Electromagnetic Interference Shielding of Graphite/ Acrylonitrile Butadiene Styrene Composites

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ABSTRACT: Dispersion of graphite within the acrylonitrile butadiene styrene matrix demonstrates enhanced electromagnetic interference shielding of composites through the use of tumble mixing technique. A shielding effectiveness of 60 dB with 15 wt % of graphite has been achieved. *D* shore hardness data revealed a little decrease in hardness of composites with rise in graphite content. DC conductivity measurements revealed a fairly low percolation threshold at 3 wt % of graphite. The conductivity exhibited by 15 wt % composite is 1.66×10^{-1} S/cm. These composites are fit for use as an effective and convenient EMI shielding material because of easy processing, better hardness, light weight, and, reasonable shielding efficiency. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1100–1105, 2011

Key words: polymer composites; fillers; hardness; dielectric properties; EMI shielding

INTRODUCTION

Electromagnetic interference (EMI) shielding problems are very common now and because of its interference with other electronic devices, these issues have become the focus of attention. The visibility of this concern has increased with the spread of digital electronics. Hasty development of appliances and devices in the field electronic information and communication has radically placed the general population under the threat of EMI or radio frequency interference. EMI not only tends to interfere with digital devices but is also a direct hazard to public health owing to its adverse effect on human being exposed to these radiations. All electronic products need to be compliant within acceptable electromagnetic radiation levels. EMI shielding in far field regions is achieved via electrically conducting materials such as typical metals, graphite, and conducting polymers.[1] Conductive plastic products are used to provide electrostatic discharge and EMI/radio frequency interference shielding.[2] Polymer-based conducting systems have been considered as versatile EMI shielding materials, because of easy synthesis, light weight, low cost during mass production, and simple processing.[3,4] These materials excel over their metallic counter parts as a result of greater variety of mechanical properties such as strength, flexibility, and environmental resistance. For fabrication of conductive polymer composites, thermoplastic and thermoset matrices filled with carbon or metallic fillers (powders and fibers) have been used. Electrical and dielectric properties of these composites depend on the filler amount, conductivity, shape, size of the filler particles, material defects, and the processing methods used.[5–7] For appropriate control of the electromagnetic behavior, special skill is required because these materials cannot be formed efficiently or easily into the required intricate forms.

This work is referred to investigation of acrylonitrile butadiene styrene (ABS)-based conducting composites for EMI shielding capability. ABS offers easy processability, better cost, and more reliable notch impact resistance. Normally, ABS plastics are used for mechanical purposes. However, they also possess good electrical properties that are fairly constant over a wide range of frequencies. These properties are little affected by temperature and atmospheric humidity in the acceptable operating range of temperatures.[8] In addition, many blends of ABS with other materials such as polyvinylchloride, polycarbonates, and polysulfones have been developed with a wide range of features and applications. In the recent past work on ABS-based polymer composites filled with conductive carbon fiber, nickel-coated conductive carbon fibers (NCF) and electroless NCFs have been studied for EMI shielding in the frequency range of 30–1000 MHz.[9–12] Maximum

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shielding efficiency (SE) reported in case of NCF/ABS was ~ 47 dB. But SE of this composite degraded during thermal treatment at 60°C in air. In such composites, nickel–phosphorus coating on filler by electroless nickel plating is considered to be better than that of nickel coating deposited by electrolytic nickel plating owing to its resistance to oxidation and corrosion. The method used for preparation of conductive ABS composites was melt processing with compression molding at ~ 240°C. However, in this work, graphite-filled ABS composites were produced through tumble mixing of powders with subsequent compression molding at elevated temperature (90°C). The measurement of SE and return loss (RL) of graphite-ABS composites were made in the frequency range of 8.0–12.0 GHz. Shielding in this so-called X-band frequency range is very important for many military and commercial applications because Doppler, weather radar, television picture transmission, and telephone microwave relay systems lie in the X-band.[13] The best EMI shielding SE of about 60 dB has been obtained for 15 wt % graphite composite. SE increases with increasing graphite mass fraction similar to DC conductivity. Both reflection and absorption of EM radiation are increasing with increase in graphite filler.

EXPERIMENTAL

Materials

ABS-92 used in this work was procured from Lanxess ABS Ltd., Baroda, India. The bulk density and resistivity of its pellet were found to be 0.9583 g cm^{-3} and 2.13×10^{-12} S cm^{-1}, respectively. Graphite powder was supplied by Graphite India Ltd., Bangalore, India. Its particle size ranges from 10 to 20 μm, with a resistivity of 7.5×10^{-5} Ω cm and density of 1.75 g cm^{-3}. Scanning electron microscopy micrograph[14] has confirmed their flake-like shape.

Processing and compression molding

The requisite ratios of powders of ABS and graphite were mixed for 200 min at room temperature using tumble mixing procedure. The resulting mixture was heated to temperature of 110°C, brought back to 90°C, and then compressed for 15 min with 75-MPa pressure in a piston–cylinder assembly. The rectangular-shaped pellets were of area 2.28×1.01 cm^2 and thickness ~ 3 mm. During tumble mixing process, the ABS particles were observed to be coated with graphite particles. On compaction of composite mixture by compression in the absence of any shear, the conductive graphite particles were believed to be located at the interfacial places between the ABS particles. Additionally, compaction decreases the number of air voids. A series of specimen pellets were produced by varying the filler concentration from 0 to 20 wt %. Five pellets were prepared for each composition. The DC resistivity of each pellet was measured within the period of initial 10 sec because polarization was assumed to be negligible during this period. Little variation in values of resistivity of five pellets of each composition confirms uniform dispersion of graphite into the ABS powder. The data reported here are the mean value.

Measurements

For resistance measurements lower than 200 MΩ, a digital multimeter was used, whereas for greater than 200 MΩ, a Keithley Pico ammeter was used. All values of resistivity reported in this work were of DC resistivity. Programmable Automatic RCL Meter PM 6306 Fluke was used for dielectric measurements. EMI SE and RL measurements were made in the frequency range of 8.0–12.0 GHz using Wiltron vector network analyzer. Specimen composites were accurately inserted in the wave guide so as to fill the entire cross-section to avoid any leakage of EM radiation. The resistivity, permittivity, and SE measurements were carried out at atmospheric pressure and room temperature ~ 25°C.

RESULTS AND DISCUSSION

Density and hardness of composites

Specimen composites of all compositions were characterized for density and hardness. Figure 1 illustrates the variation of bulk density of graphite/ABS composites with increasing mass fraction of graphite. The bulk density of the composite referred here

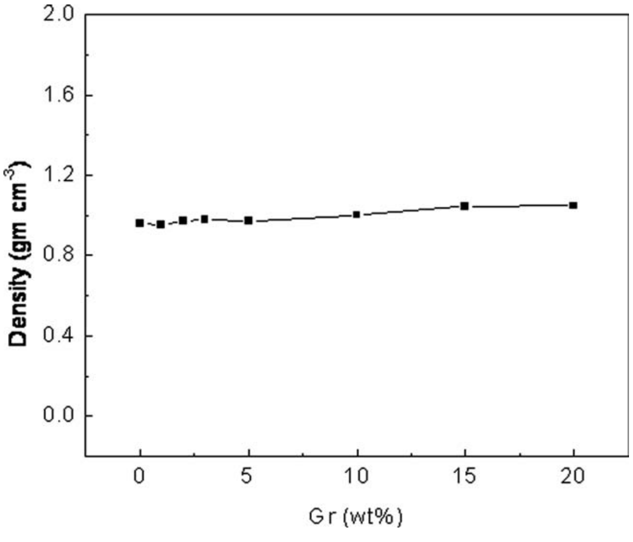

Figure 1 Density of graphite/ABS composites as a function of graphite content.

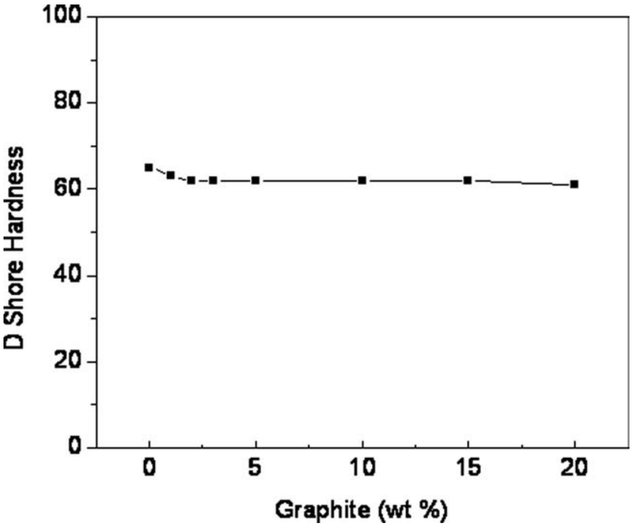

Figure 2 Hardness of graphite/ABS composites as a function of graphite content.

means the ratio of its weight to volume, despite some air voids inside, if any. It was evaluated precisely from the testing results of the microlevel measurement of the sample volume and weight. The observed density of the ABS pellet (0.9583 g cm^{-3}) is lower than the density of graphite (1.75 g cm^{-3}). On inclusion of filler particles of higher density (graphite) in ABS composites, an increase in density up to level of 15 wt % of graphite (1.0471 g cm^{-3}) has been noticed, which settles down to 1.0480 g cm^{-3} at 20 wt %. All these pellet composites were tested for hardness also. Measurements were taken on 100 scale of *D* shore hardness. Hardness behavior with increasing mass fraction of graphite is shown in Figure 2. Decrease in hardness on inclusion of graphite is small, merely 6% on addition of 20 wt % graphite.

These composites had been prepared through extensive tumble mixing of dry powders of graphite and ABS, with subsequent hot compaction. ABS particles were seen to be coated with a layer of graphite particles. On compaction, the graphite particles are assumed to be placed at the interfacial spaces between the ABS particles. The position of graphite particles within the insulating ABS matrix would contribute toward improvement of electrical and dielectric properties of the composites. This was confirmed through the electrical and dielectric measurements.

DC electrical conductivity of composites

Figure 3 shows the influence of graphite content on electrical conductivity (σ) of graphite/ABS composites. The σ of specimen of ABS pellet is 2.13 × 10^{-12} S cm^{-1}. Figure reveals that the σ of the composites is improving by increasing graphite loading. At a very low level of 1 wt % of graphite, the σ of the composites is 4.03 × 10^{-11} S cm^{-1}, which is nearly equal to that of the ABS polymer. With further increase of graphite to 2 wt %, the σ gradually increases followed by an abrupt increase to 4.90 × 10^{-4} S cm^{-1} at 3 wt % graphite content. The drastic change in the σ by several orders is believed to be a result of the formation of an interconnected network of graphite particles because of their interfacial placement across the composite. This is a usual percolation threshold as described in the literature, which recognizes the existence of network of interconnecting paths consisting of conducting graphite particles that permit a very high percentage of electrons to flow through the matrix. At a low level of 1 wt %, graphite particles implanted in the polymer matrix are secluded from each other by insulating ABS surrounding them. Hence, they do not contribute significantly toward the conductivity of the composite, and the resulting σ is little less than the constituent polymer (ABS) phase. Close to percolation threshold near 3 wt %, the graphite particles are close enough to allow the electrons to conduct across gaps between them.[8] For composition >5 wt % graphite fraction, the σ starts saturating. This implies that beyond percolation only the numbers of conductive paths have increased, which does not improve the σ appreciably. At 20 wt % concentration, the flattened conductivity facilitates the unrestricted movement of electrons. This composite has exhibited electrical conductivity of 1.56 × 10^{-1} S/cm.

Permittivity of composites

Placement of graphite particles within the interfacial places surrounded by insulating ABS matrix environment is expected to induce dielectric property by

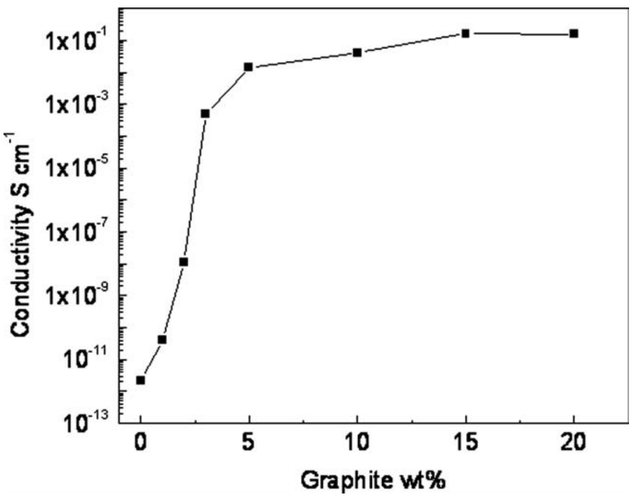

Figure 3 Conductivity of graphite/ABS composites as a function of graphite content.

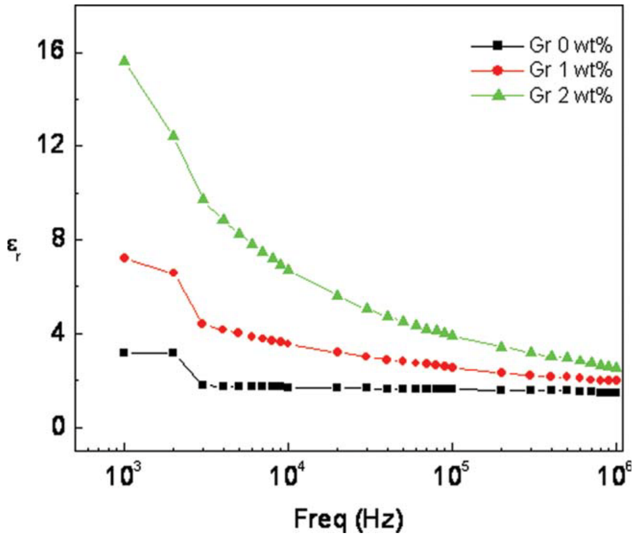

Figure 4 Relative permittivity of graphite/ABS composites as a function of frequency. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

generating space charge polarization at the interfaces.[15] The permittivity of composites was investigated in the frequency range of 10^2–10^6 Hz using available facility in this laboratory. The evaluated values were confined to lower compositions of smaller conductivity because of limitation of equipment. Corresponding values of relative permittivity (ε_r) of composites as a function of frequency for various graphite contents are illustrated in Figure 4. ε_r increases with increasing graphite content and is more than 15 at 10^2 Hz for 2 wt % graphite. The permittivity here is related to Maxwell–Wagner type of polarization that used to occur in heterogeneous dielectrics where one component has a very high conductivity compared with other. This provides an explanation for the dielectric behavior because of the interfacial polarization.[16] ε_r diminishes with rising frequency and tends toward saturation for all compositions. The trend is expected to be same in the X-band frequency range. The interfacial polarization can take place without difficulty at low frequency. As the frequency is increased, the time needed for polarization of interfacial charges or for the dipole to be aligned is delayed.[15]

EMI shielding effectiveness

The use of an EMI shielding is to put up an effective barrier that attenuates radiated or conducted electromagnetic energy. Figure 5 demonstrates the shielding effectiveness for ABS composites of various graphite contents in the X-band frequency range. SE increases with enrichment of graphite level in ABS composites. Composite containing a little amount of graphite (1 wt %) showed an SE of ∼ 4 dB followed by ∼ 14 dB at 3 wt %, and a maximum of 60 dB was observed for 15 wt % of graphite at 8.5 GHz. As evident from the conductivity data, with increasing graphite content, the graphite particles become closer. When more graphite particles were dispersed in the matrix, network of graphite pathways with exceptionally close gaps were formed. Consequently, at higher concentration, EM waves were likely to encounter more graphite particles. These particles reflected or absorbed more radiation compared with ABS-rich areas, producing an increase in SE with increasing graphite concentration. For composites with 3 and 5 wt % graphite, there is a decrease in SE with increasing frequency, whereas for 15 wt % it is almost independent of frequency in the measured range of this work. ABS composites prepared with graphite have shown comparatively improved values of SE than those prepared with other conducting fillers using melt processing compression molding technique.[9–12]

Variation of RL as a function of frequency is illustrated in Figure 6. The maximum value RL ∼ 7 dB for ABS at 8.5 GHz decreases with the addition of graphite content and is observed to be 3 dB for 15 wt % graphite. It is arbitrarily decreasing with frequency, and the variation is more unsystematic for higher compositions. Such frequency dependence may be due to some structural effects, such as the geometrical distribution of the filler along with interaction of electromagnetic waves with graphite. It is recognizable that ABS composites that have a high value of SE yield a lower value of RL.

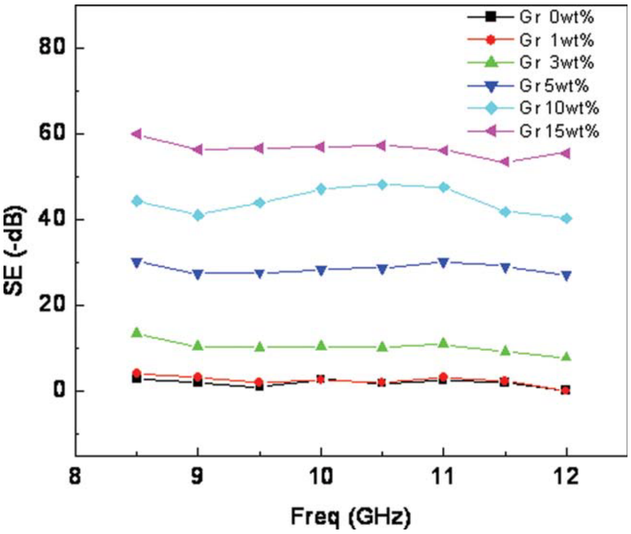

Figure 5 SE as a function of graphite concentration in graphite/ABS composites. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

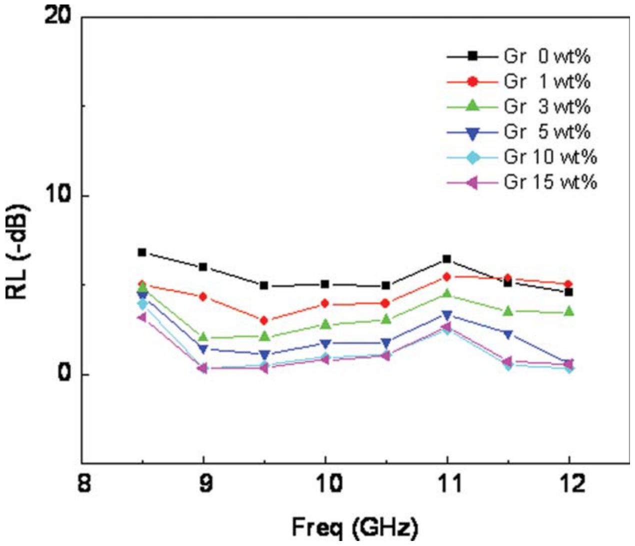

Figure 6 RL as a function of graphite concentration in graphite/ABS composites. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

SE is a measurement of attenuation of electromagnetic signal mainly through reflections and absorption after a shield is introduced. As a consequence, the total SE $= \text{SE}_{\text{ref}} + \text{SE}_{\text{abs}}$. SE_{ref} can be evaluated[17] through the relation $\text{SE}_{\text{ref}} = 10 \log_{10} (1 - R)$. Reflectance R is the ratio of reflected power density (P_r) to incident power density (P_i). In case of normal incidence, $R = P_r/P_i = \text{Anti} \log_{10} (-\text{RL}/10)$.

Contribution of SE_{ref} and SE_{abs} in total SE

Evaluated values of SE_{ref} as a function of frequency are displayed in Figure 7. Curves exhibit random frequency dependency of less than 9 dB for all compositions of composites. Contribution of SE_{ref} in EMI SE increases with graphite contents in the composites. For 15 wt % graphite, upper limit of assessed value is ~ 11 dB at 9.5 GHz.

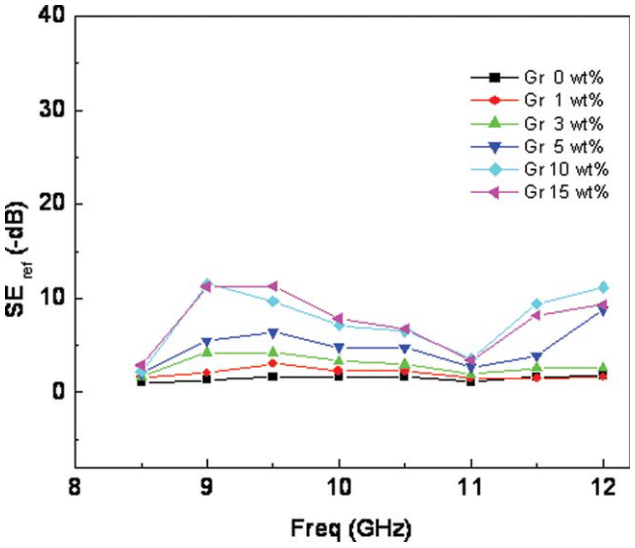

Figure 7 SE_{ref} as a function of graphite concentration in graphite/ABS composites. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

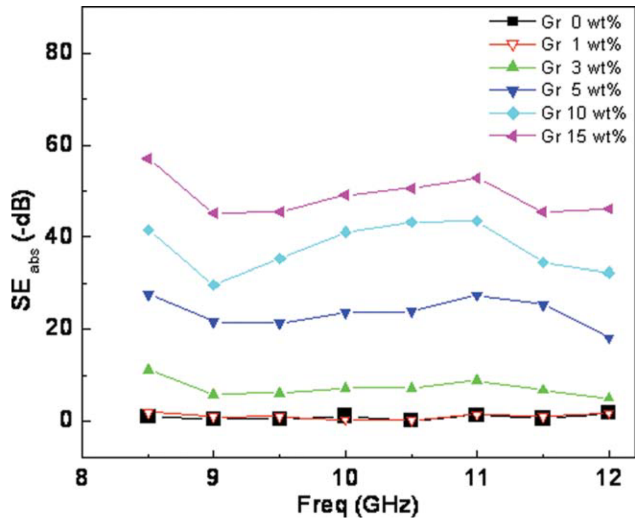

Figure 8 SE_{abs} as a function of graphite concentration in graphite/ABS composites. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

Undersized values of SE_{ref} indicate its small contribution to the total SE of the system. Figure 8 illustrates the evaluated values for SE_{abs} for ABS composites as a function of frequency for various graphite concentrations. Small random variation with frequency can be seen in SE_{abs} for higher composition of composites. Increasing graphite content increases the SE_{abs}. For ABS, SE_{abs} is only ~ 1 dB. While on growing, inclusion of graphite in ABS matrix near to percolation threshold ~ 9 dB is followed by a significant value of 53 dB for 15 wt % graphite content at 11 GHz. Investigations clearly suggest that SE of these composites is absorption dominated. During composite processing, graphite sets into ABS matrix and is assumed to show dielectric property as reported in case of carbon black.[15,18] EM wave absorption here is related to interfacial or Maxwell–Wagner type of polarization used to occur in heterogeneous dielectrics where one component has very high conductivity than the other.[16] This is an important finding, which determines the EM wave absorption. Absorption in such composite most probably occurs because of interactive loss processes of the interfacial polarization of the filler particles. Because of restrained conductivity of the composites, the larger value of permittivity may be accountable to absorption of radiation.

CONCLUSIONS

Dispersion of graphite in ABS powder with subsequent compression molding of composites at 90°C has proved better for realization of enhanced results. Higher SE using present dry mixing technique relative to melt mixing reported in the literature confirms the result. ABS composites filled with graphite would be more effective than carbon fiber, nickel-coated carbon fibers, or electroless nickel-coated carbon fibers for device applications. The required EMI shielding for different electronic devices is about 15–20 dB. Consequently, graphite/ABS composite having ~ 60 dB SE seems to be promising for its commercial use in the X-band frequency range. Little decrease in *D* shore hardness with increasing graphite content envisages its realistic application. ABS composite containing 3 wt % of graphite demonstrates SE ~ 14 dB at 8.5 GHz and cannot be used effectively for EMI shielding, but can be used where static charge dissipation is important.

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