Characterization of PVDF-Gr Composite Films for Electromagnetic Interference Shielding Application

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Abstract—Graphite receives tremendous attentions as filler for conducting composite due to its low cost and high electrical conductivities. In this work we use polyvinylidene fluoride (PVDF) as insulating matrix and graphite (Gr) as a filler to develop conducting composite films using solvent casting technique. The dielectric properties of the developed PVDF-Gr films were analysed for the frequency range of 100 kHz to 10 MHz. The morphology of the obtained films was investigated by scanning electron microscopy. The EMI shielding properties of the PVDF-Gr composite films were evaluated theoretically using ε', $\tan\delta$, and σ in the desired radio frequency region. Mechanical strength of the films was tested by universal testing machine. Due to advantages such as light weight, flexibility, and low cost the developed film with the thickness of ~ 0.15 mm had very good potential to be used for fabricating electromagnetic compatible electronic devices.

1. INTRODUCTION

In today's world electromagnetic interference (EMI) increases exponentially as technologies increase. To make a device work satisfactorily without interference from any other device in a confined frequency space is a challenging task, and to do so we have to make a device electromagnetically compatible [1, 2]. Electromagnetic interference (EMI) shielding is needed to make a device electromagnetically compatible [2]. For an EMI shielding material, electrical conductivity is the primary requirement which is the reason that initially metal was suitable for this application. Drawbacks of metal such as weight, prone to corrosion, and rigid shape had shifted the attention of researchers from metal to conducting polymer composites [3, 4]. A conducting polymer composite can be obtained with the incorporation of small fractions of non-metallic electrically conducting fillers with a non-conducting plastic matrix using techniques such as mechanical mixing, hot compression moulding, solvent casting, and insitu-polymerization [5]. Due to poor dispersion and lack of interfacial adhesion with other materials the high concentration of conducting filler can significantly decrease the mechanical strength of the composite films [6]. So good mechanical strength is always the priority in fabricating composite films for EMI shielding application.

Eswaraiah et al. [7] prepared a composite of functionalized graphene and (f-G)-polyvinylidene fluoride (PVDF), and investigated their electrical conductivity and EMI shielding efficiency. An EMI shielding effectiveness of ~ 20 dB and ~ 18 dB was obtained in different frequency bands for 5 wt.% composite. Taka [8] prepared a composites by mixing chemically synthesized poly (3-octyl thiophene) PS, PVC, and EVA in the melt state. EMI shielding efficiency at frequency range from 100 kHz to 1 GHz was measured. Shielding of the composites (3 mm thick) was ~ 45 dB with a polymer loading of 20% in the PVC matrix. In this work, due to its natural abundance and cost-effective property graphite (Gr) is used as a conducting filler material [9] and polyvinylidene fluoride (PVDF) as an insulating polymer

matrix. The developed composite films with a thickness of $\sim 0.15\,\text{mm}$ show excellent EMI shielding properties. The composites were prepared by solvent casting method. This method of fabrication of composite film is simple and less time consuming. The main advantages of using PVDF are its low weight, corrosion resistance, and mechanical flexibility. Due to these specific properties of PVDF and Gr, PVDF-Gr conducting polymer composites can be utilized as the material for EMI shielding applications. The dielectric constant, dissipation factor, and AC conductivity of these composites were analysed as a function of radio frequencies (100 kHz to 10 MHz), then EMI shielding properties were calculated theoretically. To test the mechanical strength of the developed composite films, universal tensile testing machine (Tensile test-Instron) was used. The surface morphology of the developed films was also analysed by scanning electron microscopy (SEM) images. The EMI shielding mechanism for a composite film is shown in Fig. 1 where we can see that the reflection and absorption are the two main mechanisms of shielding.
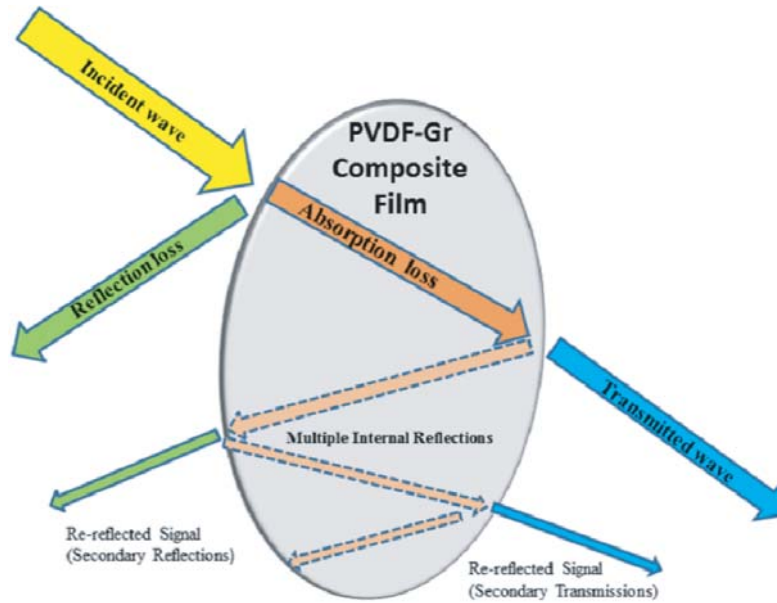

Figure 1. EMI shielding mechanism.

2. EXPERIMENTAL

2.1. Materials

Natural graphite flakes with average particle size of 10–20 μm, supplied by Graphite India Ltd. The conductivity of graphite flakes was $1.33 \times 10^4\,\text{S/cm}$ with density $1.75\,\text{g/cm}^3$. PVDF powder (Mw 440,000 g/mol) was purchased from Sigma Aldrich.

2.2. Preparation of Composite

The PVDF polymer and Gr filler powders were dry mixed thoroughly for 4 h in a glass beaker with a magnetic stirrer at the speed of 400 rpm with heating. This process coated the conducting graphite powder on the surface of the PVDF particles and is also referred to as the pre-localization of the conductive phase [6]. This mixing improves the homogeneity of the spatial distribution of the conductive particles and their uniform coating thickness on the PVDF particles. The 4 wt.%, 8 wt.%, and 12 wt.% of graphite filled polymer composites were prepared with solvent casting method as shown in Fig. 2. The mixed PVDF and Gr powder was dissolved in DMF and mixed thoroughly for 4 h in a glass beaker with a magnetic stirrer. After that, the blend solution was cast onto a glass petri dish. It was kept
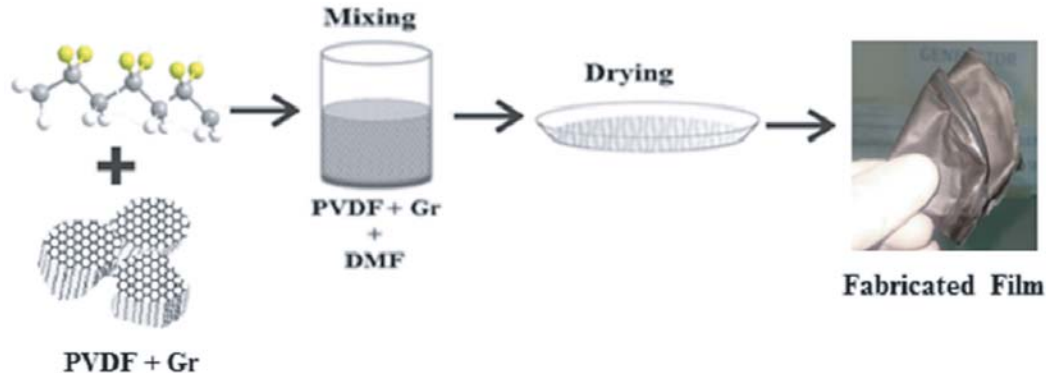
Figure 2. Fabrication process of composite films.

under vacuum at $80°$C for 24 h and then at $100°$C for 12 h to remove the solvent. The film membrane was stripped off from the glass petri dish.

2.3. Measurement of Dielectric properties

The dielectric properties (the dielectric constant (ε') and dissipation factor $(\tan \delta)$) of the samples were used to calculate the absorption loss and reflection loss of composite films. RF impedance analyser (Model No. E-4940 A) with a dielectric material test fixture was used to measure the capacitance (C) and $\tan \delta$ of the samples in the frequency range of 100 kHz–10 MHz. For the measurement after both opposite surfaces of the films were coated with conductive silver paint and copper connecting wires were bonded to the surfaces with conductive silver paint films placed in dielectric material test fixture between electrodes as shown in Fig. 3. The AC conductivity of composites is calculated from the formula $\sigma = \omega \varepsilon_0 \varepsilon' \tan \delta$ where $\omega = 2\pi f$. Thickness of conducting films was measured using electronic micrometre (Yamayo Classic-IP54). The values of reflection and absorption are accordingly calculated with the equations explained in Section 2.4.
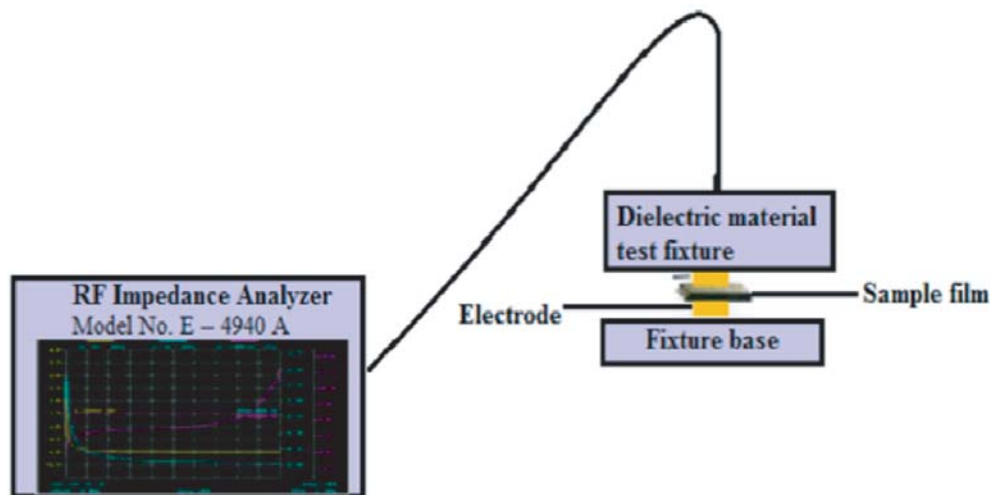

Figure 3. Measurement setup for dielectric properties.

2.4. Calculation of Shielding Effectiveness

The ability of conducting material to attenuate EM wave is known as Shielding Effectiveness (SE). The two main mechanisms of shielding are reflection (R) and absorption (A). The third mechanism, multiple

reflection correction factor (C), comes if absorption is less than 10 dB. Multiple-reflection is negligible when the thickness of a material is much greater than its skin depth [5, 10]. The calculation of SE simply consists of the addition of A, R, and C [11].

$$SE = A + R + C \tag{1}$$

For a composite film with a thickness of t, shielding by absorption loss can be defined as

$$A = 131t\sqrt{f\mu\sigma} \tag{2}$$

where f is the frequency, μ the magnetic permeability of conductive shield relative to that of free space, and σ the conductivity of film. The reflection term is mainly reliant on the relative mismatch between the incoming wave and the surface impedance of the film. The formula for Reflection loss can be defined as

$$R = 168 - 10\log_{10}\left(\frac{f\mu}{\sigma}\right) \tag{3}$$

The correction factor represents internal reflections inside a conducting film. As the resultant of multiple-reflection is an increment in transmitted wave, it has a negative influence on the overall EMI shielding. The correction factor can be defined as

$$C = 20\log_{10}\left[1 - \left(\frac{\eta 0 - \eta 1}{\eta 0 + \eta 1}\right)^2 e^{-2yt}\right] \tag{4}$$

where $\eta 0$ is the impedance of free space, and $\eta 1$ is the intrinsic impedance of shielding film.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

The composite films were analysed for their morphology using scanning electron microscopy (SEM) (Hitachi, Model S-4700). Fig. 4(a) shows the SEM image of pure PVDF, and we can see a smooth surface of PVDF without any impurity. Fig. 4(b) shows the SEM image of PVDF-Gr composite having 12 wt.% of Gr content. The blue arrow shows the conducting graphite particles on the surface of PVDF polymer. With the magnified image of the composite film in Fig. 4(c) we can see a complete conducting graphite channel forming on the interfacial region of polymer.

3.2. Dielectric Analysis

The analysis of dielectric behaviour of PVDF-Gr conducting polymer composite films is necessary for the EMI shielding application [12]. To investigate the dielectric behaviour of the PVDF-Gr composites at radio frequencies, ε' and $\tan\delta$ of the composites were calculated in the frequency range from 100 kHz to 10 MHz. Fig. 5(a) shows $\tan\delta$ of the PVDF-Gr composite films as a function of frequency for various contents of Gr. The ε' of the composite films as a function of frequency for various contents of Gr is shown in Fig. 5(b). It is clear from the graph that $\tan\delta$ and ε' increase with increasing Gr wt.%. The reason for this is the formation of graphite conducting channels between the interfacial region of polymer, which tends to increase dipole moments including $\tan\delta$ and ε' of conducting polymer composite. Fig. 5(c) shows the conductivity (σ) of PVDF-Gr composites as a function of frequency. We can see that σ was also increased with Gr wt.% in a similar manner. The reason for this is that it depends on the values of ε' and $\tan\delta$ ($\sigma = \omega\varepsilon_0\varepsilon'\tan\delta$). The PVDF-Gr composite films with 12 wt.% of Gr attained the highest value of σ at 10 MHz.

3.3. Mechanical Strength Analysis

Ultimate tensile testing machine was used to investigate the mechanical properties of the developed PVDF/Gr composite films. This analysis provides the information about change in material properties of the developed films when being subjected to a stretching or pulling force [13]. Fig. 6 shows the stress strain curve for all the developed composite films.
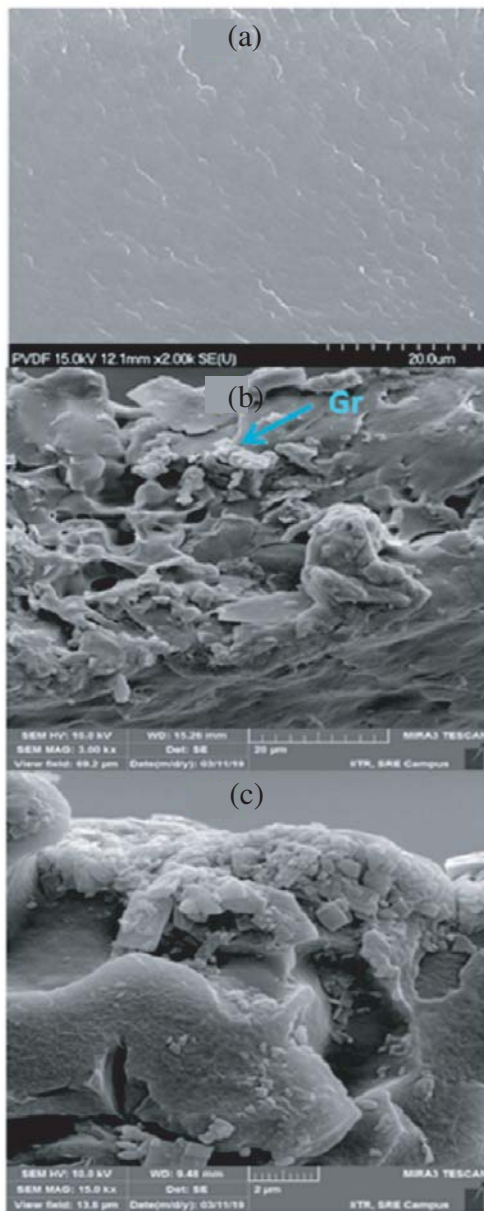
Figure 4. (a) SEM image of pure PVDF, (b) SEM image of composition with 12% of Gr, (c) magnified image of composition with 12% of Gr.
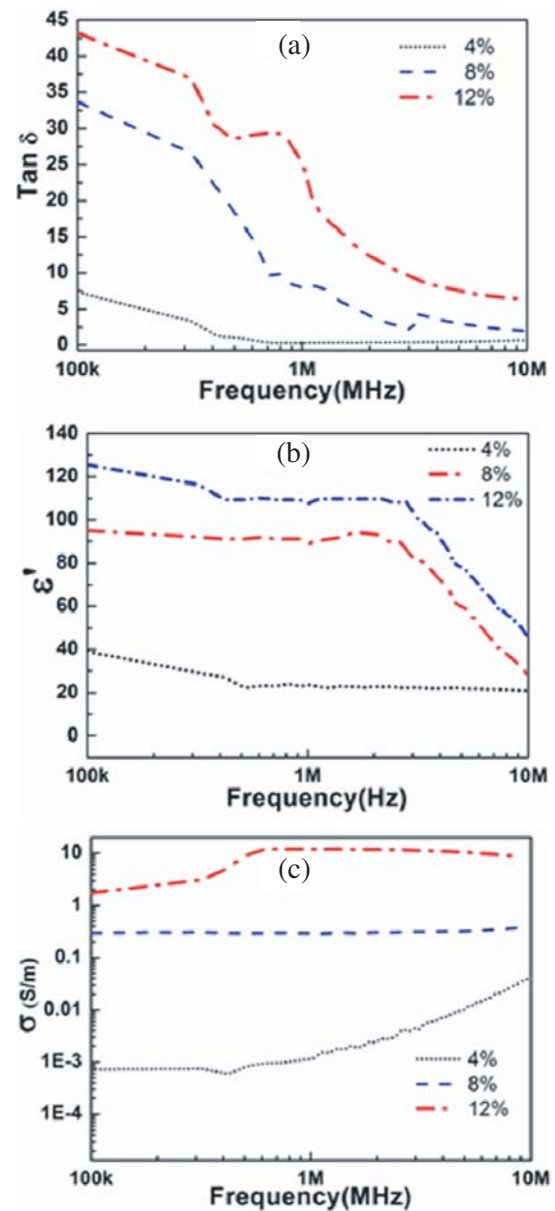

Figure 5. (a), (b), (c) ε', $\tan\delta$, and σ as a function of frequency, for different Gr wt.%.

From the stress strain curve we can observe the comparison of these three films. The film with 12 wt.% of Gr is most brittle, and film with 4 wt.% of Gr is ductile. The composite with 4 wt.% of Gr exhibits maximum elongation of 25% and ultimate tensile strength of 2.72 ± 0.2 MPa. The composite with 8 wt.% of Gr exhibits maximum elongation of 12% and ultimate tensile strength of 2.78 ± 0.2 MPa. The composite with 12 wt.% of Gr exhibits maximum elongation of 9.8% and ultimate tensile strength of 1.75 ± 0.2 MPa. It is clear from these data that all the developed films have good mechanical properties.

3.4. EMI Shielding Analysis

The calculation of SE is already discussed in Section 3.4. By using Equation (2) first we calculate A of the films for the entire frequency range of 100 kHz to 10 MHz. The A of all three compositions of
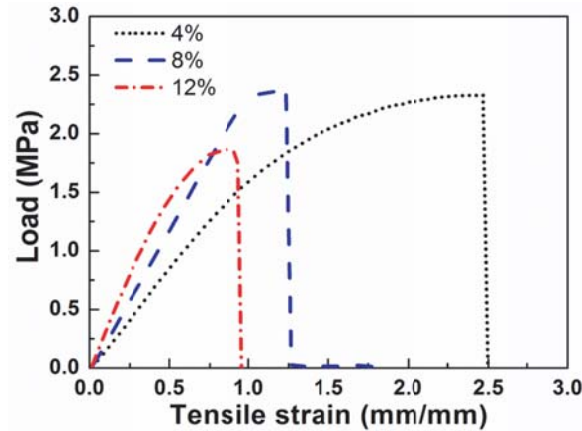
Figure 6. Stress strain curve for developed films with different Gr wt.%.
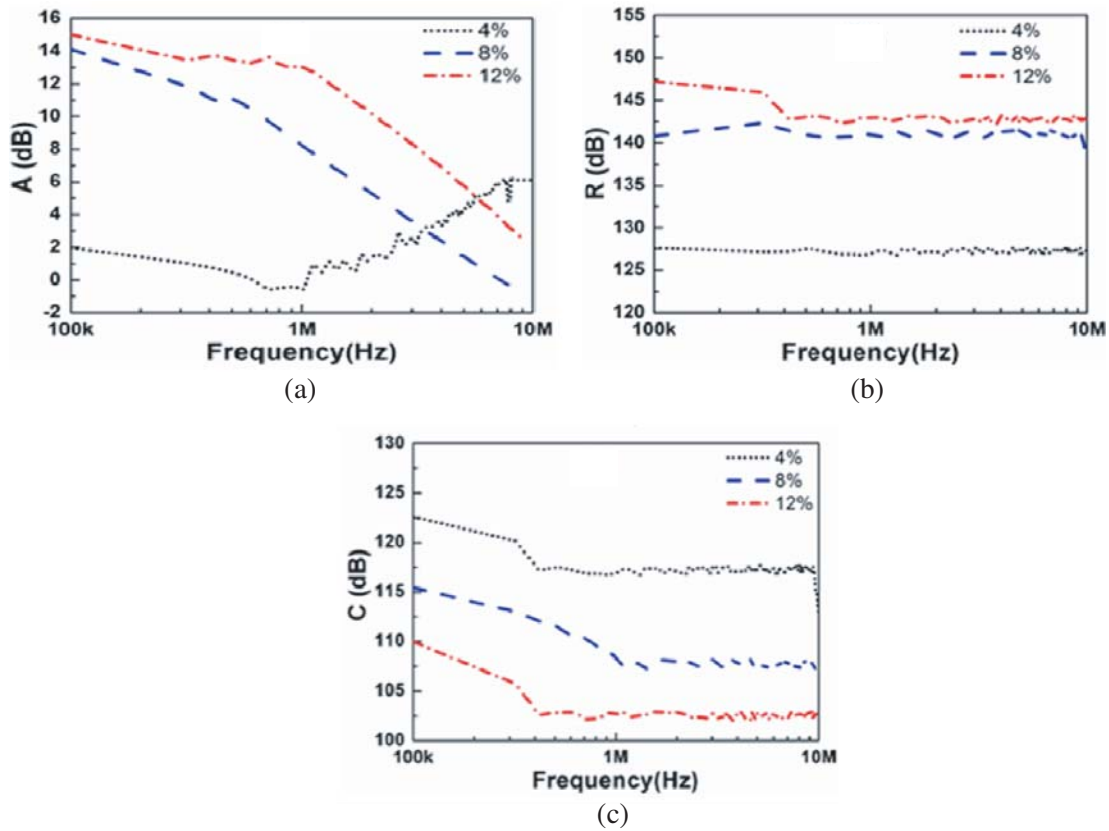

(a)

(b)

(c)

Figure 7. (a), (b), (c) A, R and C as a function of frequency for different Gr wt%.

PVDF-Gr is shown in Fig. 7(a). We can see from the graph as the concentration of Gr increases, the absorption loss increases. It is also clear from the equation that the conductivity is directly proportional to absorption. Equation (3) will be used to calculate R of the film. The R of all three composition of PVDF-Gr is shown in Fig. 7(b). Again as the concentration of Gr increases, the reflection loss also increases. Equation (4) will be used to measure C of the developed films. We can see from Fig. 7(c) that as the concentration of graphite increases, the correction factor decreases.

The total SE of PVDF-Gr is shown in Fig. 8. The value of SE increases with increase in Gr content and decreases with frequency, except the fluctuation in the value of 4 wt.% of Gr filled composite. The
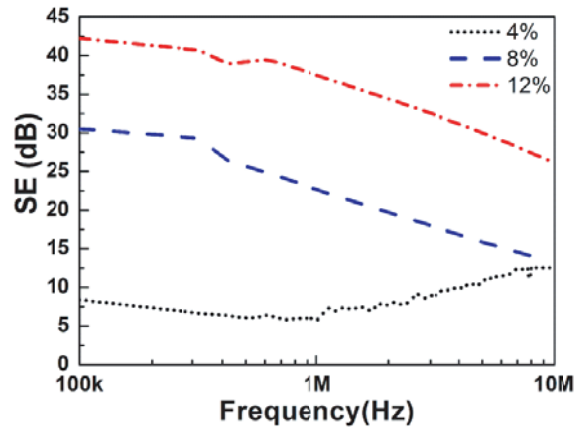
Figure 8. Total SE as a function of frequency for different concentration of Gr.

composite with 12 wt.% of Gr content shows the highest value of SE. The high value ~ 42 dB is obtained for 12 wt.% of Gr filled PVDF-Gr conducting polymer composite at 100 kHz and ~ 28 dB at 10 MHz.

4. CONCLUSION

In this work, we have developed inexpensive PVDF-Gr composites for EMI shielding application using dry mixing and solvent casting technique. With the increase of Gr content, the values of ε', $\tan \delta$, and σ increase. The PVDF-Gr composite with 12 wt.% of Gr shows high value of SE ~ 42 dB at 100 kHz and ~ 28 dB at 10 MHz. However, samples of 8 wt.% Gr also show satisfactory result of SE for the whole radio frequency region (100 kHz–10 MHz). The mechanical properties of the film also show satisfactory results. Due to the flexible nature of the composite film, the film can be coated on any electronic device to diminish the effect of EMI.

ACKNOWLEDGMENT

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