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Polyphenylene sulphide/graphite composites for EMI shielding applications

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ABSTRACT

Electrical properties of graphite flake (GF) filled polyphenylene sulphide (PPS) composites prepared by hot pressing was investigated to be used for electromagnetic interference (EMI) shielding applications. Composites exhibited an electrical conductivity percolation threshold of 5 wt%. The electrical conductivity of composites was increased fourteen orders of magnitude higher than that of pure PPS. The dielectric constants and dissipation factor of composites were measured in a frequency range of 100 KHz to 15 MHz. The dielectric constant of the composites increased several orders of magnitude and showed a strong dependence on frequencies. For example, dielectric constant of 8 wt% composite measured at 1 MHz was increased by five orders of magnitude compared to pure PPS. Similarly, dissipation factor was increased significantly. Scanning electron microscopy showed 3-dimensional conducting network of GF across the PPS matrix. Significant improvement in electrical properties shows that these composites may be useful for EMI shielding particularly at high temperature applications.

Keywords: Polymer-matrix composites; conductivity; scanning electron microscopy; dielectric property.

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Introduction

Electromagnetic interference (EMI), which is an unwanted disturbance to the electronic devices, may interrupt, degrade or limits the effective performance of the electronic devices. The protection of the devices and circuits against EMI with shielding materials has become essential issues [**1-3**]. The shielding materials must possess good electrical conductivity and dielectric constant. The metals are well suited for many EMI shielding applications. However, metals have their own shortcomings like heavy weight, susceptibility to corrosion, wear, physical rigidity etc. The conductive particle filled polymer-matrix composites score over these materials with advantages like low weight, resistance to corrosion, ease of processing and tailored coefficient of thermal expansion [**4-6**]. The electrical conductivity is imparted to the composite due to the formation of 3-dimensional (3-D) conducting paths of fillers within the matrix. The minimum loading of conducting particles at and above which 3-D network is formed within the matrix is called a percolation threshold [**5**]. The percolation threshold depends upon the aspect ratio, inherent electrical conductivity and degree of dispersion of filler in the matrix, nature of interface and interaction between the filler and matrix. Conductive polymers such as polyaniline or polypyrole filled polymer composites have been also reported as EMI shielded materials, but their poor mechanical properties and processability limit their application [**7-8**]. Therefore, use of carbon materials such as carbon nanotube (CNT), carbon black, carbon fiber, carbon nanofiber (CNF) etc. as fillers in polymer matrix for EMI shielding have been studied as they exhibit good electrical properties in addition to good mechanical properties. High aspect ratio of filler helps in attaining the percolation threshold at very low filler concentrations, i.e., 0.05–0.1 wt% for polystyrene/CNT composites [**6**] and 1-2 wt% for polyphenylene sulphide (PPS)/CNT composites [**9**]. Though percolation threshold values are low for polymer/CNT composites, CNT has certain drawbacks such as its difficulties in dispersion and alignment in the matrix and poor compatibility with polymers. Moreover, its breakage during processing or treatment with acids results in decreased aspect ratio [**10-11**]. The cost of CNT is about 500 times than that of graphite. The electrical conductivity of graphite is approximately 2.26 x 10^4 S/cm. The percolation threshold for graphite filled polymer composites varies from less than 1 to 13 vol% depending upon the aspect ratio and its distribution in the matrix [**12-13**].

In view of above, this research work aims to produce graphite flake (GF) filled PPS composites by exploiting properties of PPS and GF. Nevertheless, the PPS is a high performance semi-crystalline polymer which exhibits a glass transition temperature of 85 ºC, a crystalline melting point of 285 ºC and continuous use temperature of 240 ºC. Moreover, it has inherent fire retardant property. To the best of our knowledge, detailed studies on the electrical and dielectric properties of PPS/GF composites were not carried out yet. In this work, we report here that homogeneous PPS/GF composites can be prepared using a simple method, i.e., by dispersing commercial GF powder in PPS matrix via solvent suspension method followed by hot pressing. These composites show dramatic improvement in electric conductivity and dielectric properties with relatively low percolation threshold (5 wt%) of untreated GF. The lower percolation threshold with significant improvement in electrical conductivity for a highly crystalline PPS matrix is significant. It is to be noted that the calculated EMI shielding of these composites are comparable with that of polymer/CNT composites in addition to their low cost.

Experimental

Materials

The commercial PPS powder purchased from Aldrich Chemical Company (M_n: 10000, CAS: 25212-74-2) was used as a matrix. The graphite flake (GF) purchased from Aldrich Chemical Company was used as filler without treatment. A commercial absolute ethanol was used as a solvent medium for mixing GF and PPS powders using ultrasonic bath followed by mechanical stirring.

Fabrication of composites

Pure PPS powder and GF powder were dried in an oven for 3 h at 120 ºC. The dried GF powder was first suspended in an absolute ethanol using ultrasonic bath for 30 minutes. Then, the PPS powder was added slowly into the GF/ethanol solution with concurrent stirring and heating at 80 ºC till dried powder was obtained. The resultant powder was further dried at 120 ºC for 10 hrs in a vacuum oven. Then, the PPS/GF composites were fabricated using hot pressing technique. The dried powder was filled in a tool steel die having diameter 13 mm. The powder was heated at an average heating rate of 10 ºC/min under pressure of 45 MPa to a maximum temperature of 330 ºC. After soaking period of 30 minutes, the samples were air cooled to a temperature of 50 ºC and then samples were ejected. Thus, composites containing 0, 5, 8, 10 and 20 wt% GF were fabricated. In other words, composites have 0, 3.06, 4.96, 6.25 and 13.04 vol% GF in the PPS matrix.

Characterizations

The theoretical density of the composites was calculated by the rule of mixture (ROM) using the density of PPS 1.35 g/cm^3 and of GF 2.2 g/cc. For theoretical density (ρ_{th}), it was assumed that there were no voids and no loss of GF powder during processing. The ROM can be expressed by $\rho_{th} = \rho_m.V_m + \rho_f.V_f$, where, V_m is the volume fraction of the matrix and V_f is the volume fraction of the filler. The ρ_m and ρ_f is the density of matrix and filler, respectively. The experimental density was determined using Archimedes's Principle. SEM (JEOL JSM 6360A) operated at 20 KV was used to investigate the distribution of GF in PPS matrix. For this, samples were dipped in liquid nitrogen for 15 minutes and then fractured. The fractured surface of sample was coated with a thin layer of platinum using sputter coater and mounted on metal stub which was grounded with silver paste to minimize charging effects. For measuring electrical conductivity and dielectric properties, samples were coated with a thin layer of silver paste. The volume resistance of samples was determined by using high resistance meter (Keithley 6517B). However, when the volume resistance is below 10^6 Ω, an Agilent 6½ digital multi meter (Agilent 34401A) was used. The volume resistivity was measured by the relation $\rho = R (A/L)$, ρ is resistivity in Ω/cm, R is resistance in ohms, L is the thickness in cm and A is the cross sectional area (cm^2) of sample. The electrical conductivity was reported as the reciprocal of the volume resistivity. The dielectric constant was obtained from the measurement of capacitance (C) using Wayne Kerr Electronics precision impedance analyzer [6515B, UK] at frequencies varying from 100 KHz to 15 MHz at 30 °C. The dielectric constant (ε) was evaluated by the relation $\varepsilon = Ct/\varepsilon_0 S$, S is the surface area and t is the thickness of the dielectric material. The ε_0 is the permittivity of the free space (8.854 × 10^{-12} F/m). The dissipation factor was obtained directly from the instrument.

Results and discussion

Fig. 1 shows the theoretical and experimental density of the PPS composites. PPS has experimental density of 1.35 gm/cc. The density of the composite increased with increasing GF content due to its higher density (2.2 g/cc) than that of PPS. The experimental density is almost very close to that of theoretical density. This shows that the prepared samples are almost porosity free. However, in case of 13.04 vol% (20 wt%) composite, the experimental density is slightly lower than that of the theoretical density. This is attributed to the agglomeration of GF particles through which infiltration of molten PPS might have found

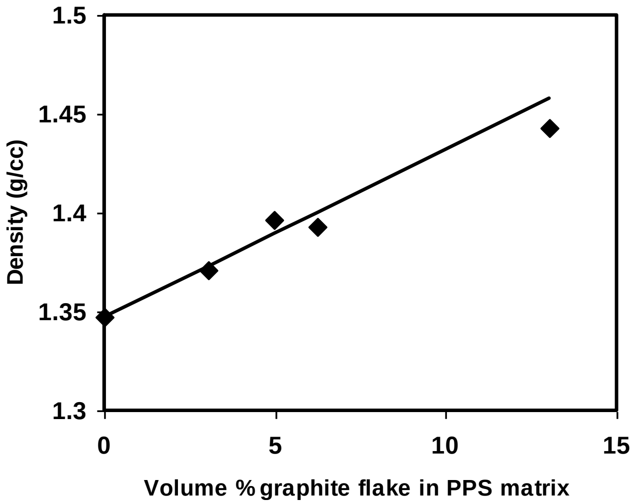

Fig. 1. Theoretical and experimental density for PPS/GF composites. Solid line represents theoretical density predicted from a rule of mixture and filled diamonds are experimental data.

conductivity of pure PPS is about 1.47×10^{-16} S/cm. It increased with increasing GF in PPS matrix, i.e., there is sharp increase in conductivity from 4.5×10^{-13} S/cm for 5 wt% composite to 4.55×10^{-4} S/cm for 8 wt%, 4.12×10^{-3} S/cm for 10 wt% and to 1.25×10^{-2} S/cm for 20 wt% composite. The low percolation (i.e., 5 wt%) may be due to the high aspect ratio of graphite flake and flat sheet like shaped particle which help in forming 3-D network. The conductivity of 8 wt% and 20 wt % composite is twelve orders of magnitude and fourteen orders of magnitude higher than that of pure PPS, respectively. It is interesting to see that the percolation threshold for multi walled carbon nanotube (MWCNT) filled PPS composites prepared by Hake mixer followed by hot pressing was reported between 5 and 7 wt% MWCT [**14**]. The reason for the high percolation threshold for PPS/MWCNT was attributed to the reduced aspect ratio by high shear stresses during processing. The lower percolation threshold with significant improvement in electrical conductivity for a highly crystalline PPS (~ 60%) with micron sized flake shaped GF particle is very interesting compared to that of high density polyethylene (14.3 vol% CNF). The insignificant improvement in conductivity after 10 wt% may be attributed to the tendency for aggregation of GF particles as confirmed from SEM images. It is interesting that mixing of polymer and filler using a simple solvent

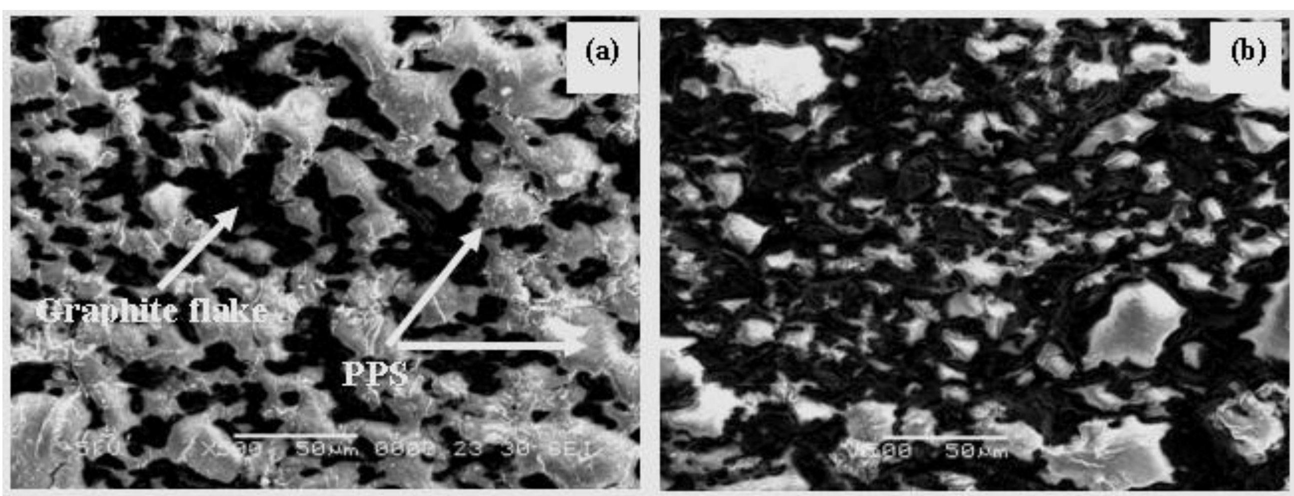

Fig. 2. SEM of fractured surfaces of (a) 8 wt% and (b) 20 wt% GF filled PPS composites.

difficulty during hot pressing. **Figs. 2a and b** show SEM of 8 wt% and 20 wt% GF filled composites, respectively at 500X magnification. From **Fig. 2a**, it can be seen that the GF is uniformly distributed in the PPS matrix and form a partly continuous 3-dimensional (3-D) network of GF across the entire cross section. This network indicates that the percolation threshold value for PPS/GF system start at 5 wt% GF in the PPS matrix. The better distribution of GF in the matrix might be due to the good processing conditions. In case of 20 wt% GF composite (**Fig. 2b**), complete 3-D network of GF was formed. However, some agglomerates of GF were also seen due to the decreased inter-particle distances as GF content increased.

Fig. 3 shows the volume electrical conductivity of PPS/GF composites as a function of GF. The electrical

dispersion method followed by hot pressing yielded low percolation threshold. The low percolation threshold would be beneficial for the industries particularly for antistatic and electromagnetic interference (EMI) shielding applications.

Fig. 4a shows the dielectric constants for the pure PPS and its composites measured at frequencies varying from 100 KHz to 15 MHz. The dielectric constants for pure PPS and 5 wt% GF composites are almost frequency independent. However, dielectric constant for composites with more than 5 wt% GF content decreased gradually with increasing frequencies. The significantly higher dielectric constants at lower frequencies are believed to be due to the Maxwell-Wagner polarization originating in the interfaces between the GF particles and the matrix [**15-16**]. The dielectric constants of 8, 10 and 20 wt % composites measured at 100 KHz are 1.7×10^7, 2.7×10^7 and 2.3 ×

10^8, respectively. It can be seen from **Fig. 4b** that dielectric constants of composites increased with increasing GF content. Similar to electrical conductivity, dielectric constant of the composites increases sharply above 5 wt% GF content. Higher aspect ratio of GF led to the formation of conductive path at lower GF content. The dielectric constants for 0 and 5 wt% composites measured at 1 MHz is 3.25 and 6.64, respectively. The dielectric constants for 8, 10 and 20 wt% composites at 1 MHz are 1.9×10^5, 2.9×10^5 and 8.3×10^6, respectively. The increased dielectric constants are primarily due to the interfacial polarization. The improvement in dielectric constant for composite with more than 5 wt% is significant compared to that of CNF filled polymer [**17-18**] composites. A high dielectric constant would be beneficial for flexible capacitors and EMI shielding applications.

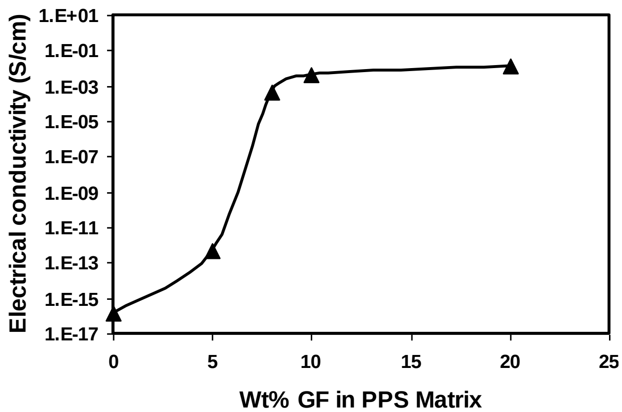

Fig. 3. Electrical conductivity of PPS/GF composites.

Fig. 5 shows the dissipation factors (tan δ) for the pure PPS and its composites measured at frequencies varying from 100 KHz to 15 MHz as a function of EG content. The tan δ for pure PPS measured at 1 MHz is 0.005. The tan δ for 0 and 5 wt% composites increases steadily with increasing frequency but it is lower than 0.1 at all frequencies. Similar to dielectric constant and electrical conductivity, significant increase of tan δ values at a constant frequency can be seen for the composites containing more than 5 wt% GF. The value of tan δ as high as ~10^{13} was obtained at 100 KHz for 20 wt% composite. The high tan δ is good for EMI shielding applications. The significant increased electrical conductivity, dielectric constant and tan δ of the PPS/GF composites are favorable for use in antistatic and EMI shielding materials [**19-22**]. Yang reported that the EMI shielding effective of 10 wt% CNF filled polystyrene composite with electrical conductivity of 10^{-3} S/cm is 13 dB in the Ku-band. Similar trends were report for CNF filled liquid crystal polymer composites. This supports that PPS/GF composites owing to comparable electrical conductivity with high interfacial area would also show good EMI shielding properties [**23**].

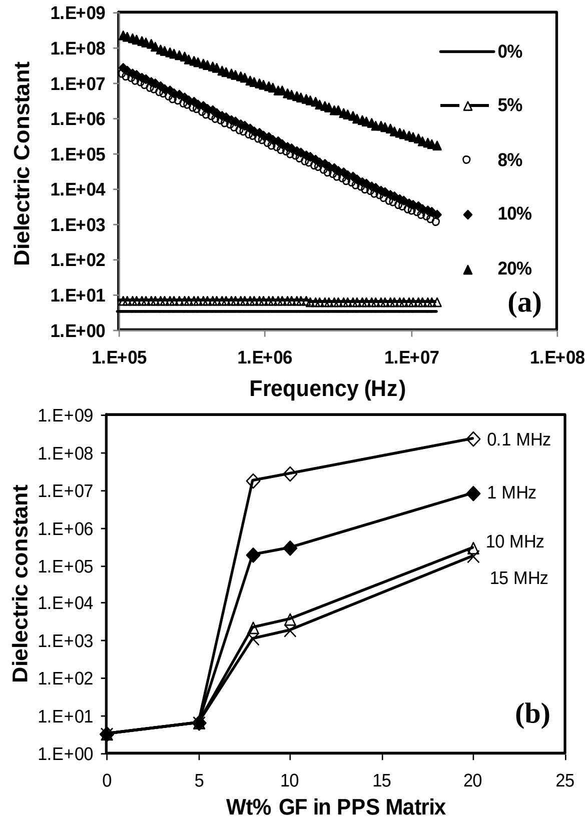

Fig. 4. Dielectric constants for composites as a function of (a) frequency and (b) GF content in the matrix.

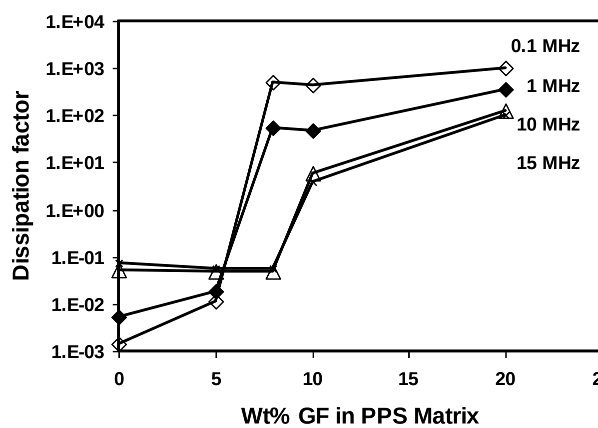

Fig. 5. Dissipation factor for composites as a function of GF content in the matrix.

Conclusion

High performance PPS/GF composites were fabricated successfully by a hot pressing technique. A percolation threshold at 5 wt% GF was obtained. The electrical conductivity was improved up to fourteen orders of magnitude higher than the pure PPS. The dielectric constant and dissipation factor for composites with more than 5 wt% GF were increased significantly but decreases with increasing frequencies. SEM showed 3-dimensional conducting path of GF particles in the matrix. The significant improvement in electrical conductivity and dielectric constant were attributed to the high aspect ratio and better dispersion of GF particles in the matrix. Based on the results, it may be concluded that these composites may prove to be the futuristic high performance materials for antistatic/EMI shielding applications particularly at higher temperatures.

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