Enhancement of microwave absorption bandwidth of polymer blend using ferromagnetic gadolinium silicide nanoparticles

Pritom J. Bora,[1] S. Gupta,[2] V. K. Pecharsky,[2, 3] K. J. Vinoy,[4] Praveen C. Ramamurthy*[1,5] and R. L. Hadimani*[6]

[1] Interdisciplinary Centre for Energy Research (ICER), Indian Institute of Science, India.

[2] Ames Laboratory, Division of Materials Science and Engineering, U.S. Department of Energy, USA

[3] Department of Materials Science and Engineering, Iowa State University, USA.

[4] Department of Electrical and Communication Engineering, Indian Institute of Science, India.

[5] Department of Materials Engineering, Indian Institute of Science, India.

[6] Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, USA.

*** Corresponding authors:**

Praveen C. Ramamurthy : onegroupb203@gmail.com

R. L. Hadimani: rhadimani@vcu.edu

Abstract

Ferromagnetic gadolinium silicide (Gd_5Si_4) nanoparticles outstandingly enhance the microwave absorption bandwidth of a polymer blend (PVB-PEDOT:PSS). These materials are critical for various military and civilian applications such as X-band (8.2–12.4 GHz) and Ku-band (12.4–18 GHz) absorption. A single 1.2 mm thick layer of PVB-PEDOT:PSS-Gd_5Si_4 (PPGS) nanocomposite film shows the most promising bandwidth (8.2–18 GHz) with a minimum reflection loss of -14 dB. Mechanistically, dielectric loss ($tan\ \delta_e \sim 2.4$) and magnetic loss ($tan\ \delta_m \sim 1.1$) contributes more efficiently, and standard microwave simulation confirms the stored energy is predominant in PPGS nanocomposite which enhances the bandwidth.

Keywords: Polymer nanocomposites, Dielectrics, Reflection loss (RL), RL bandwidth.

1. Introduction

In search of novel ultra-thin and lightweight coatable broadband microwave absorption materials, recently several polymer-metal/oxide nanocomposites have attracted tremendous attention [1-9]. Among the base coatable polymers, polyvinylbutyral (PVB) has recently drawn special attention especially in the area of organic nanoelectronics [9, 10]. Recently, PEDOT:PSS (high conducting PH1000) has been widely used as a standard conducting polymer in various applications due to its superior chemical stability [11]. Hence here, PVB-PEDOT:PSS blend is evaluated as a novel microwave dielectric material.

To the best of our knowledge, rare earth metal silicides such as Gd_5Si_4 based engineered nanocomposite for microwave absorption have not been investigated. The key interest in use of Gd_5Si_4 for microwave absorption is that it has soft magnetic property [12, 13]. In general, single layer broadband microwave absorption is challenge. To overcome this, in this work, a simple and yet very effective solution processed microwave dielectric blend is prepared and its bandwidth enhancement using Gd_5Si_4 nanoparticles is reported for films with thickness of 1.2 mm.

2. Experimental

The Gd_5Si_4 nanoparticles were synthesised by arc-melting followed by polyethylene glycol mediated ball milling, and details of the procedure are described in the supporting information [13]. Both, the PVB-PEDOT:PSS blend (PVBPS) and PVB-PEDOT:PSS-Gd_5Si_4 nanocomposite (PPGS) were prepared by solution processing. In a typical synthesis, PVB was dissolved in absolute ethanol and a suitable amount of PEDOT:PSS was added to it under constant stirring. After 30 min, Gd_5Si_4 nanoparticles were added to it and was stirred for another 2 h. The optimal weight ratio of [PVB solution]:[PEDOT:PSS]:[Gd_5Si_4 nanoparticles] was found to be 1:0.1:0.1. Finally, the mixture was casted and kept at room temperature in open air for drying (24 h). The details of relative permittivity ($\varepsilon_r = \varepsilon' - i\varepsilon''$) and permeability ($\mu_r = \mu' - i\mu''$) measurements, reflection loss (RL) calculations are given in the *supporting information*.

3. Results and discussion

Fig.1(a) shows the recorded FESEM images of the as-prepared irregularly shaped Gd_5Si_4 nanoparticles (average particle size ~ 90 nm). The cross-sectional surface morphology, EDS spectra and elemental mapping of the PPGS nanocomposite are shown in the Fig.1(b), (c) and (d) respectively. The EDS confirms the presence of the Gd and Si in the PPGS nanocomposite. As Gd_5Si_4 is in the form of irregular shaped nanoparticles, it can easily establish the linkages in the polymer matrix. The observed dense elemental mapping of the Gd and Si suggest that the percolation threshold is achieved for PPGS nanocomposite.

As shown in the Fig.2, real permittivity (ε') of PVBPS blend range from 8-4, and corresponding imaginary permittivity (ε'') changed from 23-9 in the frequency range of 8.2–18 GHz. In case of PPGS nanocomposite, the ε' in the same frequency range increased to 12-9 and corresponding ε'' varied from 29-12 (Fig.2(a) and (b)). The interfacial polarization is one of the major factors in polymer nanocomposite that contributes to absorption [8-15]. As can expected, in PPGS nanocomposite, the interfacial polarization is predominant. It can be approximated by change of ε'' value ($\Delta\varepsilon''$) [16], the $\Delta\varepsilon''$ value of PVBPS was found to be ~ 13 whereas it was increased to ~ 17 for PPGS nanocomposite. Results clearly indicate the presence of significantly higher interfacial polarization in PPGS nanocomposite due to the presence of Gd_5Si_4 nanoparticles, which also leads to enhanced heterogeneity of the films. Due to the presence of ferromagnetic Gd_5Si_4 nanoparticles (***Supporting information***) noticeable changes in both real permeability (μ') and imaginary permeability (μ'') values of PPGS were observed (Fig.2 (c) and (d)) as compared to PVBPS composite.

As illustrated in the Fig.2 (e), the obtained minimum RL of the PVBPS blend was -5 dB for the thickness of 1 mm. When the thickness was increased to 1.2 mm, 1.4 mm and 2 mm, RL value decreased to -9 dB, -12.5 dB, -15 dB respectively. The RL value of -10 dB, which corresponds to 90 % absorption, is adequate for practical applications [15]. However, PVBPS blend bandwidth (RL ≤ -10 dB) was not found to increase significantly until the thickness was increased to 2 mm. Enhanced absorption is observed for Ku-band (12.4–18 GHz) for a thickness of 1.5 mm. On the other hand, as shown in the Fig.2 (f-h), outstanding bandwidth (8.2–18 GHz) was achieved for the PPGS nanocomposite for the thickness of 1.2 mm with a minimum RL value -14 dB. In fact, for 1 mm thickness, minimum RL value of -16 dB is achieved within a broad bandwidth of 8.5-18 GHz. Thus, this work clearly demonstrates the enhancement of microwave absorption in a much broader bandwidth in PPGS. It is also verified that the presence of Gd_5Si_4 in PPGS plays a key role in bandwidth engineering. In comparison to the well-known ferrite based, porous systems, PPGS exhibit a higher bandwidth at a minimum thickness (**Table S1, *Supporting information***).

The enhancement of bandwidth in presence of Gd_5Si_4 is possible because of multiple factors as summarized in the Fig. 3(a). For magneto-dielectrics, absorption of electric and magnetic energy can be approximated in terms of dielectric loss tangent ($tan\ \delta_e = \frac{\varepsilon''}{\varepsilon'}$) and magnetic loss tangent ($tan\ \delta_m = \frac{\mu''}{\mu'}$) [8-15]. As shown in the Fig. 3(b) and (c), both $tan\ \delta_e$ and $tan\ \delta_m$ values were high for PPGS as compared to PVBPS.

A noticeable $tan\ \delta_m$ value is observed for PPGS, which indicates a pronounced magnetic loss. Eddy current may be induced due to this magnetic loss, which can reduce the absorption [15]. The factor, $\mu''(\mu')^{-2}f^{-1}$, indicates that, the eddy current is predominant if it is constant [15]. The plot of $\mu''(\mu')^{-2}f^{-1}$ with respect to frequency is shown in the Fig. 3(d). The factor, $\mu''(\mu')^{-2}f^{-1}$ is not constant for PPGS, which indicates that eddy current loss can be ignored. Further, EM attenuation can be understood from the EM attenuation co-efficient (α) value. As shown in Fig. 3(e), the calculated value of α in PPGS is much greater than PVBPS, which suggests that EM attenuation of PVBPS blend can be enhanced by an order of magnitude by loading with Gd_5Si_4 nanoparticles. Standard microwave simulation (CST-microwave studio) results of the energy stored in the PVBPS blend and PPGS nanocomposite for various thicknesses are shown in the Fig. 3(f) and (g) respectively (8.2–18 GHz). The energy stored in PPGS nanocomposite is predominant as compared to the PVBPS blend resulting excellent bandwidth.

4. Conclusions

In the development of microwave dielectric materials, use of nanostructured magnetic materials as a dopant in optimized polymer blends is a promising approach, as demonstrated by enhanced microwave absorption bandwidth in Gd_5Si_4 nanoparticles-polymer composite. A large bandwidth, 8.2–18 GHz, was achieved for the optimally prepared PVB-PEDOT:PSS-Gd_5Si_4 nanocomposite for the single 1.2 mm thick layer. An impressive minimum RL value of -16 dB was achieved for 1 mm thin layer with an excellent bandwidth in the range of 8.5–18 GHz. Gd_5Si_4 nanocomposites may present a tangible path forward for discovery of extremely efficient microwave absorbers in the near future.

Acknowledgments

PJB, KJV and PCR gratefully acknowledge the Govt. of India, Ministry of Defence Aeronautics R&D Board (ARDB/01/2031900/M/I) for financial support of this work. Synthesis of Gd_5Si_4 nanoparticles was supported by Division of Materials Sciences and Engineering of Bassic Energy Sciences Program of the Office of Science of the U.S. Department of Energy. Ames Laboratory is operated for the U.S. Department of Energy (DOE) by Iowa State University of Science and Technology under contract No. DE-AC02-07CH11358.

References

[1] Liu P, Ng VMH, Yao Z, Zhou J, Kong LB. Mater Lett 2018;229:286–9..

[2] Bora PJ, Porwal M, Vinoy KJ, Kishore, Ramamurthy PC, Madras G. Compos Part B Eng 2018;134:151–63.

[3] Qin F, Brosseau C. J Appl Phys 2012;111.

[4] Bora PJ, Porwal M, Vinoy KJ, Ramamurthy PC, Madras G. Mater Res Express 2016;3.

[5] Qin F, Peng HX. Prog Mater Sci 2013;58:183–259.

[6] Bora PJ, Azeem I, Vinoy KJ, Ramamurthy PC, Madras G. Compos Part B Eng 2018;132:188–96.

[7] Bora PJ, Lakhani G, Ramamurthy PC, Madras G. RSC Adv 2016;6:79058–65.

[8] Liu P, Li L, Wang L, Huang T, Zhao QL, Zhang KL, et al. Phys Status Solidi Appl Mater Sci 2017;214.

[9] Bora PJ, Mallik N, Ramamurthy PC, Kishore, Madras G. Compos Part B Eng 2016;106:224–33.

[10] Gupta S, Seethamraju S, Ramamurthy PC, Madras G. Ind Eng Chem Res 2013;52:4383–94.

[11] Li P, Du D, Guo L, Guo Y, Ouyang J. J Mater Chem C 2016;4:6525–32.

[12] Hadimani RL, Gupta S, Harstad SM, Pecharsky VK, Jiles DC. IEEE Trans Magn 2015;51.

[13] Hadimani RL, Mudryk Y, Prost TE, Pecharsky VK, Gschneidner KA, Jiles DC. J. Appl. Phys., vol. 115, 2014.

[14] Hunagund SG, Harstad SM, El-Gendy AA, Gupta S, Pecharsky VK, Hadimani RL. AIP Adv 2018;8.

[15] Zhao B, Guo X, Zhao W, Deng J, Shao G, Fan B, et al. ACS Appl Mater Interfaces 2007;8:28917–25.

[16] Lv H, Guo Y, Wu G, Ji G, Zhao Y, Xu ZJ. ACS Appl Mater Interfaces 2017;9:5660–8.

Figures

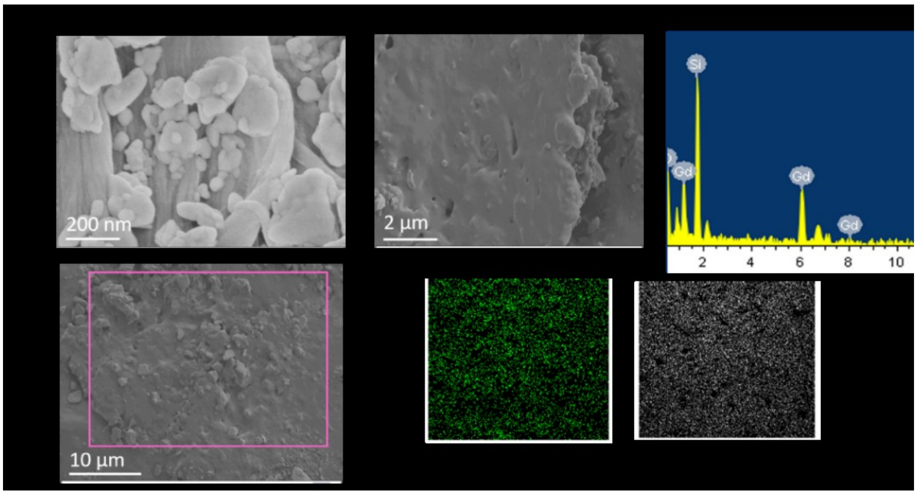

Fig.1.(a) FESEM image of the synthesized Gd_5Si_4 nanoparticles, **(b)** cross-sectional surface morphology of the PPGS nanocomposite **(c)** EDS spectra of the PPGS nanocomposite and **(d)** elemental mapping of the PPGS nanocomposite.

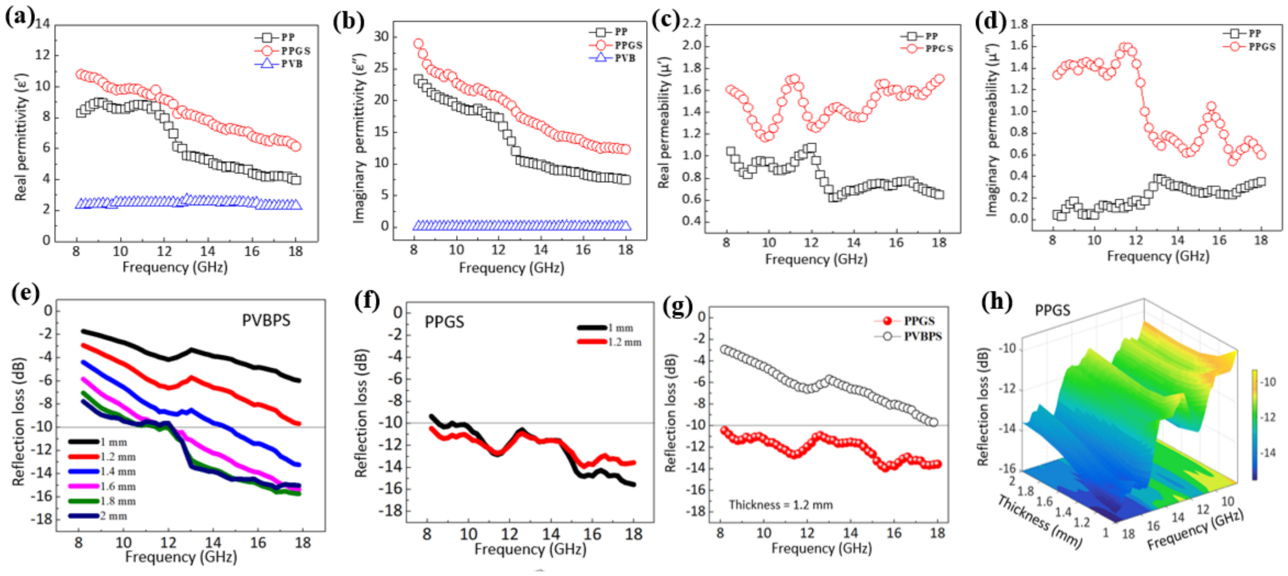

Fig. 2. Variation of **(a)** real (ε′) and **(b)** imaginary (ε″) permittivity, and **(c)** real (μ′) and **(d)** imaginary (μ″) permeability of the PVBPS blend and PPGS nanocomosite in the frequency range 8.2-18 GHz. Reflection loss, RL (dB) of **(e)** PVBPS blend, **(f)** PPGS nanocomposite for various thicknesses in the frequency range 8.2-18 GHz. **(g)** Comparison of RL (dB) of PVBPS and PPGS (thickness 1.2 mm) and **(h)** 3D plot of RL (dB) of PPGS nanocomposite for various thicknesses.

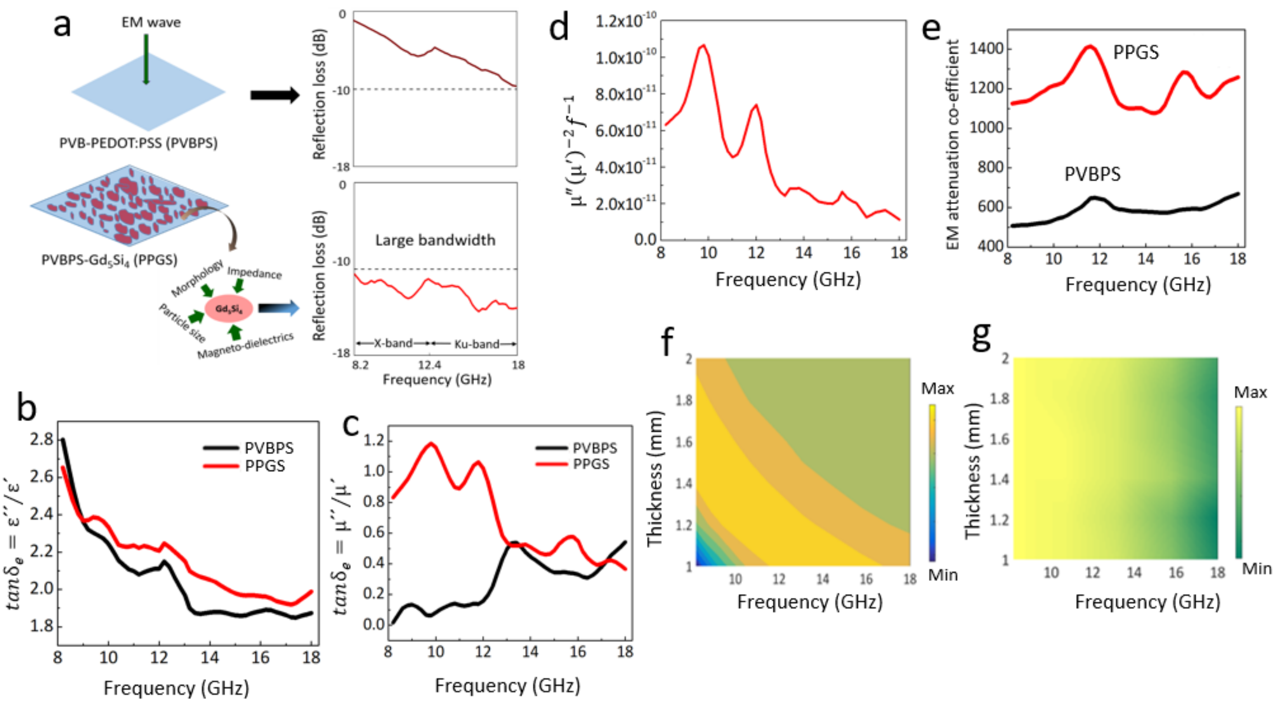

Fig.3. (a) Schematic of performance of PVBPS blend and PPGS with contributing factors, **(b)** dielectric loss tangent, **(c)** magnetic loss tangent, **(d)** variation of $\mu''(\mu')^{-2}f^{-1}$ of PPGS with frequency, **(e)** EM-attenuation constant (α), **(f)** energy stored of PVBPS blend and **(g)** energy stored of PPGS nanocomposite.