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Research Article

Keywords: Wood, Electroless Cu-Ni, Conductivity, hydrophobicity, Electromagnetic shielding

Posted Date: February 28th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1393984/v1>

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Abstract Prepare a sort of Wood-based EMI shielding materials can resist harsh electromagnetic wave environment had become a developing trend. The affect was differ from heat treatment temperatures on the wood-based composites was analyzed. The results showed that the surface roughness of metal coatings were 9.202 μm when the wood was electroless Ni and the heat treatment temperature was 120°C. When the wood was electroless Ni via 180°C heat treatment, the coatings thickness were 100.86 μm . EDS spectrums verifies the existence of Cu and Ni. The contact Angle of composite materials could reached 120.2°, and the hydrophobic property of wood was better. The average electromagnetic shielding efficiency of electroless 2Cu1Ni via 180°C heat treatment reached 91.40 dB in the frequency ranging from 300 KHz to 3.0 GHz, which verified that the composite material can shield 99.99% of the incident electromagnetic wave. The conductivity gradient structure can realize multi-dielectric interface loss and multiple reflection loss.

Keywords Wood; Electroless Cu-Ni; Conductivity; hydrophobicity; Electromagnetic shielding

1. Introduction

At present, because of the rapid development of communication technology, electromagnetic interference (EMI) and irradiation have become an emerging environmental pollutant. The electromagnetic pollution has become a serious social problem, affecting the normal operation of the electronic facility and the health of human ^[1,2]. The elimination of harmful electromagnetic waves is necessary for the protection of electronic communication equipment and the maintenance of a healthy human living circumstance ^[3-5]. The matrix of commonly used electromagnetic shielding materials is mostly non-renewable and not easy to degrade, large-scale use will bring environmental problems. Therefore, it will be an inevitable trend to prepare shielding materials based on environment-friendly materials with rich resources, renewable and degradable. As one of the natural materials, wood has the advantages of abundant resources, sustainable

development and biodegradation. If the shielding material is prepared by using wood as matrix and composite with materials with electromagnetic shielding property, the advantages of wood can be fully brought into play, and the electromagnetic shielding function of wood can also be endowed and the added value of wood can be increased. As one of the effective means to resist electromagnetic interference and reduce electromagnetic wave damage, electromagnetic shielding has become the mainstream method of purifying electromagnetic environment in the world. The growing number of powerful, sophisticated electronic devices demands excellent heat dissipation and EMI shielding materials [6]. The area of artificial forest in China ranks first in the world, but the poor wood material restricts its application range, so it is important to improve its performance through modification treatment. Heat treatment, as a very important wood modification technology, can effectively improve the dimensional stability and durability of wood properties, so it is necessary to achieve efficient and rational utilization of heat treated wood. Therefore, the preparation of electromagnetic shielding materials with high efficiency and environmental protection has been increasingly demanded by the society, wood-based electromagnetic shielding materials with renewable wood as the matrix, has a good application development prospects [7].

Wood heat treatment technology, as a green and environment-friendly physical modification method of wood, can increase dimensional stability, biological durability of wood, and effectively increase wood color [8]. Wood heat treatment is one of the ways to improve the dimensional stability and biological durability of wood, and is an effective technological means to improve the utilization rate of wood resources [9]. The carbonization of wood is mainly conducted by heating the wood at a high temperature from 160°C to 250°C to generate heat conduction between the wood and the heating medium. So that the specific material of wood produce thermal decomposition effect in a short period of high temperature state, and the carbonization process will not cause any pollution to the external environment, realize the physical and environmental protection treatment of wood [10]. In the process of heat treatment, the composition of wood degrades and brittleness increases. Compared with untreated wood, the compressive strength along grain of heat treated wood increases to some extent. The influence of high temperature heat treatment temperature on mechanical properties of larch wood is greater than that of heat treatment time [11]. Wood mechanical properties can be improved by precisely controlling the heat treatment temperature and time [12]. After high temperature heat treatment, the moisture absorption characteristics, corrosion resistance and dimensional stability of wood have been effectively improved [13] wood heat treatment refers to modification of wood at the temperature of 180°C ~ 230°C, at this time, hemicellulose and other components in wood are pyrolyzed, the equilibrium moisture content decreases, and the biological durability and resistance to shrinkage and swelling of wood are improved [14]. The way and time of heat treatment and the temperature of heat treatment are the most important elements affecting the microstructure and macroscopic properties of wood. The influence of temperature on wood chemical

composition should be considered in combination with tree species. As the heat treatment temperature and time increases, especially when the temperature is 200°C, wood mechanical strength loss is serious [15]. When the treatment temperature is below 200°C, temperature ratio has a more significant effect on the mass loss rate and mechanical properties of *Cunninghamia lanceolata* [16]. After high temperature heat treatment, the hydrophilic groups in wood are reduced, and the surface wettability of heat treatment glulam is reduced. The higher the heat treatment temperature is, the more obvious the wettability decreases [17]. The hygroscopic and desorption equilibrium moisture content of wood at different treatment temperatures gradually decreases as the heat treatment temperature increases [18]. The pyrolysis of hemicellulose at high temperature is the main reason for the modification of heat-treated wood, which reduces the number of hydrophilic groups and nutrients in wood, reduces the toughness of wood, and also affects the brightness index of wood [19]. The slowing down of water transversely along wood is mainly related to the decrease of the average pore size of the grain orifice and the small hole on the edge of the grain orifice plug. The change of chemical composition of high-temperature heat treatment wood leads to its enhanced hydrophobicity [20]. High-temperature heat treatment of wood is favored by wood processing enterprises as an environmentally friendly and relatively simple technology [11]. High temperature heat treatment technology is one of the main technologies with the highest market conversion rate and broad future prospects among wood functional technologies [21]. As with all solids, most of the properties of electroless Ni and Cu coatings are temperature-dependent. The thermal expansion coefficient affects the internal stress and bonding strength of electroless Ni and Cu coatings without high temperature heat treatment, which are thermodynamically metastable and tend to change from amorphous or microcrystalline state to crystalline state. Other conditions Under certain conditions, when the composite coatings are heat treated, atoms in the coatings will have mutual diffusion, resulting in recrystallization of amorphous or microcrystalline structure, and the formation of metallic Ni and intermetallic compounds, such as Ni₂P, Ni₃P and Ni₅P₂, etc. [22]. Generally speaking, heat treatment will change the coatings structure, and the structural change will affect the coatings performance. However, there are few reports on the relationship between heat treatment and electromagnetic shielding efficiency of Ni-Cu-P ternary wood-based composites.

In our study, the relationship between electromagnetic shielding effectiveness and heat treatment temperature of wood-based composite materials via electroless Cu and electroless Ni with different heat treatment gradient was analyzed.

2. Experimental materials and test methods

2.1 Experimental reagents and materials

HCl 12 mL/L, NaBH₄ 15 g/L, 25% NaOH, CuSO₄·5H₂O 53 g/L, NaKC₄H₄O₆·4H₂O 13 g/L, EDTA-2Na 27 g/L, K₄Fe(CN)₆·3H₂O 1.3 g/L, Formaldehyde 70 mL/L, NiSO₄·6H₂O 33 g/L, NaH₂PO₂·H₂O 28 g/L,

$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ 30 g/L, $\text{CH}_4\text{N}_2\text{S}$ 10 mg/L, ammonia water 30 mL/L, all analytically pure, were brought in Tianjin Beilian Fine Chemicals Development Co. Ltd.

Poplar was selected as the base materials, which was collected from Tumotezuqi, Hohhot, China, with a tree age of 3 or 5 years. The veneer was spin cut into rectangle piece with thickness (1.5+0.1) mm and moisture content is about 11.5%.

2.2 Experimental design

Six temperature gradients were designed. After electroless Ni and electroless Cu, wood is heat treated at 25℃, 100℃, 120℃, 150℃, 180℃ and 200℃, respectively. The experimental design is shown in Table 1. The wood was conducted via two electroless Cu and then one electroless Ni, which was marked as 2Cu1Ni.

Table 1 Experimental design

Type	Temperature (℃)					
	25	100	120	150	180	200
Electroless Ni	25	100	120	150	180	200
Electroless Cu-Ni	25-1	100-1	120-1	150-1	180-1	200-1

2.3 Preparation of specimen

2.3.1 Preparation of substrate

Select high-quality and no defect poplar flakes from poplar. Soak for 2 h at room temperature and dry. Then cut into round pieces (diameter: 9 cm), polish the wood surface with 600 mesh sandpaper, boil in water bath at 100℃ for 2 h. Clean with distilled water for several times, and suitable temperature drying (Fig.1).

Fig. 1 schematic diagram of sample preparation

2.3.2 Electroless Cu

Take 6 pieces of spare wood for processing into solution A, Stir gently with glass rod to make it fully soak and activate. Time 15 minutes to complete the first activation, after that, take 6 pieces of wood from

solution A into solution B for 90 s. The activated wood chips were put into the electroless Cu solution with pH adjusted. Stir gently for 10 s, then put the wood into the bath for electroless Cu. After 12 minutes the electroless Cu was completed, the wood chips were pulled out and put into the bath for secondary electroless electroless Cu for 12 min. Finally, the wood slices were taken out, washed with distilled water, marked and dried (Fig. 2).

Fig. 2 Schematic diagram of electroless Cu on wood surface

2.3.3 Electroless Ni

Take 6 pieces of spare wood for processing into solution A, Stir gently with glass rod to make it fully soak and activate. Time 15 minutes to complete the first activation, after that, take 6 pieces of wood from solution A into solution B for 90 s. The activated wood chips were put into the electroless Cu solution with pH adjusted. Stir gently for 10 s, then put the wood into the bath for electroless Ni. After 30 minutes the electroless Ni was completed. Finally, the wood slices were taken out, washed with distilled water, marked and dried (Fig. 3).

Fig. 3 Schematic diagram of electroless Ni on wood surface

2.3.4 Heat Treatment of 2Cu1Ni Sample

The samples were put into furnace, and the samples were clamped by fixtures. Six temperature gradients were designed. The wood was treated by electroless Ni and electroless Cu-Ni, and then heat treated at 25 °C, 100 °C, 120 °C, 150 °C, 180 °C and 200 °C, in turn, and then the performance was tested (Fig.4).

Fig. 4 Schematic diagram of heat-treated wood base composite

2.4 Test instrument and operation procedure

2.4.1 VK-X150 laser confocal microscope

Turn on the power and computer. Adjust the microscope stage. After the computer was powered on, open the microscope control software VK Viewer. Turn the lens adjustment knob. The sample observation was performed using a 20 X objective lens. Click "Simple Mode" on the control software interface, Click "Start measurement" and set automatic measurement to save pictures and data.

2.4.2 RTS-8 four-probe

Turn on the computer and the control software of the tester "RTS-8 Four-probe Test System", click "Automatic measurement", wait for the end of the measurement, and record the measured conductivity data.

2.4.3 SEM

Take dry sample, the sample was prepared and placed in the sample area to be tested. Characterized the surface morphology of the materials by Phenom scanning electron microscopy.

2.4.3 Hydrophobic performance

Turn on the meter power source, then turn on the computer, place the sample on the platform close to the needle of the drip tube. Squeeze out the right amount of water. Wait for 2 s and click the "take photos" button on the control software and record.

2.4.5 DR-S02A electromagnetic shielding effectiveness

The electromagnetic shielding effectiveness of the composites are measured in the L-band between 0.3×10^{-3} and 3.0×10^3 MHz using the DR-S02A shielding effectiveness test device (Beijing DingrongShichuang Technology Co., Ltd.) ASTM 4935-2010 international standard test. Sample thickness ≤ 10 mm. The error is from +0.5 dB to -0.5 dB, and the maximum VSWR is less than 1.2. Insertion loss (IL) < 0.5 dB.

According to Schelkunoffs theory^[23], shielding effectiveness(SE_T) of total electromagnetic interference (EMI) can be composed of reflection (SE_R), multiple reflection (SE_M) and absorption (SE_A). The detailed formulas are as follows:

$$SET(dB) = SER + SEM + SEA \quad (1)$$

$$SE_R(dB) = -10 \log(1 - S_{11}^2) \quad (2)$$

$$SE_A (dB) = -10 \log (S_{12}^2 / (1 - S_{11}^2)) \quad (3)$$

Where, S_{11} and S_{21} are the measured scattering parameters. When the multiple reflections are less than 15 dB (SE_T), Formula (1) can be simplified as:

$$SE_T (dB) = SE_R + SE_A \quad (4)$$

3 Analysis and discussion

3.1 Heat treatment coatings morphology

Fig. 5 showed the surface morphology of wood without superheat treatment. Fig. 6 was the surface topography of electroless Ni wood. Comparing Fig. 5a with Fig. 5b (3D figure), it can be clearly observed in Fig. 6b and Fig. 6c that copper and nickel were deposited on the composite material surface after electroless Ni, which partially covered the whole area, and the morphology of wood grain pores disappeared. Figure 7 was the surface topography of 2Cu1Ni electroless wood before heat treatment. The surface topography of wood was numerous ranges and uneven. The maximum surface roughness of metal coatings on wood surface were 33.805 μm (Table 2). 3D images after heat treatment (Fig. 8 and 9) showed that metal particles have covered the uneven area with the increase of heat treatment temperature, and the surface roughness of metal coatings on wood surface can be as low as 9.202 μm and 11.688 (Table 2). Tended to smooth wood surface proved that the chemical rate on the surface of the metal ion deposition in wood by matrix and sedimentary catalytic [23]. The metal coatings on the wood surface gradually flatten out with the increase of temperature, further verify the heat treatment can accelerate metal Cu and Ni particles will be rearrangement and was advantageous to the preparation of a smooth and uniform wood composite materials.

Fig.5 The wood surface laser microscope morphology 200 $\times$ (a: Surface morphology; inset showed depth map; b: 3D image)

Fig.6 Electroless Ni wood surface laser microscope morphology before heat treatment 200 $\times$ (a to k was followed by temperature 25 $^{\circ}$ C, 100 $^{\circ}$ C, 120 $^{\circ}$ C, 150 $^{\circ}$ C, 180 $^{\circ}$ C, 200 $^{\circ}$ C wood surface topography; inset showed depth map; b to l was temperature 25 $^{\circ}$ C, 100 $^{\circ}$ C, 120 $^{\circ}$ C, 150 $^{\circ}$ C, 180 $^{\circ}$ C, 200 $^{\circ}$ C of the 3D image)

Fig.7 Electroless 2Cu1Ni wood surface laser microscope morphology before heat treatment 200×(a to k was followed temperature 25 °C, 100 °C, 120 °C, 150 °C, 180 °C, 200 °C wood surface topography; inset showed depth map; b to l was temperature 25 °C, 100 °C, 120 °C, 150 °C, 180 °C, 200 °C of the 3D image)

Fig.8 Electroless Ni wood surface laser microscope morphology after heat treatment of 200°C (a to k

was followed by electroless temperature 25 °C, 100 °C, 120 °C, 150 °C, 180 °C, 200 °C wood surface topography; inset showed depth map; b to l was electroless temperature was 25 °C, 100 °C, 120 °C, 150 °C, 180 °C, 200 °C of the 3D figure)

Fig.9 Electroless 2Cu1Ni wood surface laser microscope morphology after heat treatment 200℃ (a to k was followed by electroless temperature 25 ℃, 100 ℃, 120 ℃, 150 ℃, 180 ℃, 200 ℃ wood surface topography; inset showed depth map; b to l was electroless temperature 25 ℃, 100 ℃, 120 ℃, 150 ℃, 180 ℃, 200 ℃ of the 3D figure)

Table 2. Surface roughness

Temperature (°C)	Before heat treatment (μm)	After heat treatment (μm)
25	19.676	19.676
25-1	21.006	21.006
100	33.805	14.299
100-1	16.870	11.291
120	18.281	13.859
120-1	24.293	9.202
150	21.806	11.006
150-1	19.730	12.777
180	25.394	12.713
180-1	19.534	12.712
200	21.710	11.688
200-1	20.219	12.179

3.2 Composite SEM surface topography

Figure 10 was SEM morphology of wood surface via electroless Cu-Ni. Fig.11 was SEM morphology of wood surface via electroless Ni. After electroless Cu-Ni and different heat treatments, the metal coatings distribution on the wood surface was gradually smooth, and the wood surface was flat and tended to be flat. There were obvious pore structures on the coatings surface (Fig.10a), and there were local agglomerations. The pore structures were obvious, and the number of pore structures were obviously increased (Fig.10b). The metal particles on the wood surface coatings were dispersed unevenly with the increasing heat treatment temperature. The more pore structures, the smaller grains (Fig. 10f). The morphology of electroless Cu-Ni composite coatings were ideal when the heat treatment temperature was 180°C.

After electroless Ni and different heat treatment, the uniformity of metal coatings on the wood surface decreased gradually. It can be clearly seen that there was obvious pore structure on the coatings surface (Fig.11b), and there were local agglomeration. the pore structure was obvious (Fig.11c), and the number of pore structures on the coatings surface of wood were obviously increased. With increasing heat treatment temperature (Fig. 11f), metal particles on wood surface coatings were not evenly dispersed, with more pore structure and smaller grain size. The morphology of electroless Cu-Ni composite coatings on wood surface was ideal when the heat treatment temperature was 25°C.

Figs. 12 and 13 were area scanning and local point energy spectra of composite coatings of different heat treatment treatments. In order to verify the uniform dispersion of metal particles in the coatings after

heat treatment, two different areas were selected in the composite coatings scanning image. The composite coatings mainly included Ni, Cu, P, C and O were five elements and the main elements were Ni and Cu, which further verified the results of laser confocal microscopy. At the same time, surface scanning and local point energy spectra showed that the Ni and Cu particles were tightly embedded together. Therefore, when the heat treatment temperature was 120°C, the morphology of electroless Cu-Ni composite coatings on wood surface were ideal.

Fig.10 Electroless 2Cu1Ni wood surface morphology after heat treatment (a:25°C, b:100°C, c:120°C, d:150°C, e:180°C, f:200°C)

Fig.11 Electroless Ni wood surface morphology after heat treatment (a:25°C, b:100°C, c:120°C, d:150°C, e:180°C, f:200°C)

Fig.12 Energy Dispersive Spectra of 150°C heat-treated by Electroless 2Cu1Ni (a:Area 1, b: Area 2)

Fig.13 Energy Dispersive Spectra of Electroless 2Cu1Ni (a Point 1, b Point 2, c Point 3).

3.3 SEM cross-section morphology of composites

Figure 14 and figure 15 were the cross section morphology via electroless 2Cu1Ni and electroless Ni with different heat treatment. It showed that the coatings thickness will also change with the increase of heat treatment temperature, showing a trend of first increase and then decrease. Cu and Ni particles were fully embedded in the pores of wood, and the thickness of metal coatings on the wood surface reached 100.86 μm when the electroless temperature reached 180°C (Table 3). The interface morphology of the composite material verified that the surface and interface morphology of the composite coatings were better at 180 °C. The bright white wood in the cross-sectional morphology showed that the metal Cu particles will enter the wood pores, which was conducive to the formation of dense and high strength composites. The cross-sectional morphology showed bright white in the wood pores, which further illustrated that the metal Cu and Ni particles will enter the wood pores, it was conducive to the formation of dense and high strength composites.

Fig 14 Cross section morphology of electroless 2Cu1Ni after heat treatment
(a:25°C, b:100°C, c:120°C, d:150°C, e:180°C, f:200°C)

Fig 15 Section morphology of electroless Ni after heat treatment (a:25°C, b:100°C, c:120°C, d:150°C,

e:180°C, f:200°C)

3.4 Conductivity

Figure 16 showed the relationship between heat treatment and the conductivity of coatings. Before heat treatment, Fig.16a showed the conductivity of Ni-coated composite increased first and then decreased. It was obvious that the conductivity increased sharply from 25 °C to 120 °C, and decreased sharply from 120 °C to 150 °C. Figure 16b showed the conductivity of 2Cu1Ni electroless composite decreased first and then tended to be stable, and the electrical conductivity decreased from 25 °C to 100 °C, then tended to be stable. After heat treatment, Fig. 16c showed the electrical conductivity of the electroless Ni composite was improved, the conductivity increased sharply from 25 °C to 100 °C, stabilized from 100 °C to 150 °C, decreased sharply from 150 °C to 180 °C, and increased sharply from 180 °C to 200 °C. Figure 16d showed the conductivity of electroless 2Cu1Ni composite increased at 100 °C, 150 °C, 180 °C, and decreased at 120 °C and 200 °C. It can be concluded from Fig. 16 showed the electrical conductivity of the coatings on the composite surface varies greatly after heat treatment. The main reason was the rearrangement and recrystallization of Cu and Ni accelerate during heat treatment. The Cu and Ni particles accumulated rapidly on the wood surface. The metal coatings covered the whole wood surface and the difference of materials, the uniformity and thickness of the composite coatings increased rapidly, which made the electrical conductivity of the wood composite increase.

Figure 16 showed the electrical conductivity of the wood surface increased after heat treatment. With the increase of temperature, the rearrangement and recrystallization of Cu and Ni accelerated, and the wood surface will form dense, uniform and conductive composites.

Table 3 Thickness of cross section coatings after heat treatment

Temperature (°C)	Thickness (μm)
25	70.83
25-1	36.05
100	46.87
100-1	38.37
120	97.48
120-1	39.53
150	49.48
150-1	65.77
180	69.26
180-1	100.86
200	40.63
200-1	93.3

Fig 16 Relationship between heat treatment temperature and conductivity

(a: electroless Ni coatings without heat treatment, b:electroless 2Cu1Ni coatings without heat treatment , c:Electroless Ni coatings after heat treatment, d: Electroless 2Cu1Ni coatings after heat treatment)

3.5 Hydrophobic performance

Fig 17 Hydrophobic properties of electroless Ni after heat treatment (a:25°C, b:100°C, c:120°C, d:150°C, e:180°C, f:200°C)

Fig 18 Hydrophobic properties of electroless 2Cu1Ni after heat treatment (a: 25 °C, b:100 °C, c:120 °C, d:150 °C, e:180 °C, f:200 °C)

Fig 17 and 18 were the surface hydrophobicity of the materials treated with different heat treatment. The materials heat treated at different temperatures were showed in the figure, and the heat treatment temperatures were 25 °C, 100 °C, 120 °C, 150 °C, 180 °C and 200 °C, respectively. It can be seen from the figure that the contact angles via electroless Ni and electroless 2Cu1Ni with different temperature gradients were 111.3, 108.8, 120.1, 119.1, 106.4, 108.5, 108.7, 115.8, 120.2, 100.5, 105.2 and 104.7, respectively (Table 4). When the temperature of electroless 2Cu1Ni composites reached 100 °C, the contact angle was 119.1°. When the temperature of electroless Ni composites reached 180 °C the contact angle was 120.2°. This result further verified the correctness of the SEM analysis conclusion. Compared with the hydrophobic treatment method mentioned in the literature [24], heat treatment was a simple and effective way. The composite coatings formed by heat treatment on the wood surface can improve the hydrophobic properties of the material, which proved that the metal Cu and Ni on the wood surface were tightly embedded together to form a dense composite coatings. The reason was the rearrangement and recrystallization of Cu and Ni were accelerated, and the Cu and Ni coatings were tightly embedded together. The roughness decreases gradually, the surface coatings smoothness tends to be uniform, and the particles were closely combined. Therefore, the metal coatings structure on the wood surface was relatively dense, the hydrophobic property of the composite was better. The hydrophobic property of the composite at 180 °C was better than at 200 °C. The possible reason was the thickness of the composite coatings increases gradually with the increase of temperature on the wood surface, resulting in the

difference in the local surface roughness ^[25]. Fig. 11f showed the size of the composite coatings were significantly larger than the larger island structure in Fig. 11e, which can reduce the air volume between water droplets and the surface of the composite coatings, and reduced the hydrophobic effect of the composite coatings ^[25].

Table 4 Contact angles at different time after heat treatment

Temperature (°C)	Contact angle (°)
25	111.3
25-1	108.8
100	120.1
100-1	119.1
120	106.4
120-1	108.5
150	108.7
150-1	115.8
180	120.2
180-1	100.5
200	105.2
200-1	104.7

3.6 Analysis of electromagnetic shielding effectiveness

Figs. 19 to 22 showed the electromagnetic shielding effectiveness curves of the composites, which were wood-based composites formed via electroless 2Cu1Ni and electroless Ni on the wood surface and heat treatment. From Table 5, The average electromagnetic shielding efficiency of electroless 2Cu1Ni via 180°C heat treatment reached 91.40 dB ranging from 300 KHz to 3.0 GHz (Table 5), which verified that the composite material can shield the incident electromagnetic wave.

The absorption spectra showed that the composites via electroless Ni treated at 200 °C had stronger electromagnetic wave absorption capacity. The reflection spectra showed that the electroless Ni treated at 200 °C has stronger reflection on electromagnetic waves in the frequency ranging from 2.5 GHz to 3.0 GHz (Figs. 22a and 22b). Due to good impedance matching, the incident electromagnetic wave can easily penetrate the interior of the composite coatings, a few electromagnetic waves can be reflected on the surface of the composite coatings. The porous structure of composite coatings on wood surface were not conducive to electromagnetic wave absorption, and electromagnetic wave was easy to penetrate. The absorption coatings with positive conductivity gradient and negative magnetic ^[26] gradient achieved strong electromagnetic absorption through strong hysteresis loss and dielectric loss ^[26]. Strong hysteresis loss was the main electromagnetic wave loss mode.

Fig 19 Electromagnetic shielding effectiveness of electroless 2Cu1Ni composite before heat treatment
(a: Reflection efficiency; b: Absorption efficiency; c: Electromagnetic shielding effectiveness)

Fig 20 Electromagnetic shielding effectiveness of electroless Ni composite before heat treatment
(a: Reflection efficiency; b: Absorption efficiency; c: Electromagnetic shielding effectiveness)

Fig 21 Electromagnetic shielding effectiveness of electroless 2Cu1Ni composite after heat treatment
(a:Reflection efficiency; b: Absorption efficiency; c: Electromagnetic shielding effectiveness)

Table 5 Relationship between Heat Treatment and Electromagnetic Shielding Effect

Temperature (°C)	Electromagnetic shielding effect (SE _T)/(dB)	
	Before heat treatment	After heat treatment
25	72.61	72.61
25-1	88.41	88.41
100	60.63	63.99
100-1	81.92	81.93
120	69.45	71.46
120-1	84.45	72.02
150	65.57	65.44
150-1	89.35	88.71
180	56.95	59.74
180-1	87.80	91.40
200	66.12	64.61
200-1	84.30	89.74

Fig 22 Electromagnetic shielding effectiveness of electroless Ni composite after heat treatment
(a: Reflection efficiency; b: Absorption efficiency; c: Electromagnetic shielding effectiveness)

Wood-based electroless Cu and electroless Ni have synergistic effect on electromagnetic shielding effectiveness, and the main mechanism was the separation of conductive network and specific interface polarization mechanism of composite coatings [27–28]. The ideal conductive network of the composite coatings showed superior charge storage capacity, and the polarization of the electric field promoted the absorption of more incident electromagnetic microwave energy [26–29]. During the heat treatment process, the metal Cu particles and Ni particles were fully embedded in the wood pores, which made the coatings structure compact, the pore structure shrinks or disappears, and the surface of the material tended to be ideal flat morphology. With the change of heat treatment temperature, the thickness of the coatings section were also greatly improved. For example, When the wood was electroless Ni via 180°C heat treatment, the coatings thickness were 100.86 μm (Table 3). Due to the increase of the coatings thickness of the wood-based composite and the shrinkage or disappearance of the pore structure, it was difficult for the

incident electromagnetic wave to pass through the composite. Because the conductivity gradient structure of the composite material can realize multi-medium interface loss and multiple reflection loss, the electromagnetic shielding effectiveness of the composite material was greatly improved, and the incident electromagnetic wave can be shielded efficiently. The electromagnetic shielding effectiveness of the treated wood-based composites was analyzed and composites was analyzed. The experimental data of electromagnetic shielding effectiveness of the composites before and after treatment were compared, thus demonstrated that the wood-based composites after heat treatment have ideal electromagnetic shielding effectiveness.

3.7 The mechanism of electromagnetic shielding effectiveness

Figure 23 illustrated a schematic diagram of EMSE mechanism of electromagnetic gradient structure composites. Microscopically, wood has a micro/nano multi-scale pore structure, and its natural skeleton form can be used as a matrix template for other materials. However, the poor wood material restricts its application range, so it was of great significance to improve its performance by modification. Heat treatment was a very important wood modification technology. As shown in Fig. 8 and Fig 9, after heat treatment at different temperatures, the atoms at the bump began to diffuse and tended to be flatted. Different heat treatment temperatures have different trends. At the appropriate heat treatment temperature, the surface protrusions will became smaller and disappeared until smooth. Before heat treatment, the Cu element and Ni element added in the electroless solution preferentially adsorbed on the defects of the wood surface, which greatly reduced the surface energy, promoted the adsorption of metal coordination compound ions and reducing agent ions on the metal surface ^[30], and provided catalytic activity for the nucleation of the later alloy, which greatly improved its nucleation degree and deposition rate. From the figures 23, it can be seen that the initial state of the metal coatings metal arrangement were more disordered between the metal or there will be voids. Taking the chemical composite coatings as the object, the effects of different heat treatment temperatures on the structure, wear resistance, surface roughness and morphology of the coatings were studied for our purpose to improve the electromagnetic shielding effectiveness of wood matrix composites with electromagnetic gradient structure. Studied have shown that with the increase of heat treatment temperature, the composite coatings gradually transformed into crystalline structure ^[31], and the wear resistance was improved. The surface of the wood-based composite coatings treated with temperature were smoother, denser and finer than that of the composite coatings without temperature treatment, and the surface roughness of the metal coatings on the wood surface can reach 9.202 μ m. The smaller the particle size of Cu and Ni, the denser the coatings. Figure 23 showed the temperature treated wood ^[32].

Fig.23 Diagram of electromagnetic shielding mechanism of wood-based composites

The wood surface was treated with twice electroless Cu and once electroless Ni, then treated with different temperature gradients to improve the morphology, roughness, conductivity and hydrophobicity of the wood coatings, so as to prepare the electromagnetic gradient structure composite with ideal electromagnetic shielding effectiveness. Firstly, the reason for high electromagnetic shielding efficiency was that the polarization mode in the process of microwave dielectric loss was dominated by interfacial polarization ^[33]. The electromagnetic wave passes through the wood-based composites, and a large number of free charges spontaneously accumulate in the heterojunction surface between the metal Cu coatings, the metal Ni coatings and the Cu coatings, the metal Ni coatings and the metal Ni coatings and the wood, resulting in the macroscopic dipole moment and the Debye relaxation, thus accelerating the attenuation of electromagnetic wave and realizing the multi-media interface loss ^[34]. Secondly, the

conductivity loss was undoubtedly another important factor. The better the conductivity of the material, the better the electromagnetic shielding effect [35]. In this experiment, the wood surface was treated by twice electroless Cu, once electroless Ni, and then the compactness of the coatings were improved by temperature treatment. A perfect conductive structure was formed on the wood surface, and the good conductivity of the composite accelerated the efficiency of electromagnetic energy into heat energy [26-36]. In addition, the gradient structure design will cause the electromagnetic shielding mechanism of absorption-reflection-reabsorption [37-38], which can significantly attenuate the backward scattering of electromagnetic waves [39-40], so that the shielding effect was better. At the same time, the wood showed bright white in figure 14 and figure 15, which further illustrated that metal Cu and Ni particles would enter the wood pores.

CONCLUSIONS

1. The wood surface gradually tended to gentle and the surface roughness of metal coatings on wood surface was 9.202 μm .
2. When the wood was electroless Ni via 180 °C heat treatment, the coatings thickness were 100.86 μm . The interface morphology of the composite material verifies that the surface and interface morphology of the composite coatings was better at 180 °C.
3. The electrical conductivity after heat treatment increased significantly. The electrical conductivity of wood via 200 °C heat treatment increased from 40 S/cm to 527 S/cm, which was 13 times higher than untreated wood. The electrical conductivity also increased with the increase of temperature and the extension of constant temperature treatment time.
4. When the wood was electroless Ni composites via 180 °C heat treatment, the contact angle of the composite could reach 120.2°.
5. The composite coatings with 200 °C heat treatment temperature showed more stronger electromagnetic wave absorption capacity and electromagnetic wave reflection capacity ranging from 2.5 GHz to 3.0 GHz. The electromagnetic shielding effectiveness of composites via electroless 2Cu1Ni was up to 90 dB while the average electromagnetic shielding efficiency of composite materials via electroless 2Cu1Ni with 180 °C heat treatment reached 91.40 dB ranging from 300 KHz to 3.0 GHz, which verified that the composite materials can shield 99.99% of the incident electromagnetic wave.

ACKNOWLEDGMENT

This work was supported by The undergraduate innovation and entrepreneurship training program (202110129007), Natural Science Foundation of Inner Mongolia Autonomous Region (2019BS03014), the Start-up Project of Inner Mongolia Agricultural University High-level Talents Introduction Scientific

Research (NDYB2016-24), The Colleges and Universities Science Research Project of Inner Mongolia Autonomous Region (NJZY18058 and NJZY21468), Science research innovation projects of the Inner Mongolia Agricultural University for undergraduate (KJCX2020025) and Science and Technology Innovation Leading Project of Inner Mongolia Autonomous Region (KCBJ2018013).

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