Materials Letters 236 (2019) 116–119

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

# Shape memory driving thickness-adjustable G@SMPU sponge with ultrahigh carbon loading ratio for excellent microwave shielding performance

Yongjie Yan, Hong Xia, Yiping Qiu, Zhenzhen Xu *, Qing-Qing Ni *

*Department of Mechanical Engineering and Robotics, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8576, Japan*

ARTICLE INFO

*Article history:*
Received 30 July 2018
Received in revised form 4 October 2018
Accepted 15 October 2018
Available online 16 October 2018

*Keywords:*
Carbon
Shape memory
Dipping coating
Adhesion
Functional
Microwave shielding

ABSTRACT

Shape memory driving thickness adjustable graphite (G) micro-flakes@shape memory polyurethane (G@SMPU) sponge was fabricated by two-step dipping separately in G-dispersed aqueous solution and SMPU/THF solution for high-performance microwave shielding. The sponge exhibited an ultrahigh G loading ratio (G/sponge, wt/wt) up to 490 wt%. For the first time, dipping coating of SMPU onto the sponge was proposed, and the obtained G@SMPU sponge exhibited a good recovery effect at least above 90% after thorough compression. And also, the thickness could be adjusted by utilizing its shape memory property. For microwave shielding, G-9@SMPU and G-18@SMPU sponges achieved the shielding effectiveness over 20 and 30 dB, respectively. Moreover, varying thickness or compressing repeatedly even up to 100 times would not obviously decrease the shielding effect of the G@SMPU sponge. This suggests the steady distribution and adhesion of G micro-flakes inside the three-dimensional sponge substrate due to the fixing of SMPU.



## 1. Introduction

Recently, to overcome increasingly deteriorative electromagnetic interference (EMI) and radiation hazard for human health, especially from microwave, carbon based nano/micro-composites, such as graphite [1], carbon black [2], carbon nanotube [3,4], graphene [5,6], and carbon nanofiber [7], have been widely researched for microwave shielding mainly due to their electrical conductive properties and unique one/two/three dimensional structures. Generally, higher percent of carbon content in composite would give a higher electromagnetic shielding effect [8–11]. Thus, pure carbon interface could possibly provide better reflection effect due to good interface mismatch. Although some researchers have developed free-standing pure carbon materials for electromagnetic shielding, their mechanical performances, such as elongation and deformation ability, were not enough at all [12,13].

Therefore, we are herein proposed a novel and facile approach by utilizing melamine sponge having lots of interspace for loading of typical pure carbon material, graphite (G) micro-flakes, as shown in Fig. 1a. To fix and avoid the drop of G micro-flakes from the sponge, shape memory polyurethane (SMPU) was adhered onto the surfaces of the G micro-flakes by dipping. In this approach, there would be three obvious advantages sticking out. (1) Ultrahigh carbon loading ratio could be obtained; (2) The internal porous structure of this G@SMPU sponge could be also utilized to weaken the incident electromagnetic wave energy by repeated reflection and interference; (3) Thickness adjustable G@SMPU sponge driven by shape memory effect could be obtained.

## 2. Experimental

### 2.1. Preparation of G@SMPU sponge

SMPU (MS6520, SMP Technologies Inc, Japan), reported in our previous work [14], was used as shape memory composition with $T_g$ of ~65 °C and $T_m$ of ~170 °C. G@SMPU Sponge was fabricated by sonication assisted dipping approach, as shown in Fig. 1b. Firstly, different weight of graphite (0 g, 3 g, 6 g, 9 g, and 18 g) and 300 ml distilled water were in turn added in a teflon container and subjected to sonication for 30 min. Then, melamine sponge precut into 90 mm * 90 mm * 26 mm (L * W * H) was dipped into the solution and sonicated for 60 min. After that, the sponges loading different graphite (denoted as G-M sponge, M: 0, 3, 6, 9, 18) were dried at 75 °C for one week. Secondly, the G sponge was dipped into a 300 ml 2 g/ml SMPU/THF solution for 20 min. Then,

* Corresponding authors.
*E-mail addresses:* xuzhenzhen@ahpu.edu.cn (Z. Xu), niqq@shinshu-u.ac.jp (Q.-Q. Ni).

https://doi.org/10.1016/j.matlet.2018.10.101

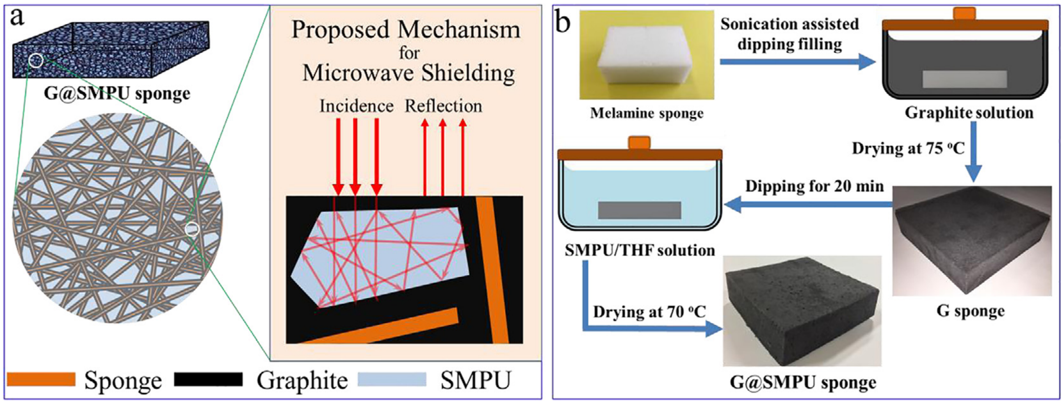


**Fig. 1.** (a) Proposed multi-reflection mechanism for microwave shielding; (b) Fabrication approach for G@SMPU sponge.

the sponge was dried for 48 h at 70 °C. Finally, G@SMPU sponges with different weight of graphite (denoted as G-M@SMPU sponge, M: 0, 3, 6, 9, 18) were obtained.

### 2.2. Characterization and evaluation

Structures of G and SMPU were characterized by X Ray Diffraction (XRD, MiniFlex300, Japan) and Nicolet 5700 attenuated total reflection Fourier transform infrared (ATR-FTIR) instrument (Thermo Electron Corp., USA). Cross sections of G sponges were observed by photographic camera. Conductivity of G sponges was measured by standard four-probe method using a MCP-HT450 conductivity meter (Dia Instruments Co.).

Shape memory evaluation of G@SMPU sponges was carried out in a dryer with a transparent glass cover for observation. For details, the heated G@SMPU sponge was cool-compressed up to 20 MPa by pressing machine and kept for 10 min for fixing. Then, the compressed G@SMPU sponge was transferred into the dryer for recovery at 80 °C. Besides, maximum compression ratio was measured by calculating the thickness before and after compression. Microwave shielding was evaluated in 7.0–16.5 GHz using transmission attenuation measurement system for microwave (KEYCOM Corp.), which connects with a vector network analyzer (37247D, Anritsu Co. Ltd.) for calculation of shielding effectiveness (SE).

## 3. Results and discussion

For SMPU, N-H stretching vibration peak revealed at 3305 $cm^{-1}$ in FTIR spectrum (Fig. 2a), suggesting its consistency with typical polyurethane. For G micro-flakes, they have the size ranging in 5–20 μm, and exhibited a sharp feature peak at 26.5° in XRD pattern (Fig. 2b), which is typical graphitic structure.

With increasing addition of G micro-flakes to dipping solution, the loading ratio of the sponge increased as well. G-18 sponge could reach up to 490 wt%, which is almost 5 times than the weight of the sponge itself. This demonstrated the sponge has a high loading ratio for carbon materials. Also, the porosities of G sponges decreased with increasing loading ratio of G (Fig. 2c-f). This is because of the filling of G inside the sponge having lots of internal space (average pore size of ∼128 μm). For G-18 sponge, there had been no obvious pores observable, indicating saturation of internal space of the sponge.

Fig. 2g presents the weight percentages of each composition in G@SMPU sponge. The weight percentage of the sponge composition showed a declining trend down to 8.3 wt% because of increas-

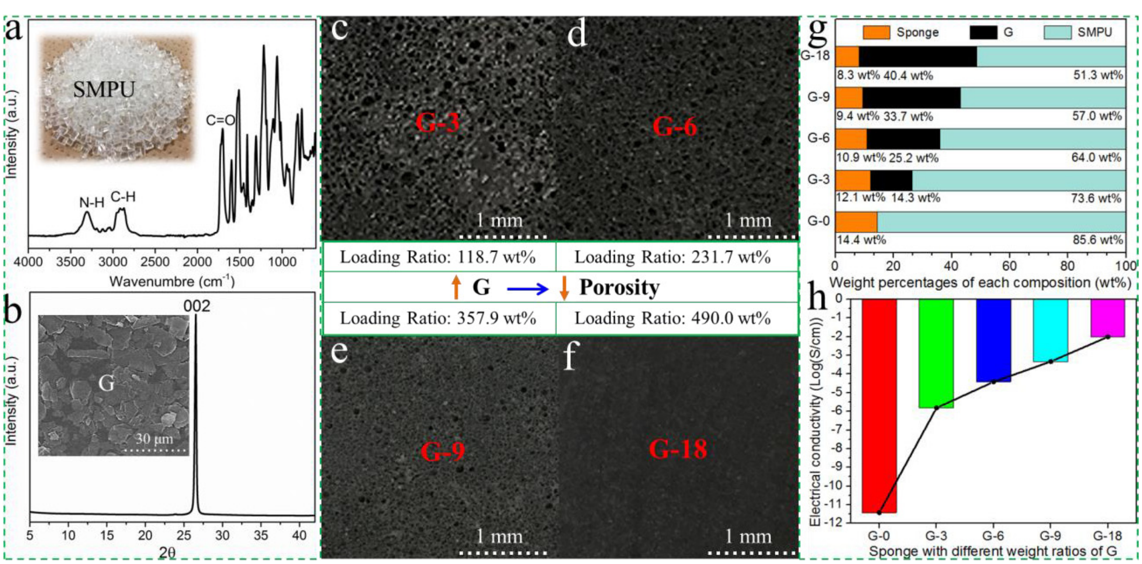


**Fig. 2.** (a) FTIR of SMPU; (b) XRD of G; (c, d, e, f) Cross sections of G sponges; (g) Weight percentages of each composition in G@SMPU sponge; (h) Electrical conductivity of G sponges.