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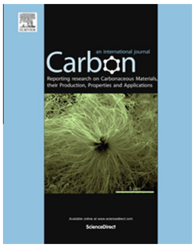

Electromagnetic interference shielding properties of polymer-grafted carbon nanotube composites with high electrical resistance

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ABSTRACT

Poly(methyl methacrylate) (PMMA)-grafted multiwalled CNTs were prepared, and then dispersed into additional PMMA matrix, yielding highly insulated PMMA–CNT composites. The volume resistivity of PMMA–CNT was as high as $1.3 \times 10^{15}\ \Omega$ cm even at 7.3 wt% of the CNT. The individual CNTs electrically-isolated by the grafted PMMA chains in PMMA–CNT transmitted electromagnetic (EM) waves in the frequency range of 0.001–1 GHz, whereas the percolated CNTs in a conventional composite prepared by blending PMMA with the pristine CNTs strongly shielded the EM waves. This result suggests that the intrinsic conductivity of the CNT itself in PMMA–CNT does not contribute to the EM interference (EMI) shielding in the frequency range of 0.001–1 GHz. On the other hand, PMMA–CNT exhibited EMI shielding at the higher frequency range than 1 GHz because the dielectric loss of the CNT itself was rapidly increased over 1 GHz. At 110 GHz, PMMA–CNT with 7.3 wt% of the CNT had EMI SE of as high as 29 dB (0.57 mm thickness), though is slightly lower than that of the percolated conventional composite (35 dB). Thus, it is demonstrated that the highly insulated PMMA–CNT has the good EMI shielding at extremely high frequency range (30–300 GHz).

1. Introduction

Polymer/carbon nanotube (CNT) composites have been paid much attention as electromagnetic interference (EMI) shielding materials because the CNTs impart high electrical conductivity and good mechanical properties to the polymer materials at low loading of the CNT [1–5]. It is well-known that the electrical conductivity enhances the EMI shielding, and the highly conductive polymer/CNT composites exhibit superior EMI shielding effectiveness (SE) [6–29]. The polymer/CNT composite becomes conductive owing to the formation of a three-dimensional conductive network of the CNTs within the polymer matrix when the CNT content exceeds a critical value, known as a percolation threshold [1–5]. At over the percolation threshold, the CNTs approach each other within several nanometers, allowing efficient electron tunneling between the CNTs (tunneling conduction) [30,31]. This conductive CNT network can strongly interact with the EM waves. In general, as mentioned above, good EMI shielding materials are always electrically conductive; this fact is not limited to the polymer/CNT composites [32–38]. On the other hand, electronic materials including

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the EMI shielding materials often require electrical insulation (e.g. EMI shielding for high frequency module and signal transmission cable). For such applications, therefore, the EMI shielding materials have to be covered with other materials with high electrical resistance. Is it impossible to produce a polymer/CNT material with both of high EMI SE and electrical insulation?

Also, it is suggested by some research groups that the electrical conductivity of the polymer/CNT composites is not the scientific criterion for the EMI shielding because the shielding does not require the conductive network of the CNTs; the mobile electrons in the CNTs interact with the EM waves [15,18,24,39]. Therefore, the conductivity of the CNT itself is essential for the EMI shielding, and the conductive network of the CNTs only improves the EMI shielding. However, the issue of the relationship between the conductivity of the CNT itself and the EMI shielding has been still unclear because the formation of the conductive networks is inevitable for the polymer/CNT composites owing to the extremely low percolation threshold of the CNTs. If the percolation of the CNTs can be forbidden, the clear understanding of the issue would be obtained, and a polymer/CNT material with both of high EMI SE and electrical insulation might be produced. A solution to prevent the percolation is polymer-grafting on the surface of the CNTs. Recently, we have reported the ultrahigh electrical resistance of poly(cyclohexyl methacrylate) (PCHMA)/multiwalled CNT composite system where all the PCHMA chains were tethered to the CNT surface [40]. The grafted polymer chains isolated the individual CNTs at a sufficient distance (>10 nm) to prevent the tunneling conduction between the CNTs [41].

Here, we report the interaction of EM waves with individual CNTs electrically-isolated by grafted polymer chains. In this study, poly(methyl methacrylate)-grafted multiwalled CNTs (CNT@PMMA) were prepared using our surface-initiated atom transfer radical polymerization (SI-ATRP) technique, and then dispersed into additional (ungrafted) PMMA matrix, yielding highly insulated polymer/CNT composites (PMMA–CNT). The EMI properties of PMMA–CNT were characterized in the broad frequency *f* range of 0.001–110 GHz, and compared to those of conventional composites prepared by blending PMMA with the pristine CNTs (PMMA/CNT). To our knowledge, this is the first report that the EMI properties are investigated for a polymer/CNT composite system with high electrical resistance.

2. Experimental

2.1. Sample preparation

Multiwalled CNT with an average diameter and length of 10 nm and 1.5 μm, respectively, was obtained from Nanocyl SA. The density of the CNT was determined to be 1.8 g cm^{-3} by pycnometry. ATRP-initiator modified CNT (CNT-Br) was synthesized as previously reported in detail [40]. An example of the procedure of the SI-ATRP of MMA using CNT-Br was as follows: *N*,*N*-dimethylacetamide (160 ml) was added to CNT-Br (1.51 g) and CuBr (85.8 mg, 600 μmol) in a N_2 atmosphere. After sonication of the mixture, 2,2′-bipyridyl (187 mg, 1.2 mmol) in MMA (80 ml) was added, and the solution was kept at 60 °C for 9 h. The resultant CNT@PMMA was precipitated in methanol and freeze-dried by benzene.

PMMA–CNT was prepared by blending CNT@PMMA with an additional PMMA matrix ($M_n = 15$ k). First, CNT@PMMA and the PMMA matrix were added in benzene and homogeneously dispersed by sonication. The dispersion was quickly frozen by liquid N_2, and then freeze-dried under vacuum. Similarly, PMMA/CNT was also prepared by blending PMMA with the pristine CNTs. PMMA/CNT and PMMA–CNT were molded by hot pressing at 130 °C into 15 mm square specimens with a thickness of ~0.85 mm for direct current (DC) electrical resistance and impedance measurements, or 150 mm square specimens with a thickness of ~0.57 mm for two types of EMI SE measurements.

2.2. Measurements

Morphologies of CNT@PMMA and PMMA–CNT were observed using scanning electron microscopes (S-4300 and S-5500, respectively, Hitachi) operated at an accelerating voltage of 2 kV. For the SEM observation of PMMA–CNT, the cross-sections of the molded composites that had been planed using an ultramicrotome, were slightly etched with oxygen plasma in order that the PMMA matrix on the surface was removed out.

The DC resistance of the composites was measured at a voltage of 500 V using a megohmmeter (SM-8220, Hioki) for PMMA–CNT with high resistance and a multimeter for PMMA/CNT with low resistance in combination with a test fixture with 10 mm square copper electrodes. In order to minimize the contact resistance between the electrodes and a specimen, two gold electrodes (11 mm square) were deposited by sputter coating on the top and bottom of the specimen at a distance of 2 mm from the edge of the specimen. The measurement system was calibrated with a copper specimen (1 mm thickness) on which the same gold electrodes were deposited in order to remove the resistance of the gold electrodes and the total contact resistances.

Dielectric spectra of the composites were obtained in the *f* range of 0.001–1 GHz using an impedance analyzer (E4991A, Agilent) equipped with a commercially available test fixture (16453A, Agilent). The test fixture was calibrated with a poly(tetrafluoroethylene) film to be minimized contact impedance between the electrode and a specimen.

EMI SE of the composites was obtained by two types of methods depending on the *f* range. In the *f* range of 0.001–1 GHz, the KEC method was used [42]. The KEC method was developed by Kansai Electronic Industry Development Center in Japan. The set-up consisted of a test fixture (MA8602B, Anritsu), an RF amplifier (8247A, Agilent), an RF preamplifier (MH-648A, Anritsu), and a spectrum analyzer (R3361C, Advantest). The test fixture is based on a transverse electromagnetic (TEM) cell that is divided into two units, and a specimen is sandwiched between the two units. In the higher *f* range than 1 GHz, the free space method was used [10]. For the free space method, 5 bands, 5.6–8.2 GHz (C band), 12.4–18.0 GHz (Ku band), 26.5–40 GHz (Ka band), 50.0–68.0 GHz (V band), and 75.0–110.0 GHz (W band), were scanned. S parameters were obtained by combination of a network analyzer (N5227A, Agilent) and a millimeter-wave controller (N5361A, Agilent). This system including spot-focusing horn lens antennas was cali-