramine and ammonium chloride were from Beijing Chemical Works; analytically purified formaldehyde were from Xilong Chemical Limited Liability Company; analytically purified ammonia were from Beijing Chemical Works; analytically purified acetic acid were from Beijing Chemical Works.

Experimental method

Preparation of wood modifier. A certain amount of formaldehyde, carbamide, and hexamethylenetetramine were mixed in the reactor with certain proportio. Carbamide were completely dissolved, then reacted 3 hours under 27~30C° through reflux condensation. After completion of reaction, acetic acid and ammonia were applied to adjust the pH level of the modifying agent to pH 7 ~ 8. Amount of stabilizer were added to the above product, to obtain a functional timber modifier, which could be used in later experiment.

The trunk portion of poplar 107 with appoximate 25cm diameter of fresh longer-diameter timber were selected to saw into square wooden of 20 × 20 × 100cm as the experiment material. Timber modifiers were impregnated into the wood internally by impregnating machine pulse, and the impregnated wood board were sawn into 100 × 10 × 3 cm planks, and compressed and dried for 120 hours at 0.5MPa pressure. The dry processed wood were processed to specimens according to GB1927-1939-2009. In each content, 10 pcs of each specimen and modified wood were randomly selected to analyse the physical and mechanical strength before and after modification. The material and modified material were produced into wood powder (100 mesh) for instruments test. The wood characterization before and after modification were detected by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy analyzer (FTIR), energy dispersive X-ray spectroscopy (EDXA).

RESULTS AND DISCUSSION

Analysis of mechanical properties

The comparison of chemical modified fast-growing wood physical properties were completely illustrated in Tab. 1. Each wook index significantly improved after modifier processed. The air-dried wood density increased from 0.30 g•cm^{-3} to 0.58 g•cm^{-3}, totally, it increased 93.33 %. The basic density increased from 0.21 g•cm^{-3} to 0.44 g•cm^{-3}, totally increased 109.52 %. The absolute dry density increased from 0.27 g•cm^{-3} to 0.51 g•cm^{-3}, totally increased 88.89 %. The modifiers filled the gap of wood during impregnated wood, made the wood internal abundance and obvious weight gained. Furthermore, the strength of the wood also has significant changed, and the flexural strength increased from 67 MPa to 85 MPa. and parallel-to-grain compressive strength increased from 37 MPa to 52 MPa, respectively increased by 26.87 % and 40.54 %,. This was because the wood modifier penetrated into the wood internal parts, and had cross-linking reaction with wood active group (Wu et al. 2010, Gonzalez-Pena and Hale 2011).

At the same time, after compression and drying process, timber modifiers inside solidified under high temperature,and increased the strength of wood.

Tab. 1: Mechanical strength of natural and modified wood.

Name	Air-dry density (g•cm^{-3})	Basic density (g•cm^{-3})	Oven dry density (g•cm^{-3})	Bending strength (MPa)	Compressive strength parallel to the grain / (MPa)	48h water absorption (%)	Swelling property (%)			Shrinkage (%)		
							Tangential	Radial	Volume	Tangential	Radial	Volume
Material	0.3000	0.210	0.2700	67.000	37.000	104.000	3.740 0	4.120 0	9.720 0	5.800 0	5.000 0	10.800
Standard deviation	0.0170	0.019	0.019 0	2.920	2.940	0.110	0.001 3	0.001 4	0.001 3	0.001 4	0.001 3	0.0015
Modified material	0.5800	0.440	0.510 0	85.000	52.000	93.000	3.140 0	3.910 0	7.030 0	2.170 0	2.430 0	5.230
Standard deviation	0.0013	0.029	0.059 0	4.330	3.980	0.048	0.000 5	0.000 7	0.000 8	0.000 7	0.000 9	0.000
Enhancement ratio	93.3300	109.520	88.890 0	26.870	40.540	-10.580	-16.040 0	-5.100 0	-27.670 0	-62.5900	-51.400 0	-51.570 0

In Tab. 1, the water absorption, swelling and shrinking had significantly changed, of which the shrinking and swelling were more obvious, due to the largely existed water absorbing groups (hydroxy). Hydroxy was the main group to affect the wood water absorption, swelling and shrinking. During the modifier processing, the wood internal modifier could have cross-linking reaction with hydroxy, and reduced the quantity of hydroxy. Thus, the water absorption was reduced. The swelling and shrinking were decreased in a large scale.

Wood was a natural three-dimensional polymer composite, and the main component of its cell wall was composed of cellulose, hemicellulose and lignin (Gwon et al. 2010; Huang et al. 2012), which contained a large amount of hydroxyl groups, which was easy to make wood interior components combined with water. Wood cell wall was the main component to support of the structure of entire timber with a decisive role on wood physical and mechanical properties and dimensional stability (Hyunjung et al. 2011, Islam et al. 2012). Wood modifier diffusion penetrated into the interior of the wood in impregnation process, polymerization curing inside and deposited on the cell walls of wood after drying, reducing internal porosity of timber, increased its density and mechanical properties. Wood modifying agent could also occur with a hydroxyl group on the wood cell walls, reduced the number of terminal hydroxyl groups, and enhanced the strength and toughness of the wood cell wall, and made the modifier and wood combined with each other more solid. Wood pores were filled and the number of hydroxyl groups in internal components was reduced, which could effectively reduce the moisture absorption of the timber, thereby increased the dimensional stability of wood. In addition, the rise in density help to improve other physical and mechanical properties of wood (Xie 2013). The density of modified wood increased significantly, which increased the added value of fast-growing wood, so fast-growing wood can be used for applications widely.

X-ray diffraction (XRD) analysis

In order to examine the impact of timber modifiers on the structure of fast-growing wood, the fast-growing wood samples were characterized by XRD before and after modification. In Fig. 1, the XRD spectrogram at 2θ of timber modifer processed fast-growing wood were 17.0°, 22.5°, 35.0°, which were still within the characteristic diffraction peaks of wood cellulose (101) (002) (040) crystal plane, which described crystal structure of modified material did not been damaged, while the peak intensity level decreases, and crystallinity decreased from the 36.89 % to 39.65 %, as the modifier was an amorphous substance (Long et al. 2008). In the hot compressed drying process, the timber modifier not only occurred cross-linked reaction itself in the timber amorphous region, but also occurred chemical reaction with other components of wood, resulting in the swelling of amorphous regions. On the other hand, the modifier contained ammonia which could break wood crystalline regions, so it could reduce intensity of diffraction peak timber during the X-ray diffraction.

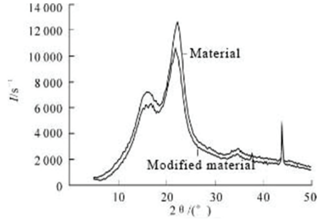


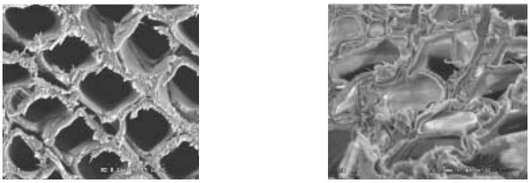
Fig. 1: X-ray diffraction diagram of natural and modified wood.

Urea was polar molecules with a strong permeability, and could penetrate into the amorphous regions of cellulose to destruct its structure, resulting in the cellulose molecular chain rearrangement to form part of the new crystalline area in the amorphous regions, so the degree of crystallinity of modified material was increased. After heat treatment, crosslinking agent of wood modification in the internal timber reduced the gap between the timber, while microfibrils distance of cellulose of wood cell wall in the amorphous region was reduced, and the narrowing in the same direction which was move closer so that microfibrils was more orderly arrangement (Lang 2013). Wood modifiers filled between the cell wall and cell microfibril cavity, and the chemical cross-linking reaction was occurred in certain active groups of the wood cell walls. When measured the X-ray diffraction, there has been a quasi-crystalline form, which may lead to crystallinity of modified material increased (Lang 2014).

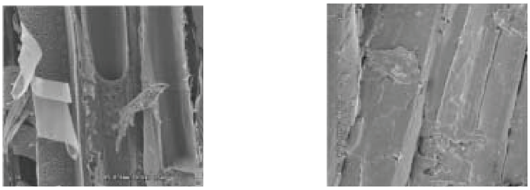
Cellulose was mainly component of wood xylem framework structure, and cellulose divided into crystalline and non-crystalline region, wherein hydrogen bonds were closely linked in the crystalline cellulose internal, and it was mainly determined by the degree of crystallinity of this part of the inner timber crystalline cellulose. Therefore, it can clearly be inferred from the increased of crystallinity that cross-linking reaction in situ polymerization has occurred between modifier and internal wood cellulose, increased crystal structure of timber, thereby enhanced the skeletal structure of wood. Therefore, it also help to improve physical and mechanical properties of timber.

Scanning electron microscopy (SEM) analysis

Fig. 2 expressed the scanned electron microscope image of the cross-section and radial section of fast-growing timber before and after modifier process. Figs. 2-A and 2-B are the cross-section scanning electron micrographs before and after the modified fast-growing wood, from the comparison, the modifier mainly penetrated into the chamber and cell gap of the wood, which indicated that the wood modifier impregnated to wood interior. Fig. 2-C and Fig. 2-D were the radial section SEM images of the fast-growing wood before and after modification, most pits of modified fast-growing wood were clogged by timber modifiers, and modifiers filled in wood internal. Because of wood modifiers polymerized in interior wood, which reduced the water absorbance and and swelling capability. The timber modilier became viscous substance and filled the wood internal structure, and had cross-linking reaction with wood interior group, thus enhanced the dimensional stability of the wood.



(A) Cross-section of creative (B) Cross-section of modified. material.



(C) Radial section of creative. (D) Radial section of modified material.

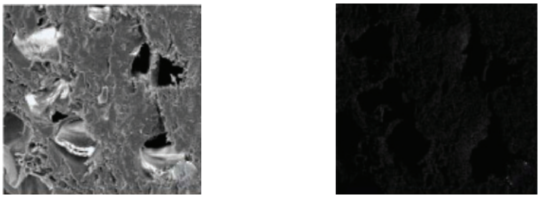
Fig. 2: SEM of natural and modified wood.

Observed by SEM, timber modifiers had evenly impregnated into the wood and duct cell gap, effectively filled the interior space of timber. There were many shades of ravines in the radial section of rough material, which were performed by radial section out the empty of timber. The diameter section of modified timber was obviously neat and smooth, which indicated that most of the fast-growing timber had been filled with pits modifiers. The filled of catheter of inner timber was large, inferred that during impregnation, the impregnating agent start to permeate into the timber through the catheter inside the timber primarily and circulated throughout the timber, and then through pressing, the modifier molecules diffused into cell gap of wood, cell walls and the cell cavity through Brownian motion to free under pressure. In the final drying process, the water evaporates, and the modifier polymerization curing and deposited wherever, played the role of filling the timber inside the pores, and thus achieved the purpose of modified, increased the density of the wood, mechanical properties, and size stability.

EDXA analysis

Fig. 3 was the wood element distribution EDXA analysis after modifier processed. It showed the mole fractions and the distribution position of nitrogen (N) carbon (C) oxygen (O) element in wood before and after modification. The evenly distribution of nitrogen (N) elements in wood cell wall and cell gap, even cell cavity, could clearly see the out.line of wood cells, which indicated that the modifier in fast-growing wood internal had a evenly distribution. The cells in fast-growing wood had a polymerization reaction with active groups. After chemical treatment, carbon (C) element was 58.78 % (mole fraction), nitrogen (N) element was 11.70%, and oxygen (O) element was 29.08 % in wood.

There were many pits in the catheter wall of poplar, which help the material conduction and switching. There were also special construction in phase at the two longitudinal conduit, which provided a theoretical basis for the various parts of the modifying agent and have the evenly penetration of wood. The figure could vividly illustrated the content and distribution of N element, O element and Si element in the modified wood, and C elements and their distribution. evenly impregnation of the wood could be obtained from the method, and the elements of N, O and Si evenly distributed in the wood cell wall and intercellular space, even in cell cavity, and outline of the cell timber, which showed the modified instructions polymerized reaction took place in the wood cells.



(A) SEM spectrum. (B) Carbon distribution.

(C) Nitrogen distribution. (D) Oxygen and nitrogen distribution.

Fig. 3: EDXA analysis about element distribution of treated wood.

FTIR analysis

Three natural polymer: cellulose, hemicellulose and lignin were made up of wood, whose main structure was a polysaccharide carbon chain, by detecting changes in their main functional groups, which could be inferred composition and location of the chemical reactions that occurred (Jebran et al. 2011, Linger et al. 2013, Willems et al. 2013). Fourier transform infrared spectroscopy was the most effective method to detect chemical functional groups. Fig. 4 was FTIR spectra of a timber before and after modification, among which the stretching vibration of hydroxyl group was at 3 500 cm^{-1}; 2 920 cm^{-1} was close to the C-H stretching vibration, including CH_2 and CH_3; 1 726 cm^{-1} was the C=O stretching vibration (xylan acetyl); 1596 cm^{-1} and 1 506 cm^{-1} were close to vibration of lignin with the benzene ring carbon skeleton; 1 460 cm^{-1} was correspondce to CH_2 bending vibration of the lignin and polysaccharides, and the vibration of carbon skeleton of the benzene ring; bending vibration 1424 cm^{-1} was correspondce to scissor vibration of CH_2 of cellulose and vibration of CH_2 of lignin; 1 374 cm^{-1} and 1 329 cm^{-1}were bending vibration of C-H and CH_2, respectively. 1 234 cm^{-1}~1257 cm^{-1} was stretching vibration of acyl-oxygen bond and a vibration of phenol ether linkages of lignin; 1 103 cm^{-1} was the absorption band with OH associated; 1 055 cm^{-1} was corresponding to stretching vibration in the C-O bond for the cellulose and hemicellulose.

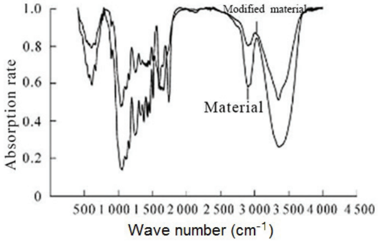


Fig. 4: FTIR analyze of modified and natural wood.

From the FTIR spectra comparison between the woods before and after modifer process, the number of hydroxyl groups of the modifier processed wood reduced significantly. The stretching vibrations of C-H decreased in 2 920 cm^{-1} area; stretching vibration of C=O (acetyl xylan) disappeared near to 1 726 cm^{-1}; carbon skeleton vibration of the benzene ring strengthened at 1 596 cm^{-1}; CO-OR bond of hemicellulose and Ph-O-R vibration of lignin weakened at 1 245 cm^{-1}; absorption band of hydroxy association weakened at 1 103 cm-1, which indicated that the timber modifiers not only filled in wood cell lumen and cell gap, but also had the cross-linking reaction with certain groups within the timber.

The analysis of functional groups by poplar infrared spectroscopy before and after modifying fully proved, timber modifiers had spread and penetrate into the wood cell wall structure, and occurred the reaction of cross-linking with terminal hydroxyl of interior wood components (mainly cellulose and hemicellulose), reduced the water main groups, which largely reduced the moisture-absorbent of wood, and improved stability of wood. The C-O-C covalent bond of this category was also very solid and stable, and it improved the retention and stability of the modifier in the timber interior. It could improve the mechanical strength of the timber.

CONCLUSIONS

Pulse pressure impregnation were performed on timber modifier modified fresh wood, then the processed wood shall perform hot compresson and dry procedure. The physical and mechanical properties were measured on woods before and after modification, and a variety of experimental instruments were employed to characterize the wood before and after modification. The results showed that, the wood density, bending strength, compressive strength parallel to grain, water absorption and other physical and mechanical strength have increased significantly after the timber modifier treatment. Through instrument characterization of XRD, FTIR, SEM and EDXA, the characteristics before and after modification proved that Wood modifier was evenly distributed in the intercellular cavity, cell wall and cell gap, had chemical cross-linking reaction with groups of internal structure in the timber, and reduced the number of hydroxyl groups in the wood, thereby increasedtheir physical and mechanical properties.

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