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Morphologies and electromagnetic interference shielding performances of microcellular epoxy/multi-wall carbon nanotube nanocomposite foams

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Microcellular epoxy/multi-wall carbon nanotube (EP/MWCNT) composite foams loaded with 0.5, 1.0, 2.0 and 3.0 wt% of multi-walled carbon nanotubes (MWCNTs) were prepared by a batch foaming process with supercritical carbon dioxide ($scCO_2$). The morphologies of EP/MWCNT composite foams were analyzed by scanning electron microscopy (SEM). It was found that there was a synergic effect between the formation of microcellular structure and the addition of MWCNTs on improving the performances of EP/MWCNT composite foams. The addition of MWCNTs promoted the formation of microcellular structure, and the growth of cells in turn induced the redistribution of MWCNTs. Furthermore, the electromagnetic interference (EMI) shielding effectiveness (SE) of EP/MWCNT solid and foamed composites was investigated. The results indicated that the foaming improved the specific EMI SE from 5.2 to 21.3 dB cm^3/g at the MWCNT content of 1.0 wt%. The introduction of MWCNTs and microcellular structure synergistically enhanced the EMI shielding performance of epoxy-based composites.

1. Introduction

The electromagnetic interference (EMI) shielding of radio frequency radiation has been a serious concern in modern society, because of the increasing use of commercial, military, communication equipment, and personal digital devices. Thus the development of novel EMI shielding materials has received increasing attention in both the scientific and industrial fields [1–3]. Traditionally, EMI prevention has mainly relied on metal-based materials, which inevitably suffer from disadvantages of high density, low corrosion resistance and bad processability [4–6]. Compared to metal-based EMI materials, polymer nanocomposites are becoming more attractive, because they not only exhibit high electrical conductivity and enhanced mechanical properties, but also possess low density, good processability, and resistance to corrosion et al [4,7,8].

Based on material and energy saving, the researchers have introduced microcellular structures into polymer nanocomposites to further decrease their density [9–11]. Interestingly, due to the existence of cellular structure, electrically conductive fillers form an electron transport path through cell walls and struts, resulting in an increase in electrical conductivity of polymer foams [3,12,13]. In addition, to achieve good shielding effectiveness, the electrically conductive fillers should have small unit size, high conductivity and large aspect ratio [1,14]. The carbon nanotubes (CNTs) fit the above demands completely. CNTs with nanometer-scale diameter and large aspect ratio, show an exceptional structural, mechanical, and electrical properties compared to the conventional metal and carbon fillers (e.g., silver nanowires and carbon black) [10,15]. Moreover, a significant advantage of CNT over two-dimensional (2D) conducting fillers (e.g., graphene nanosheets) is that its one-dimensional (1D) tubular structure makes it easier to construct more macroscopic electron transport paths at the same filler concentration [16].

Taken together, the introduction of microcellular foams and carbon nanotubes seems promising for the design of materials for EMI shielding applications. For example, Thomassin et al. [17] prepared multi-walled carbon nanotube filled polycaprolactone (PCL/MWCNT) foams with shielding efficiencies as high as 60–80 dB, presenting low reflectivities at very low vol% of MWCNTs (0.25 vol%). Tran et al. [15] reported conductive microcellular foams

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of poly(methyl methacrylate)/carbon nanotubes (PMMA/CNT) nanocomposites, and established structure/properties relationships for further optimizing EMI shielding performances of the materials. Ameli et al [18] fabricated nano/microcellular polypropylene/multiwalled carbon nanotube (PP/MWCNT) composites, and proposed that the microcellular materials were efficient for EMI shielding applications with the conductivity increasing to a range (10^{-3}–10^{-2} S cm^{-1}) when the MWCNT contents were higher than 0.4 vol%. Monnereau et al. [19] prepared polycarbonate/carbon nanotube (PC/CNT) nanocomposites foams with a gradient morphology that could be used as efficient EMI absorbers and the experimental results indicated the gradient foams were advantageous for EMI shielding compared to the homogeneous foams. Therefore, the combination of carbon nanotubes and microcellular foams has provided a viable option to fabricate EMI shielding materials.

However, the polymer nanocomposite foams always involve thermoplastic polymers, while the thermosetting polymer nanocomposite foams are rarely reported, especially epoxy-based nanocomposite foams. Considering that epoxy resin displays some attractive features including good adhesion to substrates, chemical and heat resistance, good processability, low shrinkage and low toxicity, the application of epoxy resin for preparing polymer nanocomposite foams is a good choice for the design of EMI shielding materials [20–22].

According to the previous researches, the difficulty of the preparation of epoxy-based foams is how to control the foaming process, because the viscosity of epoxy rapidly increases due to the curing reaction [23]. Recently, Ito et al [24] prepared microcellular epoxy foams using a temperature-quench physical foaming method with subcritical CO_2, and demonstrated that the microcellular epoxy foams could be obtained by maintaining the molecular weight between crosslinks (M_C) above 10^4 g mol^{-1} and the complex modulus above 6×10^8 Pa. In addition, CO_2 is stable, non-toxic, non-flammable, low-cost, easy to obtain from air and recycle, and has an easily attainable low critical temperature and moderate critical pressure [25]. In our earlier work [21,22,26], the physical foaming method with supercritical CO_2 ($scCO_2$) was used for the fabrication of thermoplastic polymer foams. It's a novel attempt of using the supercritical carbon dioxide technology in foaming of thermosetting epoxy-based materials.

In this work, the epoxy/multi-wall carbon nanotube (EP/MWCNT) nanocomposites were prepared using compression molding process. Then the nanocomposites were foamed using the supercritical carbon dioxide technology. The morphological and microstructural properties were characterized to establish a correlation between microstructure and MWCNT contents of the foamed EP/MWCNT nanocomposites, then the effect of MWCNTs on foaming was investigated. The effects of foaming on the electrical conductivity and EMI shielding effectiveness (SE) were also discussed to obtain the relationships between the electrical properties and microstructure of the EP/MWCNT solid and foamed composites.

2. Experimental

2.1. Materials

The epoxy resin used in this work is diglycidyl ether of bisphenol A (DGEBA), CYD-014U, with an epoxy value of 0.11–0.14 mol per 100 g, supplied by Yueyang Petrochemical Ltd., China. The curing agent, 2-ethyl-4-methylimidazole (2E4MZ) were purchased from Xiya Reagents Co. Ltd., China. Multi-walled carbon nanotubes (OD > 50 nm, length: 10–20 μm, SSA > 40 m^2/g, carbon purity > 90%) were supplied by Chengdu Organic Chemicals Institute, Chinese Academy of Sciences. Carbon dioxide (CO_2), with purity 99.99%, was supplied by Changte Airproduct Co., Ltd., China. CO_2 was introduced into the stainless steel vessel by a positive displacement pump (Lab Alliance Model SFC-24).

2.2. MWCNT surface oxidization

The MWCNTs needed a carboxylation treatment before using. The MWCNTs were firstly sonicated in a proportion of 2.5 g MWCNTs in 160 mL of the sulfuric-nitric acid mixture (3:1 by volume, respectively) for 4 h at ambient temperature. The mixture was then heated to maintain boiling in a refluxing system for 6 h. Subsequently, the treated MWCNTs were washed with water and vacuum-filtrated using mixed cellulose ester membranes (pore size: 0.22 μm) for multiple times until pH = 7. Finally, the modified MWCNTs were dispersed in water and freeze dried.

2.3. Preparation of EP/MWCNT nanocomposites

A solution blending and compression molding process was chosen to prepare the MWCNT-epoxy nanocomposites. That involved (a) dissolving 25 g DGEBA in 25 mL acetone at room temperature with a magnetic stirrer for 1 h, simultaneously dispersing the appropriate amount of MWCNTs in acetone by sonication for 1 h, (b) adding MWCNT-acetone suspension to the epoxy solution and continuing stirring for 1 h, (c) adding 2E4MZ (which was 5% by weight of DGEBA) to the solution and continuing stirring for 10 min (the resultant liquid was pale yellow, clear, homogeneous and viscous), (d) repeatedly degassing the mixture in a vacuum drying oven at 40 °C until the viscous liquid expanded and formed foamy solid, (e) crushing the foamy solid into powder and loading it in a $8 \times 8 \times 2.8$ mm^3 aluminum-made square cavity mold and compression moulding at 80 under 15 MPa for 30 min, (f) placing the pre-cured composite with mold in a drying oven and curing it for 4 h at 150 °C to reach essentially complete cure, (g) cooling slowly to room temperature and then demoulding, (h) cutting the cured sheets into the desired size for foaming and further testing.

2.4. Foaming with supercritical carbon dioxide

A batch foaming process was used to prepare microcellular EP/MWCNT nanocomposites foams. The nanocomposite sheets were placed into the high-pressure autoclave (Tongchan instruments, internal volume 500 mL), which was heated to 45 °C and pressurized to 8 MPa, then maintained the stable condition for 3 days to ensure the samples with sufficient sorption amount of CO_2. When the sorption process ended, the samples were removed from the autoclave and foamed by being immersed in oil at 120 °C in prescribed time (10 s, 20 s, 40 s and 60 s), then they were immediately put into room temperature water to stabilize the foams.

2.5. Characterization

The insolubility tests were conducted to measure the gel fractions (insoluble fractions) of cured epoxy resins and composites. Approximately 1.0 g of the non-foamed sample was soaked in 100 mL of acetone for 12 days at 25 °C. The acetone was replaced after 3 days with fresh acetone. After soaking, the sample was dried at 100 °C in a vacuum drying oven. Then the weight of the sample was measured when the weight was stabilized. The gel fraction (F_g) was calculated as: