

Innovations in polymer nanocomposite coatings for EMI Shielding applications

M. Joshi¹, T. Bansala¹ and S. Mukhopadhyay¹

¹ Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

Corresponding author: mangala@textile.iitd.ac.in

Abstract. Start Excessive usage of electronic gadgets, telecommunication devices and electrical appliances has led to unwanted electromagnetic interference (EMI) as side effect. The EMI pollution interferes with the performance and functioning of the electrical equipments, which is generated through the conduction or radiation of emitted electromagnetic (EM) waves. In addition to affecting the quality of electrical appliances, EMI has a huge negative impact on the health and life of living organisms. Moreover, microwave frequency operated functions such as radar surveillance systems; weather radar, military aviation, radar guns, wireless technology and satellite communication are more prone to EMI pollution and specifically with regard to stealth purposes. In this paper carbon nanomaterial based polyurethane nanocomposites have been synthesized and investigated for decreasing the EM wave pollution due to their light weight, flexibility, optimum conductivity and good dielectric properties. Three different types of graphene sheets such as thermally reduced and exfoliated graphene (TRG); chemically reduced graphene (CRG) and Polyvinyl-pyrrolidone stabilized silver nanoparticles based graphene nanohybrid (Ag-PVP-CRG) have been synthesized and characterized for EMI shielding properties. Further, TRG, CRG and Ag-PVP-CRG sheets have been dispersed in thermoplastic polyurethane (TPU) polymeric matrix to create multifunctional nanocomposite films with properties such as EMI shielding, electrically conductivity and dielectric behavior. The study presents for the first time a comparative evaluation of three different types of graphene sheets in both neat and nanocomposite form. The synthesis of Ag-PVP-CRG nanohybrids and its application for EMI shielding is novel and reported for the first time for such an application.

1. Introduction

The modern day electronic market is majorly governed by Electromagnetic waves and the major cause of unwanted electromagnetic interference (EMI) as side effect. The common examples of EMI in our daily routine are the flickering of picture and audio/video signal distortions in radio, television and computer screen. In addition to the quality degradation of electrical appliances, EMI has a huge negative impact on the health and life of living organisms. Moreover, microwave frequency operated functions such as radar surveillance systems; weather radar, military aviation, radar guns, wireless technology and satellite communication are more prone to EMI pollution and specifically with regard to stealth purposes.

In order to minimize the effect of EMI, emerging research has focused onto materials providing shielding against EMI pollution in all commercial and critical sectors. In general, the dissipation or



absorption of incident electro-magnetic waves in the form of heat, conduction, dielectric or magnetic losses by using electrically conducting and magnetic material is known as electromagnetic shielding. EMI shielding materials either reflect or absorb the EMI radiations. Metal-based shielding materials are majorly reflection-based and suffer from processing difficulties, large density and sustainable to corrosion. Absorption based shielding materials such as polymer nanocomposites are preferred because of their camouflage nature as the incident EM signals will be absorbed instead of reflected which is desirable for defense systems. Literature review suggest that the electrical, mechanical, gas barrier, dielectric and EMI shielding properties of the polymeric nanocomposites are affected by a number of parameters viz. the aspect ratio, thermal or chemical treatment, dispersion (related to processing conditions) and loading level of graphene nanosheets. Therefore, a consolidated study dealing with the preparation of different types of graphene sheets such as chemically reduced graphene (CRG), thermally reduced and annealed graphene sheets (TRG) and silver nanoparticles decorated graphene sheets (Ag-PVPCRG) and their based thermoplastic polyurethane nanocomposites has been undertaken [1]. Furthermore, the effect of different types of graphene, their morphological aspects on the final tailored properties of TPU nanocomposites such as electrical, gas barrier, mechanical dielectric and EMI shielding properties has been discussed in detail. These nanocomposites show useful properties for decreasing the EM wave pollution along with light weight, flexibility, optimum conductivity and good dielectric properties. A new material based on silver nanoparticles and graphene sheets was synthesized and reported for first time for potential applications in the field of EMI shielding applications [2].

2. Methods and Materials

2.1. Materials

Natural graphite powder was acquired from Loba chemie, India (purity 99.5%, 60 mesh size). Concentrated sulphuric acid (H_2SO_4 , 98%), potassium permanganate (KMnO_4), potassium per sulfate ($\text{K}_2\text{S}_2\text{O}_8$), di-phosphorus pentoxide (P_2O_5), hydrochloric acid (HCl , 37%), silver nitrate (AgNO_3 mol. weight 169.87 g/mol), hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 50.06 g/mol), N,N-dimethylformamide (density, 0.945 kg/L) and hydrogen peroxide (H_2O_2 , 50%) were purchased from Merck, Mumbai and methanol from Fisher Scientific, India. Polyvinyl pyrrolidone PVP (K-40) was acquired from Sigma Aldrich. Procured chemicals and solvents required for synthesis were used directly.

2.2. Methods

Firstly, graphene oxide (GO) was synthesized through modified Hummer's method, which was reduced via chemical reduction method and thermal reduction routes [1-3]. The exfoliation by chemical reduction route is limited. Hence, thermal exfoliation of GO sheets was achieved via annealing in the thermal furnace. The increase in surface area and degree of exfoliation assist in effective dispersion in N, N-dimethylformamide (DMF). The polyvinyl pyrrolidone (PVP) stabilized silver nanoparticles decorated graphene sheets were produced through solvent assisted reduction of GO sheets without the addition of catalyst [2].

3. Results and discussion

3.1. Morphological characterization using SEM and HRTEM

The surface morphologies of CRG, TRG and Ag-PVPCRG nanohybrid were investigated using SEM and HRTEM analysis. Typical SEM images are shown in Figure 1. CRG is observed as aggregated stacked sheet like structures (Figure 1a). In comparison, TRG exhibits fluffy (exfoliated) sheets with lamellar structure consisting of randomly aggregated sheets (Figure 1b). Ag-PVP-CRG nanohybrid sheets morphology is shown in Figure 1c, which reveals agglomerated CRG sheets decorated uniformly with AgNPs.

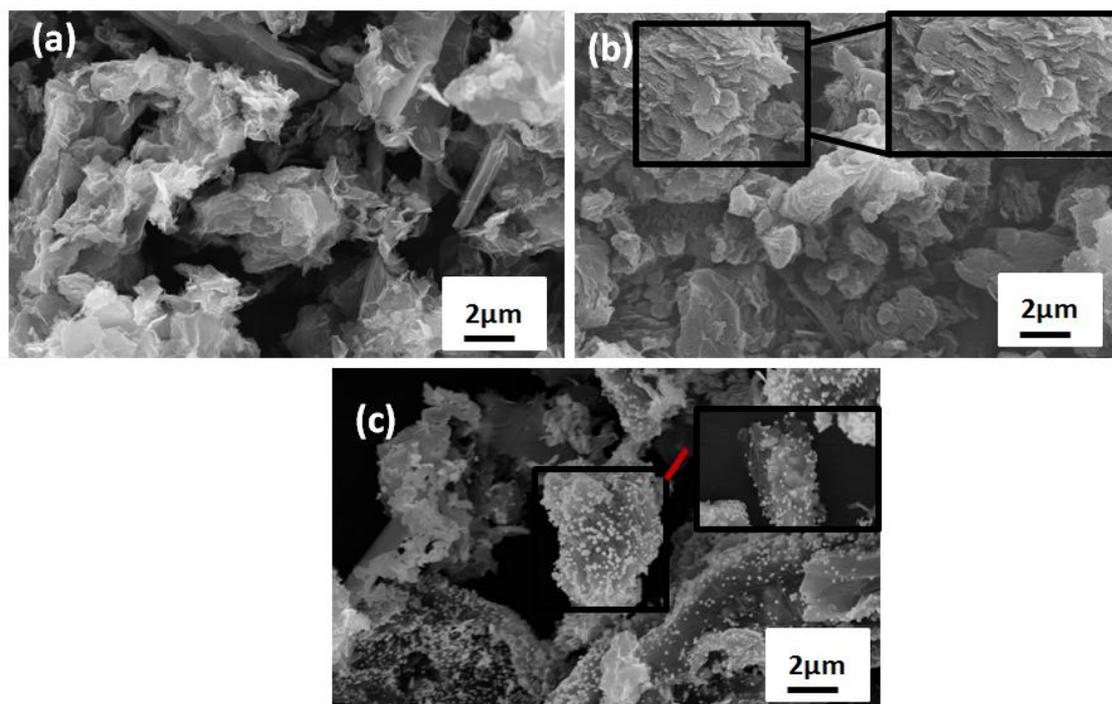


Figure 1. SEM images at 5KX of (a) chemically reduced graphene (CRG), (b) thermally reduced graphene (TRG), inset shows exfoliated wrinkled morphology at high magnification and (c) Ag-PVP-CRG nanohybrid, inset shows AgNPs presence on graphene sheets.

HRTEM micrographs of Ag-PVP-CRG nanohybrid are shown in Figure 2. The distribution of PVP stabilized AgNPs over the CRG nanosheet is evident from Figure 2a. Graphene sheets are covered by spherical Ag nanoparticles with an average particle size of approximately 15–30 nm. The selected-area electron diffraction (SAED) pattern of single silver crystallite is shown in Figure 2b, and it confirms the presence of AgNP adherence on CRG sheets..

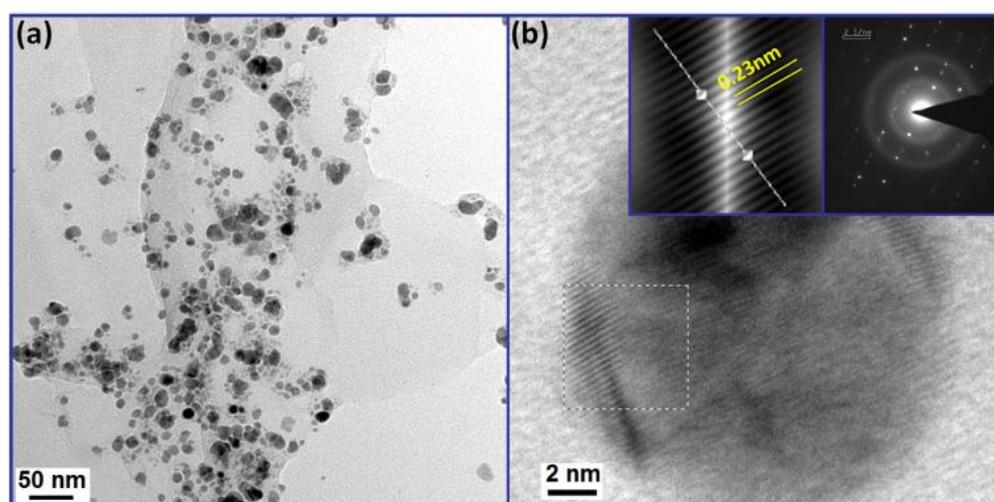


Figure 2. (a) TEM and (b) HRTEM image of Ag-PVP-CRG nanohybrid (inset shows lattice fringes and SAED pattern). The lattice-fringe spacing of silver

crystallites was measured to be 0.23 nm by HRTEM microscopy, which corresponds to the (111) crystal planes as shown in the inset of Figure 2b.

3.2. DC electrical conductivity analysis of Graphene nanosheets

Two-probe DC electrical conductivity was performed for GO, Ag-PVP-CRG nanohybrid, TRG and CRG at room temperature (30°C) as shown in Table 1. Rectangular shaped pellets measuring 2 mm in thickness were used for the measurement. The conductivity table shows the DC conductivity values as 1.2×10^{-4} , 0.25, 62.74 and 124.91 Scm^{-1} for GO, Ag-PVP-CRG, TRG and CRG respectively.

The rationale for low conductivity value in Ag-PVP-CRG nanohybrid relies upon the coating of non-conducting polymer (PVP) on the AgNP surface which hampers the conductivity of both AgNPs and graphene sheets. In the case of TRG, conductivity value is found to be lower than that of CRG which is attributed to the presence of more residual OH functional groups in TRG, which are unable to restore the graphitic structure and its exfoliated morphology that leads to the lower stacking of the sheet structures in comparison to densely stacked sheets in CRG.

Table 1. Electrical conductivity values of Graphene nanosheets.

| Graphene sheets | Electrical conductivity (S cm^{-1}) | BET Surface area (m^2/g) |
|-----------------|---|---|
| CRG | 124.91 | 18.20 |
| TRG | 62.74 | 159.61 |
| Ag-PVP-CRG | 0.25 | n/a |

3.3. EMI Shielding behavior of Graphene Nanosheets

The total EMI SE achieved for CRG, TRG and Ag-PVPCRG are $\sim -80 \text{ dB}$, -45.1 dB and -57.8 dB at 15GHz, 2 mm thickness respectively as given in Table 2. The total EMI value (SE) for CRG, TRG and Ag-PVP-CRG majorly comes from the absorption losses, SEA. In general, the value of SER mainly depends upon the electrical conductivity of the material, whereas SEA depends on its thickness, conductivity and dielectric properties. The dielectric properties in terms of real and imaginary parts of the permittivity (ϵ' , ϵ''), and tangent losses are given in Table 2 for all three forms.

The reason for highest EMI SE of CRG is attributed to (a) high conductivity of the order of 124.9 Scm^{-1} arising from increase in 3D conductive channels upon stacking of sheets, (b) the presence of clustered defects (residual functional groups) onto the sheet surface and (c) high values of dielectric permittivity. Thus, both high electrical conductivity and dielectric permittivity in terms of losses as well as stored energy plays a contributive role in attaining maximum SER and SEA value, yielding highest total SE. In comparison, TRG exhibits (a) low conductivity value (62.7 Scm^{-1}) due to highly exfoliated sheet structures, (b) lower residual bonds (oxygenic functional groups) and (c) low dielectric losses resulting in comparatively low SE value of -45 dB . The dielectric permittivity in terms of stored energy plays a contributive role in attaining -45 dB SE value for TRG. The high SE value (-58 dB) of Ag-PVP-CRG is a result of EM wave attenuation in the form of highest dielectric losses (Table 2) along with a moderate conductivity value of 0.25 Scm^{-1} . The dielectric losses $\epsilon''(\omega)$ consist of both polarization losses and conductivity losses. The dielectric behavior of Ag-PVP-CRG comprises of polarization losses in terms of (a) interface polarization occurring at the interfaces between AgNPs and CRG sheet, (b) dipole polarization caused due to the presence of residual functional groups or defects in CRG sheets. The relatively high values of ϵ'' are attributed to the synergistic coordination between dielectric AgNPs and CRG sheets and effective conducting network formation of CRG sheets and PVP-AgNPs in Ag-PVP-CRG nanohybrid. The effective ϵ'' may also result from the quick dissipation of stored energy in the form of thermal energy. The high value of thermal conductivity of carbon and AgNPs in Ag-PVPCRG structures may add up to high dielectric losses resulting in effective dissipation of thermal energy. The

electrical conductivity of TRG is higher as compared to AgPVP-CRG, even though the EM wave losses due to reflection (SE_R) terms in case of Ag-PVP-CRG nanohybrid is higher which is attributed to the presence of metallic AgNPs in Ag-PVP-CRG.

Table 2. EMI Shielding Effectiveness summary of neat graphene nanosheets such as TRG, CRG and Ag-PVP-CRG @ 15 GHz

| Material | SE_T | SE_A | SE_R | Real part of permittivity | Imaginary part of permittivity | Tangent losses |
|------------|--------|--------|--------|---------------------------|--------------------------------|----------------|
| CRG | -80 | -68 | -11.9 | 73.4 | 56.2 | 0.76 |
| TRG | -45.1 | -40.1 | -5 | 43.3 | 18.5 | 0.42 |
| Ag-PVP-CRG | -57.8 | -50.7 | -7.06 | 88.5 | 139.9 | 1.58 |

3.4. SEM Fracture surface of nanocomposite films

The cross-sectional SEM micrographs of the cryofractured TPU/Graphene nanocomposites at 10 wt.% loading of different graphenes such as CRG, TRG and AgPVP-CRG is shown in Figure 3. The SEM morphology of TPU matrix exhibits smooth and continuous surfaces, while TPU/Graphene nanocomposites (TPU/TRG, TPU/CRG and TPU/Ag-PVP-CRG) appear to be rough, more likely as dendrite structures. The Ag-PVP-CRG nanohybrid in TPU matrix at 10 wt.% loading, appeared as scattered island morphology (Figure 3b), where PVP stabilized silver nanoparticles could be seen as droplets dispersed in TPU matrix. At high Ag-PVP-CRG loading, CRG sheets seem to be agglomerated and non-uniformly distributed in TPU matrix. Thus, TPU/Ag-PVP-CRG nanocomposite at higher content of Ag-PVP-CRG nanohybrid showed poor distribution of graphene sheets, revealing the presence of thick stacked CRG sheets. This agglomeration and aggregation of graphene sheets may be attributed to the solvent evaporation step in solution casting process during nanocomposite film preparation, leading to non-uniform distribution and dispersion of Ag-PVP-CRG in TPU matrix. In TPU/CRG nanocomposites, non-uniform and poor distribution of thick stacked CRG sheets was observed in Figure 3c. The SEM images of CRG revealed thick stacked sheets. The reason for CRG sheets stacking is the final stage water removal step during CRG synthesis from CRG/water.

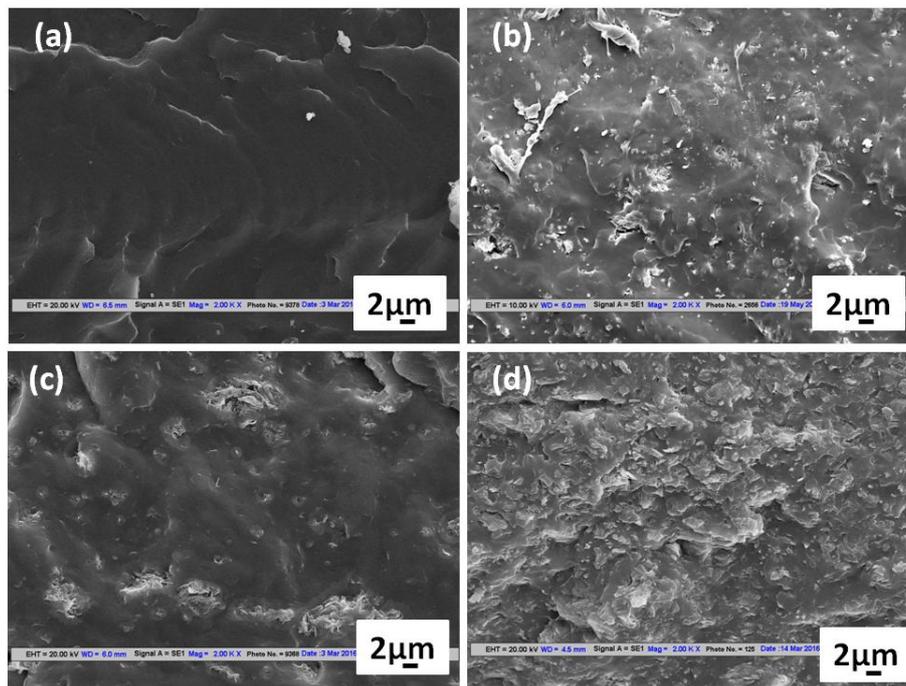


Figure 3. SEM micrographs of the fractured surfaces of (a) neat TPU, (b) 10 wt.% TPU/Ag-PVP-CRG, (c) 10 wt.% TPU/CRG, and (d) 10 wt.% TPU/TRG at 2KX magnification.

3.5. Electrical conductivity and EMI shielding property of Graphene/TPU nanocomposites

In spite of highest electrical conductivity and EMI SE values of bare CRG sheets over TRG sheets, the TPU/TRG nanocomposite showed maximum EMI SE due to excellent exfoliation, fine dispersion and distribution of TRG sheets which form an effective 3-dimensional electrically conducting network inside the insulating polymer matrix (TPU) over CRG sheets which got agglomerated and aggregated within TPU matrix as shown in Figure 4 and 5. This has also been confirmed through DC conductivity values. The lowest EMI SE value obtained for TPU/Ag-PVP-CRG nanocomposite can be ascribed to the minimum conductivity values of Ag-PVP-CRG nanosheets as compared to CRG and TRG (Figure 5), due to the insulating coating of PVP onto AgNPs. Although the neat Ag-PVPCRg nanohybrid showed highest value ~ -58 dB EMI SE, but showed poor dispersion and aggregation when mixed in TPU matrix thus resulted in reduced EMI SE values when in nanocomposite with TPU. Therefore, TPU/TRG and TPU/CRG nanocomposite can act as an effective shielding material, reducing the escape chances of incident EM wave more efficiently.

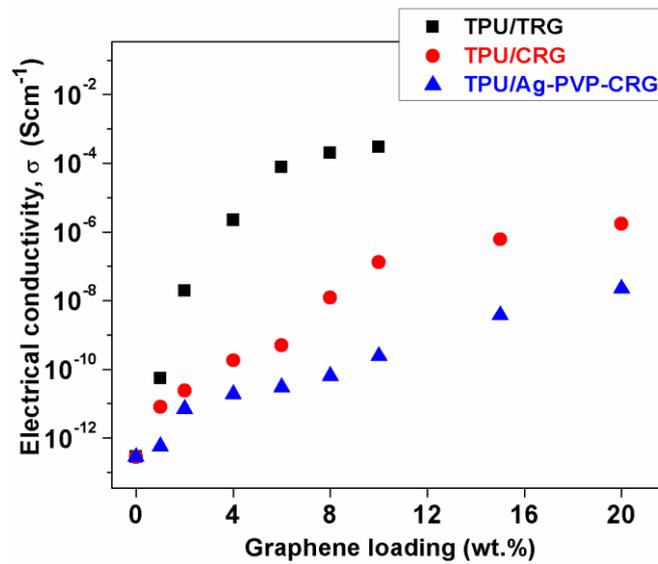


Figure 4. DC electrical conductivity TPU/Graphene nanocomposites vs. loading of graphene nanosheets.

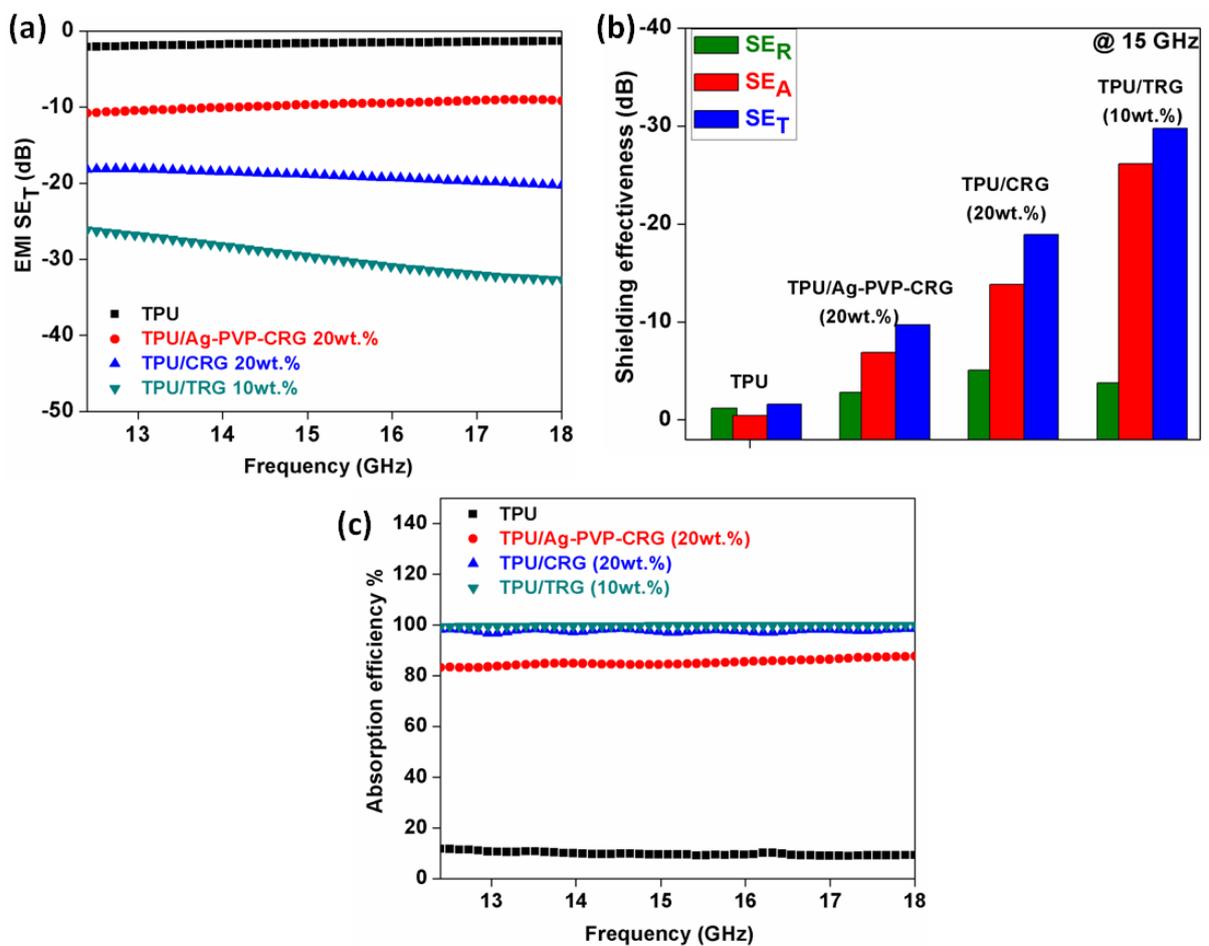


Figure 5. (a) EMI shielding effectiveness of TPU/graphene (TRG, CRG and Ag-PVP-CRG) nanocomposites with frequency (Ku Band region), (b) variation in SE_T , SE_A and SE_R with different graphene loading at 15 GHz (mid-frequency range), (c) variation in absorption efficiency.

3.6. EMI shielding behavior of graphene/TPU nanocomposites

The three different graphenes synthesized in the lab were then mixed with thermoplastic polyurethane by solution intercalation to prepare nanocomposite films and tested and characterized. A comparison of the conductivity, dielectric behavior and EMI shielding properties of TPU/graphene nanocomposites based on three different types of synthesized graphene i.e. CRG, TRG and Ag-PVP-CRG are presented in Table 3. Surface characterization via SEM of TPU/TRG showed fine dispersion of TRG sheets, due to excellent exfoliation of TRG sheets during synthesis as compared to TPU/CRG and TPU/Ag-PVP-CRG nanocomposite films which showed agglomerated CRG and Ag-PVP-CRG nanosheets. The highest DC conductivity value and lowest DC percolation threshold was obtained for TPU/TRG nanocomposite at 10 wt.% loading, comparatively at lower filler concentration as compared to TPU/CRG and TPU/Ag-PVP-CRG nanocomposites, where 20 wt.% loading could give similar property. The effective dielectric constant and tangent losses were obtained for 10 wt% TPU/TRG nanocomposites, as compared to TPU/CRG and TPU/Ag-PVP-CRG nanocomposites. TPU/TRG nanocomposite shows highest shielding effectiveness (SE) at 10 wt.% loading in comparison to TPU/CRG and TPU/Ag-PVP-CRG where SE achieved at higher loading ~20 wt.% (Table 3).

Table 3. Summary of EMI Shielding Effectiveness of different graphene (TRG, CRG and Ag-PVP-CRG) based TPU nanocomposites @ 15GHZ

| Material | SE _T | SE _A | SE _R | Absorption efficiency % |
|-----------------------|-----------------|-----------------|-----------------|-------------------------|
| TPU | -1.61 | -0.43 | -1.18 | 9.4 |
| TPU/TRG 10wt.% | -29.8 | -26.1 | -3.7 | 99.9 |
| TPU/CRG 20wt.% | -18.8 | -13.8 | -5.07 | 95 |
| TPU/Ag-PVP-CRG 20wt.% | -9.6 | -3.8 | -5.8 | 82 |

4. Conclusion

The above comparative data analysis showed that amongst the three types of nanocomposites TPU/TRG nanocomposite show the most promising EMI shielding behavior at 10 wt.% loading and thus meet the basic requirements of the commercial electrical applications against electromagnetic pollution. The reason may be that it also shows highest electrical conductivity, dielectric constant and tangent losses amongst the three nanocomposites prepared. The maximum achieved exfoliation and uniform dispersion in TPU/TRG nanocomposites further helps in giving best EMI shielding parameter.

References

- [1] T. Bansala, "Studies on Thermoplastic/graphene based nanocomposites", PhD Thesis, 2017, IIT Delhi, India.
- [2] T. Bansala, M. Joshi, S. Mukhopadhyay, R. A. Doong and M Chaudhary, "Synthesis and shielding properties of PVP-stabilized-AgNPs-based graphene nanohybrid in the Ku band" 2016, Synth. Met. vol. 221, pp. 86-94.
- [3] T. Bansala, M. Joshi, S. Mukhopadhyay, R. A. Doong, M. Chaudhary, "Electrically conducting graphenebased polyurethane nanocomposites for microwave shielding applications in the Ku band" 2017, *J. Mater. Sci.*, vol. 52, no. 3, pp. 1546–60.
- [4] T. Bansala, M. Joshi, S. Mukhopadhyay, R. A. Doong, M. Chaudhary, "Electrical and Dielectric Properties of Exfoliated Thermally Reduced Graphene Based Polyurethane Nanocomposites", 2017, *J. Nanosci. Nanotechnol.* vol. 17, no. 12, 8782-90.