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Magnetic and electromagnetic properties of ferrocenyl organic metal magnetic resin

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A B S T R A C T

To provide a new way to fabricate novel wave-adsorbing material, ferrocenyl organic metal magnetic resin (FOMR) was successfully prepared from ferrocenyl bisphthalonitrile via an effective and mild solvent-thermal route. The structure analysis of as-synthesized FOMR was performed using Fourier transform infrared spectrophotometer and ultraviolet–visible absorption spectrum. Magnetic behavior of the sample were also studied by vibrating sample magnetometer and the experimental results indicated that the magnetic material were ferromagnetic with maximum saturation magnetization of 1.3 emu g^{-1} at 300 K. Measurements of electromagnetic parameters of FOMR show that the maximum absorbing peak has a bandwidth of 7.0 GHz (RL<4 dB). The specific gravity of FOMR was about 0.86. On the basis of these results, the novel magnetic materials are believed to have potential applications in the microwave absorbing area and in biomedical field.

1. Introduction

In recent years, the increase in electromagnetic pollution due to the rapid development of gigahertz (GHz) electronic systems and telecommunication has resulted in a growing and intense interest in electromagnetic-absorber technology [1–5]. However, density of the conventional absorptive materials such as inorganic metal powder and ferrites is too high, which restricts their use in application requiring lightweight. Meanwhile, the quest for organic metal complex has generated increasing interest, both from a fundamental point of view and in terms of their excellent performances, especially for their advantages of low density, good magnetism, optical properties, electronical properties and easy preparation using chemical methods etc. [6–15]. Among these complexes, the study on ferrocenyl polymers as wave absorbing materials displayed emergent novelty. The experimental results demonstrated that ferrocenyl magnetic polymer had low density and stable electromagnetic properties in a wide temperature range [16]. Recently, our lab has done a lot of work on ferrocenyl magnetic material and organic–inorganic hybrid materials, which showed stable magnetism and special electromagnetic properties [17–18].

Herein, we report a simple and reproducible approach of preparing novel ferrocenyl organic metal magnetic resin (FOMR) by solution method at relatively low temperature. The FOMR possessed steady magnetism with the saturation magnetization (M_s) of 1.3 emu g^{-1} at 300 K. The as-prepared magnetic material, which was believed to have potential applications in the microwave absorbing area, had lightweight, good electromagnetic and wave absorption properties in a comparatively wide frequency range.

2. Experimental

All the chemicals were analytical grade. Ferrocenyl bisphthalonitrile was prepared according to the reported procedure using 4-aminophenoxylphthalonitrile, 4, 4-dihydroxybiphenyl and ferrocenecarboxaldehyde via condensation reaction [19].

Ferrocenyl organic metal magnetic resin (FOMR) was obtained though following steps: A 500 ml three necked round bottom flask equipped with a mechanical stirrer and refluxing, ferrocenyl bisphthalonitrile was taken in and then toluene and DMF were added. The reaction solution was refluxed at 110 °C for 7 h. Then the product was poured into de-ionized water, washed several times with ethanol and dried at 60 °C under vacuum.

The prepared product was characterized by Fourier transform infrared spectrophotometer (FTIR) (Shimadzu, 8000S) by a KBr pallet and ultraviolet–visible (UV–vis) absorption spectrum (Puxi TU1800). The molecular weights determination of FOMR was studied by gel permeation chromatography (GPC) (Waters 1515/2414). The magnetic properties of FOMR were studied by a vibrating sample magnetometer (VSM) (Riken Denshi, BHV-525). The electromagnetic parameters of the sample were measured on a vector net-work analyzer (Agilent 8720ET) at 1.0–18 GHz, in which the FOMR was mixed with paraffin in a mass ratio of 3:1 and compressed to standard ring shapes (outer diameter: 7 mm, inner diameter: 3 mm, thickness: 5 mm).

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3. Results and discussion

The FTIR spectroscopy of FOMR is shown in Fig. 1A. From Fig. 1A, it is concluded that the typical band at 2229 cm^{-1} can be ascribed to the cyano groups. The appearance of ferrocene (ferrous iron) at 484 cm^{-1} can be observed. The band at 1247 cm^{-1} is assigned to the C–O–C antisymmertic (in oxazine ring), while the band at 1032 cm^{-1} is assigned to the C–O–C symmetric stretch (in oxazine ring). Compared with ferrocenyl bisphthalonitrile, the intensity of these two bands becomes weaker due to the ring-opening reaction of oxazine ring [19]. Furthermore, a new peak at 576 cm^{-1} is due to the characteristic vibration of ferrocene (ferric iron) [20]. The FTIR results indicate that part of Fe^{2+} in ferrocene have been oxidized into Fe^{3+} ions.

In order to have a better understanding of the charge transport mechanisms of FOMR, we also carried out UV–vis absorption spectrum. Fig. 1B (a) shows the absorption spectra of FOMR solution. A relatively strong peak (c) about 420–460 nm can be assigned to the absorption band of ferrocene [21]. Compared with ferrocenyl bisphthalonitrile (shown in Fig. 1B), a new weak absorption peak is in UV range (shown in the inset of Fig. 1B) may be attributed to C (242 nm, d-π*) band. The broad absorption peak at about 330 nm is a derivative of two nearby absorption peaks of ferrocenyl bisphthalonitrile, which is assigned to B band (π–π* transitions of FOMR) [22]. These results show that there are abundant charge transfers in this novel system.

Fig. 2 shows the magnetic hysteresis loops of the as-received magnetic material below the magnetic field of 5 KOe at 300 K. The coercivity (H_c, Oe) is the external applied magnetic field necessary to return the material to a zero magnetization condition and the remnant magnetization (M_r) is the residual magnetization after the applied field is reduced to zero. Both values of FOMR can be read from the magnetic loops of FOMR in Fig. 2. The coercivity and remnant magnetization of FOMR are 87.8 Oe, 0.37 emu g^{-1}, respectively. Saturation magnetization (M_s) of FOMR is 1.3 emu g^{-1}. A large amount of research has been done on organic magnetic materials for a long time. Scientists have successfully prepared organic magnetic materials, such as free radical organic conjugated magnetic material and magnetic polymer containing iron [23–24]. However, these materials could be magnetic only at extremely low temperature, which is usually lower than 273 K and restricts the practical application of organic magnetic materials. By contrast, FOMR shows stable and good magnetism at room temperature. The magnetism of FOMR maybe arise from charge transfer and the mixed-valence of ferrous iron and ferric iron of ferrocene [24], which is supported by the results of FTIR and UV–vis spectrum.

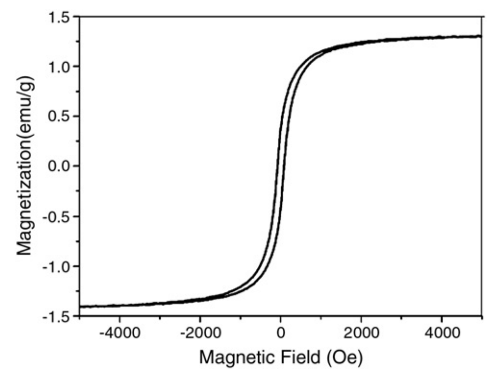

Fig. 2. Magnetic loops of FOMR.

The special sandwich structure of ferrocene might endow FOMR with particular electromagnetic properties. It is known that dielectric constant and permeability are the intrinsic parameters of electromagnetic property for wave-absorbing material. Both dielectric constant and permeability are expressed as plural under alternating magnetic field. Fig. 3 shows the electromagnetic properties of FOMR/wax in the range of 1.0–18 GHz. The imaginary part (ε'') of complex permittivity increases slightly from 0.05 to 0.20 over the 1.0–18 GHz frequency range (Fig. 3(a)). Besides, the real part (ε') remains steady within this frequency range. Moreover, it can be seen from Fig. 3(b) that the value of dielectric loss increases from 0.01 to 0.08 with the increase of frequency. Fig. 3(c) illustrates the frequency dependence of the complex permeability ($\mu = \mu' - j\mu''$) for FOMR. It can be seen that both the real part of permeability (μ') and the imaginary part of permeability (μ'') remain stable in the range of 1.0–18 GHz. As shown in Fig. 3(d), the value of magnetic loss fluctuates around 0.03 before 6 GHz and slightly increases afterwards.

According to the transmission line theory, the reflection loss (RL) is a function of the normalized input impedance Z_{in} at the surface of a single layer terminated by a metal, which is described as

$$RL = 20\log|(Z_{in} - 1)/(Z_{in} + 1)| \quad (1)$$

And the normalized input impedance Z_{in} is given by

$$Z_{in} = \sqrt{u/\varepsilon}\tanh\left[j(2\pi fd/c)\sqrt{u\varepsilon}\right] \quad (2)$$

By using the actual values of complex permittivity and permeability as shown in Fig. 3(a) and 3(c), the RL of FOMR was calculated. Fig. 4 shows that the maximum absorbing peak of FOMR obtained is 6.6 dB

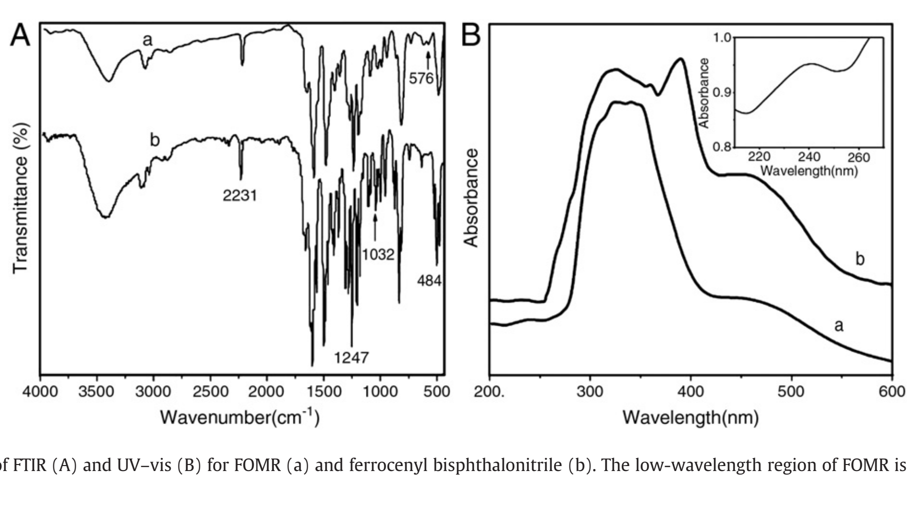

Fig. 1. Spectrums of FTIR (A) and UV–vis (B) for FOMR (a) and ferrocenyl bisphthalonitrile (b). The low-wavelength region of FOMR is shown in the inset.