

# Influence of Graphite Nanosheets on the Structure and Properties of PVC-Based Nanocomposites

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Received 26 May 2010; accepted 5 October 2010

DOI 10.1002/app.33547

Published online 14 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Polyvinyl chloride (PVC)-based nanocomposites, containing graphite nanosheets (G), which may be used as electromagnetic wave absorbers was developed and investigated. The microstructure of polyvinyl chloride/graphite nanocomposites (PVC/G) were examined by means of X-ray diffraction, scanning electron microscopy (SEM), and thermal gravimetric analyses (TGA). SEM image reveals that the graphite nanosheets were well dispersed in the PVC matrix without agglomeration. Thermal stability of the PVC/G nanocomposites is improved as a result of inclusion of graphite nanosheets. The PVC/G nanocomposites were characterized to investigate the effect of dispersion of graphite nanosheets in PVC matrix. The dielectric spectroscopy of PVC/G nanocomposites in frequency range from 1 to 12 GHz has been performed. The results show that PVC/

G nanocomposites exhibit high dielectric constant at the measured frequencies. Coefficient of attenuation and coefficient of reflection of PVC/G composites have been also examined in a frequency range from 1 to 12 GHz. The electromagnetic interference shielding effectiveness (EMI) depends on graphite volume fraction in the composite. The results show that the PVC/G represents a new class of conducting lightweight nanomaterial that can absorb electromagnetic waves at microwave frequency and may be promising for future commercial use. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3628–3634, 2011

**Key words:** graphite nanosheets; nanocomposites; microstructure; dielectric properties; electromagnetic wave shielding

## INTRODUCTION

This study is a part of an on-going research project aiming to develop a high-performance nanocomposite material for microwave devices with high attenuation, with good thermal and mechanical properties. The electromagnetic wave transport properties in disordered solids are a topic of considerable interest in condensed matter physics and for engineering purposes, for example, electromagnetic interference shielding (EMI), wave absorption, electronic packaging, vibration damping, and others.<sup>1–4</sup> With fast development of wireless communications, the electromagnetic radiation is becoming the fourth public pollution after the noise, water, and air pollution.<sup>5,6</sup> There is an increasing demand to reduce electromagnetic interference such as noise or errors in electronics devices. Such electromag-

netic radiation causes unwanted electromagnetic interference (EMI), which usually damages equipments and harm health of people. It is also needed for avoiding electromagnetic forms of spying. Electromagnetic microwave absorber composites are a critical part of electronic systems in applications such as electromagnetic shielding for air vehicles, wireless communications, and microwave devices.<sup>4–6</sup> Generally, most of the shielding materials consist of metals. Typical metals and their composites have several disadvantages such as heavy weight, easy corrosion, undurable, and effectiveness only over fixed frequency bands.<sup>4,5</sup> Hence, the high conducting polymers and their composites have been developed to replace or supplement typical metals for EMI shielding applications, which have merits such as light weight, physical flexibility, and easy control of electrical conductivity.<sup>5–8</sup> Graphite nanosheets deserve special attention because of their excellent environmental stability, high electrical conductivity, high thermal conductivity, low weight and its great promise in various practical applications to corrosion protection coatings, rechargeable batteries, reinforcements, etc.<sup>9–13</sup> Conductive filler particles in an

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Contract grant sponsors: University of Tabuk.

insulating matrix are able to dramatically increase the electrical conductivity and dielectric constant when a network develops throughout the matrix. Electrically conductive polymer nanocomposites have become increasingly important in the electronics industry in recent years and can be used for electrostatic dissipation, electromagnetic interference shielding, conductive painting, and conductive adhesive, self heating, gas sensor, pressure sensor as well as bipolar plate in fuel cells, and others.<sup>9–12</sup> Taking such considerations in mind, we fabricate new conducting nanocomposites composed of graphite nanosheets and polyvinyl chloride for the first time. The effect of graphite content on the network structure, thermal stability, and mechanical properties of nanocomposites were examined in details. The dielectric properties of nanocomposites as a function of frequency was studied and the applicability of PVC/G nanocomposites for microwave absorption properties were tested, too.

## EXPERIMENTAL DETAIL

### Materials

Natural flake graphite with an average diameter of 500  $\mu\text{m}$  used for preparing the expanded (exfoliated) graphite is purchased by Shandong Qingdao Graphite Company (Qingdao, China). Commercial concentrated sulfuric acid and nitric acid from Egyptian Chemical Company, Cairo, Egypt was used as chemical intercalant and oxidizer to prepare exfoliated graphite. Alcohol 95% (v/v) and distilled water was used as solvents for preparation of foliated graphite nanosheets. Polyvinyl chloride (PVC) was obtained from Tokyo Chemical Industry Co., Tokyo, Japan.

### Preparation of exfoliated graphite

Natural flake graphite was first dried in a vacuum oven for 24 h at 100°C. Then, a mixture of concentrated sulfuric acid and nitric acid (ratio 4 : 1, v/v) was slowly added to a glass flask containing graphite flakes with vigorous stirring. After 24 h of reaction, the acid-treated graphite flake was filtered and washed with deionized water until the pH level of the solution reached 6.4. After being dried at 100°C for 24 h, the resulting graphite intercalation compound was subjected to a thermal shock at 1100°C for 50 s in a muffle furnace to form exfoliated (expanded) graphite. The expansion ratio was about 400.

### Preparation of graphite nanosheets

In a typical synthetic procedure for obtaining of foliated graphite nanosheets, 1 g exfoliated graphite was mixed and saturated for 24 h with 400 ml alcohol solution consisting of alcohol and distilled water

with a ratio of 70 : 30. Then, the mixture was subjected to ultrasonic irradiation with a power 400 W for 24 h. After 24 h of sonication, exfoliated graphite particles were effectively fragmented into graphite nanosheets. The graphite nanosheets dispersion was then filtered and dried at 100°C to remove residual solvents. The obtained nanosheets are with thickness of 30–50 nm and diameter of 10–30  $\mu\text{m}$ .

### Preparation of PVC/G conducting nanocomposites

The obtained conducting graphite nanosheets were added to the PVC matrix and mixed by grinding machine for 30 min. The mixture was then pressed at 40  $\text{KN}/\text{m}^2$  at temperature of 185°C for 15 min. Several different batches of PVC/G weight ratios were prepared as 85 : 15, 80 : 20, 75 : 25, and 70 : 30, respectively, and abbreviated as GN15, GN20, GN25, and GN30, respectively.

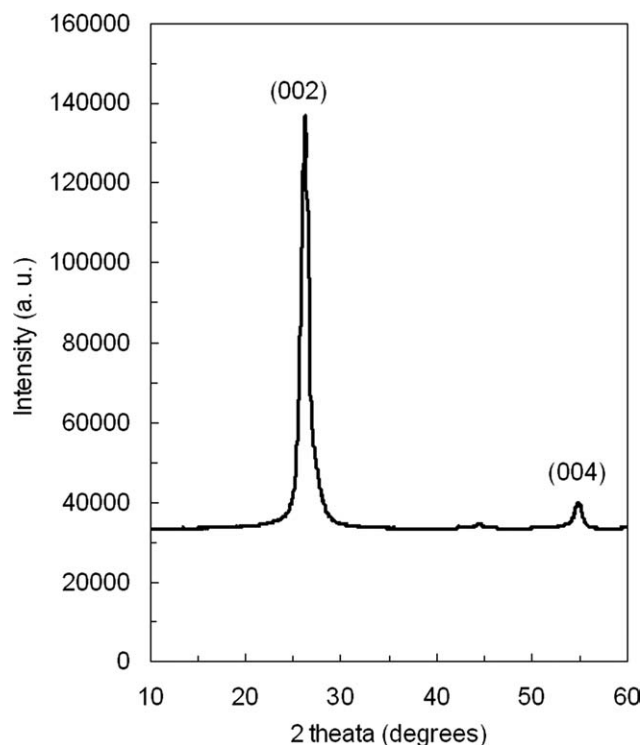
### Characterization

Crystal structures of as prepared graphite nanosheets was investigated by X-ray diffraction (XRD, D/Max 2200V, Rigaku, Japan) with  $\text{Cu } k\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. The crystallite sizes ( $D$ ) were calculated from X-ray peak broadening by Debye-Scherrer equation using the full width at half maximum (FWHM) data. The Debye-Scherrer equation is defined as [1.2] follows:

$$D = K_c \lambda / \beta \cos \theta \quad (1)$$

where  $\lambda$  is the wavelength of the X-ray radiation,  $K_c$  is a constant generally taken to be 0.9,  $\theta$  is the diffraction angle, and  $\beta$  is the full width at half maximum and is given by:  $\beta^2 = \beta_0^2 - \beta_i^2$ , where  $\beta_0$  and  $\beta_i$  are the width from the observed X-ray peak and the width due to instrumental effects, respectively.

The morphology of composites was analyzed by using a scanning electron microscopy (SEM, JSM-5310 LVB, JEOL). The specimens were coated with carbon to avoid charging using a vacuum evaporator (JEOL, GEE 500) and the voltage used was 15 kV. Thermogravimetric analysis (TGA) was carried on a Shimadzu TGA-50H thermogravimeter analyzer and the sample was heated from room temperature to 800°C at a rate of 10°C/min in a steady flow of nitrogen. The tensile strength and elongation at break of samples were examined at room temperature with an Instron universal testing machine HTE-10 KN Load cell is used and calibration done as per the ASTM procedure D-638 at a cross head speed of 2 mm/min. The dimensions of specimens were 150  $\times$  20  $\times$  5 mm. The hardness of the specimen was also measured, according to ASTM D 2240-81 using Shore D type durometer. The electrical conductivity of the samples was measured by four probe techniques



**Figure 1** X-ray diffraction pattern of the as prepared graphite nanosheets.

using a digital Keithley electrometer. Conductive copper brass electrode was applied on both surfaces for good contact.<sup>2,3</sup> The dielectric properties of the composites were measured at various frequencies by using RLC Bridge (3541 Y-Hitester, Hioki, Japan). Silver paste was used to ensure a good contact of the sample surface with copper electrodes. The electromagnetic properties were determined by a Hewlett-Packard (Palo Alto, CA) waveguide line containing spectro analyzer, power meter, coefficient of reflection meter, and coefficient of attenuation meter. The measurements were carried out in the frequency range 1.0–12.0 GHz.

## RESULTS AND DISCUSSION

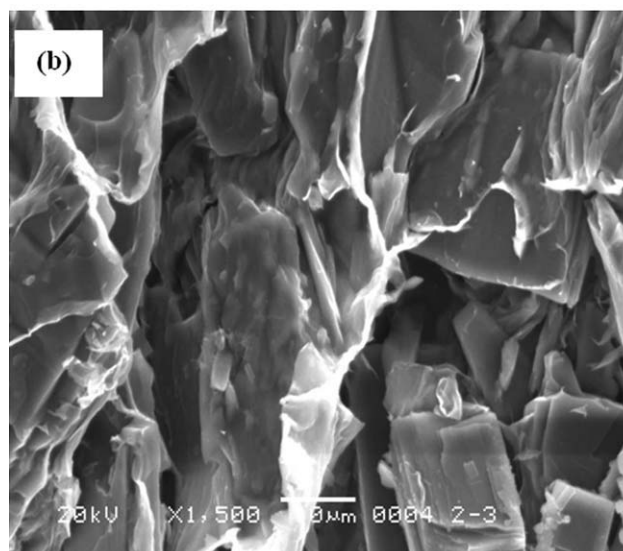
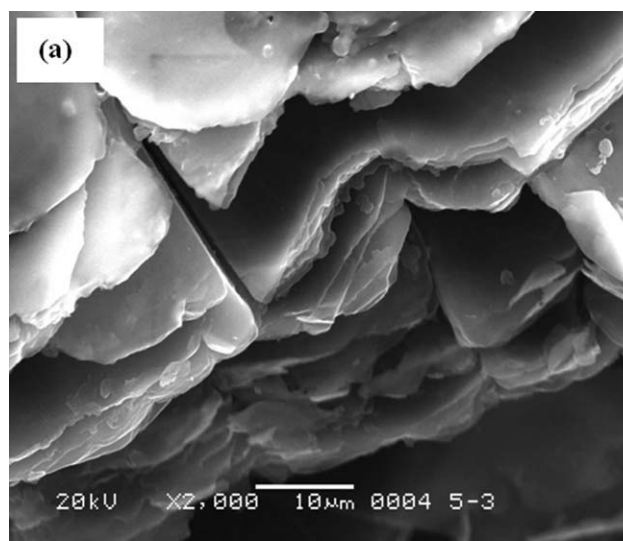
### Structure and morphology analysis

The phase identification of the prepared graphite nanosheets was performed using XRD. The XRD patterns are plotted in Figure 1. The peak positions of the (002) and (004) planes are located at  $2\theta$  values of  $26.6^\circ$  and  $56.7^\circ$ , respectively, which is attributed to the crystalline lamellae of graphite (JCPDS 41-1487).<sup>7,8</sup> Calculation based on the Scherrer equation gave the graphite crystallite size of 21 nm. The microstructure of the graphite nanosheets and PVC-based composites were examined by SEM. Figure 2(a,b) shows the SEM micrographs of graphite nanosheets and PVC composite, containing 30 wt % graphite nanosheets (i.e., G30 sample), respectively. From Figure 2(a), it is clear that the graphite shows a

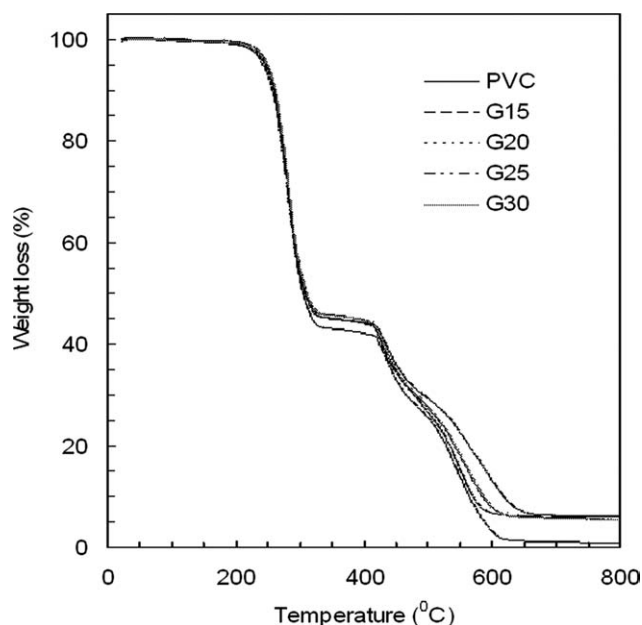
plate-like morphology. It can be seen from Figure 2(b) that the graphite nanosheets have good dispersibility in the PVC matrix. Furthermore, graphite nanosheets are located in the PVC phase and were almost well coated by the PVC matrix. In addition, the graphite nanosheets link with each other to form continuous conductive segment (i.e., infinite cluster) so that they create a conductive filament within the composite. Hence, the physical properties like mechanical properties, electrical conductivity, and dielectric constant is expected to increase with graphite loading as confirmed latter in this article.

### Thermal stability studies

TGA of the PVC/G nanocomposites was performed to identify thermal transitions and thermal stability of composites. The TGA curves of PVC/G



**Figure 2** Scanning electron microscopic (SEM) image of (a): graphite nanosheets and (b) PVC filled 30 wt % graphite (sample G30).



**Figure 3** Thermogravimetric analysis (TGA) of the green PVC and PVC/G nanocomposites.

nanocomposites are shown in Figure 3. The reduction of sample weight observed within 100°C may be attributed to the removal of moisture present in the PVC/G composite. The thermal degradation of PVC-based nanocomposites took place in two temperature ranges, namely 230–380°C and 420–710°C to nearly 89% weight loss. The main gas products released from PVC as a result of thermal degradation are methane, ethane, ethyne, hydrogen, HCl, Cl<sub>2</sub>, 1-butene, and benzene. It is seen that the onset temperature of thermal degradation of pure PVC is observed at 210°C, which is 20°C lower than the composite one. It is obvious that the thermal stability of PVC/G composite is increased compared with the green PVC, i.e., the loading with graphite nanoparticles improves the thermal stability. The increase in the starting degradation temperature was attributed to the enhancement of interaction between the PVC matrix and the graphite particles, and to the heat shielding effectiveness derived from graphite nanosheets, which limited the segmental movement of the PVC as confirmed above by SEM image and mechanical properties. The second step in degradation and weight loss is observed from 420 to 710°C. As we know the graphite is stable up to 750°C and does not degrade within the polymer matrix. The different weight losses of the samples around 500–600°C may be attributed to the different degradation of the polymer chains and backbones in the absence and presence of graphite nanosheets in different amount.

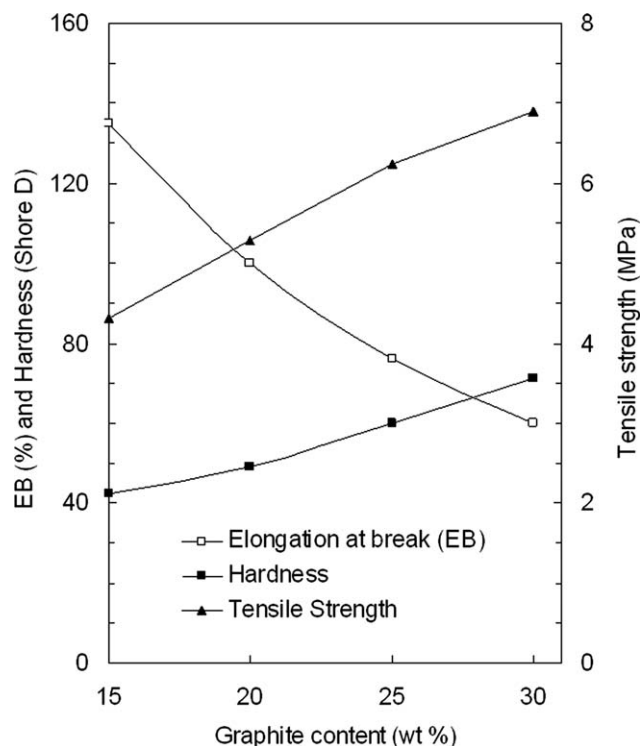
### Mechanical properties studies

To assess the influence of graphite nanosheets on mechanical properties of PVC, tensile strength, hardness

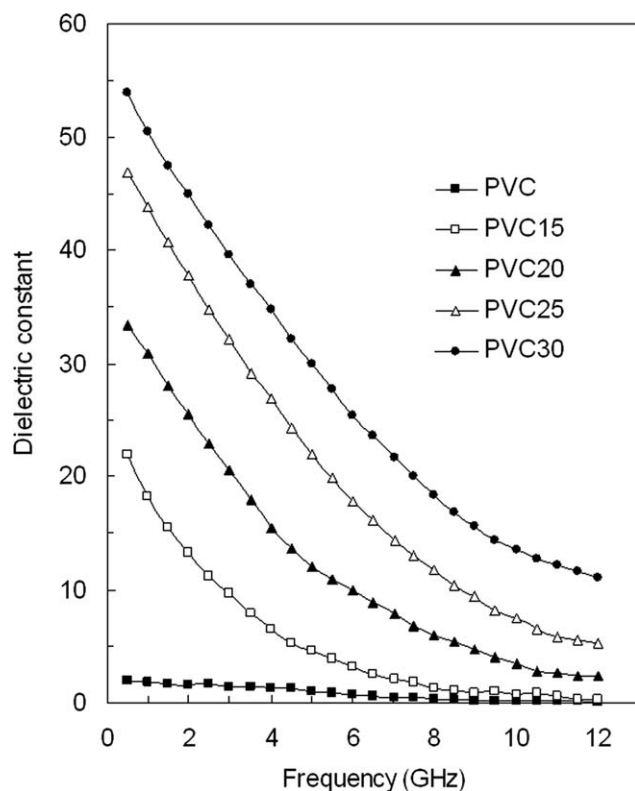
shore D, and elongation at break were measured. The tensile strength, hardness, and elongation at break of PVC/G as a function of graphite content is depicted in Figure 4. It is seen that with increasing graphite nanosheets content, the tensile strength and hardness increased consistently, whereas elongation at break decreased. The increase of tensile strength with increasing graphite content is due to the presence of graphite nanosheets having high aspect ratio.<sup>9</sup> The increase of hardness with increasing graphite content is attributed to the increase of crosslinking density (i.e., extent of filler reinforcement) and physical bonding among graphite nanosheets and PVC segments. The decrease of the elongation at break with increasing graphite content is due to decrease of the molecular mobility of composites. This suggest that the graphite nanosheets, i.e., plate-like layers can perform the role of reinforcement in PVC/G composite for the purpose of stiffening the PVC matrix.<sup>10</sup> In conclusion, the good dispersion and strong interface adhesion of graphite nanosheets entire the PVC matrix was the main reason for good mechanical properties of the composites as confirmed above by SEM image in Figure 2(b).<sup>5–7</sup>

### Dielectric properties studies

The dielectric constant are related to the structural mechanism of the composites particularly the interaction among PVC matrix and graphite nanosheets. The



**Figure 4** Influence of graphite nanosheets on tensile strength, hardness and elongation at break of PVC/G nanocomposites.



**Figure 5** Frequency dependence of dielectric constant of PVC/G composites with different graphite contents.

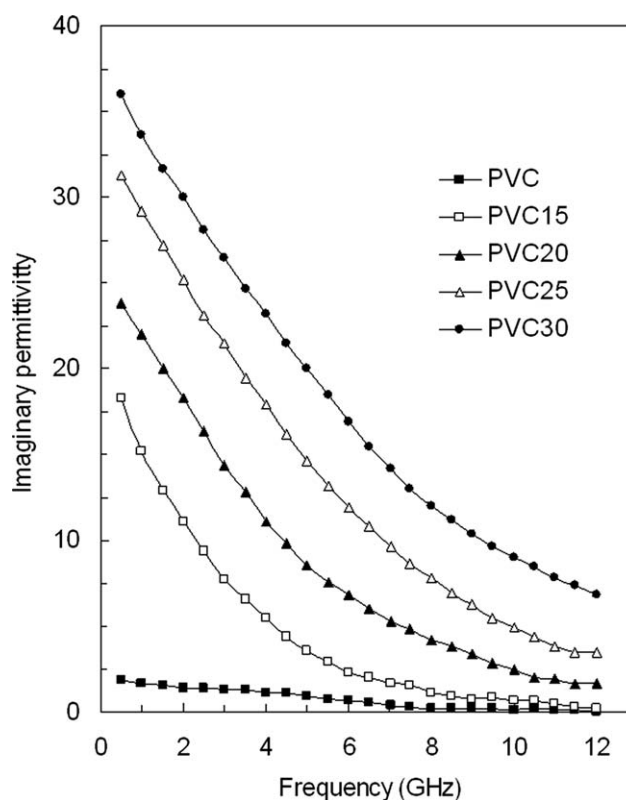
frequency dependence of dielectric constant and imaginary permittivity at room temperature for the green PVC and its PVC/G nanocomposites in the range of 1 to 12 GHz is plotted in Figures 5 and 6, respectively. It is interesting to note that the dielectric constant and imaginary permittivity of green PVC is independent of frequency. In Figure 5, it is observed that the dielectric constant increases with increasing graphite content into composites. There are three reasons evoked for increasing dielectric constant with graphite load level: First, the interfacial polarization results from the heterogeneous structure of nanocomposites, facilitating the formation of graphite network within PVC matrix. Second, the intrinsic ionic polarization of PVC matrix. Third, the increases of the density of elastically effective chains and homogenous dispersion of graphite nanosheets within PVC matrix thereby leading to an increase in dielectric constant as confirmed above by SEM in Figure 2(b) and mechanical properties in Figure 4.<sup>10</sup> It can be clearly seen that the dielectric constant for all samples presents a relatively high value at low frequency and is found to decrease with frequency. As shown in Figures 5 and 6, the imaginary permittivity in case of green PVC as well as the PVC/G nanocomposite also decreases steeply with frequency. These frequency-dependent dielectric behaviors may be related to the polarizability which depends on the dipole density and orientation polarization.<sup>11</sup> It is well known that the PVC system contains two types of charged

species, i.e., ionic and bound charges (dipoles). The ionic system is mobile and free to move along the PVC chain, whereas dipoles have only restricted mobility and account for strong polarization in the system. With increasing the frequency of the applied field, the dipoles in the system cannot reorient themselves fast enough to respond to applied electric field, resulting in the decrease in both real and imaginary permittivity.

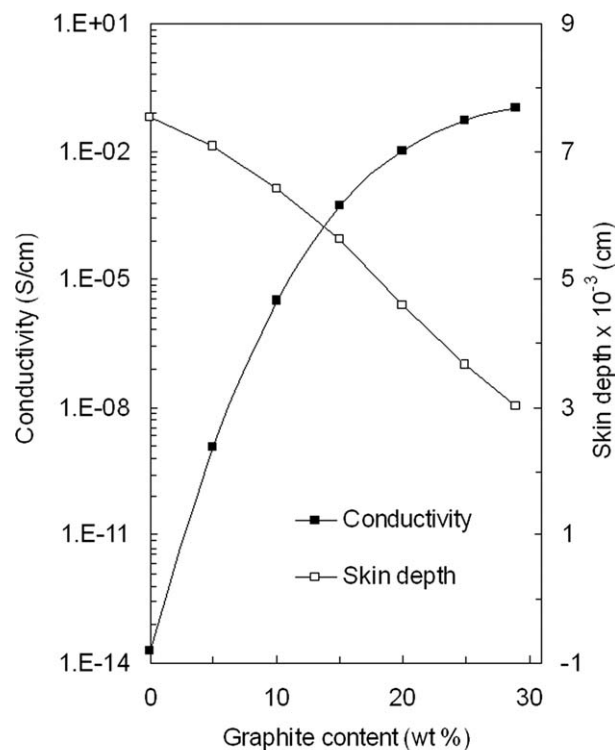
### Microwave properties studies

The electrical conductivity of PVC/G nanocomposites as a function of graphite content is depicted in Figure 7. It is observed that the electrical conductivity increase continuously with increasing graphite nanosheets content. The stronger interface adhesion and/or bonding between PVC polymer matrix and the finer dispersion of the graphite particles in PVC cause the higher electrical conductivity. Furthermore, graphite nanosheets (plate-like) offer larger effective volume and higher aspect ratio might allow for the formation of a conductive three-dimensional network throughout the nanocomposite and assisting the charge carriers to hop from conducting clusters to neighbors.

To investigate the applicability of PVC/G nanocomposites in microwave devices, the coefficient of attenuation and reflection were examined in the frequency range from 1 to 12 GHz. The coefficient of attenuation



**Figure 6** Frequency dependence of imaginary dielectric of PVC/G composites with different graphite contents.



**Figure 7** Dependence of conductivity and skin depth on the graphite content of PVC/G nanocomposites.

and coefficient of reflection as a function of graphite content are depicted in Figure 8. In Figure 8, it is seen that the coefficient of attenuation increases with the increasing of graphite content into composites. This is attributed to the high aspect ratio and good connectivity of graphite nanosheets with PVC matrix. The coefficient of attenuation reaches 62 dB/cm for 30 wt % graphite. This value of coefficient of attenuation gives a real opportunity for application of PVC/G nanocomposites as microwave absorbers. Furthermore, graphite nanosheets are interconnected to form conductive nets, PVC segment lies in the inter space of the nets [see SEM image in Fig. 2(b)], which leads to a higher absorption loss. On the other hand, the coefficient of reflection decreases with increasing graphite content into composites. This can be explained based on the skin depth ( $\delta$ ) and is given by the following<sup>8</sup>:

$$\delta = \sqrt{2/f\mu\sigma} \quad (2)$$

where  $f$  is the frequency,  $\mu$  is the permeability, and  $\sigma$  is the composite conductivity.

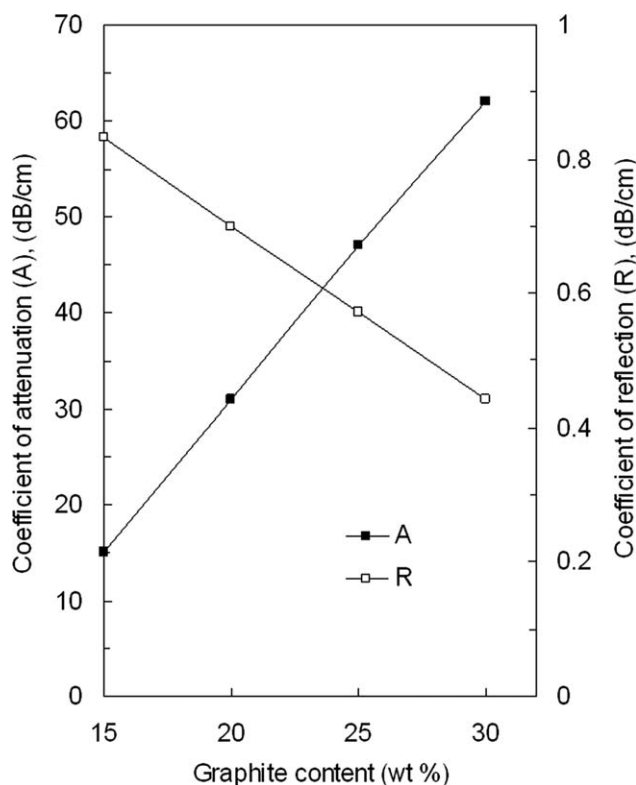
The skin depth decreases with increasing graphite content into composites as shown in Figure 5. This can be explained to homogeneity of composite to form a continuous network due to good entanglement between graphite nanosheets and PVC polymer matrix. When the thickness of the coating and size of graphite particles are much smaller than the

skin depth of the conductive nets, it leads to an increase of absorption losses due to Ohmic losses, and at the same time, the effective dielectric constant of the composite increases. It is obvious that the lower reflection coefficient and the higher absorbing frequency can be obtained as a result of inclusion of graphite nanosheets into PVC matrix.

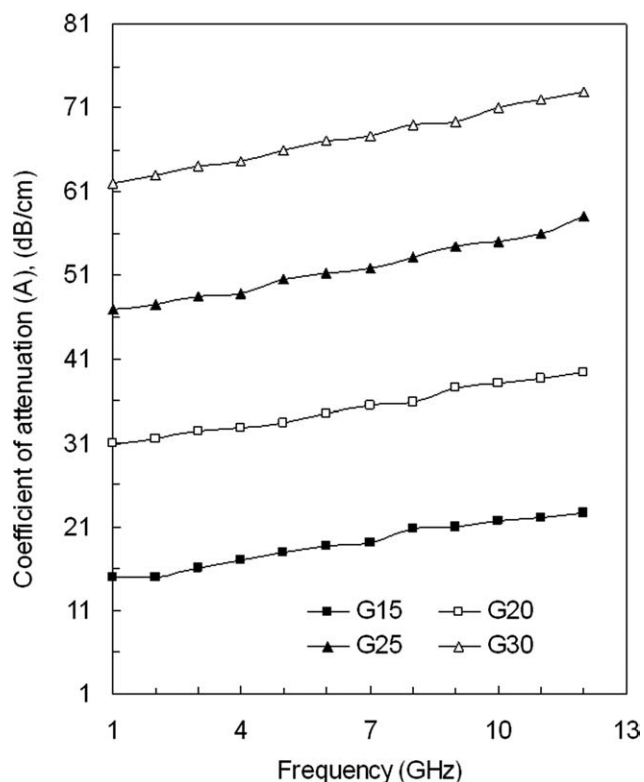
Figure 9 shows the absorption coefficient of the PVC/G nanocomposites versus microwave frequency. As it is shown in Figure 9, the absorption coefficient of the nanocomposites increases with the graphite content and frequency increasing. This result indicates that the inclusion of graphite nanoparticles into PVC matrix change the surface conditions of the composites, which make it easier for the microwave to penetrate into the core of nanocomposites and be absorbed. Furthermore, due to stronger interaction at the interface of graphite nanosheets and PVC matrix, the interface polarization and multiple scatter increase the microwave absorption. The result shows that the PVC/G nanocomposites are more suitable for a microwave absorbing material.

### CONCLUSIONS

1. The microstructure of PVC/G nanocomposites, thermal stability, and mechanical properties



**Figure 8** Dependence of coefficient of attenuation and coefficient of reflection on graphite content of PVC/G nanocomposites.



**Figure 9** Relationship between the coefficient of attenuation of PVC/G nanocomposites and frequency.

were highly enhanced by inclusion of graphite nanosheets into PVC matrix.

- The dielectric constant increases with increasing graphite content into composites. On the other hand, the dielectric constant decreases with increasing frequency up to 12 GHz. This is ascribed to interfacial polarization among filler and matrix and graphite nanosheets and the electric dipole polarization of PVC matrix. The dielectric constant and imaginary permittivity

of green PVC and nanocomposite showed a similar behavior and decreased as frequency increased.

- Electromagnetic wave attenuation potential of the PVC/G nanocomposites has been examined in 1–12 GHz frequency range. The results show that the dispersed graphite nanosheets attenuate the electromagnetic wave and the attenuation depends on particle volume fraction of the graphite into PVC matrix.

The present research is a result of an international collaboration program between University of Tabuk, Tabuk, Kingdom of Saudi Arabia and the University of Chemical Technology and Metallurgy, Sofia, Bulgaria.

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