Skin collagen fiber-based radar absorbing materials

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By using skin collagen fiber (CF) as raw material, Schiff base structure containing CF (Sa-CF) was synthesized through CF-salicylaldehyde reaction. Then a novel radar absorbing material (Fe-Sa-CF) was prepared by chelating reaction between Sa-CF and Fe³⁺. The coaxial transmission and reflection method was used to analyze the complex permittivity and complex magnetic permeability of these CF-based materials, and the radar cross section (RCS) method was used to investigate their radar absorbing properties in the frequency range of 1.0–18.0 GHz. Experimental results indicated that the conductivity of CF increased from initial 1.08×10⁻¹ⁱ to 2.86×10⁻⁶ S/cm after being transferred into Fe-Sa-CF, and its dielectric loss tangent (tan δ) in the frequency range of 1.0–17.0 GHz also increased. These facts suggest that the Fe-Sa-CF is electric-loss type radar absorbing material. In the frequency range of 3.0–18.0 GHz, Sa-CF (1.0 mm in thickness) exhibited somewhat radar absorbing property with maximum radar reflection loss (RL) of −4.73 dB. As for Fe-Sa-CF, the absorbing bandwidth was broadened, and the absorbing intensity significantly increased in the frequency range of 1.0–18.0 GHz where a maximum radar RL of −9.23 dB was observed. In addition, the radar absorbing intensity of Fe-Sa-CF can be further improved by increasing membrane thickness. When the thickness reached to 2.0 mm, the RL values of Fe-Sa-CF were −15.0−−18.0 dB in the frequency range of 7.0–18.0 GHz. Consequently, a kind of novel radar absorbing material can be prepared by chemical modification of collagen fiber, which is characterized by thin thickness, low density, broad absorption bandwidth and high absorption intensity.

skin collagen fiber, chemical modification, radar absorbing material, reflection loss (RL)

Radar absorbing materials have been widely applied in many fields [1–6]. In general, radar absorbing materials are divided into two categories, namely, inorganic and organic absorbing materials. Inorganic radar absorbing materials include iron-based absorbing materials (such as polycrystalline iron fibers and carbonyl iron), carbon-based absorbing materials (such as graphite and carbon fiber) and ceramic-based absorbing materials (such as silicon carbide) [7–9]. Organic radar absorbing materials are often derived from conductive polymers such as polypyrrole, polyaniline, macromolecule Schiff bases and macromolecule Schiff base salts [10].

Recently, the research of conductive polymer-based radar absorbing materials is developing fast because conductive polymers have the advantages of light weight, good softness, easy molding, and their conductivity and absorbing property can be adjusted by doping with metal ions [11,12]. Among those conductive polymers, macromolecule Schiff bases and Schiff base salts are one of the most important categories. It is reported that the retinyl Schiff base salt developed by Wang et al. [13] exhibited a high radar reflectivity loss (−10.0 dB), while its density was only 1.1 g/cm³.

Macromolecule Schiff bases belong to structural radar absorbing materials, which are prepared by the reaction of aldehyde and methylamine under basic conditions [14,15]. Schiff base salts are complexes synthesized by chelating reaction of Schiff bases with some metal ions such as Fe³⁺, Al³⁺, Ag⁺ and Cu²⁺ [16]. Compared with Schiff bases, the conductivity of Schiff base salts is improved, and their ab-
Skin collagen fiber (CF), a kind of structural protein, mainly comes from the skin of domestic animals, and is one of the most abundant renewable biomass resources in the world. CF is mainly used as raw material in leather making. Collagen molecule is triple-helical structure composed of three polypeptide chains. Each helical peptide has approximately 1052 amino acids and in the sequence of periodicity of Gly-X-Y [18]. CF contains high density of electron dipole and molecule bound charges in electret state, and can be polarized in electrostatic field [19]. On the other hand, a number of amino groups (-NH₂) located at the side chains of CF are capable of reacting with aldehyde to form amino acid Schiff bases and Schiff base salts [20,21]. As a result, a large number of micro conductive units can be formed in CF by the chemical modification, and therefore, it is possible to prepare radar absorbing materials by using collagen fiber as raw material. In addition, CF contains some content of water (~12.0%, wt%) because intramolecular and intermolecular interactions of collagen molecules are based on the formation of hydrogen bonds through water. After the absorption of radar waves, the temperature of CF and the infrared emission intensity may not significantly increase due to the high specific heat capacity of water. In this study, the novel radar absorbing materials were prepared using collagen fiber as raw material through reacting with salicylaldehyde and then chelating with Fe³⁺, and their radar absorbing properties were investigated.

1 Experiment

1.1 Reagent and instrument
(1) Reagents. Bovine skins were obtained from a local tannery of Sichuan Province. Salicylaldehyde, FeCl₃ and other reagents were of analytic reagents (Kelong Chemical reagent plant in Chengdu).
(2) Instruments. Collagen fiber-based membrane was prepared by ZQJ1-B-II Hand-sheet Former; Fourier Transform Infrared Spectroscopy (Perkin Elmer Spectrum One) was used for the analysis of FTIR of the samples; The membrane thickness was measured using JEB431 Thickness Tester; Electric resistance of the samples was measured by EST121 Digital Ultra-high Resistance/Micro-Current Meter; Electromagnetic parameters of the samples were tested by Agilent-8720ET Vector Network Analyzer; The radar absorbing properties were investigated in anechoic chamber using Radar Cross Section (RCS) method; The tensile strength and tearing strength of the membranes were measured by electronic AI 7000S Digital Display Pull Machine; Bursting strength of the membranes was measured by U-20GT-70B-ADP Bursting Strength Tester.

1.2 Preparation of radar absorbing materials
(1) Preparation of collagen fiber (CF). Collagen fiber was prepared according to the procedures reported in our previous work [22]. In brief, bovine skin was cleaned, limed, split, and delined according to the procedures of leather processing in order to remove non-collagen components. Then the skin was treated with an aqueous solution of acetic acid (concentration 16.0 g/L) three times to remove mineral substances. After the pH of the skin was adjusted to 4.8–5.0 with acetic acid-sodium acetate buffer solution, the skin was dehydrated by absolute ethyl alcohol, dried in a vacuum, ground, and sieved. As a result, the collagen fiber was obtained with the particle size of 0.1–0.25 mm, water content ≤12.0%, ash content ≤0.3%, and pH=5.0–5.5.

(2) Preparation of salicylaldehyde modified CF (Sa-CF). 50.0 g of CF prepared as before was added into a 500 mL three-neck bottle followed by the addition of 200.0 mL of ethanol. The pH of the mixture was adjusted to 8.0 using KOH dissolved in ethanol (10%, w/w) and then stirred at 30.0°C for 2.0 h. Subsequently, 100.0 mL of ethanol containing 0.2 mol salicylaldehyde was added into the above mixture. After stirring reaction at 30.0°C for 8.0 h, yellow Sa-CF was obtained.

(3) Preparation of Fe³⁺ modified Sa-CF (Fe-Sa-CF). 50.0 g of Sa-CF were prepared and 200.0 mL of ethanol were added into a 500 mL three-neck bottle. Then 0.2 mol of FeCl₃ dissolved in 200.0 mL of ethanol was added. After stirring at 30.0°C for 4.0 h, dark brown Fe-Sa-CF was obtained by filtration and drying. The Fe³⁺ concentration in solutions before and after the reaction was analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2100 DV), and the Fe³⁺ content in Fe-Sa-CF was determined to be 18.3% (w/w).

(4) Preparation of Fe³⁺ modified CF (Fe-CF). 50.0 g of CF were prepared and 200.0 mL of ethanol was added into a 500 mL three-neck bottle. Then 0.2 mol of FeCl₃ dissolved in 100.0 mL of ethanol was added. After stirring at 30.0°C for 4.0 h, brown Fe-CF was obtained by filtration and drying. The Fe³⁺ concentration in solutions before and after the reaction was analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2100 DV), and the Fe³⁺ content in Fe-CF was determined to be 16.5% (w/w).

(5) FTIR analysis of CF, Fe-CF, Sa-CF and Fe-Sa-CF. The FTIR analysis of CF, Fe-CF, Sa-CF and Fe-Sa-CF was carried out in KBr pellet.

1.3 Preparation of testing membranes
Testing membranes were prepared according to the laboratory papermaking method [23]. To obtain membranes with different thickness, a proper amount of CF, Fe-CF, Sa-CF or Fe-Sa-CF was molded in ZQJ1-B-II Hand-sheet Former, respectively. Subsequently, the obtained membranes were pressed under 4.0 MPa for 5.0 min, followed by the vacuum dry at 0.08 MPa and 65°C for 20 min.
1.4 Analysis and test

(1) Measurement of conductivity. Testing membranes with the thickness of 1.0 mm were prepared as Section 1.3, and then cut into 20.0 mm×10.0 mm small pieces. The conductivity of the samples was measured using EST121 Digital Ultra-high Resistance/Micro-Current Meter.

(2) Measurement of electromagnetic parameters. By using a plate flow machine, CF, Fe-CF, Sa-CF and Fe-Sa-CF were molded to 5.0 mm tube-like samples, which have an external diameter of 7.0 mm and internal diameter of 3.0 mm. Based on the coaxial transmission and reflection method, the complex permittivity and complex magnetic permeability of the samples in the range of 0.5–18.0 GHz were analyzed using Agilent-8720ET Vector Network Analyzer.

(3) Measurement of radar absorbing properties. According to the method in Section 1.3, 200.0 mm×200.0 mm testing samples with different thickness were prepared. The reflection loss of the samples in the frequency range of 1.0–18.0 GHz was measured in anechoic chamber using far-field RCS measurement.

(4) Measurement of density and mechanical strength of membrane. The mechanical strength of the membranes was measured according to the literature [24]. Samples with different size and shape were placed into a constant temperature and humidity chamber at (20±2)°C for 24 h where the relative humidity is 65%±1%. Then, the tensile strength, tearing strength and bursting strength of the samples were measured. The bulk density of the samples was calculated according to the mass and area of membranes.

2 Results and discussion

2.1 Properties of CF-based radar absorbing membranes

In practical application, radar absorbing materials are often prepared as membranes to be utilized. Therefore, it is important to investigate the properties of CF-based radar absorbing membranes. The scanning electron microscope (SEM) observation of the samples indicated that Fe-CF, Sa-CF and Fe-Sa-CF, which are obtained from the chemical modification of collagen fibers (CF), are still in fiber state (shown in Figure 1), which favors CF-base radar absorbing materials to weave each other, forming membranes with large area. According to the method in section 1.3, CF-based radar absorbing materials obtained by different chemical modifications were shaped into 200.0 mm×200.0 mm membranes with the thickness of 1.0 mm, and their physical properties were shown in Table 1. It can be seen that the CF, Fe-CF, Sa-CF and Fe-Sa-CF membranes exhibit mechanical strength in some extent, but needs to be further improved. In practical application, the mechanical strength of CF-based radar absorbing membrane can be significantly improved by complexing with polymer or substrate cloth [25–27]. In addition, CF-based radar absorbing materials have the advantages of light mass and low density. The density of CF-based radar absorbing materials is less than 0.8 g cm$^{-3}$, which is far below than those of inorganic radar absorbing materials (such as ferrite, its density is about 5 g cm$^{-3}$), and also lower than that of common Schiff base-type radar absorbing materials (1.1 g cm$^{-3}$) [13,14,17,28].

Figure 1  SEM images of CF (a), Fe-CF (b), Sa-CF (c) and Fe-Sa-CF (d).
2.2 Conductivity of CF-based radar absorbing materials

Table 2 is the conductivity of CF-based radar absorbing materials. It was observed that CF has the lowest conductivity (1.08×10^{-11} S/cm), while those of Fe-CF and Sa-CF are much higher. Notably, the conductivity of Fe-Sa-CF reaches 2.86×10^{-6} S/cm. For raw CF, the mobility of high density electron dipoles and molecules bound charges is limited, which leads to difficult transfer of charges in CF, resulting in poor conductivity of CF. After reacting with salicylaldehyde, the Schiff bases are formed in Sa-CF, in which the conjugated double bonds (–C=N–) favor the mobility of charges, and thus the conductivity of Sa-CF obviously increased [29]. As for Fe-CF, the increased conductivity is due to the fact that Fe^{3+} is able to chelate with –COOH and –NH_{2} of CF, which increases the amount of mobile charges in CF, and thus increasing the conductivity [30]. In the case of Fe-Sa-CF, Fe^{3+} ions react with Schiff bases to form salts, which promote the formation of a large number of micro conductive units, and the corresponding conductivity also significantly increased due to the interaction between –C=N– and Fe^{3+}. Therefore, Fe-Sa-CF has much higher conductivity as compared with Fe-CF and Sa-CF.

2.3 Electromagnetic parameters of CF-based radar absorbing materials

The real and imaginary parts of permittivity (\varepsilon_\prime and \varepsilon_\prime\prime) of CF, Fe-CF, Sa-CF and Fe-Sa-CF are shown in Figure 2(a) and (b), respectively. Figure 2(c) is the dielectric loss tangent (defined as \tan\delta=\varepsilon_\prime\prime/\varepsilon_\prime). It can be observed that the dielectric loss tangents of CF, Fe-CF, Sa-CF and Fe-Sa-CF are all in the order of magnitude of 10^{-1}, suggesting that they are dielectric materials [30]. Furthermore, their dielectric loss tangent in the range of 1.0–17.0 GHz follows the sequence of Fe-Sa-CF>Sa-CF>Fe-CF>CF, implying that salicylaldehyde modified CF can increase its dielectric loss ability by chelating with Fe^{3+}. In the frequency range of 1.0–15.0 GHz, the real and imaginary part of permittivity of CF-based radar absorbing materials change with the change of frequency, and the corresponding dielectric loss tangent increases with the increase of frequency (frequency response), which suggest that these materials may be used as microwaves absorbing materials with broad bandwidth [31–33].

The real and imaginary parts of (\mu_\prime and \mu_\prime\prime) complex magnetic permeability of CF, Fe-CF, Sa-CF and Fe-Sa-CF are shown in Figure 3(a) and (b), respectively. The real and imaginary parts of complex magnetic permeability also change with the change of frequency. The changing scope of real part is near to “1” while that of imaginary part is near to “0”. According to normalization method, the complex magnetic permeability of CF-based radar absorbing materials can be expressed as \mu_r=1–\omega. The value of imaginary part is 0, which suggests that CF, Fe-CF, Sa-CF and Fe-Sa-CF have no magnetic loss ability [34].

In general, the microwave absorbing mechanism includes electric-loss type (including dielectric loss and resistance loss) and magnetic-loss type. The investigations to the con-

Table 1 Density and mechanical strength of CF, Fe-CF, Sa-CF and Fe-Sa-CF membranes (Thickness 1.0 mm)

| Material  | Areal density (g/m²) | Density (g/cm³) | Tensile strength (N/mm²) | Tearing strength (N/mm) | Bursting strength (kPa) |
|-----------|---------------------|----------------|------------------------|------------------------|------------------------|
| CF        | 407                 | 0.407          | 1.61                   | 2.00                   | 105.8                  |
| Fe-CF     | 703                 | 0.703          | 1.85                   | 2.27                   | 138.6                  |
| Sa-CF     | 626                 | 0.626          | 1.83                   | 2.24                   | 141.2                  |
| Fe-Sa-CF  | 735                 | 0.735          | 1.88                   | 2.29                   | 145.3                  |

Table 2 Conductivity of CF-based radar absorbing materials

| Material  | Conductivity (S/cm) |
|-----------|---------------------|
| CF        | 1.08×10^{-11}       |
| Fe-CF     | 8.43×10^{-8}        |
| Sa-CF     | 2.52×10^{-8}        |
| Fe-Sa-CF  | 2.86×10^{-6}        |
ductivity and electromagnetic parameters of CF-based radar absorbing materials suggest that they should belong to electric-loss type. On the one hand, CF-based radar absorbing materials are polarized by the radar waves, and then the molecular electric dipole inside the materials are striving to match the changing electromagnetic vibration, which results in molecule friction, further leading to dielectric loss. On the other hand, due to their conductivity in some extent, the induced electric current can be formed within radar absorbing materials and heat is generated. As a result, a part of electromagnetic wave energy was consumed, resulting in the absorption to radar waves [34].

2.4 The absorbing properties of CF-based radar absorbing materials

Figure 4 is the radar reflection loss (RL) of CF and Sa-CF. It can be seen that CF only has weak absorption to radar wave in the frequency range of 9.0–11.0 GHz. For Sa-CF, obvious radar RL can be observed in the frequency range of 3.0–18.0 GHz, and the maximum RL value reaches –4.37 dB at 7.0 GHz.

In general, organic radar absorbing materials belong to conductive polymers [35], and often contain conjugated \( \pi \)-electron systems such as \(-C=\text{N}-) groups in macromolecule Schiff base, which provides electrons the possibility of delocalization. In CF, there are no chemical components or units that can generate conduct electricity, and therefore, CF has low conductivity (1.08×10\(^{-11}\) S/cm) and presents no radar absorbing ability. When the -NH\(_2\) groups of CF reacted with salicylaldehyde, the Schiff base structure was formed, which increases the conductivity of CF and thus the electric loss-type microwaves absorbing ability was obtained. Therefore, the microwaves absorbing ability of CF significantly increased after reacted with salicylaldehyde. Figure 5 is FTIR spectra of CF, Sa-CF, Fe-Sa-CF and Fe-CF. According to the literature [13], the characteristic peak of Schiff base is 1690–1590 cm\(^{-1}\), which is close to that of amide I-band of CF (1650 cm\(^{-1}\)). Consequently, the FTIR spectrum of CF has only one peak at 1640 cm\(^{-1}\), which exhibited somewhat red shift as compared with the peak of amide I-band of CF. This observation suggested that CF has been reacted with salicylaldehyde, resulting in the formation of Schiff base structure. In addition, the stretching vibration peak of N-H of CF-Fe at 3380 cm\(^{-1}\) is shrunk in comparison to that of CF, which suggested the chelating interaction of Fe\(^{3+}\) with the -NH\(_2\) group of CF.

Figure 6 presents the radar RL of Fe-CF, Sa-CF and Fe-Sa-CF. Although Fe-CF and Sa-CF have radar absorbing ability in the frequency range of 3.0–18.0 GHz as compared with CF, their absorption intensity is limited and the
maximum RL is only $-4.31\, \text{dB}$. As for Fe-Sa-CF, it exhibits much higher radar absorption intensity in the frequency range of $1.0$–$18.0\, \text{GHz}$, and the maximum radar RL is as high as $-9.23\, \text{dB}$. These experimental results suggest that the introduction of Fe$^{3+}$ significantly improved the radar absorbing ability of Sa-CF. Possibly, Fe$^{3+}$ ions reacted with Schiff bases in CF to form a large number of high conductive Schiff base salts, which leads to a broad absorption bandwidth and much more intensive absorption.

Some investigations suggest that the thickness of radar absorbing materials greatly affects their absorbing ability [8]. Figure 6 illustrates the RL values of Fe-Sa-CF with different thickness (0.5 mm, 1.0 mm and 2.0 mm). It is obvious that the RL of Sa-CF-Fe increases with the increase of thickness. When the thickness of Sa-CF-Fe is 2.0 mm, the RL is higher than $-15.0\, \text{dB}$ in the frequency range of $11.0$–$18.0\, \text{GHz}$, which is hardly obtained from commonly magnetic radar absorbing materials. The absorbing ability of CF-based materials to radar has close relationship with membrane thickness. Consequently, the absorption bandwidth and absorption intensity can be controlled by varying the thickness [36]. The particular advantage of CF-based radar absorbing materials is the fact that their mass is only $1/10–1/5$ as compared with those inorganic wave absorbing materials at same thickness.

3 Conclusions

Skin collagen fiber can be used for the preparation of novel radar absorbing materials through the reaction with salicylaldehyde (formation of Schiff bases), followed by the chelating with Fe$^{3+}$ (formation of Schiff base salts). The radar absorption ability of these CF-based material increases as the increase of thickness. CF-based radar absorbing materials have high conductivity and dielectric loss tangent, and therefore, their adsorption mechanism to radar should belong to electric loss-type. CF-based radar absorbing materials exhibit a broad absorption bandwidth and intensive absorption to radar waves. These novel radar absorbing materials have the advantages of low-cost, low density, light mass and easy formation of membranes with a large area. Therefore, the potential applications of CF-based radar absorbing materials can be expected.

Figure 6 Comparison of radar reflection loss (RL) of Fe-CF, Sa-CF and Fe-Sa-CF (Thickness 1.0 mm).

Figure 7 Effect of thickness of Fe-Sa-CF on radar reflection loss.
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