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Preparation and microwave absorbing properties of nickel-coated carbon fiber with polyaniline via in situ polymerization

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Abstract Electric conductive and microwave absorbing material PANI/Ni/CF was prepared by in situ polymerization of polyaniline on the surface of nickel-coated carbon fiber (Ni/CF). The morphologies and structures of CF, Ni/CF, PANI and PANI/Ni/CF were characterized by scanning electron microscope and X-ray diffraction. Results show that the CF was wrapped tightly around the nickel layer, and the Ni/CF was coated by PANI. Measurement of four probes resistance tester indicates that the electrical conductivity of PANI/Ni/CF was great improved compared with PANI and PANI/CF. Vibrating sample magnetometry shows that the magnetic saturation intensity of Ni/CF and PANI/Ni/CF was 13.8 and 2.3 emu/g, respectively. According to the vector network analyzer, the microwave absorbing properties of PANI/Ni/CF were better than those of PANI and PANI/CF, and its minimum loss value is −12.4 dB at 8.8 GHz.

1 Introduction

With the development of modern science and technology, the influence of electromagnetic radiation on the environment is increasing day by day, so wave absorbing material is a hot area in the current research [1, 2]. Absorbing material is a kind of material that can absorb the electromagnetic wave energy projected onto its surface. In engineering applications, the absorption material has a high absorption rate in a wide band electromagnetic wave, but also needs to have quality of light, heat resistance, humidity resistance, corrosion resistance and other properties [3–5]. Suction wave material loss mechanism can be roughly divided into the following three categories: First, the resistance loss, such absorption mechanisms and material conductivity of the resistive loss, the carrier induced macroscopic urge conversion of electromagnetic energy into heat energy [6–8]. Second, the dielectric loss, that is, through the medium of repeated polarization generated by the "friction" role of electromagnetic energy into heat energy dissipation. Third, the absorption mechanism is a class and ferromagnetic media dynamic magnetization process of magnetic loss [9, 10].

Some metals are always coated onto the surface of carbon materials such as carbon fiber, carbon nanotubes, graphite nanosheet to improve their electric conductivity and other properties. Among the metals, nickel (Ni) was chosen for its high magnetic properties, low price and stability. Ni is not only conductive, but also has good magnetic properties, and is widely used in the preparation of absorbing materials. Compared with carbon fiber (CF), Ni plating–carbon fiber (Ni/CF) has a higher electrical conductivity, so the addition of Ni/CF can greatly improve the shielding effectiveness of composite materials.

Conductive polymers have been widely used in the fields of electronic and optoelectronic applications. The typical intrinsic conducting polymers are poly acetylene, polyaniline, poly(thiophene) and polyaniline (PANI), which is a hot research topic due to its structural diversity, environmental stability, easy processing, low cost and special doping mechanism [11–13]. Polyaniline, a kind of high molecular compound, has special electrical and optical properties, which can be doped with electric conductivity. In the electronics industry, information engineering,

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defense engineering and other development and development have a variety of uses [14–16].

In this paper, Ni/CF was prepared by electroless nickel plating method on the surface of CF. PANI/Ni/CF was prepared by in situ polymerization in an aqueous HCl solution. The aim of this process was to prepare the composite materials with light quality, high electrical conductivity and electromagnetic shielding properties. CF, Ni/CF, PANI and PANI/Ni/CF were characterized by SEM and XRD. Properties such as electrical conductivity, magnetic performance and microwave absorbing were measured [17–19].

2 Materials and methods

2.1 Materials

Aniline (AR) was obtained from Sinopharm Chemical Reagent Limited Company and was distilled at reduced pressure before being used. Carbon fiber used in the paper is T300B and supplied by TORAY Japan. Stannous chloride ($SnCl_2{\cdot}2H_2O$) (AR), Xi'an Chemical Reagent Factory; Palladium chloride ($PdCl_2$) (AR), Tianjin Fuchen chemical reagent factory; Ammonium chloride (NH_4Cl) and sodium hydroxide (NaOH) were all obtained from Nanjing chemical industry Co. Ltd, Jiangsu, China. Nickel sulfate ($NiSO_4{\cdot}6H_2O$), 36 % hydrochloric acid (HCl), citric acid ($C_6H_7O_8{\cdot}H_2O$) (AR), sodium hypophosphite ($NaH_2PO_2{\cdot}H_2O$) (AR) were all analytical reagent grade supplied by Sinopharm Chemical Reagent Co. Ltd, China.

2.2 Preparation of Ni/CF

Using electroless plating method by nickel plated carbon fiber method is as follows (the process is shown as Fig. 1): take a certain amount of carbon fiber, agitate in 0.5 mol/L NaOH solution for 1H, filter then place in concentrated nitric acid for ultrasonic treatment for 30 min. After vacuum filtration,add it into 0.5 mol/L $SnCl_2{\cdot}2H_2O$ solution in ultrasonic for 30 min, until it was sensitized. Then, the sensitized CF was filtered with $PdCl_2$ activation treatment after dying. The reaction is as follows:

$$SnCl_2 + H_2O \rightarrow Sn(OH)Cl + H^+ + Cl^-$$
$$SnCl_2 + 2H_2O \rightarrow Sn(OH)_2 + 2H^+ + 2Cl^-$$
$$Sn(OH)Cl + Sn(OH)_2 \rightarrow Sn_2(OH)_3Cl$$
$$Sn_2(OH)_3Cl + 2PdCl_2 \rightarrow Sn_2(OH)_3Cl_5 + 2Pd.$$

Then, add the pretreated CF into the plating solution. The formula of electroless nickel plating solution is shown in Table 1, the temperature was controlled at 80 ± 5 °C, the PH was about 8 and the proportion of pretreated CF and $NiSO_4{\cdot}6H_2O$ was 1:2. The reaction is as follows:

$$Ni^{2+} + 4H_2PO^{2-} + H_2O = Ni + P + 3HPO_3^{2-} + 4H^+ + (3/2)\ H_2$$

2.3 Preparation of PANI/Ni/CF composites

PANI/Ni/CF was prepared via in situ polymerization. Certain amount of Ni/CF was added into the HCl (0.5 mol/L) solution and put the mixture under the condition of ice water bath. Then, the mixture was stirred and Aniline was added. When the temperature of the mixture was about 0 °C, another solution was added into the mixture, which contained APS and HCl (0.5 mol/L). The reaction was carried out at 0 °C for about 6 h. After the reaction, the reaction liquid was filtered, and washed several times with HCl (0.5 mol/L), then put the solid products at 120 °C for about 8 h.

2.4 Characterization

The surface morphologies of CF, Ni/CF, PANI and PANI/Ni/CF were characterized via scanning electron microscopy (SEM; JSM-6390, HITACHI, Japan). CF, Ni/CF, PANI and PANI/Ni/CF were tested by X-ray diffraction (XRD; PANalytical, Holland). The magnetic properties of Ni/CF and PANI/Ni/CF were measured by vibrating sample magnetometer (VSM, Lake Shore7307). The electrical conductivities of compounds were measured using a SZ-82 digital four probes resistance tester (Suzhou Electronic Equipment Factory, China), For measurement of electrical properties, circle samples with a diameter of 15 mm and a thickness of 2 mm were prepared by casting them into

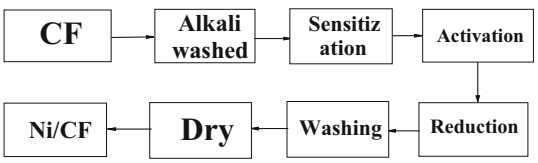

Fig. 1 Preparation of Ni/CF

Table 1 Electroless nickel plating bath formulation process

Components	$NiSO_4{\cdot}6H_2O$	$NaH_2PO_2{\cdot}H_2O$	$C_6H_7O_8{\cdot}H_2O$	NH_4Cl	Other additives[a]
Content	25 g/L	30 g/L	60 g/L	30 g/L	A few

[a] Mainly include surface active agent and stabilizer

stainless forms and cold-press. The absorption properties of PANI, PANI/CF and PANI/Ni/CF were analyzed using a HP8753D vector network analyzer, the samples were prepared using the mix of the products (20 wt%) and paraffin (80 wt%) in a mould with the size of 22.86 mm × 10.16 mm × 2 mm.

3 Results and discussion

Figure 2 shows the SEM images of CF (a), Ni/CF (b), PANI (c) and PANI/Ni/CF (d and e). As shown in Fig. 1a, the surface of pretreated CF was smooth and lustrous. After electroplating nickel, it can be found that CF was wrapped tightly around the nickel layer (Fig. 2b). Then, after the in situ polymerization, the Ni/CF covered by PANI can clearly be observed at Fig. 2d, e. Figure 2c is the image of PANI.

X-ray diffraction analysis of CF, Ni/CF, PANI and PANI/Ni/CF from $2\theta = 10°–80°$ are displayed in Fig. 3. The peak at $2\theta = 25.56°$ is corresponding the typical diffraction peak of graphite and the 3 peaks before 30° are

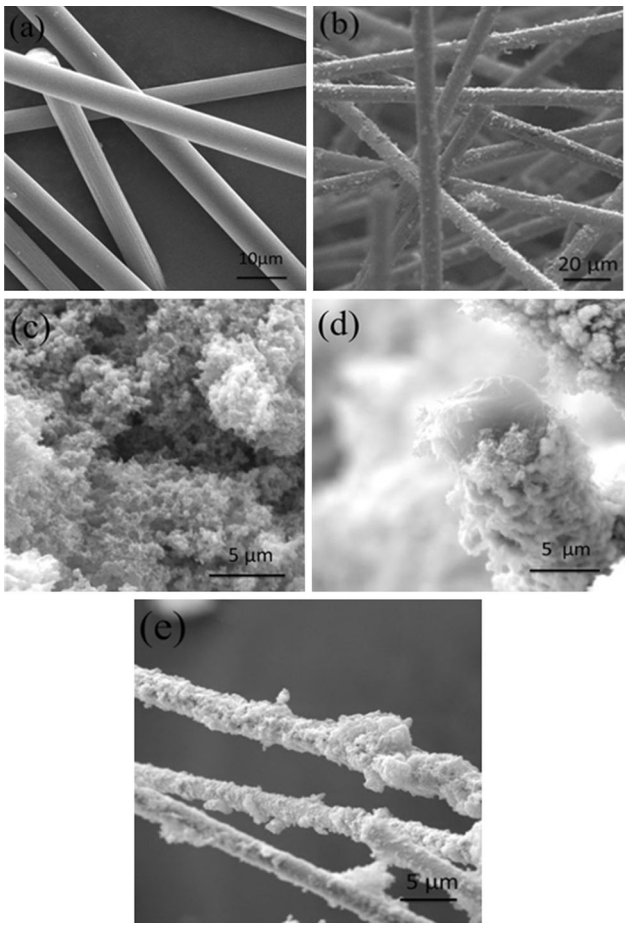

Fig. 2 SEM images of CF, Ni/CF, PANI and PANI/Ni/CF

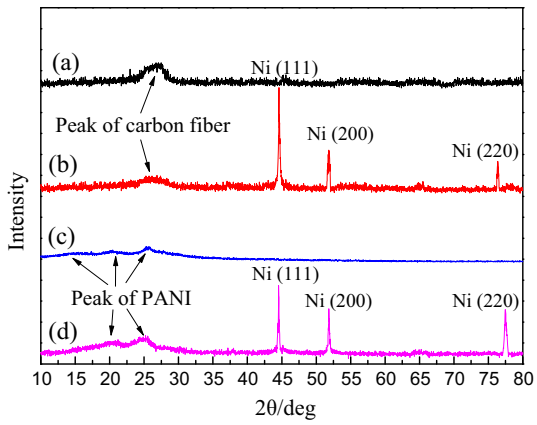

Fig. 3 XRD patterns of CF (*a*), Ni/CF (*b*), PANI (*c*) and PANI/Ni/CF (*d*)

the characteristic peak of PANI. It can easily be seen that the peak in the pattern (b) was significantly gentler than that of the pattern (a). This indicates the CF surface was covered by metal nickle after electroless plating. From curve (b) and (d), another three diffraction peaks can be observed at 44.52°, 51.84° and 76.39°, which indicate the (1 1 1), (2 0 0) and (2 2 0) planes of Ni's cubic face-centered structure (JCPDS. No. 04-0805). It indicates nickel particles are among the Ni/CF and PANI/Ni/CF.

The thermal stabilities of PANI, PANI/CF and PANI/Ni/CF were characterized by TG analysis, and the curves are demonstrated in Fig. 4. The degradation temperatures of PANI is 511 °C for the pyrolysis of its main chain. The TG curves indicate that the PANI/CF's curve and PANI/Ni/CF's curve are relatively close, while all the corresponding residual ratio of the PANI curve is lower than that of PANI/CF and PANI/Ni/CF curve. It can be attributed to the role of CF in imposing restriction on the pyrolysis of PANI chains and avoid heat concentration.

The electrical conductivities of CF, Ni/CF, PANI, PANI/Ni/CF and PANI/CF were summarized in Table 2.

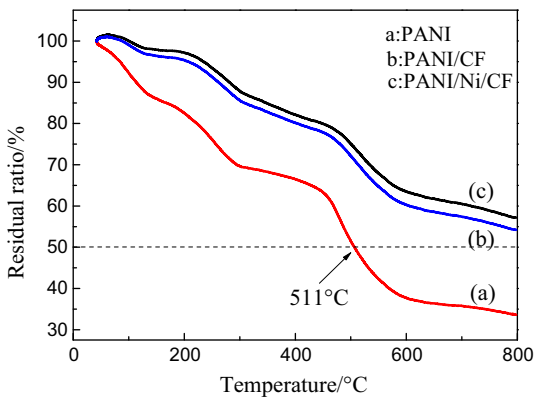

Fig. 4 TGA curves of PANI (*a*), PANI/CF (*b*) and PANI/Ni/CF (*c*)

Table 2 Electrical conductivity values of samples (S/cm)

Sample	CF	Ni/CF	PANI	PANI/Ni/CF	PANI/CF
Conductivity	3.2	1.88×10^2	0.19	1.07	0.36

According to the four probes resistance tester, the electrical conductivity of CF is 3.2 S/cm. However, its electrical conductivity increased to 1.88×10^2 S/cm after nickel plating. The electrical conductivity of PANI is 0.19 S/cm, when it was combined with the Ni/CF, the conductivity can reach 1.07 S/cm, which is approximately 4.5 times higher than PANI's 0.19 S/cm and 2 times higher than PANI/CF's 0.36 S/cm. The magnetic property of Ni/CF and PANI/Ni/CF was measured by VSM, and the result was displayed in Fig. 5. It can clearly be founded that Ni/CF and PANI/Ni/CF are all represented as typical soft and magnetic materials. The magnetization saturation (Ms) of Ni/CF is 13.8 emu/g. When combined with PANI, the magnetism drops to 2.3 emu/g. If the ratio of Ms was used to replace the content of Ni/CF, we can roughly calculate the content of Ni/CF in PANI/Ni/CF. The mass percentage of Ni/CF in PANI/Ni/CF is about: 2.3/13.8 = 16.7 %. Meanwhile, we can get the conclusion that the addition of Ni/CF greatly improved the electric conductive and magnetic property of PANI.

The microwave absorbing properties of material were closely related to its electromagnetic properties, and mainly characterized using reflection loss (RL). According to the transmit-line theory, when the electromagnetic wave vertically incidents upon the samples, the reflection loss can be calculated using the following equations:

$$R = 20\log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right|$$

$$Z_{in} = Z_0\left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2}\tanh\left[j\left(\frac{2\pi ft}{c}\right)(\mu_r\varepsilon_r)^{1/2}\right]$$

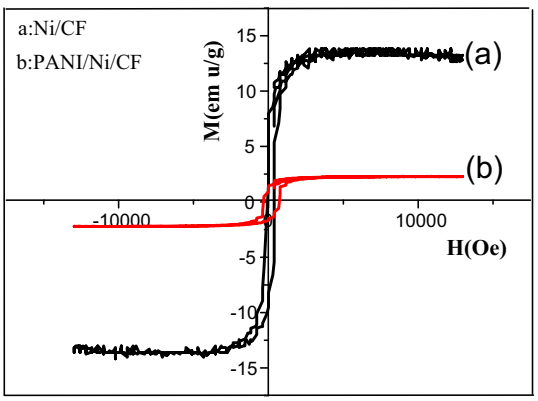

Fig. 5 Magnetization curves of Ni/CF (*a*) and PANI/Ni/CF (*b*)

where Z_0 is the characteristic impedance of vacuum, Z_{in} is the normalized input impedance relating to the impedance in free space, $\varepsilon r = \varepsilon' - j\varepsilon''$, $\mu r = \mu' - j\mu''$ is the relative complex permeability and permittivity of the material, d is the thickness of the absorber, a and f are the velocity of the light and the frequency of the microwave, respectively. It indicates that the absorption capacity of the material at the same frequency mainly depends on the thickness of the material.

The electromagnetic parameters of PANI (a), PANI/CF (b) and PANI/Ni/CF (c) were displayed in Fig. 6, and dielectric loss ($\tan\delta e = \varepsilon''/\varepsilon'$) and magnetic loss ($\tan\delta m = \mu''/\mu'$) of PANI, PANI/CF and PANI/Ni/CF were calculated. In the X band, the permittivities of PANI/CF and PANI/Ni/CF are much higher than those of PANI, confirmed that the PANI/Ni/CF and PANI/CF composites display a higher conductivity compare with PANI. The $\tan\delta e$ of PANI/CF and PANI/Ni/CF are also higher than those of PANI while the complex permeabilities and $\tan\delta m$ of all the materials are relatively close.

The calculated frequency dependence RL curves of PANI, PANI/CF and PANI/Ni/CF in a frequency range of 8.2–12.4 GHz (X band) are shown in Fig. 7. The reflection loss of proton acid doping PANI is higher than −10 dB (90 % absorption), from −1 to −8 dB. After the addition of CF, the performance of its absorption is improved, the lowest value of the reflection loss can reach −10 dB. However, the PANI/Ni/CF's curve is below the PANI/CF's curve, and its lowest point appears at F = 8.8 GHz, about −12.4 dB. It indicates that the microwave absorbing properties of PANI/Ni/CF were greatly improved compared with PANI and PANI/CF. It's mainly due to the increase of electrical conductivity and magnetic property by Ni, making the composites have better electromagnetic matching, which is able to absorb more electromagnetic waves.

The simulated RL curves of PANI/Ni/CF at different thicknesses are displayed in Fig. 8. It can be clearly observed that the thickness of the absorber has a great influence on the microwave absorbing properties. The minimum RL gradually shifts toward lower frequency with the increase of thickness, which matches the quarter-wavelength model. When the thickness is 1.0 mm, the reflection loss value is about −1 dB. However, when the thickness increased to 1.5 mm, its RL curve is ranging from −2 to −9 dB, and its microwave absorbability is poorer than the 2.0 mm PANI/Ni/CF. When the thickness reached 2.5 and 3.0 mm, its reflection loss decreased with the increase of the thickness. So we can draw the conclusion that the best match thickness of PANI/Ni/CF composites is 2.0 mm in the X band, and the RL is lower both in low and high frequency.

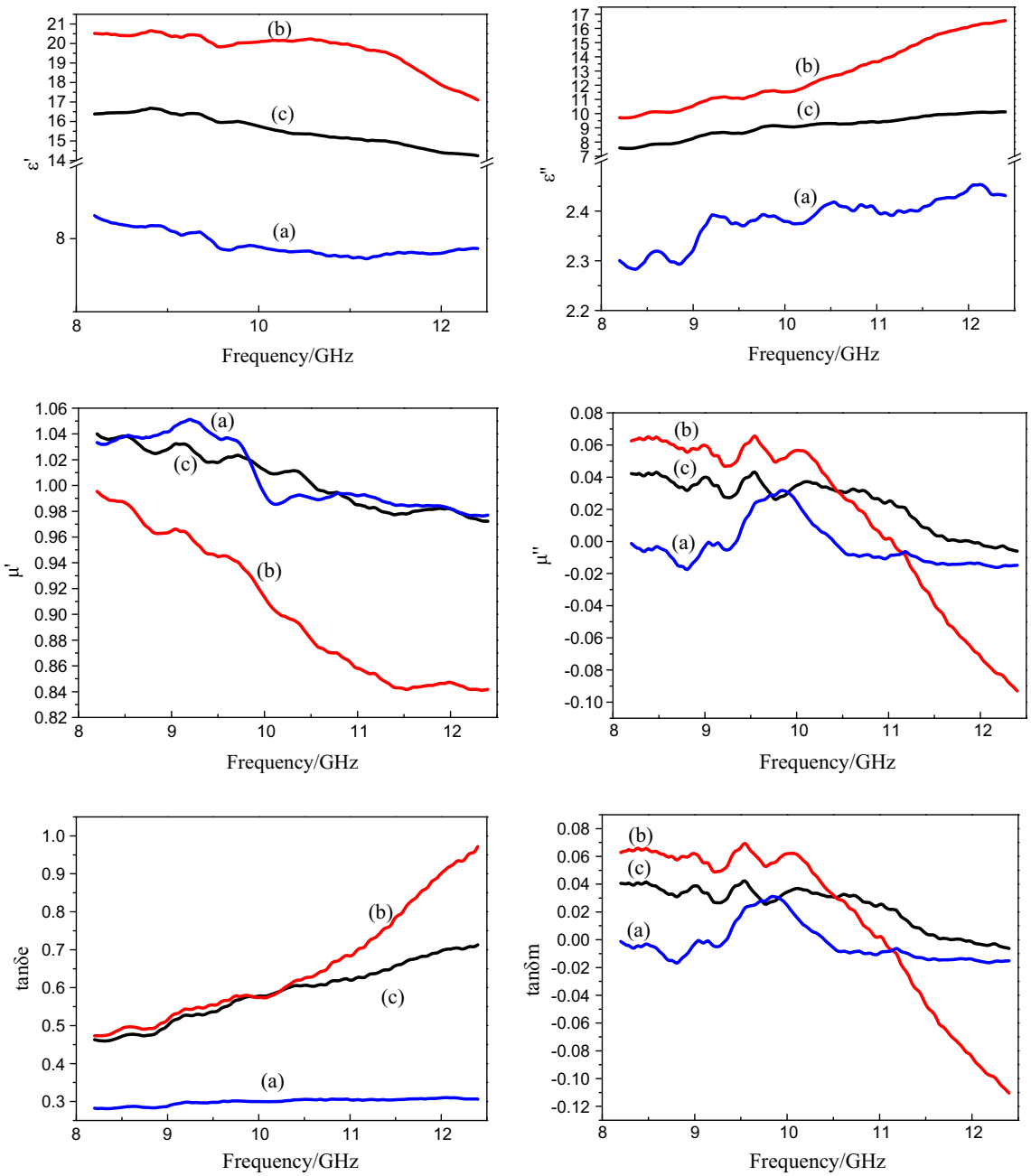

Fig. 6 Electromagnetic parameters of PANI (*a*), PANI/CF (*b*) and PANI/Ni/CF (*c*)

4 Conclusions

Ni/CF was prepared by Ni/CF was prepared by electroless plating method on the surface of CF, and PANI/Ni/CF was fabricated via in situ polymerization of PANI in the presence of Ni/CF. SEM and XRD show that the CF was wrapped tightly around the nickel layer, and the Ni/CF was coated by PANI. The electrical conductivity of PANI/Ni/CF can reach 1.07 S/cm, which is approximately 4.5 times higher than PANI's 0.19 S/cm and 2 times higher than PANI/CF's 0.36S/cm. According to VSM, the Ms of Ni/CF and PANI/Ni/CF was 13.8 and 2.3 emu/g, respectively. Measurement of microwave absorbing properties analysis, the reflection loss of PANI/Ni/CF can reach −12.4 dB, which is lower than PANI and PANI/CF, and its best match thickness is 2.0 mm. It means the microwave absorbing properties of PANI/Ni/CF are superior to those of PANI and PANI/CF.

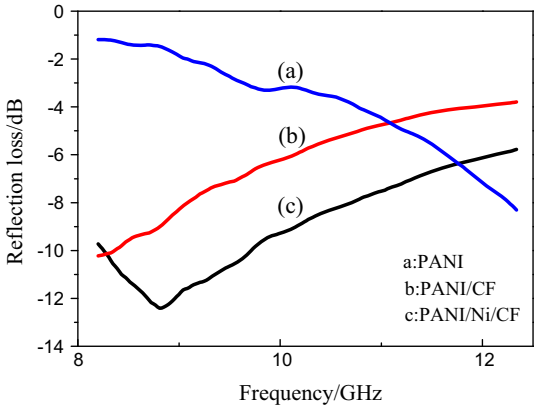

Fig. 7 RL curves of PANI (*a*), PANI/CF (*b*) and PANI/Ni/CF (*c*)

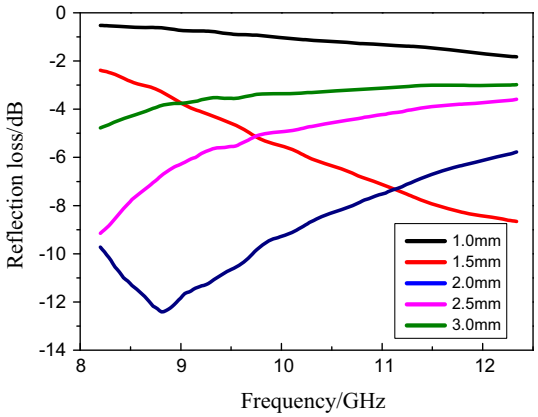

Fig. 8 RL curves of PANI/Ni/CF at different thicknesses

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