Study of dielectric properties of styrene-acrylonitrile graphite sheets composites in low and high frequency region

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1. Introduction

A conducting polymer composite can be formed by dispersing conducting filler in sufficient quantity in a polymeric resin. Graphite powder [1–4], carbon black [5–8], carbon fiber metallic powder [9,10], carbon nanotube [11–13] and piezoelectric powder [14,15] and graphite sheets or expanded graphite sheets (GS) [16–21] have been used extensively as a conducting filler, as described in the literature. Polymer and graphite sheets offer some advantages in the realization of conducting polymer composites: low weight, resistance to corrosion, flexibility, and easy processing. Conducting polymer composites can be applied as current limiters [22,23], charge storage capacitors [14,24,25] and antistatic material for electromagnetic interference shielding [26,27] of electronic devices.

The electrical conductivity of conducting polymer composites can be increased with the addition of conducting filler. The composites undergo an insulator–conductor transition at a certain filler concentration, which is known as the percolation threshold. Insulator–conductor transition behavior of the composites near the percolation threshold is explained by percolation theory [28,29]. Recently, graphite sheets have been used as the conducting filler for making conducting polymer composites because expanded graphite or graphite sheets maintain a layered structure similar to natural flake graphite but with large interlayer spacing, high aspect ratio and large surface area [16–18]. The high aspect ratio and the large surface area of expanded graphite [16,17,19] are responsible for the much lower percolation threshold and better electrical conductivity and mechanical strength of conducting polymer composites than those achieved with conventional fillers like, graphite powder, carbon powder and metal powder.
The dielectric constant of conducting polymer composites also increases with the addition of conducting filler. Especially, near the percolation threshold, a sharp change in the dielectric constant is observed. At the percolation threshold, many conducting particles are isolated by thin insulating layers. Therefore, near the percolation threshold, the composites can become a capacitor and therefore, can be applied in charge storing devices, and electroactive polymers (EAP) and decoupling capacitor applications.

High dielectric constant and dissipation factor of polymer composites are required in low and high frequency regions for various applications like a decoupling capacitor and electromagnetic interference (EMI) shielding applications. Normally, a high dielectric constant of conducting polymer composites is obtained in the low frequency region and its value decreases in the high frequency region because the dipole moment cannot follow the reversing electric field in the high frequency region. High dielectric constant and high dissipation factor are required in the high frequency region for electromagnetic shielding applications.

Various types of polymer composites have been fabricated by using different kinds of conducting fillers. These composites have been used to find methods to increase the dielectric constant. Yun-Jia Li et al. [9] fabricated metal polymer composites by mixing stainless steel fiber (SSF) with poly vinylidene fluoride. A dielectric constant of 427 was observed at 50 Hz with 10 vol% of SSF. Lan Wang and Dang [30] fabricated multiwall carbon-nanotubes/poly (vinylidene fluoride) (MWNT/PVDF) composites. Near the low frequencies, the dielectric constant of the composite with about 2.0 vol% of MWNT increased rapidly and the value of the dielectric constant was as high as 300. Huang et al. [31] investigated the electromechanical responses of a high dielectric constant (>1000 at 1 kHz) polymer composite material and fabricated the composite by combining conductive polyaniline particles within a poly(vinylidene-fluoride-trifluoroethylene-chlorotrifluoroethylene) terpolymer matrix. Shen et al. [32] investigated the permittivity and dielectric constant of a three phase, double percolating composite with Ni–Zn–ferrite/PVDF. The dielectric constant of the composite was 200 at 1 kHz with the volume fraction of Ni.

Conducting polymer composites can be also used for static dissipation and electromagnetic interference (EMI) shielding applications. Electromagnetic interference (EMI) shielding refers to the reflection and/or absorption of electromagnetic radiation by a material, which thereby acts as a shield against the penetration of radiation. Because electromagnetic radiation, particularly that at high frequencies (e.g. radio waves, such as those emanating from cellular phones), tends to interfere with electronics (e.g. electronics or computers), EMI shielding of both electronics and radiation source is needed. The advantages of conducting polymer composites as compared to metals (typically used) includes improved corrosion resistance, lighter weight, and the adaptation of shielding effectiveness properties to suit the application needs.

In this study, the composites were prepared by the mixing technique and the hot compression mold technique.

Fig. 1. Scanning Electron Microscopy (SEM) images of (a) Graphite sheets (b) Fractured surface of composite with $\phi = 0.011$ (2wt %) (c) Fractured surface of composite with $\phi = 0.027$ (5wt %) (d) Fractured surface of composite with $\phi = 0.14$ (25wt %).
The composites consisted of styrene-acrylonitrile (SAN) as the insulating polymer matrix and graphite sheets (GS) as the conducting filler. SAN is copolymer of styrene with acrylonitrile monomer. SAN is considered to have better chemical resistance and surface hardness than polystyrene. Graphite sheets (GS) with a thickness of 100–150 nm and a diameter of 1–20 μm were used. Due to these specific properties of SAN and GS, SAN–GS conducting polymer composites can be utilized as material for charge storing devices, decoupling capacitors, and anti static and EMI shielding applications. In this study, the electrical conductivity of SAN–GS composites was investigated for different volume fractions of GS (ϕ). The observed insulator–conductor transition of the SAN–GS composites is explained by the power law model of percolation theory. The dielectric constant, dissipation factor and AC conductivity of these composites were analyzed as a function of low and high frequencies. The shielding effectiveness of the SAN–GS composites were also investigated theoretically in the high radio frequency range (1 MHz–3 GHz).

2. Experimental

2.1. Materials

The polymer matrix used in this work was SAN of commercial grade in the form of granules having density 1.08 g/cm³, hardness (Rockwell M) ~84, Vicat softening point 107 °C, glass temperature (Tg) ~119 °C, melting temperature ~250 °C and melt flow rate 2.5 g/10 min. These granules were cryogenically pulverized (assumed to be brittle at very low temperature) and sieved to particles of the required size. The shapes of the particles were irregular stone like, as observed by the scanning electron microscopy (SEM) micrograph shown in Fig. 1(a). The images show that the SAN particles have an average size of 212–250 μm. Natural graphite flakes (NFG) with average particle size of 10–20 μm, supplied by Graphite India Ltd., was used as the source of the graphite sheets (GS). The conductivity of the graphite flakes was 1.33 × 10⁴ S/cm with density 1.75 g/cm³. The GS with thickness of 100–150 nm and diameter of 1–20 μm was used as the conducting filler to prepare the SAN/GS composites.

2.2. Preparation of graphite sheets (GS)

The graphite sheets (GS) were prepared according to the method described in our previous publication [33]. A mixture of concentrated sulfuric acid and nitric acid (4:1, v/v) was mixed with graphite flakes at room temperature and stirred continuously for 16 h. The acid-treated natural graphite was first neutralized with water and then vacuum filtered followed by drying at 100 °C to remove the remaining moisture. The dried particles are known as graphite intercalated compound (GIC). Acid intercalated ions occupies the space in between the carbon layers during the formation of GIC. The expansion of GIC can be achieved by providing a thermal shock in a microwave oven for 20 s to obtain expanded graphite (EG). There is a sudden expansion of about 100 times along their c-axis during expansion. EG is a loose and porous vermicular product of greatly decreased density. EG was then immersed in 70% aqueous alcohol solution and subjected to sonication in an ultrasonic bath for 8 h. The resulting dispersion was vacuum filtered and dried to get GS. The shapes of the Graphite Sheets (GS) are shown in Fig. 1(a).

2.3. Preparation of composites

Initially, the obtained graphite sheets (GS) was mixed with the polymer by pastel mortar. The mixture was further tumble mixed [34,35] thoroughly for 4 h at room temperature. This process, referred to as prelocalization of the conductive phase, involves the coating of the conducting GS on the surface of the SAN particles. Prolong mixing improves the homogeneity of the spatial distribution of the conductive particles. The tumble mixed, pre-localized powders were prepared to obtain different GS contents in the range of about 0, 1, 2, 3, 4, 5, 7, 10, 15, 20 and 25 wt% of graphite under similar conditions. The corresponding volume fraction of GS (ϕ) of these samples were 0, 0.0055, 0.011, 0.016, 0.022, 0.027, 0.039, 0.057, 0.088, 0.12 and 0.14.

The GS coated SAN powder was pressed initially for 5 min by using a hydraulic press (Shimadzu Corp., Kyoto, Japan) having ram diameter of 42.7 mm at room temperature to eliminate any void formation within the pellet. A circular mold was used in this study. The processing temperature (initial temperature) and pressure were the main parameters affecting the graphite mixed polymer composite pellets. The composites were to have good conductivity as well as hardness. After the processing temperature and pressure were optimized, all the samples were prepared at the processing temperature of 90 °C at 70 MPa and baked at 120 °C at 35 MPa for 15 min to achieve conductivity as well as hardness.

2.4. Measurements

For the measurement of conductivity, both opposite surfaces of the samples were coated with SEM grade conductive silver paint. Copper connecting wires were bonded to the surfaces with the conductive silver paint. The resistance of the samples having resistance less than 200 MΩ was measured using a conventional digital multimeter. When the resistance exceeded 200 MΩ, a Keithley Picoammeter was used to measure the resistance.

For studying the dielectric properties, the capacitance and dissipation factor of the samples were measured in two frequency ranges, 20 Hz–1 MHz and 1 MHz–3 GHz, by using an Agilent Precision LCR Meter (Model No. 4284) and RF Impedance/Material Analyzer (Model No. E–4991 A).

3. Results and discussions

3.1. Morphology

Fig. 1(a) shows the SEM images of pure GS and it can be seen from figure that GS was completely split, resulting in small graphite sheets with thickness of 100–150 nm and a
diameter of 1–20 μm. Fig. 1(b)–(d) show the SEM images of composites below ϕc, near ϕc, and above ϕc having GS volume fraction ϕ = 0.011 (2 wt%), ϕ = 0.027 (5 wt%) and ϕ = 0.14 (25 wt%), respectively. Note that the SEM images (Fig. 1(b)–(d)) were taken on fractured surfaces, which were obtained by dipping the samples in liquid nitrogen and then hammering them. Fig. 1(b) shows fractured morphology of SAN/GS composite having 2 wt% of GS. A trapped GS in interfaces of SAN particles are clearly seen from this figure. Near ϕ = ϕc in Fig. 1(c), this stage clearly shows the dispersion of GS in the interfacial regions between SAN particles. For ϕ > ϕc the SEM image (Fig. 1(d)) shows the increasing percentage of GS in the interfacial region of SAN particles and represents a conductive path for a movement of electrons throughout the composites.

3.2. Electrical conductivity

Fig. 2 shows the electrical conductivity of the SAN–GS composites as a function of the volume fraction (ϕ) of GS. The conductivity of the composites increases sharply near ϕ = 0.022, at which the insulator-conductor transition is clearly shown. According to the percolation theory, the conductivity of composites near the insulator-conductor transition can be represented by the power law model of percolation theory [28,29]:

$$\sigma \propto (\phi - \phi_c)^t$$

(1)

where σ is the conductivity of the composite, ϕc is the critical filler volume fraction at which percolation takes place, and t is the critical exponent of conductivity. The experimental values of conductivity were fitted to Eq. (1) and a log–log plot of the power law was generated, as shown in the inset of Fig. 2. The best fit of the conductivity data to the log–log plots of the power law gives ϕc = 0.020 and t = 1.62. The value of t for our composite system is found to be nearly equal to 2 which is universal value of three dimensional systems. It should be mentioned that Kirkpatrick [36] and Straley [37] obtained values of t = 1.5 ± 0.2 and 1.75 ± 0.1, respectively.

3.3. Dielectric properties in low frequency region

Conducting polymer composites possess a frequency (ω) dependent, complex dielectric constant $$\varepsilon' (\omega) = \varepsilon'' (\omega) - i \varepsilon'' (\omega)$$. The real part $$\varepsilon' (\omega)$$ represents the relative dielectric constant and the imaginary part $$\varepsilon'' (\omega)$$ accounts for the dielectric loss. The ratio of the imaginary to the real part ($$\varepsilon''/\varepsilon'$$) is the “dissipation factor”, which is represented by tan δ, where δ is called as the “loss angle” denoting the angle between the voltage and the charging current. To investigate the dielectric behavior of the SAN–GS composites in the low frequency (fL) range, the room temperature $$\varepsilon'$$ and tan δ of the composites were calculated in the frequency range from 20 Hz to 1 MHz.

Fig. 3 shows the variation of $$\varepsilon'$$ of the SAN–GS composites as a function of ϕ of GS at 100 kHz. The $$\varepsilon'$$ values increase with the increase of GS content in the composites. The $$\varepsilon'$$ of a pure SAN sample is about 11.27. The $$\varepsilon'$$ (= 468.7) of composites with ϕ = 0.005 increases rapidly after that the $$\varepsilon'$$ increases slightly up to that of the composite with ϕ = 0.022. The $$\varepsilon'$$ of the composites enhances greatly near ϕ = 0.027. The $$\varepsilon'$$ of the composites in the low frequency region greatly enhances due to the Maxwell–Wagner polarization originating in the insulator-conductor interfaces. This enhancement of the dielectric constant in the neighborhood of the percolation threshold is also predicted by the power law [38–40] as follows:

$$\varepsilon' \propto (\phi_c - \phi)^{-s}$$

(2)

where s is a critical exponent. The log–log plots of Eq. (3) are shown in the inset of Fig. 3. The value of ϕc = 0.027 was found to be slightly bit higher as that obtained with the conductivity data. The value of s was found to be 0.70, which is the universal value given by percolation theory [38].

The dependence of $$\varepsilon'$$ of the SAN–GS composites on low frequency (fL) is shown in Fig. 4. The $$\varepsilon'$$ of the composites having ϕ = 0 and 0.0055 exhibit weak frequency dependence, but when ϕ > 0.011, the $$\varepsilon'$$ of the composites exhibits strong frequency dependence and decreases sharply.
between the frequency range from 20 Hz to 500 Hz and it may be attributed to the large leakage current resulted from the high conductivity composites. At low frequency, a high value of $\varepsilon'$ of composites with $\phi > 0.011$ was observed because at low frequencies, polarization follows the change of the electric field, and dielectric loss is minimum and the contribution the dielectric constant is maximum. At high frequencies, the electric field changes too fast for the polarization effects to appear. In this case, the contribution to the $\varepsilon'$ is minimal and there are almost no dielectric losses in the system. The high value of $\varepsilon' = 1.082 \times 10^7$ is observed at 40 Hz for the composites with $\phi = 0.12$. A high value of $\varepsilon'$ would be beneficial in capacitor applications.

The dependence of $\tan \delta$ of the SAN–GS composites on low frequency ($f_L$) is shown in Fig. 5. The $\tan \delta$ maintains a maximum value up to 300 Hz for the composites having $\phi > 0$ but after this frequency, decreases with the increase of frequency. This is because the induced charge gradually fails to follow the reversing field causing a reduction in the electric oscillations as the frequency is increased. The high value of $\tan \delta = 2.13 \times 10^4$ is observed at 300 Hz for the composites with $\phi = 0.088$. The high values of $\tan \delta$ of the composites can be beneficial in decoupling capacitor applications.

3.4. Dielectric properties in the high frequency region

Dielectric properties of the SAN–GS composites in the high frequency region are necessary for the application of the EMI shielding application. To investigate the dielectric behavior of the SAN–GS composites at high frequencies ($f_H$), the room temperature $\varepsilon'$ and $\tan \delta$ of the composites were calculated in the frequency range from 0.001 GHz to 3 GHz (radio frequency). Fig. 6 shows the $\varepsilon'$ of the composites as a function of $f_H$ for various contents of GS. The $\varepsilon'$ of composite with $\phi < \phi_c = 0.027$ decreases slowly with increasing frequency and the $\varepsilon'$ of composites with $\phi \geq \phi_c = 0.027$ decreases sharply with increasing frequency and these composites ($\phi \geq \phi_c$) show complex fluctuations between $f_H = 0.1$ GHz to 3 GHz. The $\varepsilon'$ increases with increasing $\phi$ and increases sharply near $\phi_c$. The high value of $\tan \delta$ is observed at 300 Hz for the composites with $\phi = 0.088$. The high values of $\tan \delta$ of the composites can be beneficial in decoupling capacitor applications.
of $\varepsilon' = 2.1 \times 10^5$ is observed at 0.001 GHz for composite with $\phi = 0.14$ while at higher frequencies, the high value of $\varepsilon' = 470$ is observed at 1 GHz for the composite with $\phi = 0.12$. The composites possess high values of $\varepsilon'$ in the radio frequency range, indicating that the composites could be utilized as EMI shielding material.

Fig. 7 shows the $\tan \delta$ of the composite as a function of $f_H$ for various contents of graphite. The $\tan \delta$ decreases slowly with increasing $f_H$ for composites having $\phi < \phi_c$. The $\tan \delta$ shows a complex fluctuation with the measured $f_H$ for composites $\phi > \phi_c$. The high value of $\tan \delta = 7.2 \times 10^4$ is observed at 0.001 GHz for the composite with $\phi = 0.057$ while at higher frequencies, the high value of $\tan \delta = 35$ is observed at 1 GHz for the composite with $\phi = 0.057$. High values of $\tan \delta$ in the radio frequency range are useful in EMI shielding material.

Fig. 8 shows the $\sigma_{ac}$ of the composites as a function of $f_H$ (radio frequency) for various contents of graphite. The $\sigma_{ac}$ of composites with $\phi < \phi_c = 0.027$ increases sharply with the increase of $f_H$ but a complex fluctuation of $\sigma_{ac}$ is seen when $f_H \gg f_H$. For composites with $\phi > \phi_c$, the $\sigma_{ac}$ is high and remains constant with the increase of the frequency. So, because the SAN–GS composites have high AC conductivity and weak frequency dependence, they are excellent antistatic media and shielding for electromagnetic or radio frequency interference of electronic devices.

3.5. EMI shielding

For a transverse electromagnetic wave propagating into a sample with negligible magnetic interaction, the total shielding efficiency ($SE_T$) of the sample is expressed as Eq. (3) [41–43]:

$$SE_T = 10 \log \left( \frac{P_{in}}{P_{out}} \right) = SE_A + SE_R + SR_I$$  \hspace{1cm} (3)

where $P_{in}$ and $P_{out}$ are the power incident on and transmitted through a shielding material, respectively. The $SE_T$ is expressed in decibels (dB). $SE_A$ and $SE_R$ are the absorption and reflection (from both sides of the material on the condition of neglecting the multiple reflections inside the barrier) shielding efficiencies, respectively. The third term ($SE_I$) is a positive or negative correction term induced by the reflecting waves inside the shielding barrier, which is negligible when $SE_A > 15$ dB. The terms in Eq. (1) can be described as:

$$SE_A = 8.86 \frac{\alpha l}{\lambda_0}$$  \hspace{1cm} (4)

$$SE_R = 20 \log \left( \frac{1 + n^2}{4|n|} \right)$$  \hspace{1cm} (5)

$$SE_I = 20 \log \left[ 1 - \left( \frac{\exp(-2\pi f_l)\left(1 - n^2\right)}{(1 + n^2)^2} \right) \right]$$  \hspace{1cm} (6)

where the parameters $\alpha$, $n$ and $\gamma$ are defined by the following equations, $l$ is the thickness of the shielding barrier.

$$\alpha = \frac{2\pi}{\lambda_0} \sqrt{\varepsilon' \left( \frac{1 + \tan^2 \delta}{2} \right)}$$  \hspace{1cm} (7)

$$n = \sqrt{\frac{\varepsilon' \left( \frac{1 + \tan^2 \delta \pm 1}{2} \right) + i \sqrt{\varepsilon' \left( \frac{1 + \tan^2 \delta \mp 1}{2} \right)}}{2}}$$  \hspace{1cm} (8)

$$\gamma = \left( \frac{2\pi}{\lambda_0} \right) \sqrt{\varepsilon' \left( \frac{1 + \tan^2 \delta \pm 1}{2} \right) + i \left( \frac{2\pi}{\lambda_0} \right) \frac{\varepsilon' \left( \frac{1 + \tan^2 \delta \mp 1}{2} \right)}{2}}$$  \hspace{1cm} (9)

where $\lambda_0$ is the wave length, $\varepsilon'$ the real part of complex relative permittivity, the $+$ and $-$ signs are applied for positive and negative $\varepsilon'$, respectively.

Using Eqs. 4, 5, 7 and 8, the values of $SE_R$ and $SE_A$ for the SAN–GS composites were calculated. The $SE_R$ and $SE_A$ of the composites as a function of $f_H$ (0.001–3 GHz) are shown in Figs. 9 and 10, respectively. The $SE_R$ of the composites decreases slowly with the increase of $f_H$ except when the oscillations occur above 1 GHz, and increases with the increase of $\phi$. A high value (~53 dB) of $SE_R$ is obtained at 0.001 GHz for the composites with $\phi = 0.12$ (20 wt%) because the composites have high values of $\varepsilon'$ and $\tan \delta$. The $SE_A$ of composites increases with $f_H$ because $SE_A$ is directly proportional to $f_H$ as observed by Eqs. (4) and (7). The maximum value (176 dB) of $SE_A$ is obtained at

![Fig. 9. Variation of $SE_A$ of the SAN–GS composites as a function of $f_H$ for different $\phi$'s.](image-url)
1.57 GHz for composites with \( \phi = 0.12 \) (20 wt%). Using Eqs. 6, 8 and 9, the values of \( SE_I \) were calculated and \( SE_I \) of all the composites was 1. The total SET of the composites was calculated by adding SER, SEA and SEI. The SET of the composites as a function of \( f_H \) is shown in Fig. 11. The SET of the composites increases with the increase of \( \phi \) and decreases with the increase of \( f_H \) except when the oscillations occur above 1 GHz. As expected from the above data on SER and SEA, the trend of SET shows that SER comprises a major portion of the EMI SE. The maximum value (201 dB) of SET is obtained at 1.57 GHz for the composites with \( \phi = 0.12 \) (20 wt%). The high value of SET can be utilized for shielding material of various types of equipment from electromagnetic interference in the radio frequency range.

4. Conclusions

Both electrical conductivity and dielectric constant of SAN–GS composites followed the power law model of percolation theory at the percolation thresholds \( \phi_c = 0.020 \) (4 wt%) and \( 0.0271 \) (5 wt%). The dielectric constant of SAN–GS composites with \( \phi \geq 0.011 \) (2 wt%) was strongly low frequency dependent. The highest dielectric constant \( (1.082 \times 10^7) \) was obtained at 40 Hz for the composites with \( \phi = 0.12 \) (20 wt%). These composites can be used in charge storing devices. The highest dissipation factor \( (2.13 \times 10^5) \) was obtained at 300 Hz for the composites with \( \phi = 0.088 \) (15 wt%) and this property makes these composites suitable for decoupling capacitor applications.

In the GHz frequency range, the maximum values of \( e' = 470 \) was obtained at 1 GHz for the composite with \( \phi = 0.12 \) (20 wt%) and the maximum values of \( \tan \delta = 35 \) was obtained at 1 GHz for the composite with \( \phi = 0.057 \) (10 wt%). High values of \( e' \) and \( \tan \delta \) in the radio frequency range can be utilized for EMI SE applications.

The SET of composites was found to increase with the increase of \( \phi \) and decrease with the increase of \( f_H \) except when the oscillations occurred above 1 GHz. The maximum value (201 dB) of SET was obtained at 1.57 GHz for the composites with \( \phi = 0.12 \) (20 wt%). The high value of SET can be utilized in shielding of various types of equipment from electromagnetic interference in the radio frequency range.

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