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Complex permittivity and electromagnetic interference shielding properties of Ti_3SiC_2/polyaniline composites

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Abstract Ti_3SiC_2/insulating polyaniline (Ti_3SiC_2/PANI) composites were prepared by solution blending and subsequently by hot-pressing process. The dielectric permittivity and electromagnetic interference (EMI) shielding effectiveness (SE) of the composites were determined in the frequency range of 8.2–12.4 GHz (X-band). Both real and imaginary permittivities increase with the increasing Ti_3SiC_2 content, and which are attributed to the enhanced displacement current and conduction current. The EMI SE of the composites can be greatly improved by addition of Ti_3SiC_2 filler, which may be ascribed to the increase of electrical conductivity of the composites. It is also found that the reflection of electromagnetic radiation is a dominant mechanism for EMI shielding of the composite. An average EMI SE of 23 dB can be achieved in the X-band range for the composite with 25 wt% Ti_3SiC_2 content, which shows the potential of the Ti_3SiC_2/PANI composites as EMI shielding materials for commercial applications.

Introduction

Electromagnetic interference (EMI) is the electromagnetic radiation emitted by electrical and electronic equipments. This interference has increased by many folds due to increasing complexity of electronic devices and higher packing density [1–5]. To control the increasing EMI, many EMI shielding materials have been investigated. In addition to the traditional metal or metal composites, in recent years, the high conducting polymer and their composites have been developed to replace or supplement typical metals for EMI shielding applications, which have merits such as light weight, physical flexibility, and a tunable shielding response [6–10]. To obtain the polymer composites with high electrical conductivity, various types of conductive fillers, such as metal fibres, metal particulates, carbon black, graphite fiber, and carbon nanotube, have to be incorporated into polymer matrix. However, Ti_3SiC_2 material, as a novel structure/functional ceramic, has aroused researchers' interest in recent years. Ti_3SiC_2 material possesses a unique combination of mechanical, electrical, and thermal properties of both metals and ceramics [11–16]. It has excellent high-temperature properties and fatigue-damage tolerance when compared to most superalloys. Its room-temperature electrical conductivity is 4.5×10^6 $(\Omega m)^{-1}$, which is roughly twice that of pure Ti and more than four times that of near-stoichiometric TiC, and which make Ti_3SiC_2 an excellent conductive filler to create conductive composites. Hence, in our previous work [17–20], we prepared Ti_3SiC_2 ceramic composites and found that the electrical conductivity of the composites can be greatly enhanced by addition of Ti_3SiC_2 filler; in particular, in the recent work [20], we found that the EMI SE of the composites can be improved by addition of Ti_3SiC_2 filler. In the present study, we prepared Ti_3SiC_2/insulating polyaniline (PANI) composites, and investigated dielectric and EMI shielding properties of the composites in the frequency range of 8.2–12.4 GHz (X-band), to explore the potential application of the composites.

Experimental

Ti_3SiC_2 powders used in this study were synthesized using the process reported by Sun et al. [21]. Insulating

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polyaniline (PANI) used in this study was obtained from the Zheng Ji Company (Ji Lin, China). The composites were prepared by solution blending and subsequently by hot-pressing process. The starting materials of Ti_3SiC_2 (in purity of 99 wt%) and PANI were mixed in different weight fraction of Ti_3SiC_2 by ball milling, further ultrasonic dispersing and drying simultaneously in ethanol solution. Subsequently, the mixtures were molded by hot pressing at about 200 °C under 30 MPa.

Complex permittivity and EMI shielding measurements were conducted on an E8362B vector network analyzer using 201-point averaging in the frequency range of 8.2–12.4 GHz (X-band), and the thickness of all the tested samples is 1.0 mm. The microstructure of the composites was observed by scanning electron mircroscopy (SEM, Jeol-6301F, Japan).

Results and discussion

A typical SEM micrograph of fracture surface for the composite with 20 wt% Ti_3SiC_2 content is shown in Fig. 1. It can be seen that the laminated Ti_3SiC_2 grains have good disperse in the PANI matrix. Figure 2 shows the measured complex permittivity of the composite as a function of Ti_3SiC_2 content in the X-band frequency. As the Ti_3SiC_2 content is not less than 15 wt%, the real and imaginary part of the permittivity for the composites exhibit frequency independence in the measured frequency range, whereas when the Ti_3SiC_2 content is higher than 15 wt%, the real and imaginary permittivities show a complex fluctuation with the measured frequency. For example, for the composite with 20 wt% Ti_3SiC_2 content, there are five broad peaks (8.6, 9.3, 10.2, 11.2, and 12.0 GHz) in the real permittivity, correspondingly, for the composite with 25 wt% Ti_3SiC_2 content, there are six broad peaks (8.2, 8.85, 9.6, 10.3, 11.3, and 12.0 GHz) in the real permittivity, which indicates resonance behaviors in the composites, which may be attributed to the composite being highly conductive and the skin effect becoming significant [22].

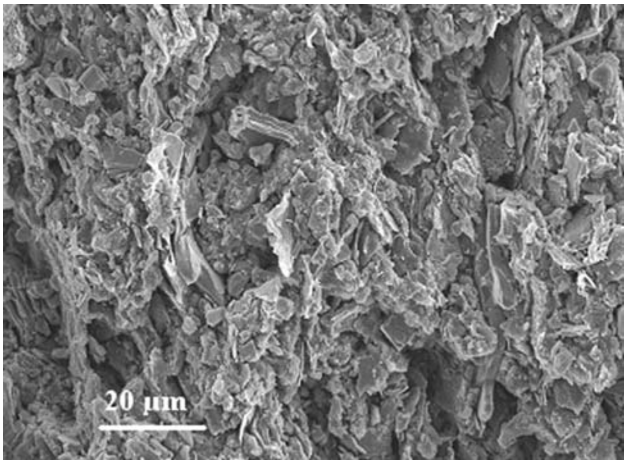

Fig. 1 SEM micrograph of fracture surfaces of composite with 20 wt% Ti_3SiC_2 content

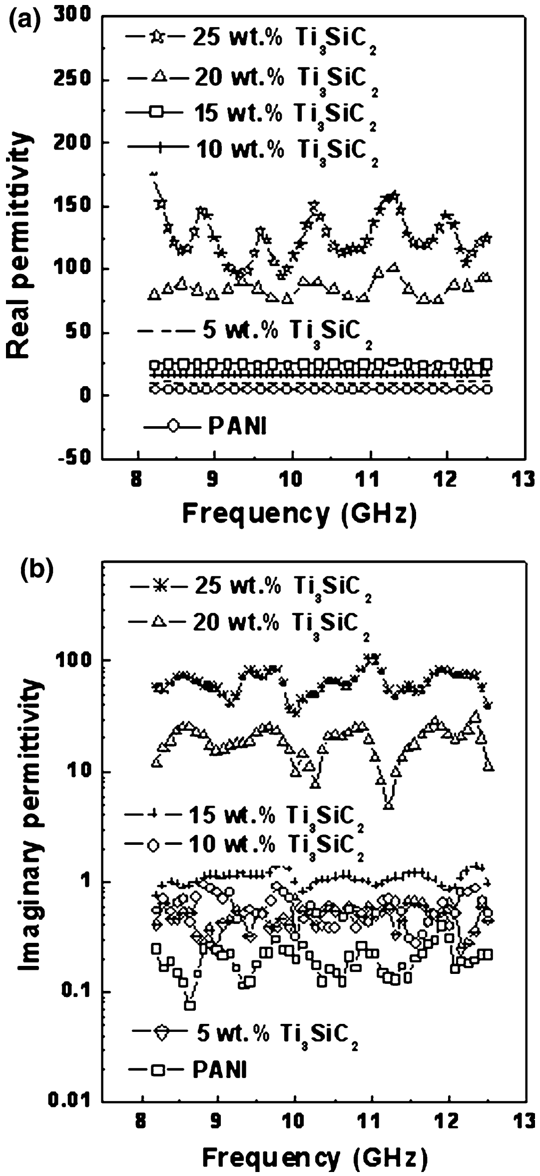

Fig. 2 Complex permittivity of Ti_3SiC_2/PANI composites as a function of the measured frequency **a** real and **b** imaginary parts

However, it can be seen that the real and imaginary parts of complex permittivity increase with the increasing Ti_3SiC_2 content. In particular, the real and imaginary parts of complex permittivity exhibit a dramatic increase with the increasing Ti_3SiC_2 content, as the Ti_3SiC_2 content is higher than 15 wt%. For example, for the composite with 25 wt% Ti_3SiC_2 content, the maximum values of the real and imaginary parts of complex permittivity are 178 and 107 in the measured frequency range, respectively.

According to the theory of complex permittivity, when the electromagnetic radiation is incident on metallic surfaces, the electric field induces two types of electrical currents within the material, i.e., the conduction and displacement currents; the former arises from free electrons and will give rise to electric loss (imaginary permittivity). The latter comes from the bound charges, i.e., polarization effect (real permittivity). Accordingly, the increase of the real part of complex permittivity can be mainly ascribed to dielectric relaxation and space charge polarization effect, and the increase of the imaginary part of complex permittivity can be attributed to the enhanced electrical conductivity of the composites. However, the Ti_3SiC_2/PANI composites with the high value of complex permittivity, as the Ti_3SiC_2 content is higher than 15 wt%, also indicates high displacement and conduction currents in the material, and suggests that the composites are suitable for use as EMI shielding materials in the measured frequency range.

The EMI SE of a material can be defined as the ratio of transmitted power (P_o) to incident power (P_i) of an electromagnetic wave. The SE is measured in the unit of decibels, and is given by [23]:

$$\mathrm{SE} = 10\log\left(\frac{P_i}{P_o}\right) = \mathrm{SE_R} + \mathrm{SE_A} + \mathrm{SE_M}$$

where P_i is the incident power and P_o is the transmitted power. $\mathrm{SE_A}$, $\mathrm{SE_R}$, and $\mathrm{SE_M}$ are the shielding effectiveness due to absorption, reflection, and multiple reflection, respectively. Assuming that the shielding materials have nonmagnetic properties (magnetic permeability, $\mu r = 1$), they are explicitly written as:

$$\mathrm{SE_A} = 8.686\alpha d$$

$$\mathrm{SE_R} = 20\log\left(|1+n|^2/4|n|\right)$$

$$\mathrm{SE_M} = 20\log\left|1 - \exp(-2(1+i)\alpha d)(1-n)^2/(1+n)^2\right|$$

$$\alpha = (\omega/c)\left[(|\varepsilon_r|/2)\left\{(1+\tan^2(\sigma/\omega\varepsilon_0\varepsilon_r))^{1/2} \mp 1\right\}\right]^{1/2}$$

where α is the absorption coefficient, ε_r is the real part of dielectric constant, and it can be calculated from the measured S_{11} and S_{12} parameters, d is the sample thickness, the signs correspond to positive and negative ε_r, respectively, ε_0 is the vacuum dielectric constant, n is the complex index of refraction, σ is the electrical conductivity of the material, and ω is the angular frequency.

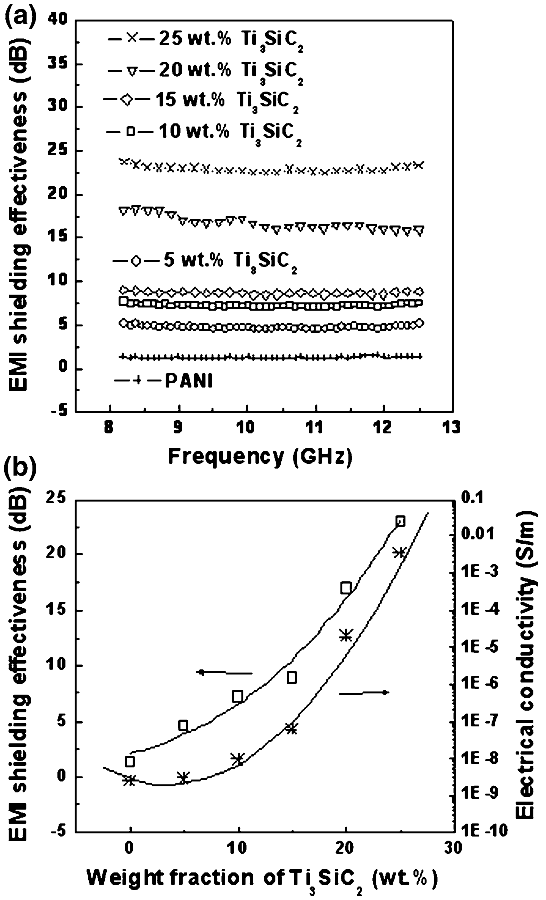

Fig. 3 EMI shielding effectiveness of Ti_3SiC_2/PANI composites as a function of **a** the measured frequency and **b** the Ti_3SiC_2 content

Figure 3a shows the EMI SE of the composites as a function of the frequency range of 8.2–12.4 GHz. It can be noted that the EMI SE of the composite is almost independent of the frequency in the measured frequency range, except that the EMI SE of the composite with 20 wt% Ti_3SiC_2 content exhibits a little fluctuation. Figure 3b shows the EMI SE and the electrical conductivity of the composites as a function of Ti_3SiC_2 content at 10 GHz. It can be observed that the EMI SE and the electrical conductivity of the composites all increase with the increasing Ti_3SiC_2 content. This may be attributed to the high electrical conductivity and high aspect ratio derived from layered microstructure of the Ti_3SiC_2, which makes it easy to form conducting networks, and it is the Ti_3SiC_2 conducting networks in the composites that may interact with electromagnetic wave radiation to attenuate electromagnetic wave. The increasing electrical conductivity of the composites with the increase of Ti_3SiC_2 content suggests the increase of contribution to the imaginary permittivity with the increase of Ti_3SiC_2 content. Therefore, the average EMI SE as high as 23 dB can be achieved for the composite with 25 wt% Ti_3SiC_2 content, indicating that the composites can be used as an effective EMI shielding material for commercial applications.

The S_{11} and S_{12} parameters of the two-port network system represent the reflection and transmission coefficients, respectively. According to the analysis of S parameters, the reflectivity (R), transmissivity (T), and absorptivity (A) can be described as:

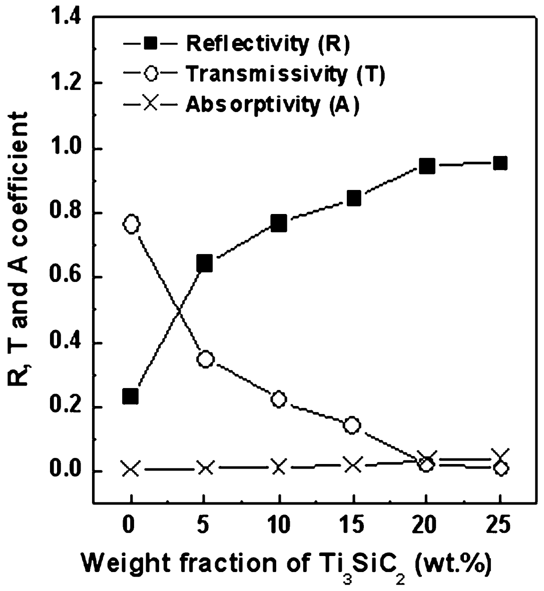

Fig. 4 The reflectivity (*R*), transmissivity (*T*), and absorptivity (*A*) of the composites as a function of Ti_3SiC_2 content

$$T = |S_{12}|^2$$

$$R = |S_{11}|^2$$

$$A = 1 - T - R$$

Figure 4 shows the reflectivity (*R*), transmissivity (*T*), and absorptivity (*A*) of the composites as a function of Ti_3SiC_2 content at a frequency of 10 GHz. With the increasing Ti_3SiC_2 content, the reflectivity increases greatly increase, whereas the transmissivity exhibits a dramatic decrease, and the absorptivity only increases a little. This result suggests that the composites should be more reflective and less absorptive to electromagnetic radiation, i.e., the primary EMI shielding mechanism of the composites is dominant by reflection rather than by absorption in the X-band frequency. This result is in agreement with the investigation of the shielding mechanism of carbon fiber and nanotube-filled polymer solid composites [8, 24].

Conclusions

Ti_3SiC_2/insulating PANI composites were prepared by solution blending and subsequently by hot-pressing process. The dielectric permittivity and EMI SE of the composites were measured in the frequency range of 8.2–12.4 GHz (X-band). The experimental results show that both real and imaginary permittivities increase with the increasing Ti_3SiC_2 content, and which are attributed to the enhanced displacement and conduction currents due to the addition of Ti_3SiC_2 filler. An average EMI SE of 23 dB can be achieved in the X-band range for the composite with 25 wt% Ti_3SiC_2 content. This may be ascribed to the increase of electrical conductivity of the composites, and shows the potential of the Ti_3SiC_2/insulating PANI composite as EMI shielding materials for commercial applications. It is also found that the reflection of electromagnetic radiation is a dominant mechanism for EMI shielding of the composite.

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