Electromagnetic Interference Shielding Efficiency in the Range 8.2-12.4 GHz of Polymer Composites with Dispersed Carbon Nanoparticles

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Abstract

In the present work, electromagnetic interference shielding properties of polymer composites with dispersed cup-stacked carbon nanotubes, graphite nanoparticles and carbon black were investigated. The polymer composites with carbon nanoparticles content from 1 to 5 w% were successfully prepared by the coagulation method, and composite sheets with thickness from 0.25 to 0.77 mm were formed by the hot press technique. The electromagnetic interference shielding efficiency measured in the frequency range of 8.2~12.4 GHz (X-band) of cup-stacked carbon nanotubes/polymer composite was considerably higher than that of carbon black and graphite nanoparticles polymer composites at the same contents of carbon nanoparticles, and contribution of absorption to the shielding efficiency was found to be higher than that of reflection.

Introduction

Carbon materials have been intensively investigated as electromagnetic interference (EMI) shielding materials [1-6]. Colloidal graphite has been applied in shielding pastes [2], and conductive carbon black has shown good characteristics in composite radar absorbing structures [3] and in rubbers composites at high content [4]. Recently multi-walled carbon nanotubes (MWCNT) have attracted a lot of attention from the viewpoint of their potential application as EMI shielding additives to polymers due to their high shielding characteristics at low contents [5]. However, one of difficulties in dealing with carbon nanotubes is their dispersibility in polymers, which can strongly influence shielding characteristics of the composites [6]. Quality of shielding is decided by properties of an active component (carbon nanotubes) and its distribution (dispersibility, connectivity and uniformity) in the matrix (polymer). To achieve better distribution, both the method of preparation and dispersibility of carbon nanotubes themselves are important. A new type of carbon nanotubes, which is known to have improved dispersibility in solvents, is cup-stacked carbon nanotubes (CSCNT) [7]. CSCNT are different from MWCNT, which are formed by graphene sheets rolled into coaxial tubes, in arrangement of graphene layers. CSCNT consist of stacked graphene truncated cones organized into a long tube. As a result CSCNT have abundant active edges on their surface, which promote their dispersibility in solvents. Different arrangement of graphene layers leads to difference in other properties such as electrical conductivity, namely while MWCNT are good conductors, CSCNT are reported to have semiconducting characteristics [7]. Since it is well known that electrical conductivity strongly influences EMI shielding efficiency (SE) [5], it would be very interesting to investigate CSCNT shielding characteristics. However, up to now no studies have been performed on CSCNT from the viewpoint of their EMI shielding properties.

The method of carbon nanoparticles/polymer composite preparation, applied in the present work, is a coagulation method [8]. The Single-Walled Carbon Nanotubes (SWCNT)/polymer composites produced by the method have demonstrated

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superior electromagnetic shielding characteristics comparing to those made by melt-extrusion method [6].

The purpose of the present work is to investigate EMI shielding properties in the range of 8.2 to 12.4 GHz (X-band) of polymer composites prepared by the coagulation method with three kinds of dispersed carbon nanoparticles: carbon black, graphite nanoparticles and CSCNT.

Experimental

The carbon nanoparticles/polymer composites were prepared by the coagulation method, described in [8]. As a polymer matrix poly-methyl-methacrylate (PMMA, MW: 120000, Sigma Aldrich) was used. Carbon black (Mitsubishi Chemicals, Ltd.), graphite nanoparticles (SEC Carbon, Ltd.), and CSCNT (Sankei Giken, Ltd.) powders were used as received. PMMA (7.3 g) was dissolved in 100 ml of DMF, and then carbon nanoparticles were suspended in the solution under ultrasonic treatment. Thus obtained stable dispersion was poured into 300 ml of water, which caused immediate coagulation of the polymer and trapping carbon nanoparticles due to their insolubility in water/DMF mixture. After filtration of the coagulated composites, they were dried in vacuum at 120 degrees C for 12 hours. Then the composites were hot-pressed into disc-like sheets with diameter about 5 cm and thickness from 0.25 to 0.77 mm.

The particle size and morphology of carbon nanoparticles were observed using Scanning Electron Microscope (SEM, JSM-6610LA, JEOL). Small amount of the powders was pressed onto a conductive carbon film and observed at 10 kV accelerating voltage. The uniformity of the composite sheets was checked by a digital optical microscope (Keyence VHX-600) in the transmission mode. The thickness of the sheets for the observation was less than 1 μm. Shielding efficiency was measured using an Agilent Vector Network Analyzer (VNA, model E8364A). The samples were fixed between two waveguide ports, connected to the ports of VNA, and power of transmitted and reflected waves was measured in the frequency range of 8.2~12.4 GHz (X-band).

Results and discussion

According to the observation by SEM, shown in Fig. 1, carbon black represents round shaped particles with mean size about 100 nm; graphite nanoparticles have flake shape with flake size less than 5 micron and thickness of 100 nm; CSCNT have diameter about 50 nm and length from 1 micron to several microns.

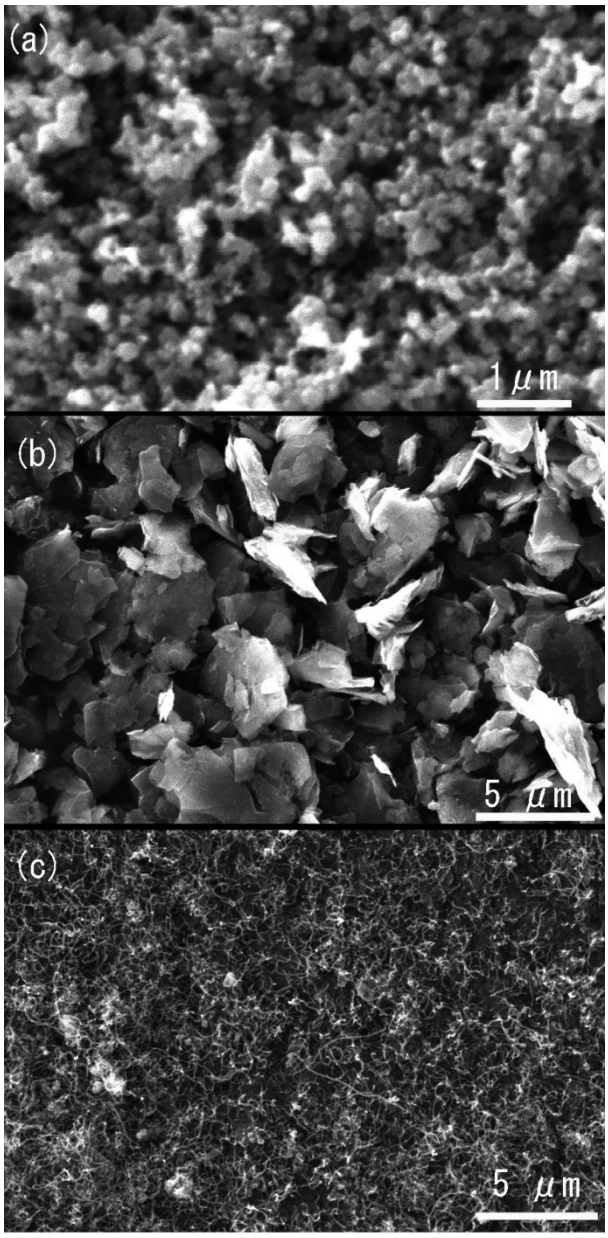

Fig. 1. SEM images of carbon black (a), graphite nanoparticles (b), and CSCNT (c).

Obtained composites represented smooth black sheets with uniformly dispersed carbon nanoparticles. The optical microscope images of the composites sheets with carbon nanoparticles content of 1 w% are shown in Fig. 2. The distribution of carbon black (Fig. 2 (a)) and CSCNT (Fig. 2 (c)) in the composite sheets appear to be

more homogeneous than that of graphite nanoparticles (Fig. 2 (b)). Mean particle size calculated from the optical images was 720±120 nm for carbon black, 930±370 nm for CSCNT, and 2200±1100 nm for graphite nanoparticles.

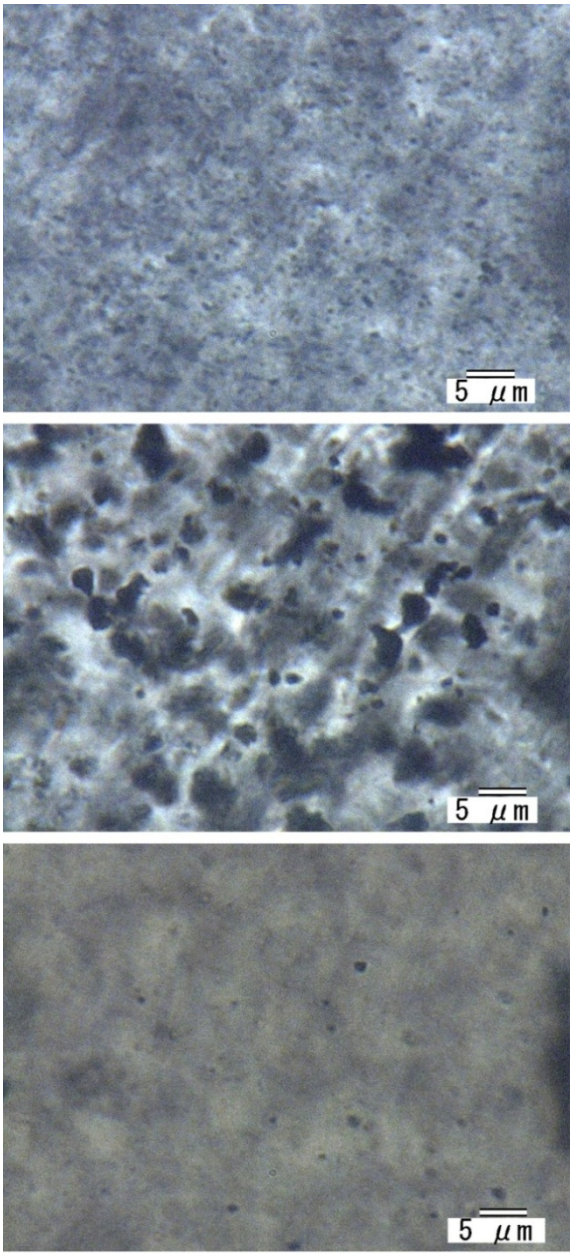

Fig. 2. Optical images of polymer sheets with dispersed carbon black, 1 w% (a), graphite nanoparticles, 1w% (b), and CSCNT, 1 w% (c).

Results of the SE measurements are shown in Figs 3-5. SE is the logarithm of the ratio of the incident power E_I to the transmitted power E_T, and it is commonly expressed in decibels (dB):

$$SE = 10 \cdot \log(E_I/E_T)$$

There are three main mechanisms of EMI shielding: reflection, absorption and multiple-reflection:

$$SE = SE_A + SE_R + SE_{MR},$$

where SE_A is the shielding efficiency by absorption, SE_R is the shielding efficiency by reflection, and SE_{MR} is the shielding efficiency by multiple-reflection.

For reflection of the electromagnetic waves by the shield, the shield must have mobile charge carriers; it means it must be electrically conductive. The reflection is the primary mechanism of shielding by metals. For absorption of the radiation by the shield, there must be electric or magnetic dipoles capable to interact with incident electromagnetic waves. Materials like Fe_3O_4 or mumetal show high shielding characteristics due to effective absorption. The third mechanism is multiple-reflection, when incident electromagnetic waves are reflected by various interfaces existing in the shield. This mechanism can play a significant role in composite materials with dispersed particles possessing high surface area.

Figure 3 demonstrates transmission SE (total SE), reflection SE_R and absorption SE_A spectra of CSCNT/polymer composites in X-band. The content of CSCNT here is 4 w% and thickness of the composite sheet is 0.77 mm. The maximum total SE was 3.0 dB at 12.1 GHz, maximum adsorption (1.9 dB) was at 12.0 GHz, and maximum reflection at 8.2 GHz (1.3 dB). It can be seen from the spectra that excluding frequencies lower than 9.2 GHz main contribution to SE was provided by absorption of electromagnetic radiation.

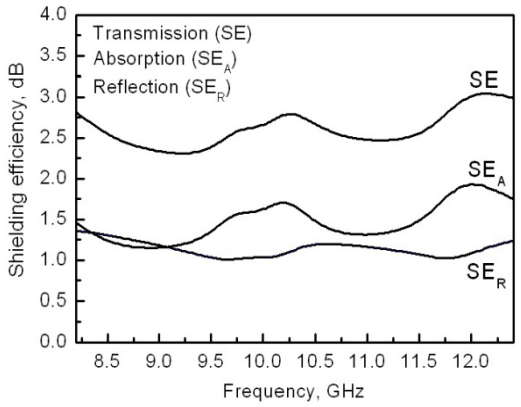

Fig. 3. Transmission, absorption and reflection of CSCNT(4 w%)/polymer composite (thickness 0.77 mm).

Calculated by averaging SE values measured between 8.2 and 12.4 GHz, mean EMI SE of carbon nanoparticles/dispersed polymer composites as a function of the nanoparticles content is shown in Fig. 4 and gradients k_1 (dB/w%) of linear fitting are summarized in Table 1. The thickness of the composite sheets was 0.77 mm. As can be seen from the Figure, composites with graphite nanoparticles and carbon black demonstrated close values, which were at the same level as for PMMA. The values of SE increased with content at 0.03±0.01 dB/w% gradient for carbon black and 0.05±0.01 dB/w% gradient for graphite nanoparticles. Much higher values of SE were measured for CSCNT polymer composites, which increased with CSCNT content at 0.52±0.10 dB/w% gradient and reached 2.6 dB at 4 w%.

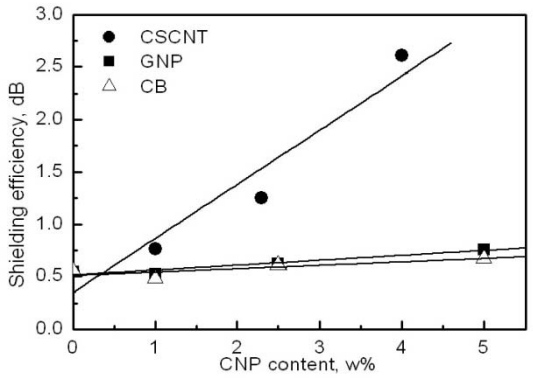

Fig. 4. Shielding efficiency of carbon nanoparticles (CNP) dispersed polymer composites as a function of CNP content.

Table 1

Gradients of linear fitting: k_1 – gradient of linear fitting for SE (dB) as a function of content (w%), and k_2 – gradient of linear fitting for SE (dB) as a function of thickness (mm).

Composite	Gradients of linear fitting	
	k_1, dB/w%	k_2, dB/mm
CSCNT	0.52±0.10	3.21±0.20
GNP	0.05±0.01	0.96±0.04
CB	0.03±0.01	0.84±0.04
PMMA	-	0.62±0.09

In Fig. 5 dependence of mean SE in X-band as a function of the sheets thickness is shown and gradients of linear fitting k_2 (dB/mm) are depicted in Table 2. It can be seen from the Figure that SE linearly increased with thickness for all composites and PMMA. The fastest growth of SE with thickness was demonstrated by CSCNT/PMMA composite (gradient k_2 is 3.21±0.20), followed by graphite nanoparticles/PMMA composite (k_2=0.96±0.04), carbon black/PMMA composite (k_2 0.84±0.04) and PMMA (k_2=0.62±0.09).

Different results for CSCNT, graphite nanoparticles and carbon black can be explained from the following considerations. In case of graphite nanoparticles and carbon black the content was not sufficient to reach the percolation threshold, therefore no conduction network was formed and SE was low. Depending on carbon black properties percolation thresholds in polycarbonate matrix were found to be from 5 to 10 w% [9], and SE values of 10 dB for carbon black/rubber composites were measured at loadings higher than 30 w% [4]. Concerning CSCNT, their high electrical conductivity together with high aspect ratio (ratio of length to diameter is more than 20) and uniform dispersion in the PMMA can lead to formation of conducting network even at very low loadings (less than 1 w%), in the same way as was observed for MWCNT [5, 10] and SWCNT [9], and as a result to the higher SE.

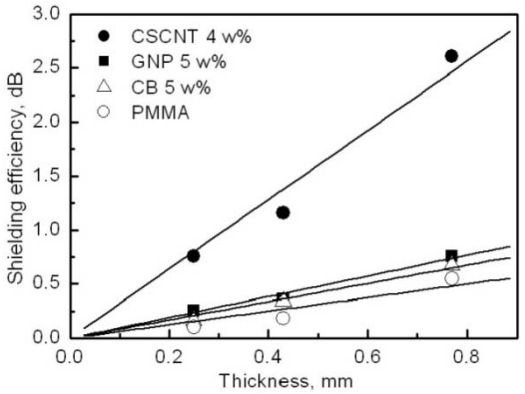

Fig. 5. Dependence of shielding efficiency on the sheets thickness.

Comparing to the data for MWCNT / polypropylene composites, reported in [5], the values of SE measured in the present work for CSCNT/PMMA composites are lower, that can be explained by lower electrical conductivity of CSCNT in comparison with MWCNT, but this requires additional studies. Better technological characteristics of CSCNT, such as good dispersibility in solvents and polymers, may increase the potential of this material for future applications in EMI shielding polymer composites.

Conclusions

Composites of PMMA and carbon nanoparticles were successfully prepared by the coagulation method, and their electromagnetic interference shielding efficiency (EMI SE) in the frequency range of 8.2~12.4 GHz (X-band) was investigated as functions of carbon nanoparticles content and composite sheets thickness. The coagulation method provided good dispersion of carbon nanoparticles in PMMA with mean particle size of 720±120 nm for carbon black, 930±370 nm for CSCNT, and 2200±1100 nm for graphite nanoparticles. The highest value of the averaged EMI SE of 2.6 dB was measured for CSCNT/PMMA composite with CSCNT content of 4 w% and 0.77 mm thickness. EMI SE for carbon black and graphite nanoparticles was found to be much lower, that was explained by insufficient content of the particles to reach the percolation threshold and form conductive networks. High axial ratio of CSCNT and their high electrical conductivity together with good distribution in the polymer matrix provided formation of conductive network, which lead to SE increasing with thickness and content of CSCNT. From the comparison between impacts of reflection and absorption to the total SE, it was found that for CSCNT/PMMA composites absorption of electromagnetic radiation played the decisive role.

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