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Constructing multiple interfaces in polydimethylsiloxane/multi-walled carbon nanotubes nanocomposites by the incorporation of cotton fibers for high-performance electromagnetic interference shielding and mechanical enhancement

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ABSTRACT

Reflection of electromagnetic waves at multiple interfaces and then absorption in the matrices has been well demonstrated to efficiently improve electromagnetic interference (EMI) shielding of conductive polymer composites (CPC). In this study, a large number of multiple interfaces were constructed in polydimethylsiloxane/multi-walled carbon nanotubes (PDMS/MWCNT) nanocomposites by the incorporation of cotton fibers (CTF). The electromagnetic radiation was efficiently attenuated by the wave reflection at the multiple interfaces and then absorption at the interfaces of PDMS/CTF and CTF/MWCNT in the nanocomposites. The EMI shielding effectiveness (SE) of the PDMS/MWCNT nanocomposites with 2.0 and 3.0 vol% MWCNT increased from ~16 to ~30 dB, ~20 to ~41 dB by adding 15 vol% CTF, respectively. A relatively dense MWCNT network, which was also formed in the PDMS/MWCNT/CTF nanocomposites because of the volume occupation effect of CTF, resulted in the high electrical conductivity and low percolation threshold. For example, the electrical conductivity of the PDMS/MWCNT nanocomposites with 0.5 vol% MWCNT increased from 1.65×10^{-4} to 0.23 S/m, and the percolation threshold of the composites deceased from 0.44 to 0.2 vol% by the addition of 15 vol% CTF. In addition, the mechanical properties, especially the Young's modulus and tensile strength, of PDMS/MWCNT nanocomposites were enhanced by the incorporation of CTF and the flexible property was maintained because of the high interfacial interaction between PDMS and CTF and the high aspect ratio of CTF. Furthermore, the samples exhibited highly reliable EMI SE even after bending 6000 times, suggesting the potential application in body protection and flexible electronic devices.

1. Introduction

Conductive polymer composites (CPC) have been well demonstrated to be electromagnetic interference (EMI) shielding materials because of their light weight, low cost, excellent processability and high-performance EMI shielding [1–3]. The conductive fillers are dispersed in polymer matrix to form conductive networks, which can attenuate electromagnetic waves [4–6]. Graphene, graphene nanoplatelets and carbon nanotubes were usually used as conductive fillers [7–9]. When an electromagnetic wave strikes CPC, the total EMI shielding effectiveness (SE) can be defined as the logarithmic ratio of incoming (P_{in}) to outgoing power (P_{out}) of electromagnetic radiation [10]. Normally, reflection, absorption and multiple-reflection happen simultaneously in CPC to attenuate electromagnetic waves. At this respect, the total EMI SE can also be summarized of the absorption (SE_A), reflection (SE_R), and multiple reflection shielding effectiveness (SE_M) [11].

$$SE_{total} = 10\log(P_{in}/P_{out}) = SE_A + SE_R + SE_M$$

In a homogenous material, reflection shielding is related to mobile charge carriers (electrons or holes), while absorption shielding is dependent on the electrical or magnetic dipoles of materials [12]. The multiple-reflection represents the internal reflection within the shielding materials. The multiple-reflection can be ignored if the sample is thicker than the skin depth, because the reflected wave from the internal surface will be absorbed by the sample [13–16]. However, for CPC, the shielding mechanism becomes more complex due to the multiple interfaces in CPC [17–19]. For example, according to the mechanism in a homogenous material, the reflection shielding should

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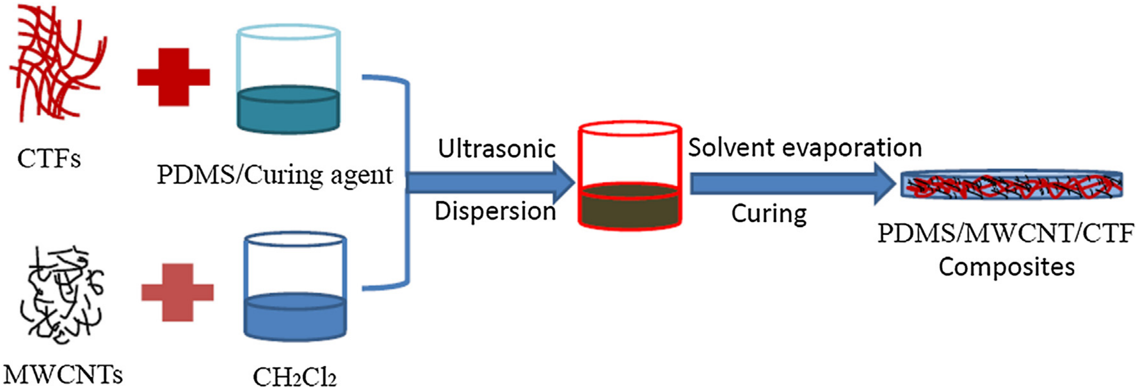

Fig. 1. Schematic description of the processing procedure for the PDMS/MWCNT/CTF composites.

be the primary shielding mechanism in CPC with high electrical conductivity. However, most CPC exhibited the absorption-dominated materials [20–25]. The distinguished mechanism between the homogenous materials and CPC was related to the multiple interfaces in CPC available for reflection and multiple-reflection [26–29]. The reflected electromagnetic wave from the multiple interfaces was attenuated by the absorption shielding in CPC. Therefore, to construct the large number of multiple interfaces is probably an efficient strategy to improve EMI SE of CPC.

The simple method to increase the number of interfaces is to increase the content of conductive fillers [30–32]. However, the high content of conductive fillers usually leads to the deterioration of mechanical and processing properties of CPC [33–35]. Therefore, construction of larger number of interfaces in polymer composites at low content of conductive fillers has been gaining great attention for the improvement of EMI SE. Double-percolation and segregated structures have been found to efficiently construct multiple interfaces, which enhanced EMI SE of CPC [36–42]. For the double-percolation structure, the conductive fillers are selectively located in one continuous phase or interfaces to get high conductivity and EMI SE [43]. For the segregated structure, the conductive fillers are selectively located in the continuous polymer phase or interfaces among the polymer particles [44–46]. As a result, the CPC with segregated structures has high electrical conductivity and EMI SE at low filler loadings [47–49].

In addition, the fast-growing micro-robots, electronic paper, foldable displays, and wearable devices urgently require the development of flexible or even stretchable EMI materials with high performance. Normally, rubbers and thermoplastic elastomers have serviced as flexible matrices to develop EMI materials with high flexible performance [50–56]. For example, the EMI SE natural rubber could reach 44.7 dB with a thickness of 250 μm and maintain high tensile strength and toughness by adding 70 wt% multi-walled carbon nanotubes (MWCNT) [57]. The waterborne polyurethane/20 wt% poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS) exhibited a high EMI SE of about 62 dB over the X-band frequency range at a film thickness of only 0.15 mm and also keeping an elongation at break of about 32.5% [58]. With the addition of 5 wt% hybrids of carbon nanotube/graphene, the minimum value of reflection coefficient for electromagnetic wave of polydimethylsiloxane (PDMS) reached −55 dB at 10.1 GHz without sacrificing the flexible property [59].

In this study, we developed a flexible conductive polymer composite with high performance EMI shielding via constructing a large number of multiple interfaces in the composites. The cotton fibers (CTF) were used to create the multiple interfaces because of the high interfacial interaction between PDMS and CTF [60–62]. PDMS and MWCNT were used as the flexible matrix and conductive fillers, respectively. The electrical conductivity and EMI shielding performance of the PDMS/MWCNT composites abruptly increased with the addition of CTF, which created a large number of multiple interfaces, including the interfaces of PDMS/CTF and CTF/MWCNT. The electromagnetic waves were reflected at the multiple interfaces and finally absorbed in the composites. Furthermore, the Young's modulus and tensile strength of PDMS/MWCNT composites were enhanced by the incorporation of CTF and the flexible property was maintained because of high aspect ratio of CTF and the high interfacial interaction between PDMS and CTF.

2. Experimental

2.1. Materials

Polydimethylsiloxane (PDMS, Sylgard 184), including a base elastomer and curing agent, was purchased from Dow Corning (USA). Cotton fibers (CTF) with a diameter of ~5 μm, the aspect ratio of ~2500 and a density of 0.44 g/cm^3 were obtained from Chongqing Shang Kun Medical Equipment Co., Ltd. (China). Multi-walled carbon nanotubes (MWCNT, NC 7000, purity > 90%) with an average diameter of ~9.5 nm and an average length of ~1.5 μm were provided by Nanocyl S.A (Belgium).

2.2. Preparation

For PDMS/MWCNT composites, the MWCNT and PDMS/curing agent were first dispersed in dichloromethane with ultrasonic assistance. The weight ratio of PDMS base to curing agent was 10:1. Subsequently, the MWCNT and PDMS/curing agent solution were directly mixed to form a uniform mixture, and then dichloromethane was removed, degassed and finally cured at 80 °C for 2 h to get the PDMS/MWCNT composites with 1.2 mm thickness. The pure PDMS sheets without MWCNT were also prepared at the same procedure.

For PDMS/MWCNT/CTF samples, the cotton fibers were first mixed with PDMS/curing agent to let CTF well coated PDMS base and curing agent. After that, the PDMS/curing agent/CTF mixture was mixed with the MWCNT/dichloromethane solution with ultrasonic assistance to get uniform dispersion. The weight ratio of PDMS base to curing agent was also 10:1. The dichloromethane was removed and the mixture was degassed and cured at 80 °C for 2 h to obtain the PDMS/MWCNT/CTF composites, as shown in Fig. 1. The sheets with a thickness of 1.2 mm were fabricated for the conductive and mechanical investigation.

2.3. Characterization

Field-emission scanning electron microscope (SEM, JEOL, JSM-7800F) was used to investigate the dispersion of CTF and MWCNT distribution in the PDMS elastomers. The accelerating voltage was 5 kV. Before the SEM observation, the samples were firstly cryo-fractured in liquid nitrogen, and then coated with a layer of platinum in a vacuum chamber. The electrical conductivity and percolation threshold of the samples were evaluated by a digital high resistance machine (PC68,