Research progress and practical application of magnetic composite absorbing materials

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Abstract. The update and iteration of communication technology, the continuous emergence of new electronic devices, smart home appliances and new energy vehicles, and the widespread use of military electromagnetic technology have caused serious electromagnetic radiation problems. Nanomagnetic materials have special electromagnetic properties and become the continuous research object of absorbing materials, especially in the development of low-frequency absorbing materials. This paper reviews the theoretical basis and research status of nanomagnetic materials in low-frequency absorbing materials and composite absorbing materials that are "thin, light, wide, and strong". In addition, the basic research is aimed at realizing the final application, and this paper also summarizes the application status of the absorbing agent in practical application.

Keywords: magnetic materials, Low frequency, Absorbing composite materials.

1. Introduction

Nanomagnetic materials possess physicochemical properties that are not found in conventional long-range ordered magnetic materials and have become the main direction for the current development of magnetic materials. Table 1 summarizes the magnetic properties of the magnetic nanomaterials. From the application point of view, magnetic materials are divided into soft magnetic materials, hard magnetic materials and functional magnetic materials as shown in Fig.1.

Nanomagnetic materials have been widely studied in the field of wave absorption due to their unique electromagnetic properties and rich compositions. Microwave absorption materials (MAMs) do not have the problem of secondary pollution and can fundamentally consume electromagnetic wave energy, which has become a research hotspot in the field of wave absorption in recent years. With the continuous development of 3G and 4G communications (1.8~2.7 GHz), household appliances (0~3.5 GHz) and radar decimeter waves, the problem of electromagnetic radiation pollution in low-frequency regions is becoming more and more serious. Magnetic materials have become the main components of low-frequency absorbing materials due to their high magnetic permeability and high saturation magnetization. In addition, to achieve microwave response behavior in the high frequency region, broadband absorption in the entire band, thin matching thickness and low load, it is necessary to develop an electromagnetic composite absorbing material that integrates component regulation and structural design.

This paper reviews the design principles and research status of low-frequency absorbing materials, the theoretical basis and research status of high-performance electromagnetic composite absorbing materials, and the application forms of absorbing agents in practical applications. It is believed that the magnetic electromagnetic composite absorbing material still has important economic value and research significance in the development of absorbing materials in the future.

Table 1. Magnetic properties of magnetic nanomaterials.

Type	Features
Small size effect	Disorder transition, maximum coercivity value.
Quantum size effect	In the environment of a lower magnetic field or lower temperature, the magnetic susceptibility is no longer constant and changes with temperature.
Surface effect	Greater specific surface area, surface anisotropy.
The macroscopic quantum tunneling effect	Magnetization of magnetic particles, the magnetic flux in quantum coherent devices

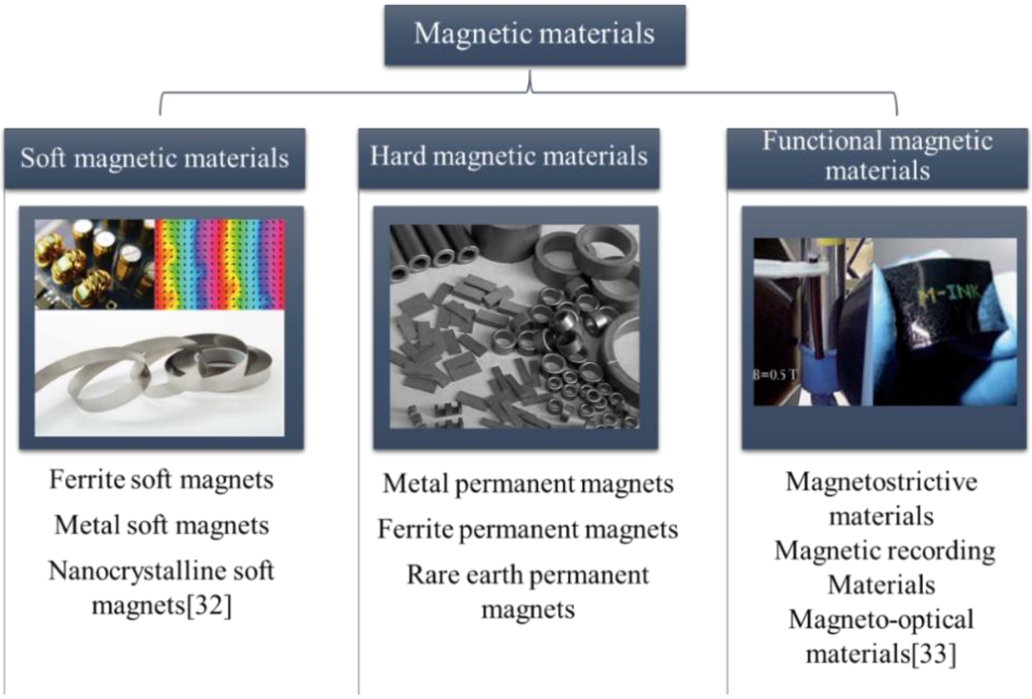


Fig.1 Classification of magnetic materials.

2. Magnetic-based low-frequency MAMs

At present, with the development of communication technology, the low-frequency microwave communication frequency band is more crowded, and the electromagnetic wave of small electronic devices is usually lower than 4 GHz, which makes low-frequency electromagnetic compatibility and electromagnetic pollution an urgent problem. This section outlines the design theory of low-frequency absorbing materials, and summarizes the current research status of low-frequency absorbing materials.

2.1. Theoretical basis

In the case of not triggering the impedance mismatch, the greater the dielectric and permeability of the material, the better the attenuation of electromagnetic waves can be obtained, from Equation 1 and Equation 2. At low frequencies, magnetic materials have higher permeability [1] than dielectric materials. Therefore, low-frequency absorbing materials generally use magnetic metal materials with high permeability, good impedance matching, and strong magnetic loss capability.

$$\tan\delta_u = \frac{\mu''}{\mu'} \tag{1}$$

$$\tan\delta_\varepsilon = \frac{\varepsilon''}{\varepsilon'} \tag{2}$$

Where $\tan\delta_\varepsilon$ is the tangent value of dielectric loss， $\tan\delta_\mu$ is the tangent value of magnetic loss.

Table 2. Magnetic Loss Mechanisms of Absorbers[2].

Type	Features
Hysteresis loss	The rotation of the magnetic domain lags the rotation of the external magnetic field.
Domain Wall Resonance	The vibration frequency of the domain wall is consistent with the alternating frequency of the applied magnetic field.
Eddy current loss	During the magnetization process, eddy currents are induced inside the material, resulting in losses.
Natural resonance	The vibration frequency of the easy magnetization axis of the internal magnetic field of the crystal is the same as the alternating frequency of the external magnetic field.

Shape anisotropy is of great significance for the magnetic properties of materials. Equation (3) describes the relationship between the initial permeability of the isotropic spherical absorber and the magnetic resonance frequency. Equation (4) describes the correlation between the initial permeability of the flake particles or ferromagnetic thin films and the magnetic resonance frequency. From this, using a material with high saturation magnetization helps to obtain high permeability. Equation (5) is a formula describing the limit value of the bandwidth to thickness ratio. It shows that the low-frequency absorbing material with high magnetic permeability can obtain wider effective absorbing width with thinner thickness. Besides, the snoek formula states that there is an inverse relationship between materials μ_i and f_r. Compared with spherical absorbents, flake particles or ferromagnetic films are easier to obtain greater magnetic permeability under the same resonance frequency, breaking the Snoek limit of the magnetic properties of isotropic absorbing materials. In summary, the composition and shape anisotropy of magnetic absorbents have positive significance in improving the magnetic permeability and regulating the magnetic resonance frequency, and are the key to obtaining high magnetic permeability and high magnetic loss.

$$(\mu_i - 1)f_r = \frac{1}{3\pi}\gamma M_s \tag{3}$$

$$(\mu_i - 1){f_r}^2 = \left(\frac{1}{2\pi}\gamma M_s\right)^2 \tag{4}$$

$$|lnp_o|(\lambda_{max} - \lambda_{min}) < 2\pi^2\mu_s d \tag{5}$$

where μ_i is the initial permeability, f_r is the resonance frequency, γ is the gyromagnetic ratio, and M_s is the saturation magnetization, P is the target reflection value, μ_s is the initial permeability.

2.2. Research progress

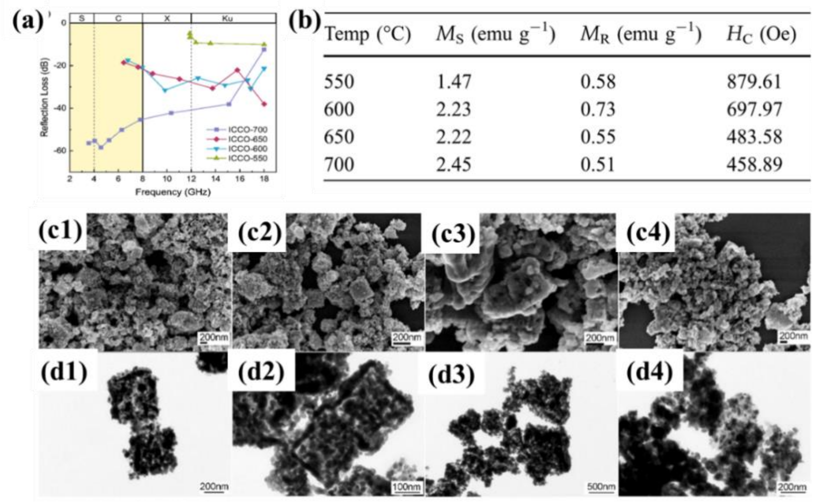
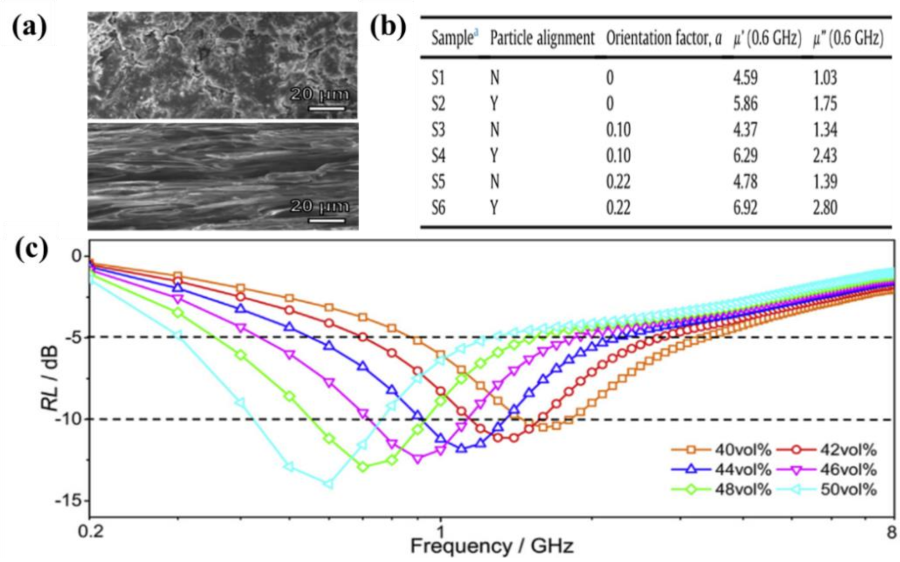


Fig.2 (a) RLmax values of different samples. (b) Magnetic properties of the Fe/C@Co_3O_4 nanocomposites with different heat treatment temperatures. (c1-c4) and (d1-d4) SEM and TEM images of Fe/C@Co_3O_4 nanoparticles: ICCO-550, ICCO-600, ICCO-650 and ICCO-700[31].

The saturation magnetization (Ms) is an intrinsic parameter of the material. As mentioned earlier, high Ms is good for permeability and thus for microwave absorption. Compared with other materials, magnetic metals and metal alloys have higher Ms, and thus become important and commonly used electromagnetic wave absorbing materials at low frequencies. In addition to selecting materials with high Ms, improving the shape anisotropy of the absorber, reducing the Hk of the absorber, reducing the grain size, and controlling the grain orientation are also effective strategies to improve the low-frequency magnetic permeability.

Guan et al. [1] developed a new method for inducing grain orientation to prepare flaky carbonyl iron particles (CIPs) with (200) crystal planes and easy axes. The textured structure reduces the in-plane magnetic anisotropy field of the sheet-like CIP. In addition, the textured structure produces additional magnetic resonance at low frequencies, greatly increasing the material's own magnetic permeability. The sample exhibits strong absorption (RL < -10 dB) in the range of 0.4 to 2 GHz with a thickness of only 1 mm. Deng et al. [2] realized FeSiAl@ZnO@Al_2O_3 (FZA) hybrid structure with atomic-level precision by atomic layer deposition technique. FZA achieved a minimum reflection loss value of -50.6 dB at 3.4 GHz with a matching thickness of 3.72 mm. Iang et al. [3] synthesized Fe/C@Co_3O_4 nanocomposites with different structures of metal-organic frameworks (MOFs) by controlling the calcination temperature. The minimum reflection loss value of the nanocomposite heat-treated at 700°C (ICCO-700) reaches -58.5 dB at 4.57 GHz when the absorber layer thickness is 2.5 mm. Yao et al. [4] synthesized nanocrystalline Ni-Zn ferrites ($Ni_{0.5}Zn_{0.5}Nd_xFe_{2-x}O_4$) with different neodymium contents by sol-gel combined with self-propagating combustion method. The results show that adjusting the content of Nd has a significant effect on improving the microwave absorption capacity of the material, especially at low frequencies.

Ferrite materials are also considered potential candidates for excellent MAs at low frequencies because of their high saturation Ms, low coercivity (Hc), and good dielectric properties. Table 3 summarizes the low-frequency microwave absorption properties of typical ferrite composites. Large matching thicknesses and narrow effective absorption bandwidth are the current improvement directions for low-frequency ferrite absorbing materials.



Sample[a]	Particle alignment	Orientation factor, α	μ' (0.6 GHz)	μ'' (0.6 GHz)
S1	N	0	4.59	1.03
S2	Y	0	5.86	1.75
S3	N	0.10	4.37	1.34
S4	Y	0.10	6.29	2.43
S5	N	0.22	4.78	1.39
S6	Y	0.22	6.92	2.80

Fig.3 (a) Top view and cross-section view SEM image of CIPs. (b) The influences of the particle alignment and grain orientation factor of flaky CIPs. (c) Reflection loss (RL) curves [2].

Table 3. Low-frequency microwave absorbing properties of typical ferrite composite.

Material	Absorption peak/GHz	d/mm	RL_{min}/dB	EAB/GHz	Ref.
Fe_3O_4/Fe	1.2	4.5	-42	< 2.0	[5]
$ZnFe_2O_4$@C/MWCNTs	0.81	2.5	-40.65	0.97	[6]
RGO/$ZnFe_2O_4$/Ni	4.21	2.5	-22.57	1.0	[7]
Biochar/nickel ferrite /$FeNi_3$	1.30	6.0	-59.29	1.34	[8]
$Ni_{0.5}Zn_{0.5}Nd_xFe_{2-x}O_4$	4.4	8.5	-20.8	3.2	[9]
C/$CoLa_xFe_{2-x}O_4$	4.96	3.83	-49.56	< 2.0	[10]
flower-like Co_3O_4-MWCNT	3.44	~7	-61.4	< 3.0	[11]
dendritic Fe_3O_4	2.2	4	-53	< 2.0	[12]
$NdFe_{1-x}Ni_xO_3$	~5	5	-49	< 2.0	[13]

3. Magnetic-based high-performance MAMs

Magnetic materials mainly rely on magnetic loss to achieve attenuation of electromagnetic waves. However, only using a single loss principle is not conducive to the development of broadband microwave absorption. Furthermore, the Snoek limit also limits the response of most magnetic materials in the high-frequency region. Therefore, in order to meet the needs of the new era, researchers have effectively integrated magnetic loss and dielectric loss to provide a reasonable way to design advanced microwave absorbing materials with excellent comprehensive properties of "thin, light, wide, and strong". This section mainly reviews the research status of magnetic-based broadband absorbing materials from the theoretical basis, material component design and new structure design.

3.1. Theoretical basis

The Reflection Loss (RL) value is a parameter that directly reflects the absorbing ability of the material. The relative impedance matching value (Z) is a parameter for judging the proportion of electromagnetic waves entering the material. The closer the Z value is to 1, the better the impedance matching properties of the material are. Analogous to the concept of effective absorption (RL≤-10 dB), the researchers derived the concept of effective impedance matching region (Equation 3), which is more flexible to compare the impedance matching performance among materials. The attenuation constant (α) characterizes the ability of a material to lose electromagnetic waves entering the system. According to the transmission line theory and the metal backplane model based on the performance test, the reflection loss, Z and α formulas for a single-layer absorbing material with a specified thickness are as follows:

$$\mathrm{RL(dB)} = 20\log\left|\frac{Z_{in}-Z_0}{Z_{in}+Z_0}\right| \tag{6}$$

$$Z = \frac{Z_{in}}{Z_0} = \sqrt{\mu/\varepsilon}\,\tanh\left[j(2\pi fd/c)\sqrt{(\mu\varepsilon)}\right] \tag{7}$$

$$0.52 \le |Z_{in}/Z_0| \le 1.93 \tag{8}$$

$$\alpha = \left(\frac{\sqrt{2}\pi f}{c}\right) \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu'\varepsilon'' + \mu''\varepsilon')^2}} \tag{9}$$

Where $\tan\delta_\varepsilon$ is the dielectric loss tangent value, $\tan\delta_\mu$ is the magnetic loss tangent value, λ_0 is the wavelength of the electromagnetic wave in a vacuum in cm, the complex permittivity and complex permeability are $\varepsilon_r = \varepsilon' - j\varepsilon''$ and （$\mu_r = \mu' - j\mu''$）, respectively, and Z_{in} is the medium The impedance of , Z_0 is the impedance of free space, f is the frequency, and d is the matching thickness.

3.2. Research progress

The microwave absorbing material requires the microwave energy to fully enter the matrix and be effectively dissipated, which requires good impedance matching and strong attenuation ability. A single magnetic material cannot have good impedance matching. Currently, compositional regulation around magnetism mainly relies on dielectric and conductive materials to achieve an effective balance between electrical and magnetic losses. Finally, a bi-component or multi-component magnetic-based composite absorbing material is realized. Table 4 summarizes the magnetic matrix composite absorbing materials with excellent comprehensive properties that have been reported so far.

Table 4. Comprehensive properties of electromagnetic composite absorbing materials.

Material	d(mm)	Load(wt%)	EAB(GHz)	RL_{min}(dB)	Ref.
Ni@Co/C@PPy	2.0	/	5.1	−48.76	[14]
$NiSe_2$-$CoSe_2$@C/$Ti_3C_2T_x$	2.6	40	5.68	−60.46	[15]
Ti_3C_2/Fe_3O_4/PANI	1.9	/	5.2	−40.3	[16]
$ZnFe_2O_4$@carbon@MoS_2/FeS_2	2.23	50	4.98	−52.5	[17]
MOF/Co/Co_3O_4/CNTs/RGO	2	20	5.7	-59.2	[18]
$MgFe_2O_4$/MgO/C	2.7	/	3.9	−56.94	[19]
	1.43	/	4.6	−59.6	[20]
Ni/NiO/C	1.9	25	5.67	-47.72	[21]
Fe/Fe_3O_4/C	1.8	/	5.2	-50.05	[22]

The improvement of microwave absorption performance by enriching the absorber composition is limited. From the relationship between structure and performance, the absorbing properties of materials are also closely related to the structure of the absorber. Recently, researchers have developed a new type of absorbing material that integrates component control and structural design. Structural design mainly builds porous and heterostructures, and derives bayberry-like structures [23], yolk-shell structures [24], one-dimensional nanochains [25], two-dimensional structures [26], and three-dimensional structures [27].

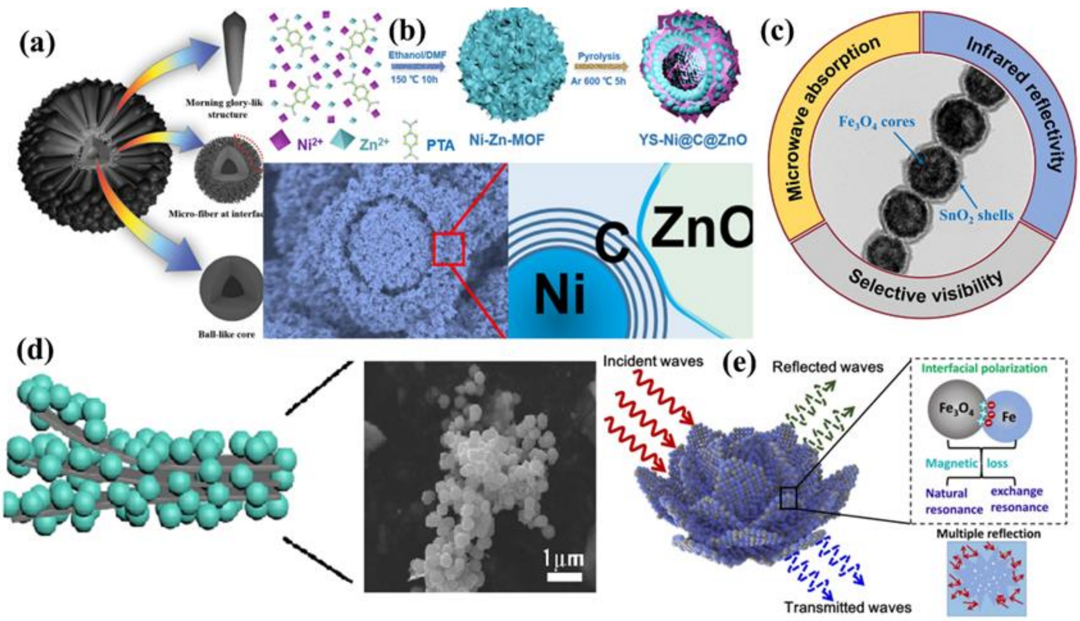


Fig.4 (a) Carbonized waxberry with hierarchical structure [23]. (b) MOF-derived yolk-shell Ni@C@ZnO Schottky contact structure [24]. (c) Core-shell Fe_3O_4@SnO_2 nanochains [25]. (d) Two-dimensional titanium carbide ($Ti_3C_2T_x$) and $NiCo_2O_4$ composites [26]. (e) Three-dimensional flower-like heterogeneous Fe_3O_4/Fe particles [27].

4. Practical application of MAMs

The absorbing material is mainly composed of absorbing agent and polymer matrix. In the laboratory, paraffin is often selected as the matrix to be combined with the absorbing agent for performance testing. However, the actual application scenarios are complex and diverse, and the form of the absorbing agent and the polymer matrix is also more complex. Absorbers and polymer binders are often compounded into various forms such as foam [28], patch [29], coating [30], rubber sheet [31] and absorbing putty.

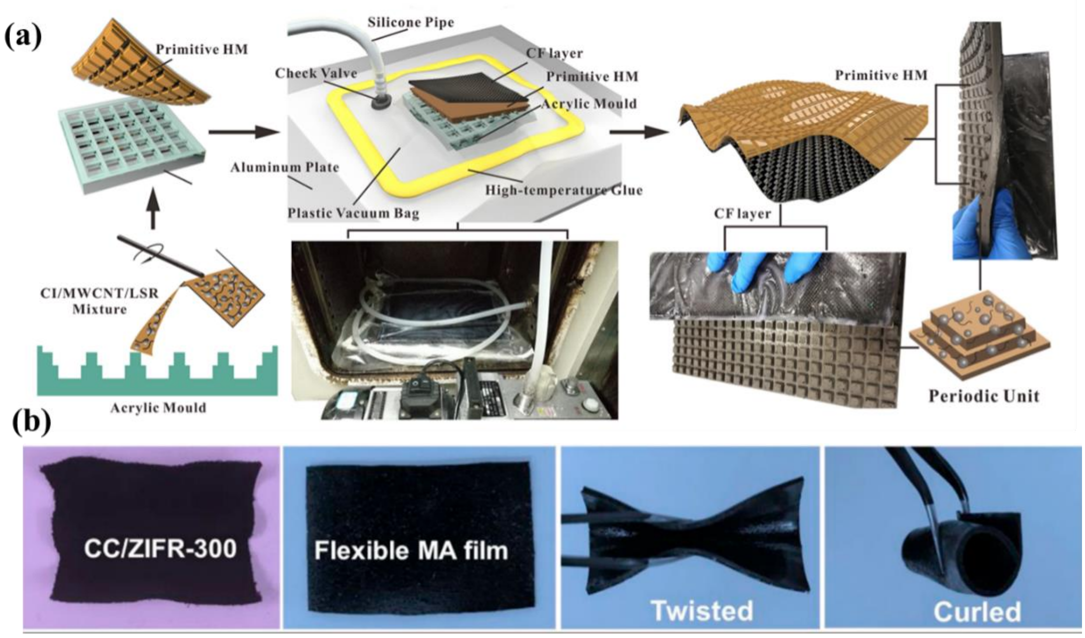


Fig.5 (a) Fabrication process and final product of CF-reinforced HM [28]. (b) The preparation process of flexible MA films using PDMS as substrate and digital physical photos of CC/ZIFR-300 and flexible MA films [29].

5. Summary and prospects

Although the development of magnetic absorbing materials has a long history, it is still an indispensable part in the current absorbing field, especially in the construction of low-frequency absorbing materials. However, the narrow absorption bandwidth and thick matching thickness of low-frequency absorbing materials are still the factors that limit their application. In the future, it is necessary to focus on the functional compounding of different materials, select appropriate process methods and dosages, and at the same time improve the low-frequency absorbing performance of radar waves, give absorbers new property and expand their application scope.

In addition, the high-performance wave absorber itself has excellent wave absorption performance, but it is difficult to achieve effective combination with the organic matrix, achieve good dispersion, and maintain performance stability. The surface modification of the absorbing agent, the optimal combination process of different organisms and the absorbing agent, and the final buildable product state of the absorbing material may all be the development directions proposed for the absorbing material in practical applications in the future.

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