

Fabrication of Hydrophobic Surface on Wood Veneer via Electroless Nickel Plating Combined with Chemical Corrosion

Zhaojun Tang, Changhong Shi, Shu Wu, Zengfu Jiang, and Lijuan Wang *

Birch veneers were coated with Ni-P films by a combined process of KBH_4 activation and electroless plating. The plated veneers were further chemically corroded to obtain hydrophobic surfaces on wood. The effect of chemical corrosion on the contact angle of the veneers was investigated. The hydrophobic veneers were characterized by X-ray photo electron spectroscopy (XPS), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The surface contact angle of birch veneer before and after it was plated with Ni-P alloy coating was 41° and 121° , respectively. The contact angle reached 136.7° when the nickel-coated veneers were corroded in CuSO_4 aqueous solution for 30 min. XPS analysis showed that Cu^0 cluster doped with little CuO formed on the corroded surface of Ni-P alloy film after chemical corrosion. SEM and XRD showed that rough copper clusters formed on the surface of the wood veneer and revealed the reason of the surface hydrophobicity. This study provides a new pathway for fabricating hydrophobic wood.

Keywords: Birch veneer; Hydrophobicity; Electroless plating; Chemical corrosion; Contact angle

Contact information: Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, 26 Hexing Road, Harbin 150040, China;

* Corresponding author: donglinwlj@163.com

INTRODUCTION

Wood is a renewable, natural composite material with many superior properties, including high strength-to-mass ratio, low thermal conductance, and a beautiful natural grain (Jiang *et al.* 2014). However, one of the key potential disadvantages of pristine wood is its hydrophilicity, which is due to its cellulose, hemicellulose, and lignin components (Devi *et al.* 2003). High hydrophilicity results in distortion and damage by fungi and termites, which limits its applications and decreases the service life of wood or wood-based products. To hinder water adsorption, hydrophobic surfaces are fabricated on wood *via* physical or chemical modifications such as acetylation and silylation (Mohammed-Ziegler *et al.* 2008), polymer coating (Magalhaes and de Souza 2002; Fu *et al.* 2012), nanocrystal coating (Li *et al.* 2010b; Sun *et al.* 2010), or other methods (Shi *et al.* 2014; Zheng *et al.* 2015).

Electroless plating is a method for depositing metals such as nickel and copper onto an insulating substrate through the catalyzed chemical reduction of solution-phase metal ions at the substrate surface (Fujii *et al.* 2014). Nickel, copper, and nickel-based alloy coatings have been deposited onto wood surfaces to prepare electromagnetic shielding materials (Wang *et al.* 2005, 2011; Li *et al.* 2010a; Wang and Liu 2011; Wang and Li 2013). The coatings are uniform and continuous, exhibiting high conductivity and

electromagnetic shielding effectiveness. However, fabrication of hydrophobic wood surfaces *via* electroless plating has not been reported.

In this study, nickel films were plated on birch veneer *via* a simple process. The plated veneers were immersed in a copper ion solution for chemical corrosion, which resulted in a rough surface. The effects of corrosion time on the hydrophobicity were investigated. The surface changes were characterized by XPS, SEM, and XRD. This study provided a new pathway to improve dimensional stability for application in electro-conductive and electromagnetic shielding fields.

EXPERIMENTAL

Materials

Birch wood veneers with a thickness of 0.6 mm were purchased from a plywood factory. The veneers were polished by emery papers to remove fine fibers or dust on the surface and cut into squares of 50 mm × 50 mm. Only analytical grade chemicals were used. The composition of the electroless bath and the operation conditions are listed in Table 1. The pH of the bath was adjusted with ammonium hydroxide (NH₄OH) solution.

Activation and plating procedure

Birch veneers were first dipped in a potassium borohydride (KBH₄) solution containing 3 g/L sodium hydroxide (NaOH) for 10 min at room temperature. The veneers were air-dried for 1 min to allow KBH₄ to diffuse to the inner pores. Next, veneers were placed in the plating bath at 70 °C. The plated specimens were rinsed in water for 1 h and dried at 100 °C for 1 h.

Table 1. Composition and Operation Condition of Electroless Nickel Plating

Chemicals	Content (g/L)
NiSO ₄ ·6H ₂ O	30
NaH ₂ PO ₂ ·H ₂ O	30
C ₃ H ₆ O ₃	35
NH ₄ Cl	20
pH	8.25
Temperature (°C)	68

Corrosion procedure

The plated birch veneers were immersed into a copper sulfate (CuSO₄) solution (0.25 M) for a set amount of time, washed with water to remove residues, and dried in an oven at 100 °C for 1 h. This procedure is illustrated in Fig. 1.

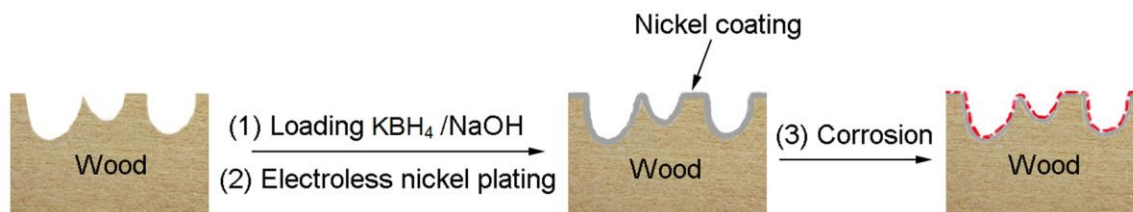


Fig. 1. Fabrication of hydrophobic surface on birch veneer

Characterization Methods

The chemical composition and state of coatings before and after chemical corrosion were analyzed by X-ray photoelectron spectroscopy (XPS, model PHI 5700 ESCA System, America Physical Electronic Company, USA) after etching by argon ion sputtering for 30 s.

The surface morphologies of the samples were determined by scanning electron microscopy (SEM, Quanta 200, Philips-FEI Co., The Netherlands). The phase structures of the birch veneers after various treatments were investigated *via* X-ray diffraction (XRD, D/max2200 diffractometer, Rigaku, Japan) using a Cu K α radiation generator operated at 1200 W (40 kV \times 30 mA).

Measurement of contact angle

The wettability of the samples was determined by the sessile drop method using a contact angle measurer (OCA20, Dataphysics Company, Germany). A 20- μ L drop of distilled water was placed on the film surface. The angle between the drop and the film surface was measured.

RESULTS AND DISCUSSION

Effect of CuSO $_4$ ·5H $_2$ O on Corrosion Time

Corrosion time is an important parameter. The plated birch veneers were corroded in CuSO $_4$ ·5H $_2$ O solution to obtain roughness on the surface. As shown in Fig. 2, the surface contact angle of the nickel plated wood was 121° and the surface contact angle increased from 130.2 to 136.7° with an increase in corrosion time from 20 to 30 min. Then the contact angle decreased from 136.7 to 130.1° with further corrosion time. The maximum value occurred at 30 min.

The purpose of chemical corrosion is to obtain roughness by breaking the continuous nickel film. Suitable corrosion time results in a rough microstructure for the fabrication of the hydrophobic surface. In the time range from 20 min to 40 min, longer corrosion time erodes too much of the deposited nickel film, which leads to fabrication failure.

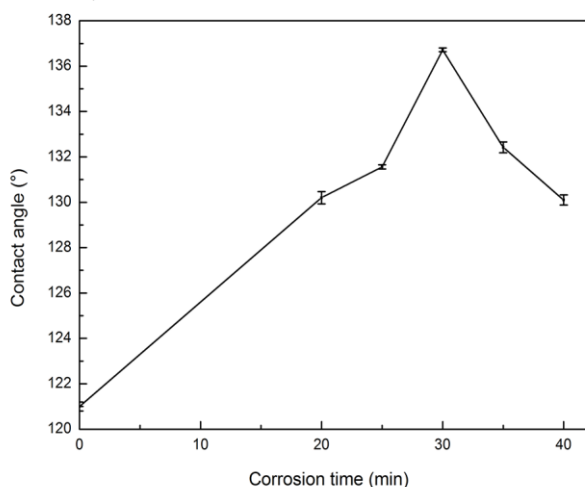


Fig. 2. The effects of corrosion time on hydrophobicity

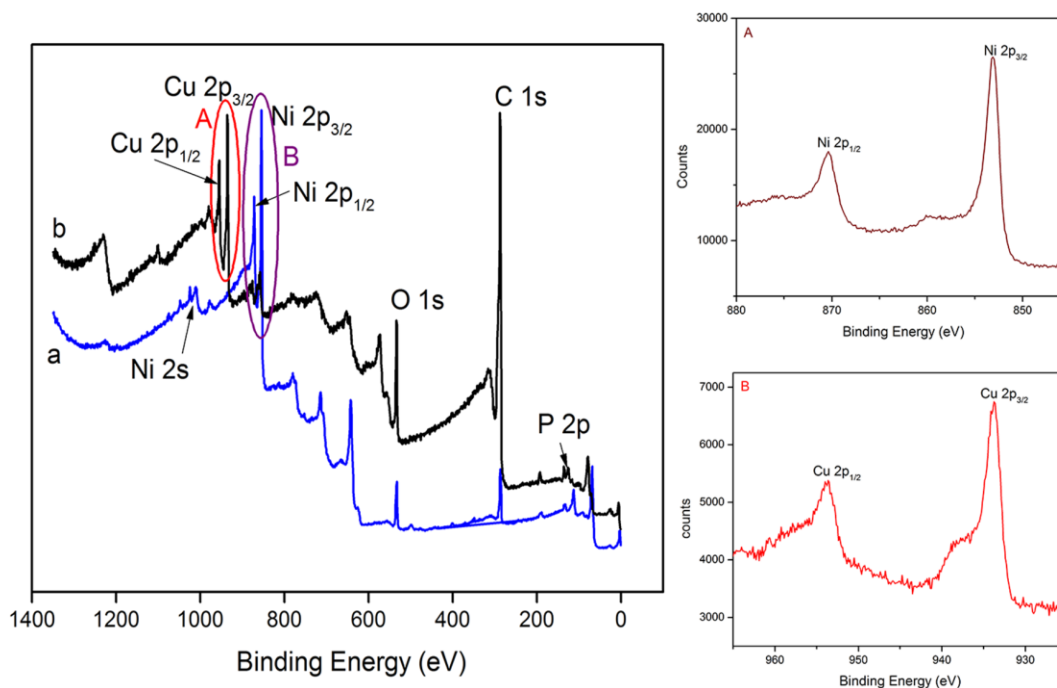


Fig. 3. XPS spectra of Ni-P alloy-coated birch veneer before (a) and after (b) corrosion in CuSO_4 aqueous solution

XPS Analysis

XPS analysis was used to examine the chemical state of the coating. Representative XPS wide spectra of the plated veneer surface before and after chemical corrosion indicated the presence of Cu, P, O, and C (Fig. 3).

The peaks of $\text{Ni}2\text{p}_{3/2}$ and $\text{Ni}2\text{p}_{1/2}$ were stronger and thinner in the XPS high-resolution scan of Ni2p (Fig. 3A), showing that Ni^0 is the main component of the coating. Therefore, the Ni-P alloy coating was successfully deposited on birch veneer by the following set of reactions:



Because XPS only detects to a depth of several nanometers, the observed C and O came from the surface of the coating, suggesting that the surface was polluted by absorbed components in the plating solution.

After corrosion in Cu^{2+} solution, the XPS spectrum showed decreased Ni peaks, but Cu, O, and C increased noticeably. There was a shoulder peak at 935.88 eV in the XPS high-resolution scan of Cu2p (Fig. 3B), which indicated that Cu^{2+} was present. In addition, O and C came from the wood surface because the Ni-P coating under Cu clusters became rougher, and wood elements were detected at the thinner part after etching by argon ion sputtering for 30 s.

These observations further demonstrated that chemical corrosion caused the roughness on the surface.

SEM Observation

The nickel-plated birch veneer was immersed in CuSO_4 aqueous solution to obtain rough copper clusters on the surface of the nickel coating. Copper clusters were deposited following the chemical reaction below:



Figure 4 shows the morphologies of nickel-coated wood veneer before and after corrosion in CuSO_4 aqueous solution. A compact and continuous nickel coating was deposited on the wood surface, and the surface was entirely covered by the coating. After corrosion, the morphology changed. Some rough clusters built from rod-shaped particles formed on the surface. The increased roughness favors increased hydrophobicity on the surface.

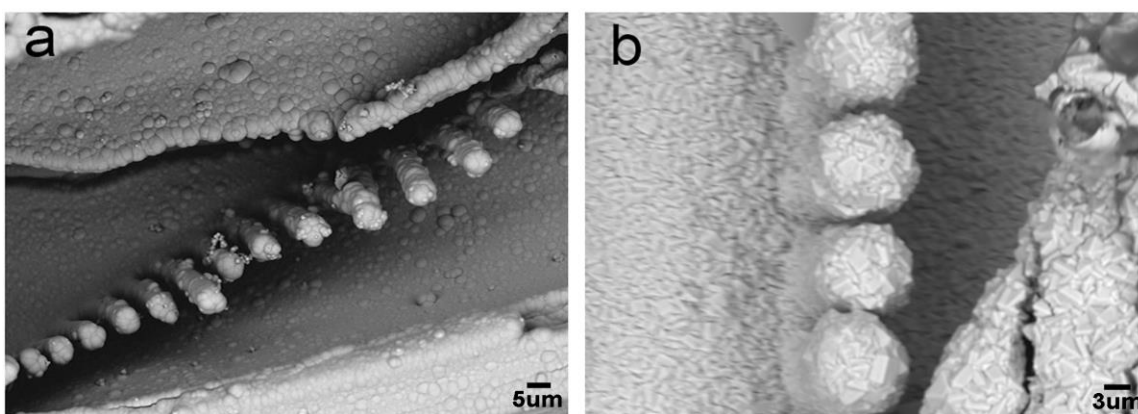


Fig. 4. SEM photographs of nickel-plated birch veneer (a) before and (b) after corrosion in CuSO_4 aqueous solution

XRD Analysis

Figure 5 shows the XRD patterns of birch veneers after various processes. The peak at $2\theta = 22.02^\circ$ is the characteristic peak of cellulose in birch veneer.

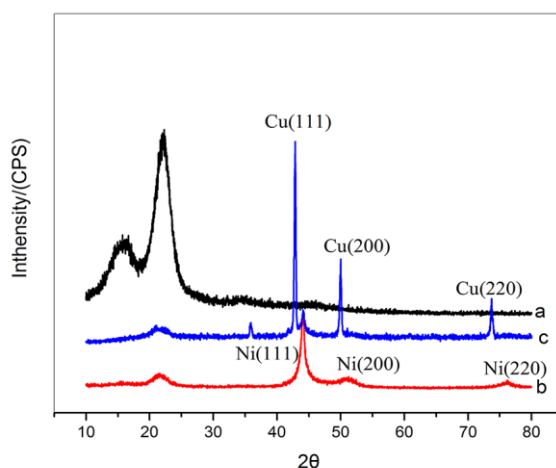


Fig. 5. XRD patterns of (a) the birch veneer, (b) the plated birch veneer, and (c) the corroded birch veneer

In the case of birch veneers coated with a nickel layer, the peaks at $2\theta = 44.11^\circ$, 51.10° , and 76.41° (Kong *et al.* 2002) can be attributed to Ni (111), Ni (200), and Ni (220), respectively, which indicates the face-centered cubic phase of nickel. Moreover, the peak at $2\theta = 22.02^\circ$ became weaker, indicating that the birch veneer surface was entirely covered by the continuous nickel layer. After chemical corrosion, the new peaks at $2\theta = 42.78^\circ$, 49.98° , and 73.81° were attributed to Cu (111), Cu (200), and Cu (220), which show the face-centered cubic phase of copper (Sun *et al.* 2012). Moreover, the characteristic peak of Ni (111) became weaker, demonstrating that the nickel layer was successfully corroded. Furthermore, the intensity of the peak at $2\theta = 22.02^\circ$ did not change; thus, the corrosion did not break the continuity of the nickel coating on wood surface. All XRD results were in agreement with the SEM photographs.

Comparison of Wettability

The wettability of pristine birch veneer and nickel-coated birch veneers before and after chemical corrosion is shown in Fig. 6. The surface of pristine wood was highly hydrophilic, with a contact angle of 40° . After nickel plating, the contact angle rose to 121° . The contact angle further increased to 136° after chemical corrosion. While water droplets spread on the surface of pristine wood, they adopted spherical shapes on treated surfaces.

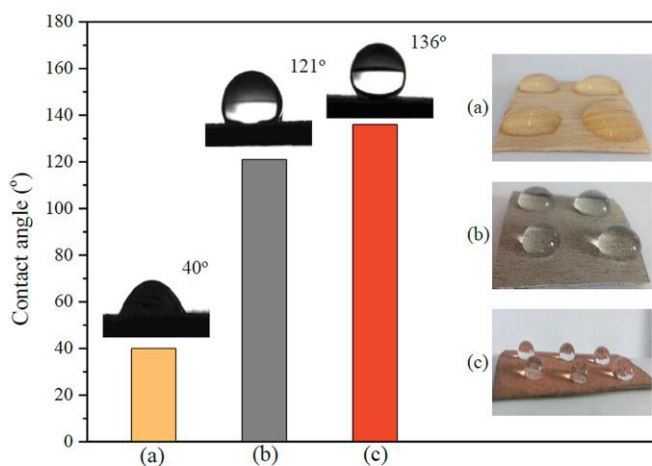


Fig. 6. The contact angle and water droplet photos of (a) pristine birch veneer and nickel-coated birch veneers (b) before and (c) after chemical corrosion

CONCLUSIONS

1. Hydrophobic surfaces on birch wood were successfully obtained by electroless nickel plating followed with chemical corrosion.
2. The corrosion time in Cu^{2+} solution was optimized to increase hydrophobicity on the plated surface. The contact angle increased to 136.7° after 30 min of corrosion.
3. XPS, SEM, and XRD results show that the chemical corrosion produced rough copper clusters on the surface, which markedly improved surface hydrophobicity.

- This report demonstrates a facile and well-controlled method to fabricate hydrophobic surfaces on wood materials.

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