

Pre-localized graphite/polyvinyl chloride composites for electromagnetic interference shielding in the X-band frequency range

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The paper reports the development of compression moulded pre-localized graphite/polyvinyl chloride (graphite/PVC) segregated composites with different concentrations of graphite and their application to the shield effectiveness of electromagnetic radiation in the X-band frequency range 8–12 GHz. The incorporation of graphite is related to the formation of conducting channels. It is found that conducting channels are formed above 3 wt. % of graphite. The electrical conductivity is also found to be strongly dependent on the graphite content, and the data are analysed using a percolation model. Variations in SE with graphite loading, due to changes in the conductivity of the composite, have been investigated.

Key words: *polymer composite; conducting filler; shielding efficiency; percolation*

1. Introduction

With the ever-growing applications of advanced electrical and electronic devices emitting electromagnetic radiation, their biological safety becomes of prime importance. Their adverse effect on the human body may well be predicted from their application to roasting in microwave ovens. Moreover, EM pulses can disrupt neighbouring equipment such as computers, or sensitive electronic/electrical measuring instruments. Therefore, it becomes essential to limit and shield all ill effects of EM radiation.

An electromagnetic interference (EMI) shielding material is one that attenuates radiated electromagnetic energy or provides protection by reducing signals to levels at which they no longer adversely affect equipment and can no longer be received by human beings. To reduce the impact of EM radiation, better and more versatile EMI

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shielding materials have always been the topic of investigation and research. Metals have been used for EMI shielding due to their high conductivity. Metals suffer, however, from the inherent disadvantages of corrosion, heavy weight, and poor processibility. Moreover, with the miniaturization of equipment and integration of circuits in limited areas, the possibility of leakage increases as the gaps between circuit units become narrower. Also, the conducting material setting on a circuit for EMI shielding can act as an antenna causing malfunctions in the electronic equipment.

Polymers are lighter in weight, less expensive, corrosion resistant, flexible for complex designs and aesthetically appealing compared to their metallic counterpart. They are electrically insulating and transparent to EM radiations, however, and they are not directly suitable as EMI shielding materials. The easiest way to make them electrically conducting for EMI shielding is to disperse a conductive filler such as black carbon into an insulating polymer matrix [1]. Electroconductive polymer composites can easily be moulded into various complicated shapes even by traditional methods of extrusion and injection moulding. Conductive fillers include metal powders, stainless steel, and carbon and graphite powders [2–4]. Metallic powders generally suffer from oxidation, which deteriorates electrical properties of the composite due to the nonconductive nature of oxide layers.

The segregated distribution of the conductive filler phase in an insulating polymer matrix can impart high electrical conductivity. A comparatively low critical content of conductive filler is needed for a conductive network to form. One way to attain the segregated distribution is to pre-localise of conductive filler phase onto the polymer particles by chemical plating or vacuum coating. Another way is to polymerise a monomer phase and subsequently compact the coated polymer powder by compression moulding around its glass transition temperature and at high pressure. During processing, some of the filler sheaths around polymer particles are expected to break due to compression, permitting polymer particle-to-particle fusion while maintaining a conductive network [5–8]. Such an approach is complicated, however, and industrial production would be expensive. Further, thin brittle conductive layers are very likely to strip off during processing.

The present study deals with the EMI shielding effectiveness (SE) of pre-localized graphite/PVC electroconductive composites. The processing of these composites is cost effective, simpler, and commercially viable [9]. SE, along with the parameter return loss (R_L), is investigated for composites with different concentration of graphite over the X-band frequency range of 8–12 GHz. The aim of this work is to design a polymeric composite material for EMI shielding with a smaller amount of conducting filler and retaining desirable mechanical strength.

2. Experimental

The matrix polymer used in this work is a commercial grade PVC resin suspension (K 67-01) with a particle size of 105–150 μm , from Reliance Industry Ltd., India. The

density of the compression moulded PVC sample was found to be 1.12 g/cm^3 . The electrical conducting filler was a graphite powder with particle sizes ranging from 10 to 20 μm , supplied by Graphite India Ltd. The conductivity of graphite with density 1.75 g/cm^3 is $1.33 \times 10^4 \text{ S/cm}$. The higher particle size ratio of PVC resin and graphite ensures a segregated distribution and lower percolation concentration. Composites with low electrical resistivities have been achieved by pre-localising flakes of graphite onto the PVC particles and compacting by compression moulding [9]. Processing and preparation are the same as described in earlier works. The graphite-coated PVC particles were compacted in a 2.54 cm^2 die by compression moulding at $78 \text{ }^\circ\text{C}$ and 105 MPa for 15 min. A monotonic increase in microhardness with graphite content, as observed in earlier works, confirms uniform coating on PVC particles and the lack of stripping off while processing. A decrease in hardness with increasing graphite content is assumed to be due to a smaller extent of PVC interparticle fusion during processing, owing to the compaction pressure. This also confirms the uniform coating of PVC particles with graphite. The uniform coating of graphite flakes on PVC particles in a composite sample of 20 wt. % graphite has also been observed in scanning electron microscope (SEM) micrographs [9].

A series of specimens of PVC/graphite conductive composites with graphite contents of 1–20 wt. % were prepared. All these samples were baked at $120 \text{ }^\circ\text{C}$ and nominal pressure for 15 min. The surface morphologies of these composites were examined by SEM. Variation in conductivity with graphite volume fraction was studied at room temperature. The baked samples with a thickness of $\sim 0.15 \text{ cm}$ were cut to fit in the cross section of the X-band rectangular wave guide. The size of the sample was $2.28 \times 1.01 \text{ cm}^2$. The sample was inserted in the wave guide cell so that it filled the entire cross-section, in order to prevent any leakage of EM energy. Measurements of incident, transmitted, and reflected power were made in the frequency range of 8.0–12.0 GHz.

3. Result and discussion

The morphological studies of PVC/graphite conductive composites with different graphite contents using SEM have indicated that networks of graphite conductive channels/paths form due to the presence of graphite particles in the interfacial regions between PVC particles [9]. In the sample with 1 wt. % graphite content, conductive graphite particles are initially apart from each other and found to be increasingly closer in samples with increasing graphite loading (above 3 wt. %). The graphite particles are flakes, while PVC particles are irregular in shape. Aggregates of small particles of graphite are formed between the interfacial regions of the irregular shaped PVC particles. Increasing graphite content leads to larger aggregates of graphite particles. Further increase in graphite content would increase the number of graphite particles touching each other in the composites that form the continuous conductive net-

work, leading to the formation of a conductive mesh structure in the insulating polymer matrix. The increased number of filler particles (graphite) in the conductive mesh of composites leads to better SE by the composites.

Figure 1 illustrates the room temperature electrical conductivity σ of the PVC/graphite composites as a function of graphite volume fraction P , assuming the density of PVC and graphite to be 1.12 g/cm^3 and 1.75 g/cm^3 , respectively. It is seen from the figure that σ is strongly dependent on P up to ~ 0.04 volume fraction. Such a drastic change in conductivity is related to the dispersion of filler in the polymer matrix, with the formation of a network of graphite conductive channels being evident from SEM images [9]. Critical graphite content may make electron hopping possible, which would result in a sharp increase in conductivity. An abrupt increase in the electrical conductivity is found to occur at $\sim 0.005_5$ (0.85 wt. %) volume fraction of graphite concentration.

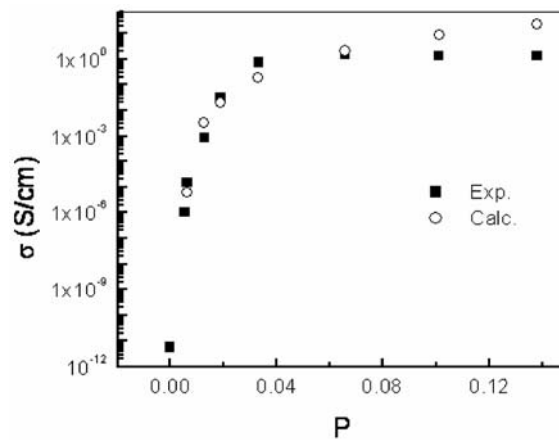


Fig. 1. The conductivity σ as a function of the volume fraction P of graphite in pre-localized graphite/PVC composites

Such a behaviour of σ with P is commonly analysed by percolation theory [10, 11]. The expression for σ can be written as

$$\sigma = \sigma_0 (P - P_c)^t \quad (1)$$

where σ_0 is the conductivity of filler particles, P_c is the volume fraction of conductive filler at the percolation threshold, i.e. the volume fraction below which the conductivity falls to a very small value, and t is the critical index of conductivity. The plot of $\log \sigma$ vs. $\log (P - P_c)$ is shown in Fig. 2. The best linear fit has been obtained for $P_c = 0.005$ (~ 0.78 wt. % graphite), which is in good agreement with the experimental value of 0.85 wt. % graphite content composite. The values of t and σ_0 as estimated from the slope and intercept are found to be 3.07 ± 0.26 and $1.13 \times 10^4 \text{ S/cm}$, respectively. Such a value of σ_0 is close to the conductivity of the filler graphite (1.33×10^4

S/cm). It should be mentioned that Kirkpatrick [12] and Straley [13] have obtained values of $t = 1.5 \pm 0.2$ and 1.75 ± 0.1 , respectively. Wang and Rubner [14], however, have reported the value of $t = 3.2$ for this system. To test the validity of percolation theory for pre-localized graphite/PVC composites, a comparison between theoretically calculated values using Eq. (1) with the estimated values of t (3.07) and σ_0 (1.13×10^4 S/cm) has been made and is illustrated in Fig. 1. A good agreement is observed, except for composites above 0.066 volume fraction (10 wt. %) of graphite content. The values above 10 wt. % probably fall in region III [15], while the theoretical fitting of this work is assumed to be for region II.

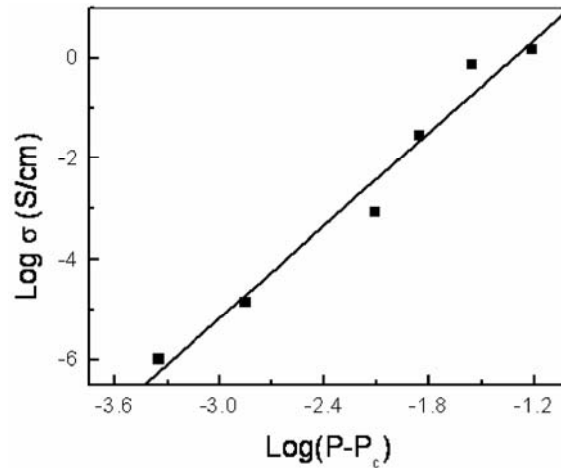


Fig. 2. The conductivity σ as a function of the excessive volume fraction $P - P_c$ of graphite in pre-localized graphite/PVC composites

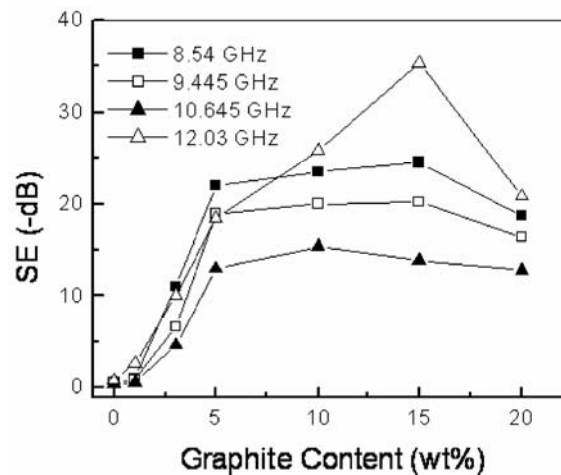


Fig. 3. The variation of shielding effectiveness SE as a function of graphite content in pre-localized graphite/PVC composites

The variation of shielding effectiveness (SE) for PVC/graphite composites with graphite content of 0 to 20 wt. %, over the frequency range of 8–12 GHz, is shown in Fig. 3. The variations in SE are more or less similar to the changes in conductivity with graphite loading (Fig. 1). It is interesting to note that SE increases sharply up to a graphite loading of 5 wt. % at all the frequencies. For higher graphite loadings, except for 12.03 GHz, SE saturates at 15 wt. % of graphite and starts to decrease with further increase of graphite content. In the case of 12.03 GHz, the system becomes more efficient in shielding at higher loadings up to 15 wt. %, and SE increases up to ~35 dB. The variation of insertion loss (R_L) as a function of frequency is shown in Fig. 4.

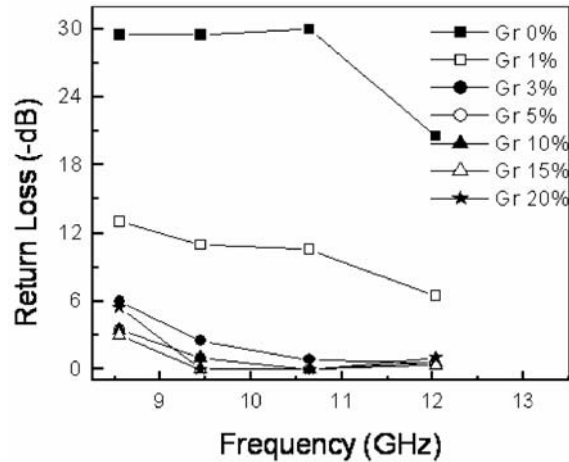


Fig. 4. The Variation of return loss R_L in pre-localized graphite/PVC composites as a function of frequency in the X-band

It is clear from the figure that composites that have a high value of SE yield a lower value of R_L . The range of these variations was found to be less than 6 dB over the whole X-band, except for the specimen with 1 wt. % of graphite concentration. The marginal frequency dependence of R_L may be due to some structural effects, such as the geometrical distribution of the filler and the interaction of electromagnetic waves with graphite.

The variation of SE with graphite loading can be linked to changes in the conductivity of composites with graphite. After a conductive barrier is inserted between a point in space and the source, SE can theoretically be expressed at that point by [16].

$$SE = 10 \lg \left(\frac{P_i}{P_t} \right) = (A + R + B) \text{ dB} \quad (2)$$

where P_i is the incident power density at a measured point before the shield is in place, P_t is the transmitted power density at the same point when the shield is in place, A is the absorption of the shield, R the reflection at both surfaces, and B is the multi-

ple internal reflection, which can be either positive or negative and is negligible for $A > 15$ dB. The return loss due to reflection can be represented as

$$R_L = 10 \lg \left(\frac{P_r}{P_i} \right) \quad (3)$$

P_r stands for the reflected power density at the same point.

The value of A depends on the σ of the sample (relative to copper) as

$$A = 1.32d(\sigma\mu f)^{1/2} \quad (4)$$

where μ is the magnetic permeability of the sample relative to vacuum or copper ($\mu = 1$), f is the frequency of radiation in MHz, and d is the thickness of the sample in cm. It will be appropriate to say that for effective EMI shielding, the dispersion of the conductive material in the polymer matrix should enhance the conductivity to a large extent since SE depends on σ , which in turn is a function of the dispersed filler, its size, structure, and distribution in the matrix [17]. The distribution of the filler in the matrix determines the void space between filler aggregates.

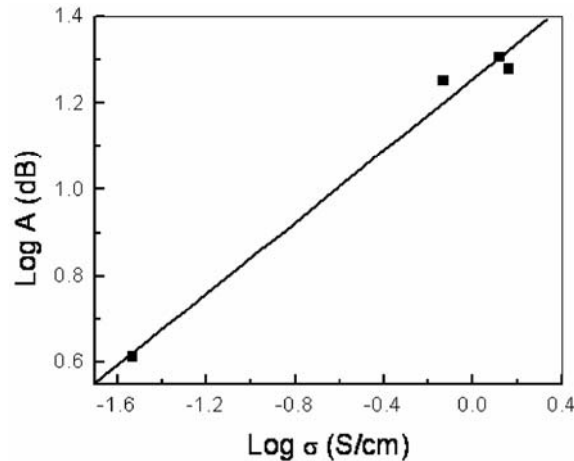


Fig. 5. The variation of the calculated value of $\log A$ as a function of $\log \sigma$ at a frequency 9.45 GHz for graphite/PVC composites

By pre-localizing the filler onto the polymer phase [8, 9], one can achieve high electrical conductivity in an insulating polymer with small amounts of electrically conductive filler with better mechanical strength. The segregated distribution of the conductive filler phase with pre-localization ensures a close-packed array throughout the matrix, so that the filler particles are arranged in a manner similar to a very fine conducting mesh that could be used for EMI shielding. The voids in the conductive composites effect absorption and R_L , owing to their effect on internal reflection. The

frequency dependence of SE is mainly due to the distribution of the filler in the polymer matrix.

The theoretical validity of Eq. (4), which predicts that absorption is proportional to the square root of conductivity, has been examined for the present investigation. Figure 5 shows the plot ($\lg A$ vs. $\lg \sigma$) within the X-band frequency range, centred at 9.45 GHz. The value of A is obtained by putting the data for SE and R_L into eq. (2). It is assumed that the contribution of B to SE is negligible. The variation of absorption with conductivity is found to be in accordance with Eq. (4), with the slope of 0.41 ± 0.03 . This is close to the theoretical value of 0.5. Using Eq. (1) in (4), the behaviour of absorption as a function of graphite content can also be predicted based on percolation theory.

4. Conclusions

Segregated composite systems with graphite pre-localized onto the PVC phase exhibit relatively high conductivity at very low filler loadings. SEM micrographs [9] confirm that graphite particles touch each other at higher graphite concentrations. At all frequencies of the incident radiation, SE increases and R_L decreases with the filler loading. Above a critical concentration of graphite, SE reaches a saturated value. The variation of A with conductivity is found to be in accordance with the theory for metal fillers within the X-band frequency range centred at 9.45 GHz. A is directly related to the thickness of the shielding. In the present study, the thickness of the sample was ~ 0.15 cm. By increasing the thickness, an increase in SE is expected. The shift from low to very high conductivity of the composite (above a critical filler concentration) is well accounted for by the percolation model. The EMI shielding of the polymer composites as a function of graphite content can be predicted by considering the power law in the percolation model.

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