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Microwave absorbing properties of alternating multilayer composites consisting of poly (vinyl chloride) and multi-walled carbon nanotube filled poly (vinyl chloride) layers

Xiaoyan Gao, Jiang Li*, Yuan Gao, Shaoyun Guo, Hong Wu, Rong Chen

The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu, Sichuan 610065, China

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The application of dielectric lossy absorbent, multi-walled carbon nanotubes (MWCNTs) filled polymer as a microwave absorbing material (MAM) is limited because of the high loading level. Optimizing the distribution of MWCNTs in a polymeric matrix was a key factor in obtaining better microwave absorption while keeping the MWCNT content low. According to the theory of transmission lines, we designed an alternating multilayer structure with MWCNTs distributed in the continuous and parallel layered spaces of a poly (vinyl chloride) matrix to improve its microwave absorbing properties. The effect of the layer number on the microwave absorbing capacity was studied by theoretical calculations and experimental measurements. The results showed that the −10 dB absorbing bandwidth and the absolute value of the minimum reflection loss of alternating layered samples were higher than those of a conventionally blended sample with the same MWCNT content and increased with the increasing layer number. This improvement of the microwave absorbing capacity was mainly attributed to the multi-reflection of microwaves between the layered interfaces. Interestingly, the matching frequency of the alternating layered MAMs could be adjusted by changing the layer number. The measured microwave absorbing properties were well predicted by the theoretical model. In addition, the mechanical properties improved with an increasing number of layers.

1. Introduction

With the escalation of electromagnetic pollution and the development of stealth technology for military platforms, much attention has been devoted to microwave absorbing materials (MAMs) [1–3]. Therefore, polymeric composites have been widely used in the design and realization of MAMs because they can be easily processed by many methods to obtain desirable shapes and simultaneously achieve good mechanical properties and tailored wideband microwave absorbing performance [4–6].

Currently, most of the polymer-based MAMs have been prepared by addition of one type of absorbent into a matrix [7–9]. To obtain low reflectivity, numerous absorbents are generally required; however, this would tremendously decrease the processing properties of the composites, limiting the applications of these MAMs as a result of heavy weight and poor mechanical properties. Therefore, it has been the goal of many researchers to enhance the absorbing effectiveness of MAMs while maintaining a low absorbent content.

Modification of the absorbent or employing a new absorbent [10–12], which can adjust the electromagnetic parameters to achieve better microwave absorption in a wide band, were considered as two efficient methods to decrease the concentration of the absorbent. Nevertheless, these techniques had some problems, such as complicated preparation processes and high costs.

The distribution of functional fillers in a matrix has a significant effect on the functionalization and mechanical properties of polymeric composites [13–16]. Therefore, some scientists have investigated the relationship between the dispersion of absorbents and microwave absorbing performance [17–19]. Most of the results have indicated that a uniform distribution of absorbents may improve the absorbing properties of MAMs [20]. For example, F. Nanni et al. used two different methods [17], employing an organic solvent that was removed either by evaporation or filtration, to prepare carbon nanofiber/epoxy composites. The resulting microstructures of the sample in the two cases showed good and poor

* Corresponding author.
E-mail address: li_jiang@scu.edu.cn (J. Li).

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dispersion, respectively, whereas the former achieved lower reflectivity with equal filler content. However, some researchers found that proper agglomeration was beneficial for the absorption of microwave radiation [21].

As a special morphology, the laminar structure with absorbents preferentially distributed in each layer was regarded as a potential choice for fabricating MAMs [22]. Based on whether the content of absorbents in the filled layer is changed, the layered MAMs can be divided into two types, i.e., gradient or alternating multilayer MAMs [23–26]. For example, Huynen et al. designed a gradient multilayer MAM with a gradually increasing concentration of carbon nanotubes (CNTs) in a foamed polycaprolactone (PCL) matrix [23]. With the same CNT content, the reflectivity of the gradient multilayer CNT/PCL composites was 5 dB lower than that of the single layer MAMs with CNTs evenly dispersed in the PCL because a gradual increase in conductivity allowed the wave to propagate deeper into the material.

According to the theory of transmission lines, which will be further discussed in the results and discussion section, the alternating multilayer structure with neat polymer and absorbent-filled polymer layers alternatively arranged can also lead to MAMs with good absorbing effectiveness [24]. For example, Lee et al. found that two-layer MAMs consisting of a glass/epoxy layer and a CNT-filled glass/epoxy layer exhibited excellent microwave absorbing properties [21]. Although the potential advantages of the alternating multilayer structure have been discovered in the fabrication of MAMs, to the authors' best knowledge, the MAMs with a higher layer number have rarely been studied and the relationship of microwave absorbing properties and layer number is still ambiguous.

Our previous work showed that the performance of alternating multilayer composites, such as conductive [27], dielectric [28] and mechanical [29] properties, depends heavily on the number of layers and that these properties would be improved with an increasing number of layer. In these studies, the parallel arrangement of layered interfaces in the alternating multilayer composites played a key role in the improvement of material properties. For example, the dielectric permittivity significantly increased with increasing layer number because of the accumulation of electrical charges at the interfaces, providing a potential application in microwave absorption [28]. Moreover, the mechanical properties of alternating multilayer composites, including the modulus, yield and tensile strength, were also enhanced because of the synergetic effect provided by the layered interfaces [29]. These layered interfaces dissipate the microwaves as a result of the impedance mismatch between the different layers. Therefore, it was proposed that the alternating multilayered design of MAMs could greatly change microwave absorbing properties.

In this work, we fabricated alternating multilayer MAMs with dielectric lossy absorbents alternately distributed in the continuous layered space of the polymer matrix and studied the effect of layer number on the microwave absorbing and mechanical properties. Polyvinyl chloride (PVC) was used as the polymer matrix because of its desirable properties, such as low-cost, high mechanical strength and convenient production [30]. Multi-walled carbon nanotubes (MWCNTs) were selected as the dielectric lossy absorbent because of their large aspect ratio and fascinating physicochemical properties [31].

2. Experimental

2.1. Materials

The MWCNTs (NC 7000™, nanocyl company) used in this study were produced by the Chemical Vapor Deposition process with an average diameter of 9.5 nm, an average length of 1.5 μm, a carbon purity of 90%, a metal oxide content of 10% and a surface area of 250–300 m^2/g. The PVC resin (SG-5, Tianjin Dagu Chemical Factory, China) was of commercial suspension grade with a degree of polymerization of 1000.

2.2. Specimen preparation

Five single-layer MWCNTs/PVC samples (CNT-0, CNT-1, CNT-5, CNT-10, and CNT-15) filled with 0, 1, 5, 10, and 15 phr (parts per hundred of resin), respectively, were fabricated as described below. The MWCNTs were first blended with PVC on a two-roll mill at 140 °C for 10 min. Then, the blends were compression molded into sheets under 10 MPa at 170 °C for 10 min and cooled to ambient temperature under the same pressure.

The alternating multilayer samples, shown schematically in Fig. 1, were prepared by hot compression of CNT-0 and CNT-10 layers with different thicknesses (1, 0.5, and 0.25 mm). The total thickness, width and length of the samples were 2, 180 and 180 mm, respectively. CNT-0 and CNT-10 layers were arranged alternately along the Z direction and the thickness of each layer was the same. 2L, 4L and 8L denote samples with a layer number of 2, 4 or 8, respectively.

2.3. Characterization and testing

The electromagnetic parameters (complex relative permittivity and permeability) of CNT-0, CNT-1, CNT-5, CNT-10 and CNT-15, which were processed in toroidal samples with an outer diameter of 7.0 mm and an inner diameter of 3.04 mm, were measured by a vector network analyzer (N5230A, Agilent Technologies Co., LTD) in the 2–18 GHz range.

The MWCNT dispersions in samples CNT-0, CNT-1, CNT-5, CNT-10 and CNT-15 were observed by scanning electron microscopy (SEM, JEOL JSM-5900LV) under an accelerating voltage of 20 kV. The samples were cryofractured in liquid nitrogen and the fractured surfaces were coated with a layer of gold in a vacuum chamber prior to visualization by SEM.

The electrical resistivities of CNT-0, CNT-1, CNT-5, CNT-10 and CNT-15 were obtained using a programmable insulation resistance tester (YD9820, Changzhou Yangtze electronics co., LTD) consisting of a multivoltage source and resistance meter. The sizes of all samples were 100 mm in length (l), 10 mm in width (w) and 2 mm in height (h). The contact faces were coated with copper paste to reduce contact resistance between the sample edges and the electrode of the conduction tester. A constant voltage of 50 V was applied to the samples unless otherwise specified. The electrical resistivity, ρ, was calculated by the following equation:

$$\rho = R_v \frac{wh}{l}$$

where R_v is the tested electrical resistance. At least five samples were tested for each condition, from which average values were calculated.

The alternating layered structures of 2L, 4L and 8L MAMs were observed by polarized optical microscopy (POM, Leica, DM2500P, Germany). A 20 μm slice for the POM observation was cut from each specimen using an ultrathin freezing microtome (Leica, RM2265, Germany).

The microwave absorbing characteristics of samples 2L, 4L and 8L were evaluated by directly measuring the reflection loss (R_L) with an N5230A vector network analyzer and standard horn antennas in an anechoic chamber in the testing frequency band of 2–18 GHz. The samples being tested were positioned on an