

Ionic Liquid-Gr Attached PVDF Composite Film for Shielding of Microwave Radiations

Vikas Rathi, Varij Panwar*, and Divya Kuriyal

Abstract—To diminish electromagnetic interference (EMI) for microwave radiations, effects of graphite (Gr) modified by a long alkyl chain ionic liquid (IL) 1-Butyl-3-methylimidazolium hydrogen sulphate ([BMIM][HSO₄]) on poly(vinylidene fluoride) (PVDF) was investigated. The pre-localized Gr coated polymer powders were fabricated, using solvent blending method, with different concentrations of Gr over PVDF matrix to prepare a series of PVDF/Gr/IL composites. The surface morphology of the fabricated composite films was examined by scanning electron microscopy (SEM). The composites, with a thickness of ~ 0.15 mm, exhibit good EMI shielding properties, besides low cost production and flexibility. The enhanced properties are due to high ionic conductivity of the IL and formation of a connecting network by Gr facilitating electron conduction. Absorption is the key factor due to which the total shielding effectiveness in the frequency band of 12 to 18 GHz has been improved significantly.

1. INTRODUCTION

The abundance of electronic appliances and their application in microwave frequency range has generated an inaudible invisible pollution recognized as electromagnetic interference (EMI). Due to EMI, there is unacceptable degradation in the performance of these devices, and also it affects the lifespan and efficiency of commercial or military electronic devices [1, 2]. In addition to this, electromagnetic radiation has been found to be very unsafe for living organisms. In literature, various scientists have claimed that a regular prolonged contact to electromagnetic radiations considerably increases the risk of skin related problems, cardiac problems, headache, cancer, and various other diseases [3, 4]. This EMI effect can create an undesired perturbation in communication which should be avoided and get shielded. Therefore, it is important to diminish complex EMI problems either by eliminating or by reducing them, using a high performance EMI shielding material.

The conducting polymer composites with advantage of their low price, light weight, corrosion resistance, and excellent processibility show efficient properties to be used as EMI shielding materials in comparison to usual metal-based materials [5]. Generally, the use of conductive shield is the most well-known method for solving EMI problems where reflection is the key mechanism of shielding. Nowadays, many devices operate at tens of GHz, with harmonic noise emissions in this high frequency region. At these frequency levels, the reflected signal in a conducting system can cause severe complications, for the shielded device itself or for other neighbouring components in the system. So it needs time to develop a shielding material, with absorption as a focal mechanism of shielding through which the secondary EMI noise pollution can be minimized. Absorption property of composites can be improved, by reducing its reflection property. Producing porosity in composite is an effective technique, to make the shielding materials light weight besides great microwave absorption ability for various scientific and industrial applications [6, 7].

Received 21 May 2020, Accepted 4 August 2020, Scheduled 17 August 2020

* Corresponding author: Varij Panwar (varijpanwar@gmail.com).

The authors are with the Department of ECE, Graphic Era University, Dehradun, Uttarakhand 248002, India.

Plane waves when propagating through heterogeneous medium suffer absorption and also get scattered. From the previous studies [8] it is known that absorption efficiency of charged nanoparticles is much higher than that of neutral nanoparticles. This happens due to phenomenon of charge induced resonance. The charged particles resonate with the incident electromagnetic radiation, and this resonance occurs between incident wavelength and charged nanoparticles surface excitations. This leads to in-phase oscillation. Surface resonance is only generated when the size of nanocrystal is small compared to wavelength of incident wave. The conductivity of the surface force excess surface charge to oscillate in synchronization with the incident electromagnetic wave which results in modified scattering pattern.

To fabricate a highly conductive composite, it is essential to concentrate on the microscopic organization of the composites. The objective is to produce an extremely porous outer surface. When the radiation is imposed on top of the material, it becomes dispersed among the pores and their walls. Large percentage of the reflected radiation commences reflections from the pore walls; reflections from the inner portion of the pores are comparatively lesser. Therefore, the pores formed on the surface of a conducting film can be used as a significant tool for change in the phenomenon of reflection of electromagnetic waves [9,10]. With the decrease in reflection of radiation, a large percentage of the incident radiation will spear into the material, so there will be the possibility to eliminate it by mechanism of absorption. Hence, managing the porosity in conducting composite films may become a method to find absorbing materials for electromagnetic waves [11].

In our work, Polyvinylidene fluoride (PVDF) was used as insulating polymer matrix. PVDF with its well-known ferroelectric, piezoelectric and pyro electric properties also have the properties such as easy processing, excellent mechanical properties, high thermal stability and dielectric strength, and good chemical resistance makes it very applicable for the purpose of EMI shielding [12]. Micro-sized graphite particles (Gr) are the mostly used conductive filler due to its outstanding electrical properties, cost effectiveness, and rich source. The presence of 1-Butyl-3-methylimidazolium hydrogen sulphate [BMIM][HSO₄] as ionic liquid (IL) helps in making the porous surface structure of the films. IL is in the form of molten salt at room temperature with a large number of organic cations and inorganic anions. It exhibits properties like non-flammability, low viscosity, high thermal stability, and low vapour [13]. The chemical behaviour of IL plays an important part in improving the surface structure and crystallinity of composites by providing stronger molecular bonds in the composite films [14]. With the above mentioned properties, we developed a porous conducting polymer composite film through solution cast method with great EM microwave absorption ability in the frequency range of 12 to 18 GHz. Fig. 1 shows the EMI shielding mechanism from the proposed composite film. Due to porous structure of the film less fraction of incident wave is reflected, so absorption is the foremost mechanism of shielding microwave radiations.

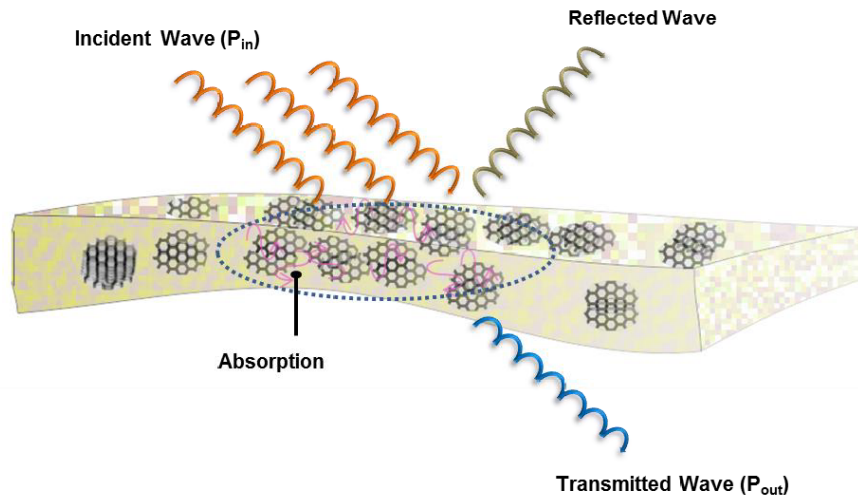


Figure 1. EMI shielding mechanism.

2. EXPERIMENTAL

2.1. Materials

For preparing the composite films, PVDF was bought from sigma Aldrich with average molecular weight (Mw) of 534,000 g/mol by the trade name 182702, having density of 1.74 g/ml at 25°C in powdered form. Natural graphite flakes (NFG) used as a filler were supplied by Graphite India Ltd. Ionic liquid (IL) was supplied by sigma Aldrich USA under the trade name 57457 with Molecular Weight (Mw) 236.29 g/mol. N,N-Dimethylformamide (DMF) as a solvent was also purchased from sigma Aldrich.

2.2. Fabrication of Composite Film

2.2.1. Pre-Localized Process and Solvent Blending Method

Figure 2(a) explains the fabrication process of composite films. Initially, the PVDF polymer powder and Gr were thoroughly mixed for 5 h in a beaker with a magnetic stirrer without heating. By this process conducting graphite powder coated on the surface of PVDF particles, which is known as the pre-localized process of the conductive phase on the polymer [15]. The pre-localized graphite coated powders were prepared with different concentration of graphite. After pre-localization of Gr with polymer powder, the IL was mixed with the pre-localized graphite powder and dissolved in DMF for mixing it in a beaker speed of ~ 800 rpm until the blend converts into a uniform mixture. Following this, the mixed solution was cast onto a glass petri dish. To remove the solvent, it was heated at 80°C for 24 h and then at 100°C for 12 h, and after cooling the film was taken off from the petri dish. The chemical structure and interaction of PVDF, Gr, IL, and formation of PVDF/Gr/IL composite films are shown in Fig. 2(b). In our work, we have fabricated different compositions of PVDF/Gr/IL at specific ratios of 60/40/00, 60/30/10, 60/20/20, and 60/10/30.

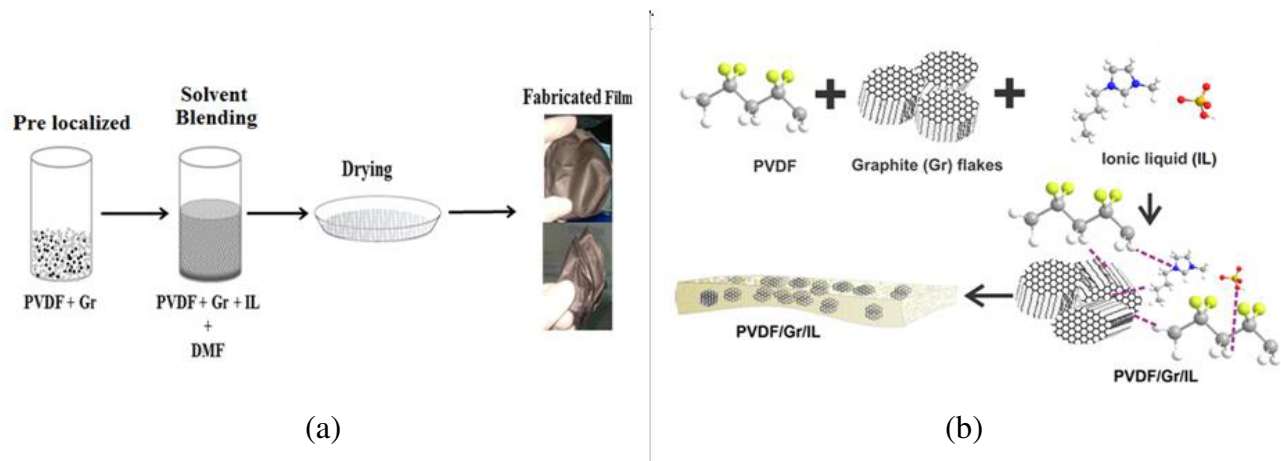


Figure 2. Fabrication process and mechanism of composite film.

2.3. Characterization and Microwave Measurement

The surface morphology of the fabricated films was examined using scanning electron microscopy (SEM), (Hitachi, Model S-4700). Electronic micrometer (Yamayo Classic-IP54) was used to measure the thickness of the composite films. The measurement of shielding effectiveness was carried out using waveguide transmission line technique [16]. In this technique, the samples were placed fit tightly in a section of waveguide, and after that the two ports scattering parameters were measured with the help of a microwave network analyzer. For these purposes the composite films are fixed in between the two ports of the Ku band waveguide adapter and connected to PNA microwave network analyzer (keysight, PNA, N5224A) as shown in Fig. 3.

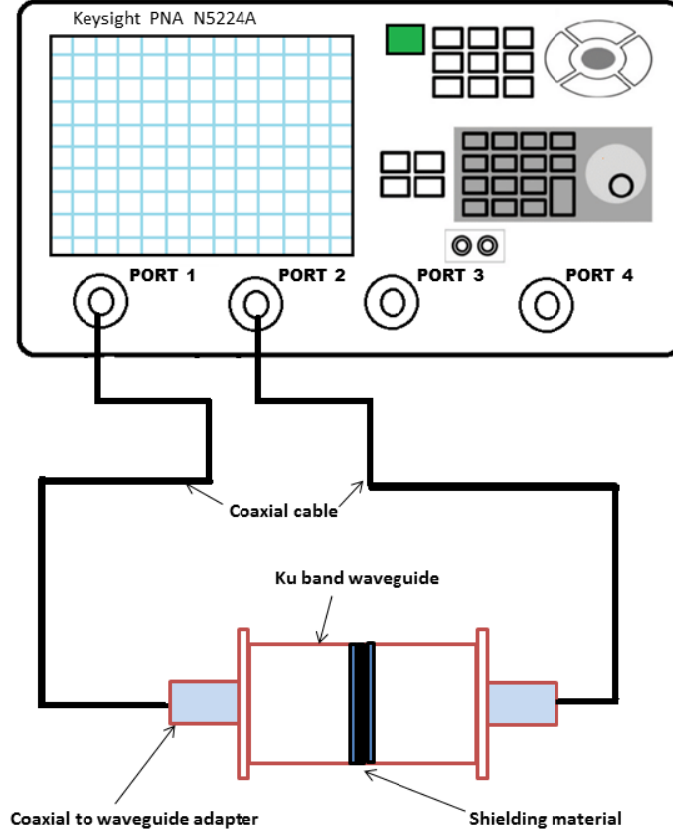


Figure 3. Measurement setup.

The network analyzer was calibrated, and the scattering parameters of the composite films corresponding to reflection (S_{11}) and transmission (S_{21}) of the incident waves were measured. The total EMI shielding effectiveness (SE_T) can be defined as amount of reduction in the intensity of electromagnetic radiation after it passes through the film; it can be expressed as:

$$SE_T = 20 \log \frac{P_{in}}{P_{out}} \quad (1)$$

where P_{in} and P_{out} are the incident and transmitted powers from the composite film.

Further SE_T can be recognized as the contributions of shielding due to reflection (SE_R), shielding due to absorption (SE_A), and shielding due to multiple reflections (SE_M). So, the equation for SE_T can be rewritten as

$$SE_T = SE_R + SE_A + SE_M \quad (2)$$

If SE_T is greater than 10 dB, SE_M can be neglected, so SE_T will depend on SE_R and SE_A . The power coefficients of reflection (R), absorption (A), and transmittance (T) are related through each other by the equation:

$$A + R + T = 1 \quad (3)$$

These coefficients can be calculated by measuring S parameters as: $R = |S_{11}|^2$, $T = |S_{21}|^2$. Shielding efficiency of materials by reflection and absorption can be expressed by the following equations [17]:

$$SE_R = 10 \log \left(\frac{1}{1 - R} \right) = 10 \log \frac{1}{1 - |S_{11}|^2} \quad (4)$$

$$SE_A = 10 \log \left(\frac{1 - R}{T} \right) = 10 \log \left(\frac{1 - |S_{11}|^2}{|S_{21}|^2} \right) \quad (5)$$

Shielding effectiveness can easily be calculated, using these formulae.

3. RESULTS AND DISCUSSION

3.1. Surface Morphology of Composite Films

SEM was applied to reveal the morphological variations of fabricated films. Fig. 4(a) shows the top surface of pure PVDF, and it is clear from the image that the surface is neat and clear without any impurity or pores. Fig. 4(b) shows the fractured SEM image of PVDF/Gr composites that show graphite embedded polymer surface. The yellow arrow shows the white colour conducting graphite particles via interfacial region of polymer [18]. Figs. 4(c)–(e) show the IL attached PVDF/Gr composites that exhibit that the incorporation of IL in the polymer matrix destroys the dense structure of the PVDF and become porous. The porosity of the samples increases with the increase in concentration of ionic liquid. In Fig. 4(f), the porous surface structure of sample 60/10/30 can be seen with high magnification. However, there is variation in the surface morphology of the films, but the crystalline behavior does not show any obvious change for different concentrations of the films.

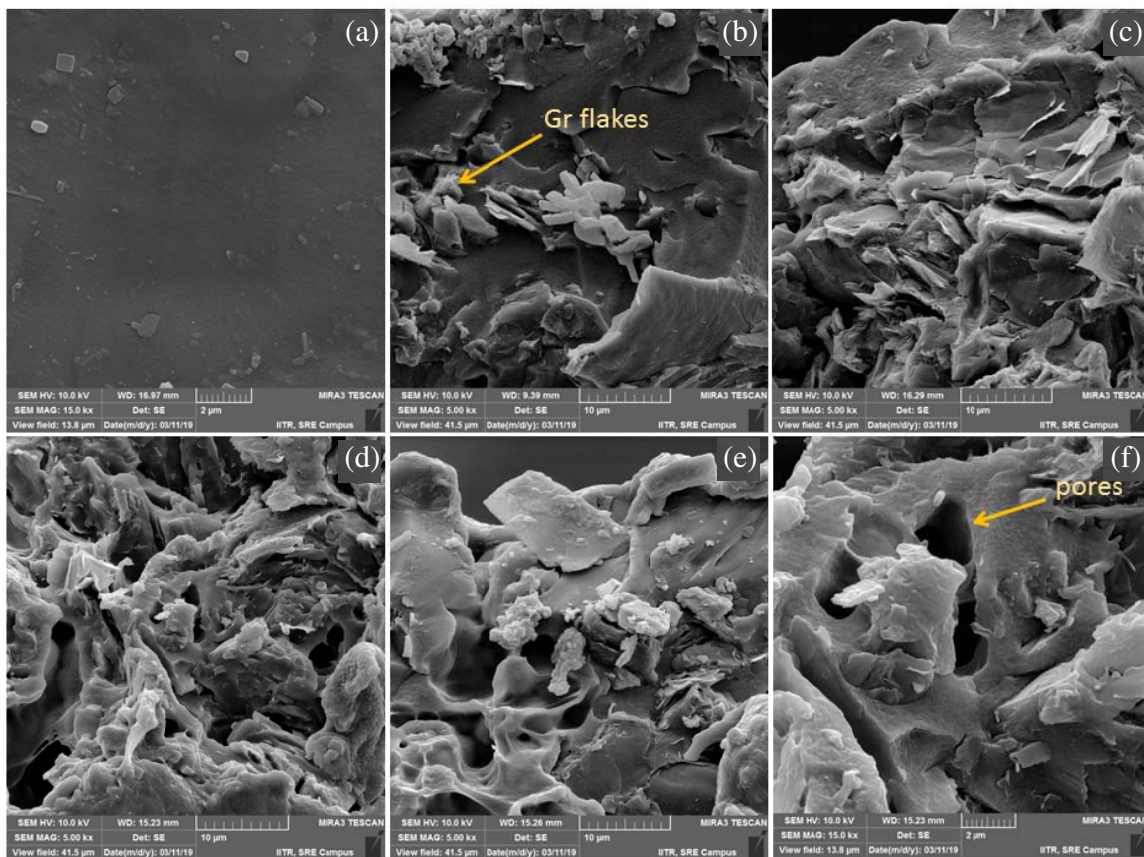


Figure 4. SEM images of (a) pure PVDF; (b)–(e) SEM images of composition 60/40/0, 60/30/10, 60/20/20, 60/10/30 of PVDF/Gr/IL respectively; (f) magnified SEM image of 60/10/30.

3.2. Mechanical Strength Analysis

The mechanical properties of the obtained PVDF/Gr/IL composite films were examined using an ultimate tensile testing machine. All fabricated films of PVDF/Gr/IL were under test, and the stress strain curve of various films is shown in Fig. 5(a). From the obtained curve, we can say that 60/10/30 is the most ductile material, and 60/40/0 is most brittle. The brittle nature of the graphite reinforcing particles plays a significant role in decreasing the ductility because graphite as a soft reinforcement is brittle in nature and increases the brittleness in the composite which in-turns decreases the ductility

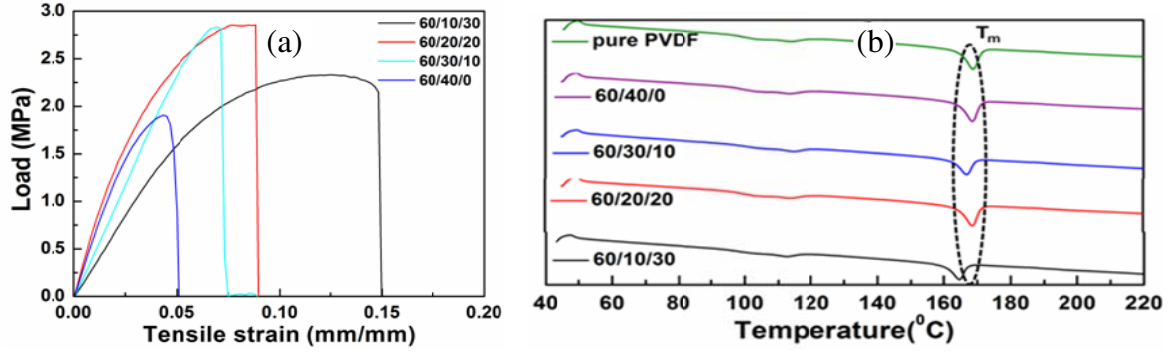


Figure 5. (a) Stress-strain curve, (b) DSC analysis.

of the composite [18]. We can see from the curve as the concentration of IL increases the tensile strain increases, i.e., the film becomes more flexible. The ultimate tensile strength of composition 60/40/0 is 1.92 ± 0.2 MPa, and its Young's modulus is 5.8 ± 0.5 MPa with an elongation of only 5%. The tensile strength of composition 60/30/10 is 2.84 ± 0.2 MPa with Young's modulus of 4.7 ± 0.5 MPa and elongation of nearly 7.5%. For composition 60/20/20 tensile strength is 2.86 ± 0.2 MPa, and its Young's modulus is 5.3 ± 0.5 MPa with an elongation of 9%. The composition 60/10/30 exhibits the maximum elongation of 15% with ultimate tensile strength of 2.32 ± 0.2 MPa and Young's modulus of 3.4 ± 0.5 MPa.

3.3. DSC Analysis

The effect of temperature on the films was examined by the differential scanning calorimetry (DSC) measurements. Fig. 5(b) shows the variation of the heat flow versus temperature for all PVDF/Gr/IL composite films. In the curve we can see a peak at melting temperature (T_m) related to the melting phase transition. T_m of pure PVDF is at around 168°C . With the penetration of Gr and IL in the PVDF matrix, it is very much clear from the obtained graph that T_m remains nearly the same, which means there is no change in the crystalline structure of the PVDF/Gr/IL composite film with temperature. In spite of the interaction with the matrix, Gr and IL do not have an effect on the normalized enthalpies of the melting transitions.

3.4. EMI Shielding Analysis

We calculate SE_T by using scattering parameters obtained from the PNA microwave network analyzer. Fig. 6(a) depicts the change in the SE_T with frequency for various PVDF/Gr/IL composites. The SE_T value increases with the increase of IL percentage in the composite films. SE_T of composites varies in the range of ≈ 15 dB to ≈ 32 dB as the concentration of IL increases from 0 to 30 wt%.

The shielding efficiencies of the composites due to absorption and reflection are depicted in Figs. 6(b) and 6(c), respectively. It is clear from the figures that SE_A value is predominantly higher than the SE_R values. The highest SE_A value corresponding 60/10/30 has been found to be 28 dB while SE_T is around 32 dB for the entire frequency band of 12 to 18 GHz. Low reflection loss is due to the highly porous structure of the films, which allows the incident wave to penetrate into the composite for dissipation. So, it decreases reflection, and thus, absorption is the foremost mechanism for shielding with obtained films. The shielding by absorption increases from ≈ 5 dB to ≈ 28 dB with the increase of IL concentration from 0 to 30 wt%. Fig. 6(d) shows the percentage contribution of absorption and reflection in the total EMI shielding for various composite ratios. It can be seen that reflection decreases, and absorption increases as the concentration of IL increases.

The SE of the samples is also calculated with the help of dielectric properties [18]. The calculated SE (SE_{cal}) for all fabricated samples is shown in Fig. 7. It is very much clear from the graph that it is in accordance with the measured shielding effectiveness. SE_{cal} of composite with composition of 60/10/30 depicts the highest value due to high concentration of IL that shows the similarity to measured results.

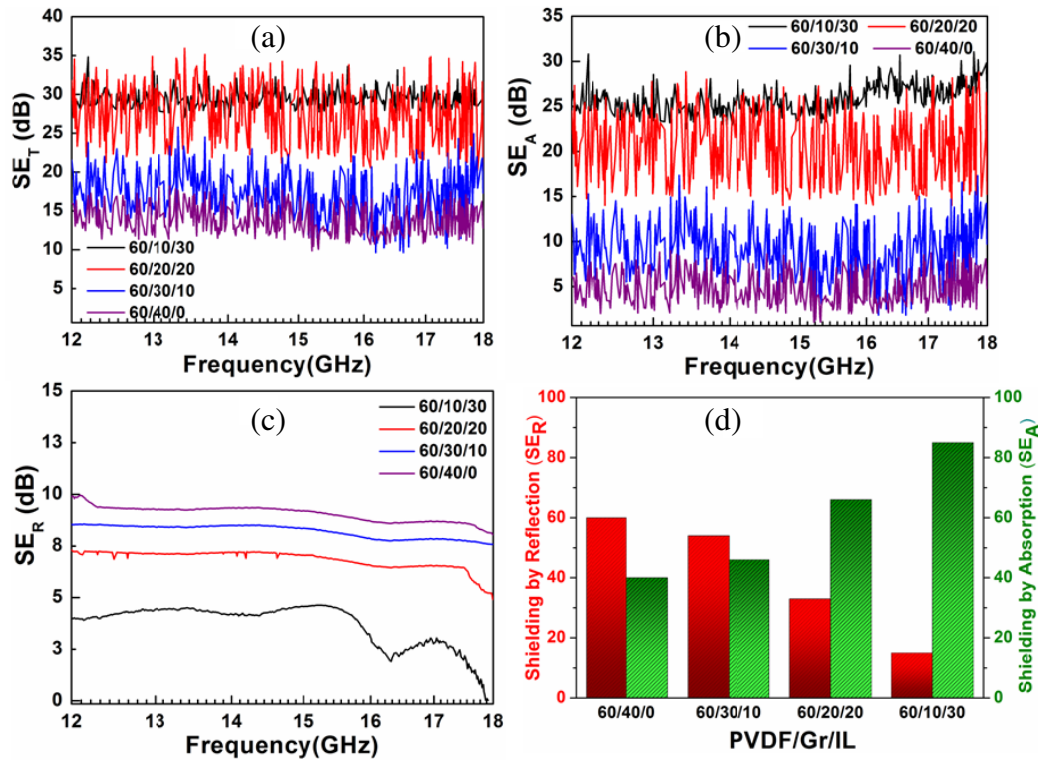


Figure 6. (a)–(c) Total shielding effectiveness (SE_T); shielding by absorption (SE_A) and shielding by reflection (SE_R) respectively as function of frequency; (d) percentages of the absorption and reflection components of total shielding for different PVDF/Gr/IL blend ratios.

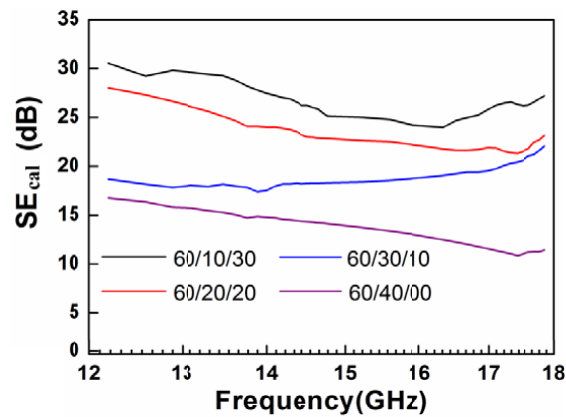


Figure 7. Calculated shielding effectiveness.

4. CONCLUSION

In summary, a light weight, thin, and flexible film of a polymer composite has been obtained for the shielding of microwave radiation. SE_T of the obtained films increases with the increase in the concentration of IL. The porous structure and conductive network developed by IL in PVDF/Gr composites are responsible for such a high shielding effectiveness with absorption as the foremost mechanism of shielding. From the shielding effectiveness and mechanical strength results analysis, we can say that the material with composition 60/10/30 gives the most satisfactory result as its SE_T is 32 dB with 15% elongation. The fabrication of a porous PVDF/Gr/IL composite film unlocks the prospect for

the application of conducting composite as flexible and shapeable high efficient EMI shielding materials. The potential applications of these composites may have a vast range from defense to flexible and portable electronic devices.

REFERENCES

1. Kong, L. B., Z. W. Li, L. Liu, R. Huang, M. Abshinova, Z. H. Yang, C. B. Tang, P. K. Tan, C. R. Deng, and S. Matitsine, "Recent progress in some composite materials and structures for specific electromagnetic applications," *International Materials Review*, Vol. 58, No. 4, 203–259, 2013.
2. Geetha, S., K. K. Satheesh Kumar, C. R. K. Rao, M. Vijayan, and D. C. Trivedi, "EMI shielding: Methods and materials — A review," *Journal of Applied Polymer Science*, Vol. 112, No. 4, 2073–2086, May 2009.
3. Morgan, D., *Handbook of EMC Testing and Measurement*, Vol. 8, Institution of Electrical Engineers (IEE), London, 1995.
4. Kheifets, L., A. A. Afifi, and R. Shimkhada, "Public health impact of extremely low frequency electromagnetic fields," *Environ. Health Persp.*, Vol. 114, No. 10, 1532–1607, Oct. 2006.
5. Rathi, V., V. Panwar, G. Anoop, M. Chaturvedi, K. Sharma, and B. Prasad, "Flexible, thin composite film to enhance the electromagnetic compatibility of biomedical electronic devices," *IEEE Transactions on Electromagnetic Compatibility*, Vol. 61, No. 4, 1033–1041, Nov. 2018.
6. Song, W. L., X. T. Guan, L. Z. Fan, W. Q. Cao, C. Y. Wang, and M. S. Cao, "Tuning three-dimensional textures with graphene aerogels for ultra-light flexible graphene/texture composites of effective electromagnetic shielding," *Carbon*, Vol. 93, 151–160, Nov. 2015.
7. Kuang, T., L. Chang, F. Chen, Y. Sheng, D. Fu, and X. Peng, "Facile preparation of lightweight high-strength biodegradable polymer/multi-walled carbon nanotubes nanocomposite foams for electromagnetic interference shielding," *Carbon*, Vol. 105, 305–313, Aug. 2016.
8. Kocifaj, M., J. Klačka, F. Kundracik, and G. Videen, "Charge-induced electromagnetic resonances in nanoparticles," *Annalen der Physik*, Vol. 527, Nos. 11–12, 765–769, Dec. 2015.
9. Sampath, U., Y. Ching, C. Chuah, J. Sabariah, and P. C. Lin, "Fabrication of porous materials from natural/synthetic biopolymers and their composites," *Materials*, Vol. 9, No. 12, 991, Dec. 2016.
10. González, M., M. Crespo, J. Baselga, and J. Pozuelo, "Carbon nanotube scaffolds with controlled porosity as electromagnetic absorbing materials in the gigahertz range," *Nanoscale*, Vol. 8, No. 20, 10724–10730, 2016.
11. Shen, B., Y. Li, W. Zhai, and W. Zheng, "Compressible graphene-coated polymer foams with ultralow density for adjustable electromagnetic interference (EMI) shielding," *ACS Applied Materials and Interfaces*, Vol. 8, No. 12, 8050–8057, Mar. 2016.
12. Gargama, H., A. K. Thakur, and S. K. Chaturvedi, "Polyvinylidene fluoride/nanocrystalline iron composite materials for EMI shielding and absorption applications," *Journal of Alloys and Compounds*, Vol. 654, 209–215, Jan. 2016.
13. Plaquevent, J. C., J. Levillain, F. Guillen, C. Malhiac, and A. C. Gaumont, "Ionic liquids: New targets and media for α -amino acid and peptide chemistry," *Chemical Reviews*, Vol. 108, No. 12, 5035–5060, Dec. 2008.
14. Lins, L. C., S. Livi, M. Maréchal, J. Duchet-Rumeau, and J. F. Gérard, "Structural dependence of cations and anions to building the polar phase of PVDF," *European Polymer Journal*, Vol. 107, 236–248, Oct. 2018.
15. Panwar, V., B. Kang, J. O. Park, S. Park, and R. M. Mehra, "Study of dielectric properties of styreneacrylonitrile graphite sheets composites in low and high frequency region," *European Polymer Journal*, Vol. 45, No. 6, 1777–1784, Jun. 2009.
16. Nanni, F., P. Travaglia, and M. Valentini, "Effect of carbon nanofibres dispersion on the microwave absorbing properties of CNF/epoxy composites," *Composites Science and Technology*, Vol. 69, Nos. 3–4, 485–490, 2009.

17. Bera, R., S. Paria, S. K. Karan, A. K. Das, A. Maitra, and B. B. Khatua, "NaCl leached sustainable porous flexible Fe_3O_4 decorated RGO-polyaniline/PVDF composite for durable application against electromagnetic pollution," *eXPRESS Polymer Letters*, Vol. 11, No. 5, 419–433, May 2017.
18. Rathi, V., V. Panwar, and B. Prasad, "Characterization of PVDF-Gr composite films for electromagnetic interference shielding application," *Progress In Electromagnetics Research Letters*, Vol. 88, 105–112, 2020.