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Graphene-ferrites interaction for enhanced EMI shielding effectiveness of hybrid polymer composites

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Abstract

Hybrid polymer composites based on poly vinylidene fluoride (PVDF) matrix are fabricated by dispersion of few layered graphene (FLG) and nickel spinal ferrites (NSF) for improving EMI shielding effectiveness. The FLG loading is kept constant at 3 wt% while NSF content is varied from 15–30 wt% in PVDF using solution processing technique. The shielding effectiveness in the frequency domain of 1–12 GHz is enhanced ranging 25 dB–45 dB for PVDF/FLG composite as compared to ~0 dB for neat PVDF. With addition of NSF up to 15 wt%, the attenuation is increased to 30 dB–53 dB, clearly indicating the effective interaction and network formation of FLG and NSF in PVDF matrix. Moreover, the shielding effectiveness trend is reduced to 12 dB–43 dB as the NSF loading is increased to 30 wt% owing to its agglomeration. Absorption is the dominant phenomena in obtaining the total shielding effectiveness of ~53 dB for PVDF/FLG–3 wt%NSF–15 wt% hybrid polymer composites. Additionally, the I-V curves provide the electrical conductivity trend while scanning electron microscope (SEM) confirms the network formation in hybrid composite.

Introduction

Hybrid polymer composites are used in various areas of applications due to their ease of processing, non-corrosiveness, light weight and flexibility. One such utilization is to employ them for the growing concern of EMI pollution especially in digital electronics & communication field [1–9]. The choice of both matrix and fillers may be tailored according to their content and related interaction. Furthermore, to attenuate both electric and magnetic part of EM waves; the canvas for fillers is certainly broadened. In this regard, carbonaceous and ferritic fillers are most sort out materials mainly due to their ability to interact with EM waves and attenuate the electric and magnetic parts respectively [10]. Earlier the most followed route for polymer composites was to disperse either metallic or carbonaceous particles to impart the EMI shielding properties. Current trend is certainly more towards fabrication of hybrid composites, for instance dispersing both carbonaceous and ferritic nano fillers in polymer matrix. In case of carbon fillers, carbon nanotubes are extensively applied [11]. The experimental discovery of graphene has surpassed the CNTs use mainly due to the cost effectiveness and equivalent set of properties. There is an increasing trend of blending graphene with other fillers such as CNTs and ferrites for bettered EMI shielding properties of PNCs [12]. Graphene’s interaction with the ferritic nano particles is the basis for current work to enhance the EM shielding effectiveness. After a series of attempts; the composite sampling has been chosen, which have been evaluated thoroughly for the intended application in the frequency range of 1–12 GHz.
Materials and methods

Few layered graphene (XG sciences) and PVDF pellets-\textsubscript{M\textsubscript{w}} = 180,000 (Sigma Aldrich) are utilized along with synthesized nickel spinal ferrites (NSF) for the preparation of hybrid polymer composites. Chemical reaction route is followed to synthesize NSF from nickel and iron nitrates in the form of salts. Both these salts are separately dissolved in distilled water (0.1 M & 0.2 M) and mixed together at temperature of 80 °C–85 °C [13]. Likewise, another solution is set (3 M) with adding sodium hydroxide. NaOH is added in dropwise manner for 60 min as the temperature reached up to 80 °C–85 °C. The solution is washed numerous times to achieve a pH value of 7.0. The extracted precipitates were then dried and calcined in an electric furnace at a temperature of 850 °C for 6 h; followed by crushing and grinding processes in a mortar. The composites are prepared via solution casting method. All the three constituents, PVDF (50 mg ml\textsuperscript{-1}), FLG (5 mg ml\textsuperscript{-1}) and NSF (10 mg ml\textsuperscript{-1}) are separately dissolved in DMF. The samples are prepared with different weight ratios as shown in table 1.

For dispersion of FLG, the solution is magnetically stirred for 24 h and ultra-sonicated for 30 min. After adding NSF into the solution, it is mechanically stirred for 4 h. Afterwards, the solution is poured into the petri dishes and dried in vacuum oven at 80 °C and 300 mbar pressure. The dried films are used for the characterization.

SEM (JOEL JSM-6490A) is used for the morphological analysis. SEM images of fractured surfaces (in liquid nitrogen) are analysed for the microstructure of composite films. Figure 1 shows the representative images for morphology of neat PVDF (a) and the hybrid composites (b)–(c). The dispersion of fillers inside polymer plays an important role especially for the intended application here, EMI shielding, where a network formation is required for maximum outcome. The fillers seem to be dispersed homogeneously for all the sample composites supporting to form an electrically conducting network.

Results and discussion

The basis of this work is to form an electrical conducting network inside polymeric composite. At first, cyclic voltammetry (BioLogic VSP electrochemical workstation) is used to find out the I-V characteristics of the composite samples. A reference electrode (Calomel), a counter electrode (platinum wire) and working electrode (sample composite (1 × 1 cm\textsuperscript{2})) scheme is utilized in 1M solution of Sodium Sulfate (Na\textsubscript{2}SO\textsubscript{4}) electrolyte to attain the I-V plots as shown in figure 2(a). The DC conductivity of PVDF/FLG-3 is around 0.0012 S cm\textsuperscript{-1}. It further enhances to 0.0015 and 0.0018 S cm\textsuperscript{-1} as the NSF content are added up to 15 and 30 wt%, respectively (figure 2(b)). These results are averaged for 3 sample measurements. Graphene has obviously imparted its electrical characteristics to the polymer; which is further strengthened with the inclusion of NSF, confirming the probable interaction of these filler particles. The interaction of these nanofillers is useful in achieving EMI shielding properties. EMI shielding phenomena may be expressed schematically as shown in figures 3(a)–(b) [14]. The incoming electromagnetic waves are either reflected or transmitted through the shielding material, whereas a considerable amount of EM waves may be attenuated due to absorption by the inclusion of fillers. S-parameters are utilized to quantify the effect of reflection, absorption and transmission expressed as R, A and T respectively [5].

\[
R = S_{11}^2
\]
\[
T = S_{21}^2
\]
\[
A = 1 - R - T
\]

The relevant shielding effectiveness parts for reflection, absorption and their sum (total) are calculated as under:

\[
SE_T = SE_R + SE_A
\]
\[
SE_R = 10 \log \left( \frac{1}{1 - |S_{11}|^2} \right)
\]
In the above-mentioned equation (4) for total shielding effectiveness, the multiple or internal reflections part is neglected as for attenuation $>10$ dB, it is considered as part of absorption [15]. The electrical conductivity effect has been clearly translated into the EMI shielding properties of these hybrid polymer composites. The insulating behavior of neat PVDF is evident from the shielding effectiveness ($SE_T$) graph as shown in figure 4(a). Both the absorption as well reflection parameters trends are such that the base line SE remains mostly along $≈0$ dB with a slight hump observed around 6–8 GHz frequency range. Graphene inclusion clearly enhances the shielding effectiveness few folds. The $SE_T$ of PVDF/FLG-3 is $≥25–32$ dB around 2 GHz frequency range reaching up to increased attenuation of 35–40 dB at 5–9 GHz. The maximum enhancement in $SE_T$ is observed beyond 10 GHz.

\[
SE_T = 10 \log \left( \frac{1 - |S_{11}|^2}{|S_{21}|^2} \right)
\]
which is $\sim 45$ dB (figure 4(a)). For PVDF/FLG-3, the dominant part is absorption which is around 30 dB for most part of the frequency region (2–8 GHz) and reaches up to $\sim 35$ dB at 12 GHz (figure 4(b)). The maximum reflection $\sim 10$ dB is observed around 6–8 GHz (figure 4(c)). The addition of NSF to the PVDF/FLG composite should enhance the shielding effectiveness mainly due to the availability of magnetic domains for EM waves to tackle. The shielding effectiveness trend (blue line) for PVDF/FLG-3/NSF-15 composite is shown in figure 4(a). The shielding effectiveness is 30–40 dB around 2 GHz and increases gradually from 40–50 dB beyond this frequency. The maximum shielding effectiveness is observed around 6–8 GHz and 12 GHz which is $\sim 50–53$ dB. Similar to PVDF/FLG-3; the dominant shielding phenomena is absorption here as well. The maximum absorptive and reflective shielding effectiveness for PVDF/FLG-3/NSF-15 are $\sim 40$ dB and 13 dB respectively (figures 4(b)–(c)). The electromagnetic energy dissipation inside the materials may be explained with the following equation (7).

$$ SE_A = -8.68t\sqrt{\pi \omega \sigma_{AC} \mu} $$

Where $t$ is thickness, $\sigma_{AC}$ is the AC conductivity and $\mu$ is the permeability of the composite sample. The range of frequency is denoted by $\omega$. The EM waves are attenuated inside mostly by the micro capacitive effect along with the joule heating effect formed due to the few layered graphene. Multiple internal scattering inside polymer composite also dissipates the EM waves particularly the electric part. The ferritic content dissipates the other part, termed as magnetic loss which mainly occurs due to the ferromagnetic resonance, eddy current loss, hysteresis loss and domain-wall displacement. Both the dielectric and the magnetic losses add up to enhance the shielding effectiveness of the polymer composite [3, 16]. Another aspect which should positively affect the outcome is the possibility of graphene-ferrites interaction with the polymer chains. The different materials characteristics will cause inhomogeneities, thus creating the interfaces. The charge and magnetic dipoles accumulation at the interfaces may cause the enhanced shielding effectiveness due to absorption phenomena. Interestingly as the ferritic content is increased further to 30 wt%; the shielding effectiveness trend has been reduced and even gets lower than PVDF/FLG-3. It is because of the agglomeration effect affecting the shielding effectiveness performance of the hybrid composite at higher loading levels of NSF. The electromagnetic shielding
effectiveness achieved in current work is shown in comparison with other related works in Table 2. It also must be taken into account that the thickness of the hybrid polymer composites film in our work is around 250 micron.

**Conclusion**

Hybrid polymer composites based on the few layered graphene nanosheets and nickel spinal ferrites have been prepared for EMI shielding application in 1–12 GHz frequency regime. Both the fillers, few layered graphene and nickel spinal ferrites, enhanced the shielding effectiveness of polymer composites considerably to ∼45 dB and ∼53 dB (maximum) for PVDF/FLG-3 and PVDF/FLG-3/NSF-15 respectively. Dielectric and magnetic losses are the main factors arise due to the graphene and ferrites for the increased attenuation. The interfacial interaction may also be considered as the probable reason for enhanced absorption of EM waves. Further increase in ferritic content (30 wt%) has a compromised shielding effectiveness as compared to the above-mentioned samples mainly due to the aggregation issue. Moreover, the film thickness effect on the total shielding effectiveness will be further investigated for these types of hybrid polymer composites. Such hybrid...
polymer composites may find a prospect for future EMI shielding applications in broadband frequency spectrum both for human safety as well as in smooth operation of digital electronics.

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