

Poplar Wood-Methylolurea Composites Prepared by *In Situ* Polymerization

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ABSTRACT: Chemical modification of wood is a potential way to obtain high quality wood. In this study, methylolurea was used to modify the poplar wood by *in situ* polymerization. The mechanical properties and dimension stability of the wood-methylolurea composites were investigated, and the modified samples were also characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The mechanism of *in situ* polymerization was presented in graphs. The test results showed that the mechanical properties and dimensional stability of natural wood were improved remarkably. FTIR analysis suggested that the methylolurea polymerized with the active groups of wood cell wall. XRD test showed that the crystallinity of wood increased after modification. Finally, the SEM analysis proved that the good interfacial adhesion of wood modifier between wood fiber and polymer. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Wood modification is a generic term describing the application of chemical, physical, and biological methods to improve the properties of wood. The aim is to improve the performances of the wood, including improvements in dimensional stability against moisture and bio-deterioration, mechanical property and weathering resistance.¹ The modification usually takes advantage of physical, thermal, and chemical methods. In the case of chemical modification, this involves the treatment with various chemical polymers to reduce the content of hydroxyl groups.^{2,3} The presence of hydrophilic groups (hydroxyl) in the three major wood polymeric components (cellulose, hemicellulose, and lignin) is the main factor for the unfavorable attributes, such as swelling, dimensionally unstable, and poor mechanical properties.^{4,5}

The properties of wood can be improved considerably by chemical treatment.^{6–8} The chemicals react with the hydroxyl groups of wood cell wall and subsequently polymerize by addition to the new formed hydroxyl group which arise from the chemical reagent. The reagent penetrates into the cell wall and that it is nonleachable in service. Many reagents, including polyaniline,⁹ methyl polymethacrylate,¹⁰ tetraethoxysilane, methyltriethoxysilane,¹¹ glutaraldehyde,^{12,13} vinyl acetate, acetic anhydride,¹⁴ furfuryl alcohol,^{15,16} lactic acid oligomers,¹⁷ and 1,3-dimethylol-4,5-dihydroxyethyleneurea are used to chemical modification.^{18,19} To improve its overall performance, fast-growing

poplar is modified using the method of vacuum-pressure-vacuum impregnation with a urea-formaldehyde resin-sodium montmorillonite intercalation as the modification solution.²⁰ The combined hydro-thermo-mechanically process is also used to improve the rot resistance of poplar wood. Bami and Mohebbi used a combination of two wood modification techniques, including hydrothermal wood modification and densification of wood, to improve the rot resistance of poplar wood.²¹ The special predrying rather than green logs were need in the process. However, the extra pretreatment will make the process of wood modification more complicated.

Chemical modification and thermal treatment can be operated simultaneously. After the wood was impregnated with monomers, the *in situ* polymerization was carried out under the heat of thermal treatment. It is possible to synthesize the intrinsically conductive polymer *in situ* within the wood structure of Southern yellow pine veneers. The polymer uniformly dispersed in the wood structure according to the light microscopy. The preferential formation occurred in the wood structure and cell wall, rather than in the lumen. The furfuryl alcohol molecules penetrated into the wood cell wall and polymerized with the wood cell. However, it is unclear whether the chemical bonds exist between the furfuryl alcohol polymer and the wood. Thus, much works still needed to identify the chemical differences between the wood and furfuryl alcohol prepolymers by investigating the leachate of furfurylated wood. A new

Table I. The Physic-Chemical Properties of Prepolymer

| Name | Density (g/cm ³) | pH | Viscosity (mPa s) | Solid content (%) | Free formaldehyde content (mg/100 g) |
|-------------|------------------------------|-----|-------------------|-------------------|--------------------------------------|
| Pre-polymer | 1.25 | 8.0 | 11 | 55.52 | 0.08 |

nonformaldehyde crosslinking system was composed of citric acid and 1,2,3,4-butanetetracarboxylic acid, which were representative polycarboxylic acids. The formation of polymerization between the wood and the reagent components led to an improvement on the tensile strength retention.²² Wood and lactic acid biopolymers have been used as constituents of an innovative biocomposite material, which exhibited remarkable properties for bending, stamping or flooring industrial uses. Different systems were made by soaking lactic acid oligomers into solid wood and then oven heating to induce *in situ* polymerization. The composite materials are expected to be useable for bending, stamping and flooring industrial uses, depending on their physical condition. A novel route to wood modification by trans-esterification of vinyl esters is developed in recent study. The reaction between unsaturated vinyl esters and the hydroxyl groups of maritime pine sapwood was catalyzed by potassium carbonate.²³

However, some reagents are ineffective to improve the properties of wood. In addition, some chemicals do not react with cell wall polymers which belong to a so-called substitution reaction. Many polymers, even though formed *in situ*, only fill the empty lumens in wood, resulting in a mixture of two materials rather than a real interaction.²⁴ In the present work, we have carried out chemical modification of poplar wood with methylolurea and carbamide. The impregnated wood was dried in a conventional drying kiln. The aim of this study was to evaluate the characterizations of wood-methylolurea composites prepared by *in situ* polymerization. The modified wood has been characterized in terms of the mechanical properties and dimensional stability, the reactivity of the functional groups, the crystallinity and their microstructure.

MATERIALS AND METHODS

The Wood Materials and Chemicals

The fresh poplar (*Populus euramevicana* cv. 'I-214') used were obtained from Beijing (China), which had initial moisture contents ranged from 60 to 70%. Urea, formaldehyde and ammonia were used for synthesis of methylolurea. Treatment of wood species was performed using methylolurea and urea solution. All chemicals used were of analytical grade.

Preparation of the Methylolurea

A three-necked flask was charged with urea (64%, w/w), formaldehyde (25%, w/w) and ammonia (11%, w/w). The reaction mixture was stirred and heated to 40°C for 3 h. Finally, sodium hydroxide and hydrochloric acid were used to adjust the pH of the prepolymer (methylolurea) to 7–8. The physic-chemical properties of prepolymer were listed in Table I.

Preparation of the Poplar Wood-Methylolurea Composites

The dimension of wood samples for impregnation was 20 cm in diameter and 100 cm in length. The fresh poplar wood was

impregnated with a pulse-dipping machine at the pressure of 0.7–0.8 MPa for 45 min. The composition of chemical reagent for wood impregnation was shown in Table II. Then, the impregnated samples were sawn into blocks about 7 × 14 × 100 cm³ (*T* × *R* × *L*) for thermal treatment. Thermal treatment was performed under atmosphere in an oven for 48 h. The oven temperature was increased from room temperature to 170°C.

Characterization

Ten specimens of natural and modified were analyzed using a universal mechanical testing machine (MWW-50). Tests were carried out according to GB/T 1933–2009 (Method for determination of the density of wood, China), GB/T 1936.1–2009 (Method of testing in bending strength of wood, China), GB/T 1936.2–2009 (Method for determination of the modulus of elasticity in static bending of wood), GB/T 1935–2009 (Method of testing in compressive strength parallel to grain of wood, China), GB/T 1941–2009 (Method of testing in hardness of wood), GB/1934.1–2009 (Method for determination of the water absorption of wood), GB/1932–2009 (Method for determination of the shrinkage of wood), GB/T 1938–2009 (Method of testing in tensile strength parallel to grain of wood) and GB/1934.2–2009 (Method for determination of the swelling of wood).

X-ray powder diffraction (XRD) patterns were recorded by a X'Pert PRO MPD diffractometer (Cu K α radiation, $\lambda = 1.5405 \text{ \AA}$) operating at 40 kV and 30 mA. The 2θ ranged from 10° to 50°. Fourier transform infrared (FTIR) spectroscopy spectra were obtained with a spectrometer Nicolet 510, using the KBr disk method. The FTIR spectra were recorded with detector at 4 cm⁻¹ resolution and 64 scans per sample. Scanning electron microscopy (SEM) images were obtained by a Hitachi 3400N scanning electron microscopy.

RESULTS AND DISCUSSION

Mechanical Properties

The average values of the mechanical properties of natural and modified wood are shown in Table III. According to Table III,

Table II. Chemical Reagents for Wood Impregnation

| Name | Methylolurea (%) | Urea (%) | Catalyst (%) |
|------|------------------|----------|--------------|
| A | 5 | 20 | 5 |
| B | 10 | 20 | 5 |
| C | 15 | 20 | 5 |
| D | 5 | 15 | 5 |
| E | 10 | 15 | 5 |
| F | 15 | 15 | 5 |

Table III. The Physical and Mechanical Properties of Natural and Modified Wood

| Name | Basic density (g/cm ³) | Bending strength (MPa) | Modulus of elasticity in static bending (MPa) | Compressive strength parallel to grain (MPa) | End hardness (N) | Tangential hardness (N) | Radical hardness (N) | Tensile strength (MPa) |
|--------------|------------------------------------|------------------------|---|--|------------------|-------------------------|----------------------|------------------------|
| Natural wood | 0.37 | 72.2 | 6786 | 41.3 | 3032 | 1348 | 1259 | 94.6 |
| A | 0.47 | 102.5 | 8402 | 65.9 | 3420 | 2034 | 1987 | 127.4 |
| B | 0.49 | 116.8 | 10,720 | 68.3 | 4142 | 2631 | 2527 | 136.7 |
| C | 0.52 | 131.4 | 12,287 | 69.1 | 4809 | 2938 | 3014 | 145.1 |
| D | 0.40 | 92.1 | 8295 | 56.6 | 3296 | 1910 | 1830 | 115.8 |
| E | 0.43 | 117.6 | 9272 | 60.0 | 3920 | 2315 | 2346 | 129.3 |
| F | 0.47 | 129.1 | 9920 | 63.1 | 4628 | 2673 | 2741 | 140.8 |

the mechanical properties of wood increased with the increasing amount of methylolurea and urea. Compared with the natural wood (0.35 g/cm³), the basic density ranged from 0.40 to 0.52 g/cm³ with the amount of methylolurea ranged from 5 to 15%. Hardness implies the ability of material to resist deformation. The modified wood exhibited much higher hardness than that of natural wood. The tangential hardness, radical hardness and end hardness of modified wood increased by 41.7–117.95%, 45.35–139.40%, and 12.8–58.6%, respectively. Meanwhile, the modification caused an obvious enhancement of bending strength, compressive strength parallel to grain and modulus of elasticity static in bending. The tensile strength of modified wood also increased compared to the natural wood, and such increases become higher as the content of modifying agents was increased, especially for sample C. These results could be explained by that the adhesion and compatibility between wood fibers and the polymer were enhanced by the reaction between methylolurea and wood cell. The methylolurea had participated in the *in situ* polymerized reaction to form complicated large molecules, which increased the viscosities of the wood modifier. The modifier had an ability to fill the void spaces and the strong branched polymer inside wood which can enhance the mechanical properties. It was well known that changes of the hemicelluloses play significant roles in the mechanical properties of wood at high temperatures. Hemicelluloses were less

resistant to the heat than cellulose and lignin during the thermal treatment. Improvement of mechanical properties of modified woods could also be attributed to the degradation of hemicelluloses.

The Dimensional Stability

Water absorption of the modified and natural wood at the soaking time of 72 h is demonstrated in Table IV. Lower moisture and water absorption is an indication of good shape stability. The water absorption decreased from 116.6 to 76.2% (Sample C) after modification. The results showed that the water absorption of modified wood dropped with the increasing amount of methylolurea and urea. The trend coincided with the changes in the swelling of natural and modified wood in transection, radicalsection and volume. It was reasonable to assume that methylolurea can polymerize with the wood fiber, which would decrease the amount of hydroxyl groups (—OH) of wood. The methylolurea not only covalently linked with hydroxyl groups but also interacted with the wood fiber through *in situ* polymerization. Therefore, the amounts of free hydroxyl groups (—OH) in the wood cellulose were reduced because some of them interacted with methylolurea agent. The swelling data was consistent with the result of FTIR spectra. According to the theory of moderate hydrogen bonds, the length of the hydrogen bonds was considered as an indication of the bond strength. The literature provided information about the hydrogen bond length

Table IV. The Dimension Stability of Natural and Modified Wood

| Name | Water uptake 72 h | Over-dried to air-dried | | | Over-dried to the maximum water absorption | | |
|--------------|-------------------|-------------------------|--------------------|------------|--|--------------------|------------|
| | | Transection (%) | Radicalsection (%) | Volume (%) | Transection (%) | Radicalsection (%) | Volume (%) |
| Natural wood | 116.6 | 3.2 | 3.6 | 6.7 | 4.9 | 7.3 | 10.8 |
| A | 91.8 | 2.8 | 3.9 | 6.2 | 4.7 | 5.4 | 10.2 |
| B | 88.2 | 2.1 | 4.3 | 5.8 | 4.3 | 5.3 | 9.8 |
| C | 76.2 | 2.3 | 3.2 | 4.6 | 3.7 | 5.6 | 9.6 |
| D | 110.2 | 2.3 | 2.9 | 6.1 | 4.3 | 4.8 | 10.2 |
| E | 109.3 | 2.0 | 2.7 | 5.3 | 2.9 | 6.8 | 10.0 |
| F | 85.1 | 1.9 | 2.4 | 4.3 | 2.7 | 6.4 | 9.6 |

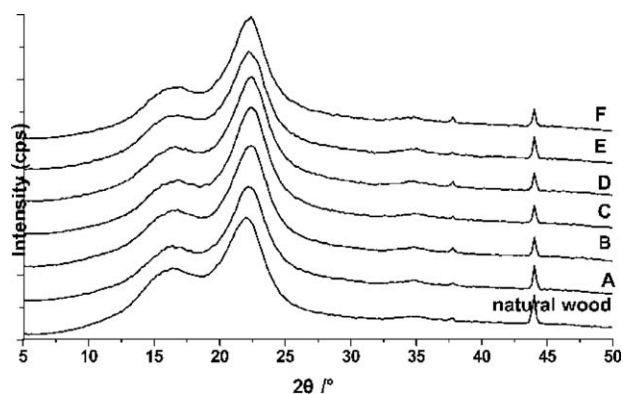


Figure 1. XRD patterns of natural and modified wood.

between water and the donor, the acceptor groups of polyamide (NH, C=O) and cellulose (C—OH).²⁵ Simultaneously, the hydrolysis of hemicelluloses during hot-press could reduce the hygroscopicity of the wood fiber. The good dimensional stability was also due to the bulking effect of the polymer. The hydrophobic characteristic of monomers shielded the wood surface and remained in the cell wall and lumen, which resulted less impregnation of water and moisture impregnated in wood. Consequently, the wood modifier dispersed and adhered in the fiber lumens, pit holes, and other void spaces in the matrix.

XRD Characterization

XRD is used to identify the intercalated structure of wood. Figure 1 presents the curves of natural and modified wood samples. The natural wood owed a typical cellulose I diffraction angles around 17°, 22.5°, and 37.5° corresponding to the cellulose crystallographic planes I_{101} , I_{002} , and I_{040} , respectively. After

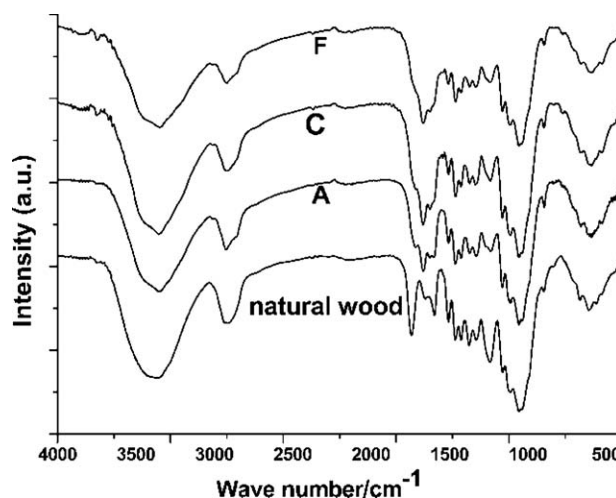


Figure 2. FTIR spectra of natural and modified wood.

modification, the crystallinity of modified wood increased to 36.91, 37.11, 37.37, 37.03, 37.12, and 37.78%, respectively. Although, the crystallinity of wood increased with the increasing content of carbamide, the location of the peaks did not change, indicating that the ordered structure of the crystalline region on the remaining cellulose was not disrupted during the modification.²⁶ This suggested that the functional groups were grafted onto the wood cell walls, and thus, the wood modifier mainly bonded to the wood cell walls. The crosslinking reaction occurred between the groups of methylolurea and the surface hydroxyl groups of wood. It can be inferred from the results that a quasi-crystalline form was generated in the X-ray diffraction. The presence of quasi-crystallites was an important factor to enhance the mechanical properties of wood. Furthermore,

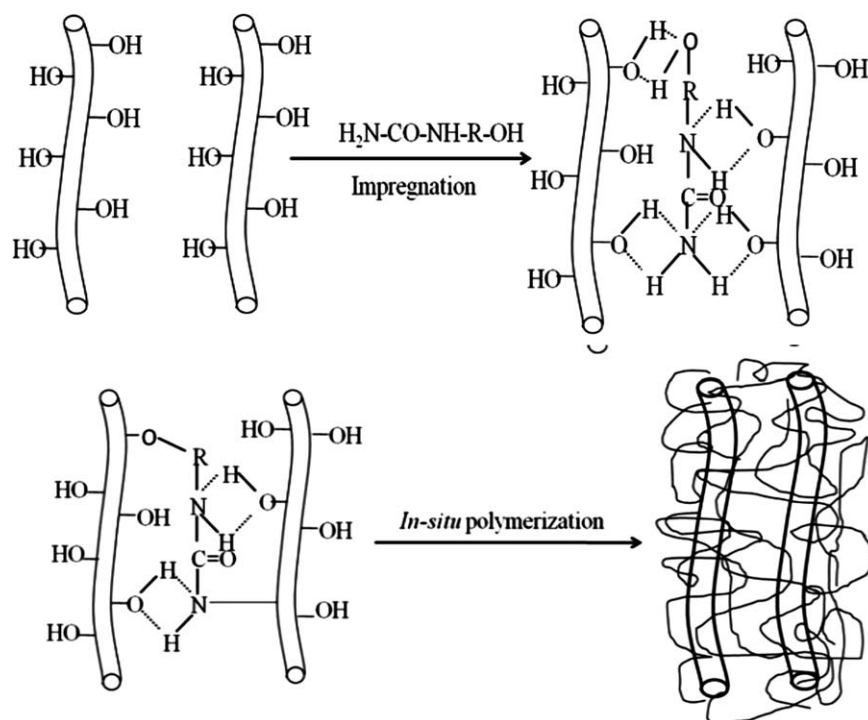


Figure 3. A schematic representation of *in situ* polymerization.

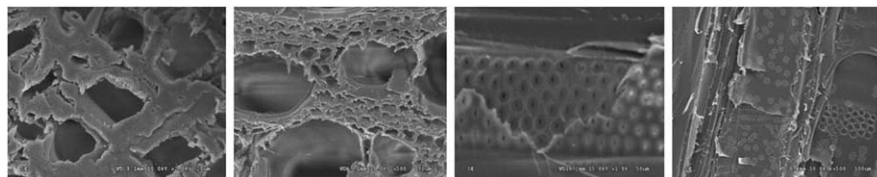


Figure 4. SEM micrographs of natural and modified wood.

carbamide was a kind of polar molecules, which can penetrate into amorphous region of wood cellulose cell wall. Hence, after impregnation of carbamide, a crystalline region can be formed by rearranging the cellulose molecule chains.

Fourier Transforms Infrared Spectroscopy Analysis

The FTIR spectra are shown in Figure 2, corresponding to sample A, C, and F as compared to the natural wood. Obviously, the unambiguous evidence for *in situ* polymerization was the emergence of the N—C=O band and the decrease of the hydroxyl groups stretching band. The intensity of N—C=O group was found to increase at 1700 cm^{-1} which suggested the formation of *in situ* polymerization. The reaction due to the bond between the function groups of —NHCH₂OH from the methylolurea groups and the wood carboxyl C=O. The characteristic peak at 3400 cm^{-1} assigned to the stretching of hydroxyl groups. However, the absorbance of hydroxyl groups shifted to lower wavenumber ($3400\text{--}3340\text{ cm}^{-1}$) after modification, which also gave an evidence of the reaction between wood hydroxyl groups and methylolurea. Simultaneously, the hygroscopicity of wood was also significantly reduced by the decrease of hydroxyl groups which was in agreement with the conclusion of water uptake and moisture absorption. The intensity of absorption bands at 1421 cm^{-1} assigned to the —CH₂ also decreased after *in situ* polymerization, possibly due to the degradation of methylene groups at the end of hemicelluloses and lignin. In the modified wood, the decreasing in stretching frequency at 1511 cm^{-1} confirmed that the degradation of lignin occurred during the thermal treatment. In addition, the *in situ* polymerization reaction between the methylolurea groups of wood modifier and wood fiber may affect the absorption of —CH₂. The $1335\text{--}1316\text{ cm}^{-1}$ doublet assigned to the cellulose component was related to the contents in crystallized I and amorphous cellulose.²⁷ A decrease in the ratio $1335/1316\text{ cm}^{-1}$ signified an increase in crystallinity, which was in agreement with the XRD analysis.

The Mechanism of In Situ Polymerization

The FTIR data shows the chemical reaction occurred between the function groups of —NHCH₂OH from the methylolurea groups and the wood carboxyl C=O. Moreover, the OH groups and NH₂ groups from methylolurea groups *in situ* polymerized with the hydroxyl groups (wood). The reaction mechanism for *in situ* polymerization involving two steps as shown in Figure 3. The presence of hydroxyl groups has shown to be critical for the *in situ* polymerization, because they can act as active groups that could lead to the polymerization of methylolurea and wood fiber. The first step of the reaction is that the impregnation of wood modifier. Then, the hydrogen bonds formed

between the OH groups (wood) and the NH₂ groups and OH groups (from methylolurea groups). In second step, ester linkages were generated by the dehydration of hydroxyl groups involving wood fiber after the thermal treatment. Furthermore, the *in situ* polymerization between OH groups and NH₂ groups, and the network polymer interlaced with the wood fibers. The covalently crosslinked network exhibited a great potential for improving the mechanical properties and the dimensional stability.

Scanning Electron Microscopy (SEM) Analysis

Figure 4 shows the SEM micrographs of natural wood and modified wood. The natural wood samples exhibited a highly void structure [Figure 4(A)]. After impregnation, the cell wall and vessels were filled with chemicals. It can be seen that the methylolurea prepolymer homogeneously dispersed in the cell wall. The radical sections of natural and modified wood are shown in Figure 4(C,D). It was clear visible that the natural woods were covered with an uneven layer with a number of void spaces. The empty cell wall, the pit, and parenchyma could be observed in the micrographs. The surface of modified wood was smooth and substantially regular than that of the natural wood. The SEM studies provided evidences that the wood modification resulted in better dispersion of the methylolurea prepolymer in wood fiber and other vertical cells. Moreover, the chemical particles of wood modifier had better interfacial adhesion between wood and polymer. The good dispersion of modifier led to a significant improvement in mechanical properties of wood-methylolurea composite.

CONCLUSIONS

On the basis of the characterization and analysis of wood-methylolurea composites, we drew the following conclusions.

The mechanical properties of wood-methylolurea composites, including density, bending strength, modulus of elasticity in bending, compressive strength parallel to grain, and hardness, were significantly enhanced compared to the natural wood. The *in situ* polymerization was shown to have significant contribution on the dimensional stability of the wood-methylolurea composites. The wood modifier mainly existed in the wood cell walls as the amorphous form. Meanwhile, the methylolurea was *in situ* polymerized with the wood cell walls and formed network polymers. 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 methylolurea. The modified method will speed up the development of wood product and increase the utilization of woods.

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