# ELECTROLESS NICKEL PLATING ON CHITOSAN-MODIFIED WOOD VENEER

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An activation process involving chitosan was conducted to prepare electroless nickel plated wood veneers for electromagnetic interference (EMI) shielding. In this process Pd(Ⅱ) ions were chemically adsorbed on wood surface modified with chitosan. Then they were reduced and dipped into a plating bath in which Ni-P co-deposition was successfully initiated. The coatings were characterized by SEM-EDS and XRD. The metal deposition, surface resistivity, and electromagnetic shielding effectiveness were measured. The morphology of the coating observed by SEM was uniform, compact, and continuous. EDS results showed that the coating consists of 1.8 wt.% phosphorus and 98.2 wt.% nickel. XRD analysis indicated that the coating was crystalline, which is supposed to be related to the low phosphorus content. The plated birch veneers exhibited electro-conductivity with surface resistivity of 0.24 $\Omega\cdot cm^{-2}$ and good electromagnetic shielding effectiveness of over 50 dB in frequency range from10 MHz to 1.5 GHz.

*Keywords: Electroless nickel plating; Activation; Chitosan modification; Wood veneer; Electromagnetic shielding effectiveness*

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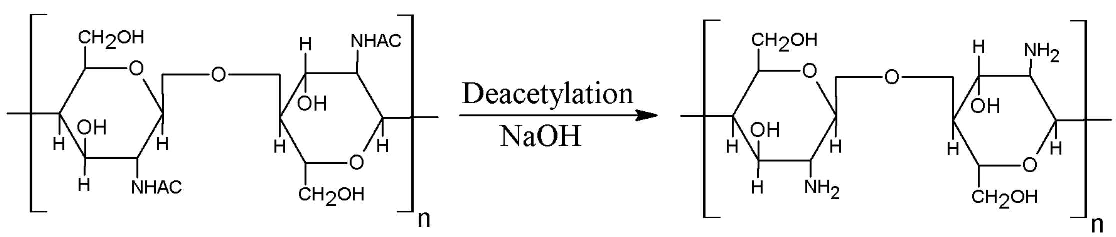
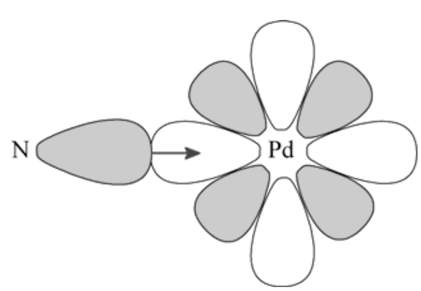
## INTRODUCTION

With the popularization of modern electronic devices such as portable computers, cell phones, etc., electromagnetic radiation is becoming a more and more serious issue. It is not only harmful to human health but also may interfere with the normal operation of other electronic devices. Generally we use metal or metal-coated plastic to shield electromagnetic radiation. But these materials are derived from non-renewable resources and are expensive. Comparatively, wood is a natural renewable polymer with better performances in sound insulation, heat insulation, humidity control, and ratio of strength to weight. However, wood has no ability to prevent electromagnetic radiation or signal, due to its non-conductivity. Electroless plating method is frequently used to deposit a metal film such as copper and nickel onto the surface of wood materials in order to improve their electromagnetic shielding effectiveness (Nagasawa et al.1989, 1990, 1991, 1992, 1999; Wang et al. 2006, 2007, 2008; Huang and Zhao 2004). In the traditional electroless plating process, the substrate to be coated is activated by adsorbing a palladium layer on its surface after being etched by Cr(VI)/$H_2SO_4$ solution, then the substrate is immersed into an electroless plating solution in which the substrate is metallized (Deonath 1981; Przyluski 1987; Mandich 1991; Garg 1993). Certainly, wood is full of pores and naturally coarse on its surface. So, wood does not require an etching process. But there is some disadvantage associated with the wood surface; palladium clusters are mainly attached in the micropores of the substrate by physical adsorption, which can make part of the palladium clusters drop off, resulting in the self-decomposition of the plating solution (Stremsdoerfer et al. 1993). Recently, coupling agents containing nitrogen, such as amino silane, have been used to improve the adhesive between the substrate and the catalyst by researchers. Liu et al. have successfully used aminosilane to modify birch and *Fraxinus mandshurica* veneers and plated nickel coating on the modified veneers (Liu et al. 2010a, 2010b).

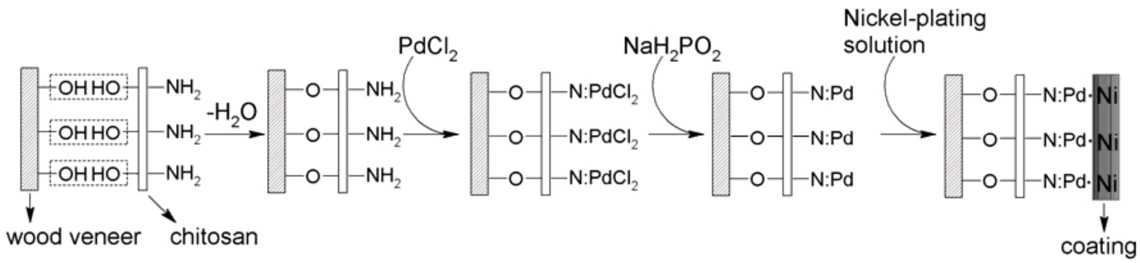
In this work, electroless nickel-coated wood veneers for electromagnetic interference (EMI) shielding were prepared by employing chitosan modification. Chitosan is produced commercially by deacetylation of chitin (Scheme 1), which is derived from the shells of crabs, shrimp, etc. Before plating, wood veneers (without being etched) were pretreated with chitosan, and a thin chitosan membrane was coated on wood veneers. Chitosan-modified wood veneers were successively dipped into palladium chloride and sodium hypophosphite solutions. In this process, the hydroxyl groups of chitosan were supposed to link wood through hydrogen bonds and connect with palladium via N-Pd coordinate bonds (Scheme 2), respectively (Renbutsu 2008; Tang 2008; Xu 2002). This process, as shown in Scheme 3, can improve the immobilization of Pd(II) to the substrate and the catalyzing effect for the electroless nickel plating. In our work, the metal deposition, surface resistivity and EMI of metallized wood veneers were measured. The relationships between the deposition and surface resistivity and the immersing time of chitosan modified veneers were investigated. Besides, the morphology of the coating was observed by Scanning Electron Microscopy (SEM) and its structure was determined by X-ray diffraction (XRD).




**Scheme 1.** Deacetylation of chitin to chitosan




**Scheme 2.** Formation of N-Pd coordinate bond




**Scheme 3.** Proposed mechanism of the activation and plating process

## EXPERIMENTAL

### Materials

Birch wood veneers of 0.6 mm thickness were purchased from a plywood factory. Chitosan (degree of deacetylation: 85+%, viscosity: 300 mPa·s) was obtained from Jinan Haidebei Marline Bioengineering Company Limited. Palladium chloride (99.5+%) was purchased from Shenyang Jinke Reagent Factory. All the other chemicals used were of analytical grade.

### Activation and Plating

The specimens were polished by emery papers to remove timbering residue or dust on the surface. Then they were immersed into 6 g•$L^{-1}$ chitosan solution (containing 6 mL acetic acid glacial per liter) for 6 min at room temperature. Next they were dried by hot air, which made the substrate become covered firmly with a film of chitosan. After this, the samples were dipped into 0.2 g•$L^{-1}$ palladium chloride solution (containing 15 mL 37% hydrochloric acid per liter) for a certain time at room temperature in order to allow the Pd(II) ions to complex with the amino groups of the chitosan, and then the substrates were washed by distilled water to remove uncomplexed ions. The Pd(II) ions were then reduced to $Pd^0$ by soaking in 2 g•$L^{-1}$ sodium hypophosphite solution at 40 $^oC$. Finally, the activated wood veneers were coated a plating bath at 70 $^oC$ for 20 min. The composition of the bath is listed in Table 1.

**Table 1.** Composition of Nickel-Plating Solution

| Chemicals | Content(g·$L^{-1}$) |
|---|---|
| $NiSO_4·6H_2O$ | 25 |
| $NaH_2PO_2·H_2O$ | 25 |
| Lactic acid | 25 |
| $NH_4Cl$ | 30 |
| Thiourea | 0.002 |
| pH | 8.5 |

### Characterization

*Metal deposition*

The raw wood veneers were dried at 103±2 °C to constant weight and weighed (with the weight denoted as $G_0$). The nickel-coated samples were also dried to constant weight and weighed with a mark $G_1$. The metal deposition was calculated as follows:

$$\text{Metal deposition (\%)} = (G_1 - G_0)/G_0 \times 100 \qquad (1)$$

*Electromagnetic shielding effectiveness*

The shielding effectiveness of the metallized wood veneers was measured by using an Angilent E4402B spectrum analyzer and standard butt coaxial cable line with flange based on Chinese industrial standard SJ20524-95.

*Morphology and phase structure*

The surface morphology and element compositions of the coatings were characterized by SEM-EDS (Quanta 200). Specimens were not sprayed with gold prior to analysis. Additionally, the phase structure of the coatings was clarified by XRD (Rigaku D/max2200 diffractometer) using Cu Kα radiation generator operated at a power of 1200 W (40 kV × 30 mA).

## RESULTS AND DISCUSSIONS

### Activation Process

It is well known that activation is the key to electroless nickel-plating for non-conductive materials. In the activation process, a film of uniformly distributed palladium clusters on the substrate surface is expected to initiate the subsequent nickel-plating reaction. The mechanism is that the nitrogen atoms of chitosan, which has a couple of isolated electrons that can occupy the empty orbital of Pd(II), adsorb the Pd(II) ions through N-Pd chelate bonds (Tang 2008). Thus, tests were carried out to determine the influence of the adsorbing time of Pd(II) ions to chitosan on the electrical performance of the nickel-coated wood veneers; results are shown in Fig. 1.

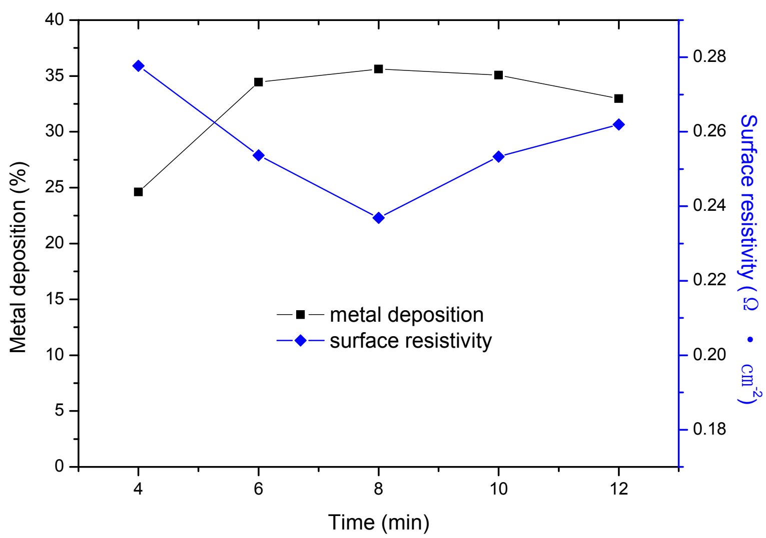



**Figure 1.** Influence on metal deposition and surface resistivity by the coordination between chitosan and Pd (II)

It can be seen that the metal deposition reached the maximum at 8 min and then declined slightly as the time increased. This indicates that it takes about 8 min for the chitosan film on the wood veneer to adsorb enough Pd (II) ions to approach saturation. However, further prolonging absorbing time can cause a small part of chitosan to become swollen and further dissolved into the acid palladium chloride solution, which affects the activation effect and makes the metal deposition decrease. In addition, the surface resistivity and the metal deposition are negatively correlated; that is, the greater the amount of metal deposition, the smaller the surface resistivity. The minimum surface resistivity reached about 0.24 $\Omega \cdot cm^{-2}$, while the metal deposition was around 36 %, when chitosan-treated wood veneers were immersed in palladium chloride solution for 8 min.

## Morphology and Phase Structure of the Coating

Figure 2 shows SEM micrographs of the raw and plated wood veneers. By comparison, the plated veneers (Fig. 2c) exhibited a bright, metallic sheen. The substrate surface including the pores was fully covered by the metal coating and the coating was uniform and continuous, as shown in the photo at a higher magnification (Fig. 2d).

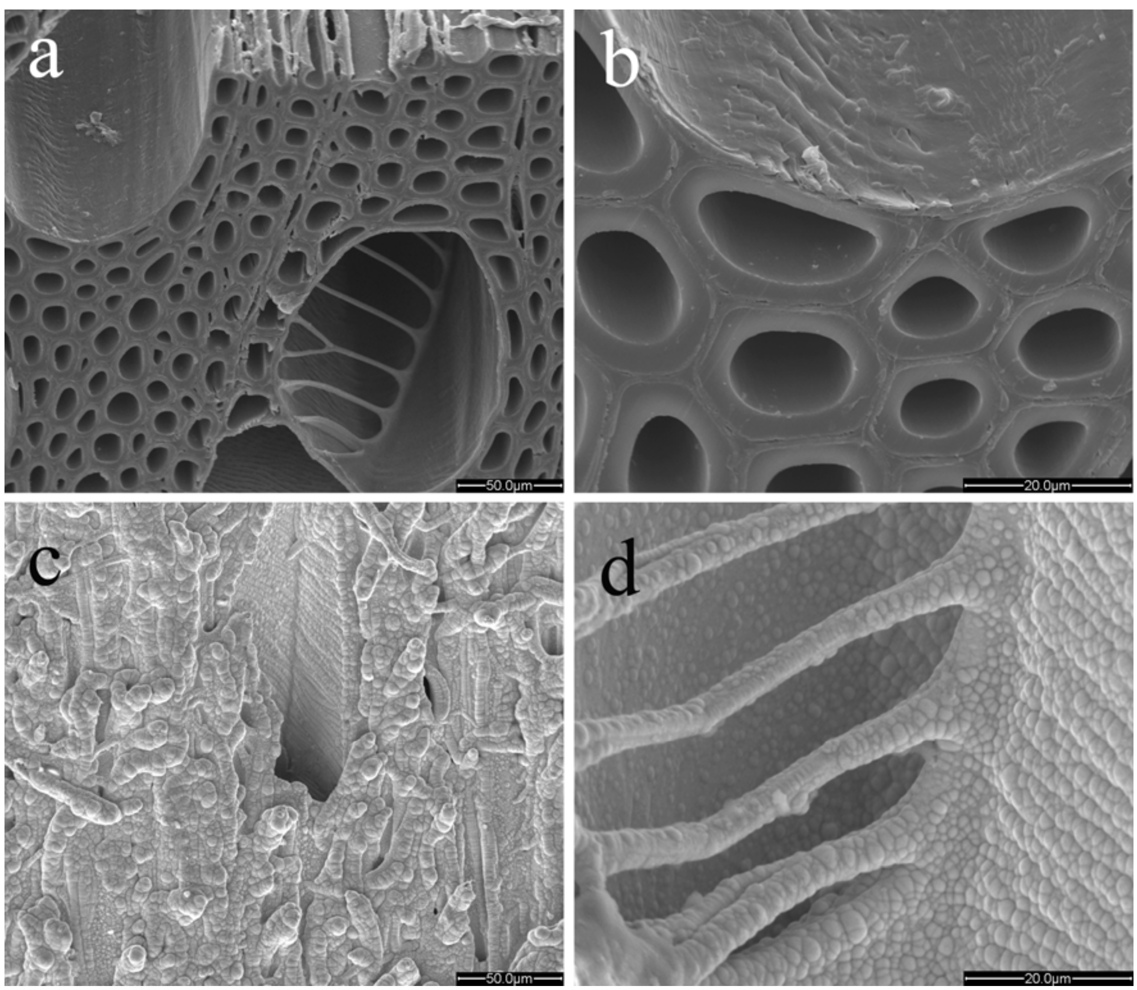



**Figure 2.** SEM photographs of the raw (a×500, b×1000) and plated wood veneers (c×500, d×1000)

Figure 3 shows the EDS spectra of the plated wood veneer. The peak of nitrogen derives from chitosan, and carbon, and oxygen are from both chitosan and wood. As shown, the presence of a palladium peak indicates that the Pd(II) ions were successfully coordinated by chitosan in activation process. The peaks of nickel and phosphorus are attributed to the coating, and their content are 98.2 wt.% and 1.8 wt.%, respectively. At the beginning of the electroless plating process, catalyzed by palladium, the $Ni^{2+}$ ions are rapidly reduced to $Ni^0$, which in return catalyzes the subsequent Ni-P co-deposition. The process can be written as follows:

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Ni\downarrow + 2H_2PO_3^- + 2H^+ + H_2\uparrow \quad (2)$$

$$3H_2PO_2^- + 2H^+ \rightarrow 2P\downarrow + H_2PO_3^- + 3H_2O \quad (3)$$

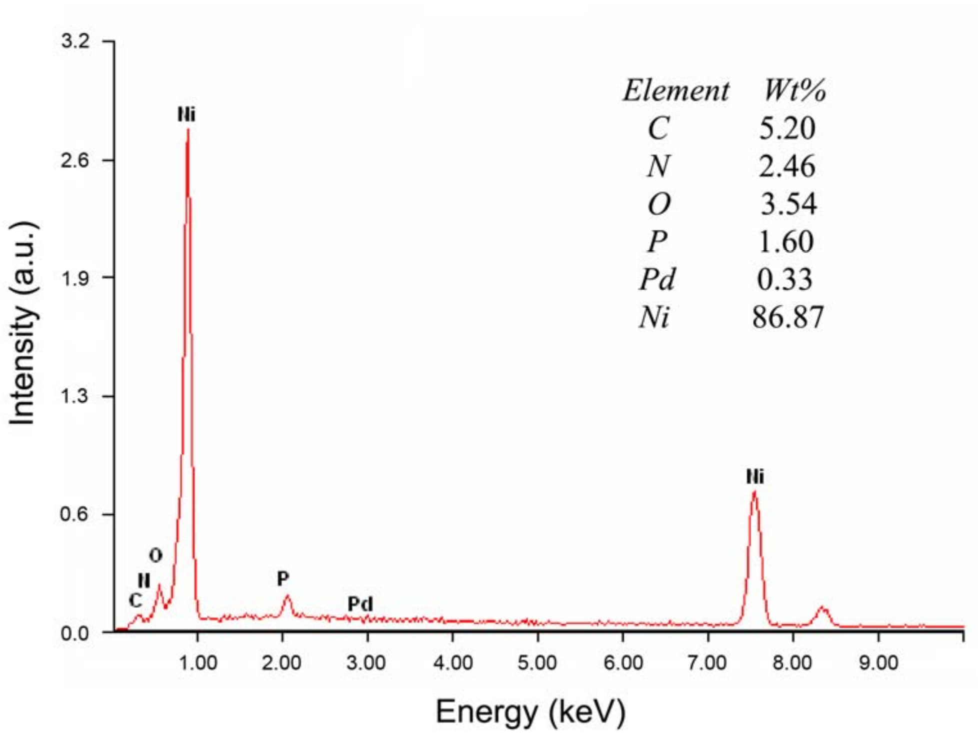



**Figure 3.** EDS spectra of the plated wood veneer

Figure 4 shows the XRD patterns of the plated wood veneer. Peaks at $2\theta = 44.6^o$, $51.5^o$, and $76.5^o$ are attributed to Ni(111), Ni(200), and Ni(220), which indicates the face-centered cubic phase of nickel (JCPDS: 04-0850) and the crystalline nature of the coating. This result is mainly related to lower P content and largely attributed to little distortion of crystallinity of nickel caused by phosphorus atoms. Additionally, the peak at $2\theta = 22^o$ is a characteristic peak of cellulose (JCPDS: 03-0289). However, Fig. 5 indicates that its intensity is very small relative to the peak of Ni(111), meaning that the wood veneer is entirely and compactly covered by a Ni-P coating, and the thickness of the coating reaches at least micron-size (Li et al. 2010).

## Shielding Effectiveness

As shown in Fig. 6, the electromagnetic shielding effectiveness of the plated wood veneer was higher than 50 dB in frequencies ranging from 10 MHz to1.5 GHz. The raw birch veneer had almost no shielding performance. Therefore, the plated wood veneer has a good shielding effectiveness and can be used in the fields of anti-EMI.

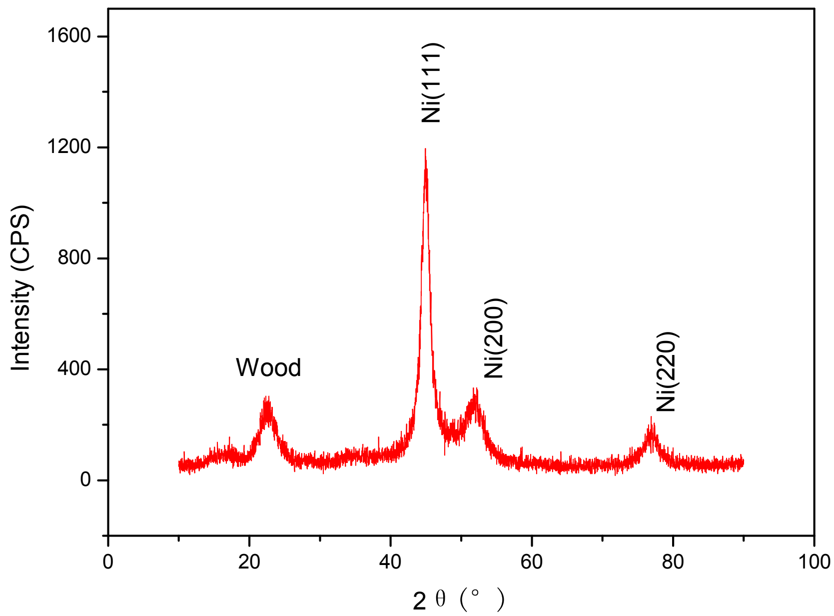



**Figure 4.** XRD pattern of the plated wood veneer

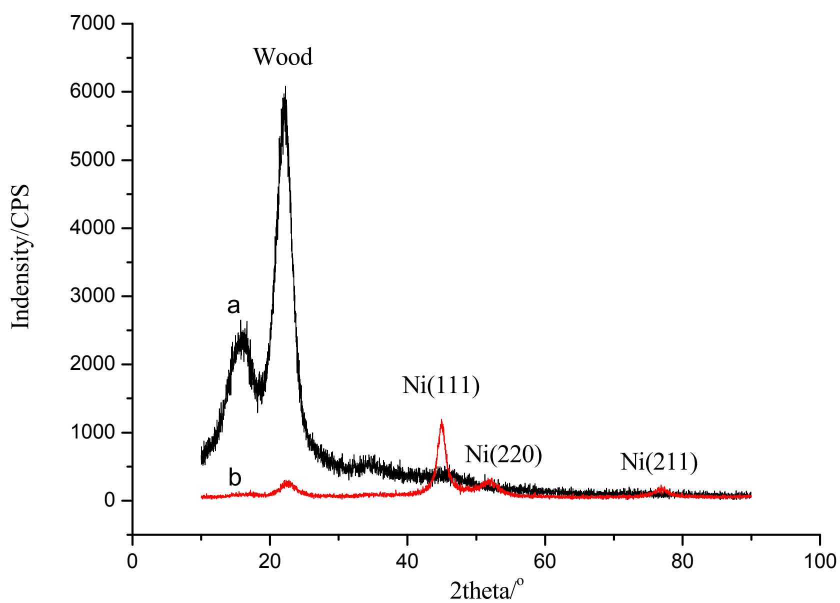



**Figure 5.** XRD patterns of the pristine (a) and the plated wood veneer (b)

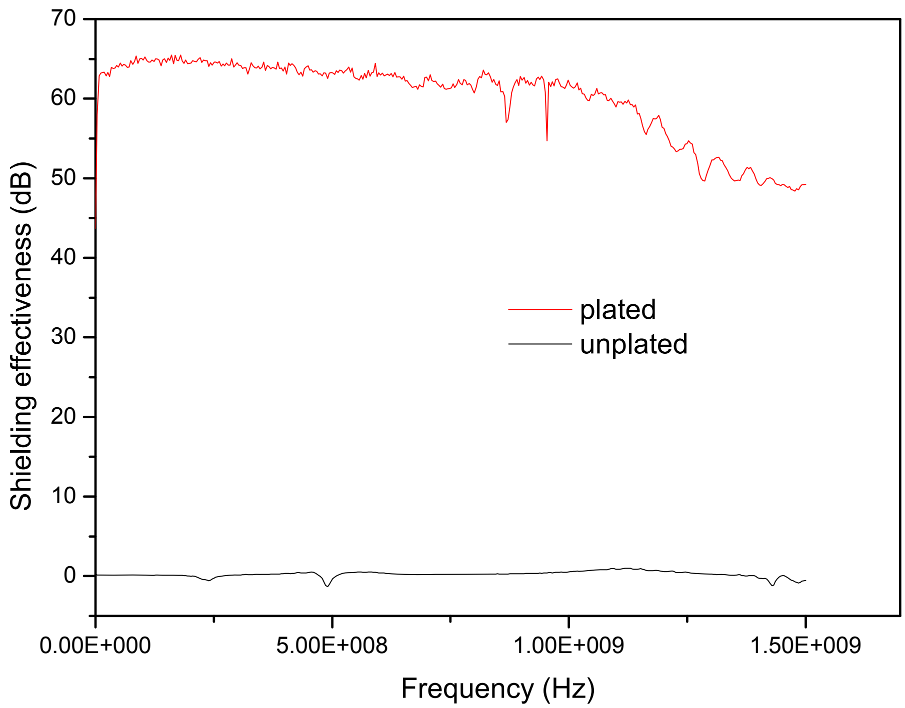



**Figure 6.** Electromagnetic shielding effectiveness of wood veneers before and after plating

## CONCLUSIONS

1. A new activation process for electroless nickel plating on birch veneer has been achieved. In the process, the veneers were modified with chitosan, and Pd(II) was used as activator.
2. A uniform, compact, and continuous Ni-P coating with crystalline structure was plated on birch wood surface. It consisted of 1.8 wt.% phosphorus and 98.2 wt.% nickel, which indicates that the coating was a low-phosphorus one. The surface resistivity was $0.24\Omega\cdot cm^{-2}$, which shows high conductivity.
3. The metallized birch veneers showed good performances in electromagnetic shielding. The electromagnetic shielding effectiveness of the plated veneers was higher than 50dB in the frequency range from 10MHz to1.5GHz, which is promising in the areas of anti-EMI.
4. This research also offers a new way for application of chitosan.

## ACKNOWLEDGMENTS

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