Chemical Engineering Journal 353 (2018) 381–393

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Synergistic effect of carbon nanotube and graphene nanoplates on the mechanical, electrical and electromagnetic interference shielding properties of polymer composites and polymer composite foams

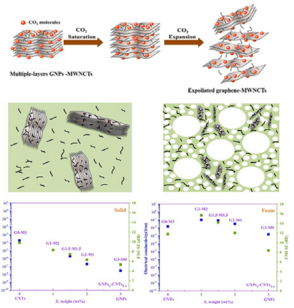
Hongming Zhang, Guangcheng Zhang*, Meng Tang, Lisheng Zhou, Jiantong Li, Xun Fan, Xuetao Shi, Jianbin Qin

Department of Applied Chemistry, MOE Key Lab of Applied Physics and Chemistry in Space, School of Natural and Applied Sciences, Northwestern Polytechnical University, Xi'an 710072, China

HIGHLIGHTS

- A bimodal composite foam with CNT-GNP hybrids was prepared.
- CNT and GNP show limited effect in improving electrical properties of composites.
- CNT and GNP synergistically enhance electrical properties of composite foams.
- The synergistic mechanism of CNT and GNP in composite foams is clarified.
- The bimodal composite foams can be used in EMI shielding.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Bimodal microcellular foam
Synergistic effect
Supercritical fluid
Electrical conductivity
Electromagnetic shielding interference

ABSTRACT

Novel PMMA composites were fabricated using two different dimensional nanofillers of MWCNTs and GNPs as bifillers to explore their synergistic effect on the final mechanical and electrical properties. MWCNTs and GNPs display limited effect on the final electrical properties while they show obvious synergistic effect in influencing the mechanical performance. The well-dispersed MWCNTs-GNPs in polymer matrix provide plenty of 1D-2D interconnections for efficient stress transferring when exposed to stress tensile, but the critical distance between nanofiller is not enough for effective electron movements and the significant Schottky barrier between nanofiller contacts has restricted the synergistic effect for electrical properties. Afterwards, PMMA composite foams with microcellular structure were prepared by supercritical fluid assisted processing. The ternary bimodal composite foams present better tensile, electrical and EMI shielding properties than the unimodal composite foams. MWCNTs and GNPs reveal prominent synergistic effect in influencing the tensile and electrical properties of ternary composite foam systems. The obvious enhancement of electrical conductivity results from the in situ exfoliation of GNPs, high-level orientation and redistribution of nanofillers, moderate physical foaming with bimodal microcellular structure as well as attenuated Schottky barriers at few-layer graphene/MWCNTs junctions. The dramatic improvement of EMI shielding performance is attributed to the elevated electrical conductivity, unique foam microstructures and special 1D-2D (MWCNTs-GNPs) hybrid structure. This study paves a feasible road to prepare lightweight and novel composites with superior electrical properties.

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* Corresponding author.
E-mail address: zhangguc@nwpu.edu.cn (G. Zhang).

https://doi.org/10.1016/j.cej.2018.07.144
Received 13 May 2018; Received in revised form 11 July 2018; Accepted 22 July 2018

1. Introduction

In recent years, the proliferation of telecommunications and wireless electronic instruments, like cell phones, radars and various electronic terminals have generated considerable electromagnetic (EM) pollutions [1–3]. These undesirable EM radiations would severely interfere the operation of nearby devices and threaten the physical health of human beings [4,5]. Hence, several methods are being explored to efficiently restrain EM pollution. Conductive polymer composites (CPCs), which are prepared by blending various conductive fillers with polymers, display great potential to fabricate lightweight and high-performance EMI shielding materials due to their superior electric conductivity and outstanding process-ability [6–11]. Among these conductive fillers, carbon nanotubes (CNTs) and graphene nanoplates (GNPs) are of particular favor on account of the unique structures and remarkable conductivities [12,13]. However, in previous work, a high content of nanofiller was required to establish effective conductive network to increase EM shielding capacity [14–16]. Such high loading levels of nanoparticles would result in agglomeration, thus restricting their mechanical performance and increasing the cost. Considered these factors, it is urgently required to prepare advanced EMI shielding materials consisting of nanofillers well-dispersed in a matrix at lower concentrations [17–20].

To further reduce the filler content and undesired agglomerations, several strategies, such as introduction of surface-functionalised nanofillers [19] or use of hybrid fillers, have been proposed for the preparation of polymer composites [21]. One most effective method is to introduce the hybrid fillers which contain two or more kinds of carbon nanoparticles differing in geometries [21–25]. Using two geometrically different fillers, like carbon nanofibers (CNFs) and carbon black (CB) or CNTs and GNPs, could induce the formation of a co-supporting network of the two fillers and thus a decrease of the total filler loading. These high-aspect-ratio fillers (CNTs and CNFs) act as bridge to connect layered fillers (GNPs) or particles (CB) to form regular global conductive pathways in composite foams with relatively lower filler content [13,24]. In previous reports, the synergistic effect (“1 + 1 > 2” phenomenon) [2,26] between graphene and CNTs have also been proved to be effective to improve various properties (mechanical property [27–29], thermal conductivity [30–32], and flame-retardant property [33–35]). However, the synergistic effect between CNTs and graphene in influencing electrical conductivity and the related properties is still controversial and not fully understood. Hong et al. [36] and Kong et al. [37] reported that functionalized MWCNTs and graphene have obvious synergistic effect in enhancing the electrical properties. But Haddon et al. [30] and Chandrasekaran et al. [38] pointed that there was no synergistic effect of MWCNTs and graphene in affecting the electric conductivity in their work. Their results suggested the graphene layers restricted MWCNTs in limited areas and thus induced a great amount of agglomeration and decreased the chance of effective contacts. As a result, graphene-MWCNTs hybrids showed an opposite effect on electrical and EMI shielding performance. The final properties of polymer/graphene-MWCNTs composites may be greatly contingent on the distribution state of nanofillers, different degree of crystallinity, processing parameters and ratios between graphene and MWCNTs.

Recently, a facile and environmentally benign supercritical fluid (SCF) assisted processing technology [39,40] based on the traditional conductive polymer composites has been proved to be beneficial to promote the exfoliation of 2D multilayers materials [41] and facilitate the orientation and redistribution of nanofillers [42,43]. For example, Park et al. [44] fabricated GNPs-polymer nanocomposites by SCF assisted processing. After SCF treatment and physical foaming, the multilayer graphene nanoplates exfoliated into few-layer graphene and then uniformly dispersed in the polymer matrix. Ozisik and his group [42] prepared polycarbonate/graphene nanocomposite foams via one-step SCF process, and the resulted foams with 0.5 wt% GNPs loading exhibited an EMI specific shielding effectiveness (SE) of 39 dB cm^3/g. Furthermore, this technology has succeeded in inducing CB and CNTs [13] to synergistically improve the electrical conductivity of composite foams in previous literature. However, there are limited studies to report on the polymer nanocomposite foams containing carbon nanofillers of two different geometries, like MWCNTs and GNPs. The mixture of one dimensional (1D) MWCNTs and two dimensional (2D) GNPs may generate heterogeneous nucleation in a completely different manner. Composite foams containing MWCNTs and GNPs may also display a different mechanism and performance of synergistic effect than solid composites. All these questions need to be answered.

Herein, the objective of this work is to explore the synergistic effect of two different dimensional nanomaterials on the final mechanical, electrical and EMI shielding properties of composites and composite foams. In this work, Polymethyl methacrylate (PMMA) has been widely used in the fabrication of lightweight and multifunctional composite foams due to its excellent ability to reserve CO_2 and good affinity with carbon fillers. PMMA based CPCs containing MWCNTs, GNPs, GNPs-MWCNTs hybrids at various loadings were fabricated by anti-solvent precipitation process, respectively. The rheology, tensile, electrical and EMI shielding behaviors of those three composite systems were first investigated respectively to examine the potential effect of MWCNTs and GNPs on the mechanical and electrical properties. A supercritical fluid batch foaming process was then applied to prepare composite foams with the same relative density. The final morphology, tensile, electrical and EMI shielding properties of those composite foams were further studied to explore how GNPs-MWCNTs hybrids influence the final performance of ternary composite foams.

2. Experimental section

2.1. Materials

The commercial PMMA with a grade name of DF23-8N was purchased from Evonik Industries AG. DF23-8N has a density of 1.19 g/cm^3 with a weight-average molecular weight of 350,000 g/mol. Graphene nanoplatelets (GNPs, XF021) with the thickness of 3–10 nm, average platelet diameter value of 5–10 μm and the bulk density value of 2.2 g/cm^3 were provided by Nanjing XFNANO. Materials Tech Co., Ltd. Carboxyl group functionalised MWCNTs (diameter: 30–50 nm, length: 10–20 μm) with approximately 95 wt% carbon purity and possessing 3 wt% COOH groups were supplied by Chengdu Organic Chemicals Co., Ltd. Carbon dioxide (CO_2) with a purity in excess of 99.9% was chose as the blowing agent. Tetrahydrofuran (THF) and methanol were purchased from Sigma-Aldrich.

2.2. Preparation of PMMA/GNPs-MWCNTs nanocomposites

PMMA composites containing both GNPs and MWCNTs (PGx-My, where x and y represents the weight ratios of GNPs and MWCNTs, respectively.) were prepared by a solution-mixing method. For a typical sample preparation (filler loading of 3 wt% and GNPs:MWCNTs weight radio 1:2), 9.7 g of PMMA pellets were first dissolved in 150 ml THF under continuous sonication for 30 min. Hundred milligrams of GNPs and 0.2 g MWCNTs were dispersed in 100 ml THF by water bath sonication for 20 min, followed by ultrasonication with a wand sonicator for 10 min. Subsequently, 100 ml GNPs–MWCNTs/THF suspension obtained above were gradually poured into the PMMA solution. After being carefully mixed for 10 min, the mixture was put into methanol under vigorous stirring to facilitate precipitation. The cotton-like materials were filtered and dried in oven at 75 °C until the weight reached a constant value. Nanocomposites for the following foaming were then molded with Dongguan BL-6170-20T hot press. For comparison, neat PMMA and PMMA composites with single fillers were also developed in the same way.