ELECTROMAGNETIC INTERFERENCE SHIELDING PERFORMANCE OF POLYANILINE/GRAPHENE NANOCOMPOSITES IN KU BAND

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A B S T R A C T

Carbon-based conducting polymer nanocomposites have potential application as electromagnetic interference (EMI) shielding materials due to their high conductivity and dielectric constant. In the present investigation, the highly conducting graphene(GNS)/polyaniline(PANI) nanocomposites were prepared by in-situ polymerization with different concentration of functionalized GNS. GNS/PANI nanocomposites showed semiconducting nature as that of PANI with improved dielectric and EMI shielding properties. The EMI shielding effectiveness (SE) and dielectric constant of nanocomposites found to be increased with increasing GNS content and is absorption dominated also, SE of nanocomposites is greater than the required commercial application and hence can be used as lightweight EMI shielding.

Keywords: Polyaniline, Graphene, Nanocomposites , EMI Shielding, Dielectric constant

1. Introduction

Electromagnetic Interference (EMI) reacts with any electronic devices to degrade the performance of systems in the same environment. As commercial, military, and scientific electronic devices, EMI shielding of radio frequency radiation continues to be a more serious concern in this modern society. For the safe operation the shielding protection is required which must be strong, low cost and lightweight. Conventionally, metals is an effective EMI shielding material, but though they are good for EMI shielding, they are expensive, heavy and prone to corrosion, poor to chemical resistance, oxidation, difficult in processing and high cost of manufacturing processes (Eswaraiah, Sankaranarayanan, & Ramaprabhu,2011). Conducting polymer composites offer a potentially cost-effective and process-friendly alternative to metal (Mohammed,&Uttandaraman,2009, Gelves, Mohammed, & Uttandaraman,2011). Conducting polymers are very efficient in various EMI shielding applications (Leo´n, Campbell, Smith, & Walsh, 2008). Among all organic conjugated polymers, polyaniline (PANI) received considerable attention in recent years due to its high conductivity in the doped state (1 S/cm) (Virji, Kojima, Fowler, Villanueva, Kaner, & Weiller, 2009). It is inexpensive, it shows excellent environmental and electrochemical stability (Youssef, Kamel, El-Sakhawy, & El Samahy, 2012). Polyaniline not only reflects but also absorbs electromagnetic waves and can attain high level of shielding performance (Tzu-Hao, & Kuo-Hui, 2013). The carbon based materials such as graphite, expanded graphite, carbon black, carbon nanotubes and graphene have been explored for possible applications in EMI shielding. Graphene is a two-dimensional hexagonal lattice; one-atom-thick planar sheet of sp^2 bonded carbon atoms originated from graphite and emerged as conductive nanomaterial (Liu, Liu, Li, Dong, Yao, Kiddi, Zhang, Li, & Tian, 2012, Brownson, Kampouris, Banks, 2011). Graphene is promising in handling terahertz frequency signals and thus can be used for electromagnetic interference shielding material (Kuilla, Bhadra, Yao, Kim, Bose, & Leea, 2010). The nanocomposites show improvements in properties even at very low filler loading in the polymer matrix (Fazli, Moosaei, Sharif, & Ashtiani, 2015). Nanocomposites of graphene-based polymers have high electrical conductivity, high optical transmittance in the visible range of spectrum and high carrier mobility (Wei-Li, Wang, Li-Zhen, Li, Chan-Yuan, & Mao-Sheng C.,(2014). All these properties make GNS/PANI composites a new trend for developing high strength light weight structural polymer composites for automobile, aerospace, electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding (Udmale, Mishra, Gadhave, Pinjare, & Yamgar, 2013, Kumar, Dhakate, Saini, & Mathur, 2013). Chen et al fabricated polyaniline composites filled with graphene decorated with silver nanoparticles, and graphene decorated with nickel nanoparticles and EMI shielding effectiveness (EMI SE) of the composites with different filler loadings (0.5, 1.0, 3.0, and 5.0 wt.%) were investigated. The PANI composite containing 5.0 wt. % graphene decorated with silver showed the highest EMI SE of 29.33 dB (Chen, Li, Yip, Tai, (2013). Singh et al developed a new material γ-Fe_2O_3 decorated reduced graphene oxide /polyaniline core–shell tubes for absorbing electromagnetic interference pollution, which shows high shielding effectiveness ($SE_T \sim 51$ dB) at a critical thickness of 2.5 mm (Singh, Mishra, Sambyal, Gupta, Singh, Chandra & Dhawan, 2014). Joshi et al prepared GNS/PANI composite in the epoxy matrix. As the percentage of the GNS/PANI composite in the epoxy matrix increases from 2.5 to 5 wt%, the shielding effectiveness increases from an average value of 34 dB to 44 dB for 3.4 mm thickness (Joshi,Bajaj, Singh, Anand, Alegaonkar & Datar, 2015). So, in the light of importance of graphene nanosheets (GNS), in the present work, the GNS nanocomposites were synthesized by in-situ chemical polymerization to investigate the electromagnetic interference shielding along with electrical conductivity, permittivity, and permeability by changing the graphene contents in the polyaniline matrix.

2. Experimental

2.1. Materials

Aniline (99%, mol. wt 93.13 g/mol), Hydrazine monohydrate (N_2H_4 mol. wt 32.042), Potassium permanganate ($KMnO_4$ mol. wt 158.03) were supplied by Sigma Aldrich. Sulphuric acid (H_2SO_4 mol. wt. 98.079g/mol), hydrochloric acid (HCl mol. wt. 36.46094 g/mol) and nitric acid (HNO_3 mol. wt. 69.71g/mol), sodium nitrate ($NaNO_3$, mol. wt. 84.9947 g/mol), hydrogen peroxide (H_2O_2, mol. wt. 34.0147) were procured from Merck Ltd., India. Ferric chloride ($FeCl_3$, mol. wt. 162.20g/mol) and ethanol (mol. wt. 46.07) were procured from Himedia. Graphite flakes were made available from National Physical Laboratory, New Delhi (India). All chemicals were of AR grade and used as received except aniline which was distilled under reduced pressure and kept below 4^oC before used for synthesis. De-ionized water was used in all synthesis.

2.2. Materials synthesis

Graphite oxide (GO) was synthesized from natural purified graphite flakes by the Hammers method, and graphene nanosheets (GNS) were prepared by exfoliation of GO (Chen, Qui, Zhu, Che, Zhang, Zhang, Li, Wang, Wang, 2014, Hanifah, Jaarfar, Aziz, Ismail, Othman, & Rahman, 2015). The preparation of GO and GNS and the functionalization of GNS were conducted as per our previously reported work (Modak, Kondawar, & Nandanwar, 2015). GNS was functionalized by acid treatment to obtain a surface suitable for making chemical interaction with polymers (Cordero& Alonso,2007, Bautista-Flores, Sato-Berrú & Mendoza,2015).. The GNS/ PANI composites were synthesized by an in-situ polymerization of aniline in the presence of GNS. The weight percent of GNS to aniline was varied from 0% to 5%. The solution of 0.2M HCl in 50 ml of de-ionized water was divided into two parts. In one part 0.2M aniline and functionalised GNS was added and the mixture was ultrasonicated for 30 min. After the ultrasonication the mixture was kept for stirring for about 5 hrs at 5ºC to get the better yield. To another part 0.2M ammonium persulphate (APS) was mixed and added drop by drop to the stirring monomer solution. After mixing the reactants, the solution starts showing greenish tint and afterward it turns violet. The black precipitate was obtained after 6 to 7 hrs. This precipitate was kept for overnight and diluted with de-ionized water until the filtrate became colourless. Finally, it was washed with ethanol and dried overnight in oven at 80ºC

(Kondawar, Anwane, Nandanwar & Dhakate 2013, Deshpande & Kondawar, 2016).

3. Results and discussion

3.1. Morphology

SEM images were recorded on Carl Zeiss EVO-18 scanning electron microscope. SEM images of as-synthesized pure PANI and GNS/PANI nanocomposites for 1%, 3% and 5% GNS are shown in Fig. 1. The pure PANI shows the spherical grain structure which is well interconnected forming a net like structure but not uniform throughout. The surface of the GNS seems to be coated with a layer of PANI. No free GNS can be seen in GNS/PANI composites which mean that the PANI covers the GNS surface uniformly. In the case of 5% GNS composite, the aggregation of PANI particles is clearly observed in (Fig. 1C) with the destruction of the three-dimensional (3-D) framework structures (Dubin, Gilje, Wang, Tung, Cha, Hall, Farrar, Varshneya, Yang, & Kaner, 2010).

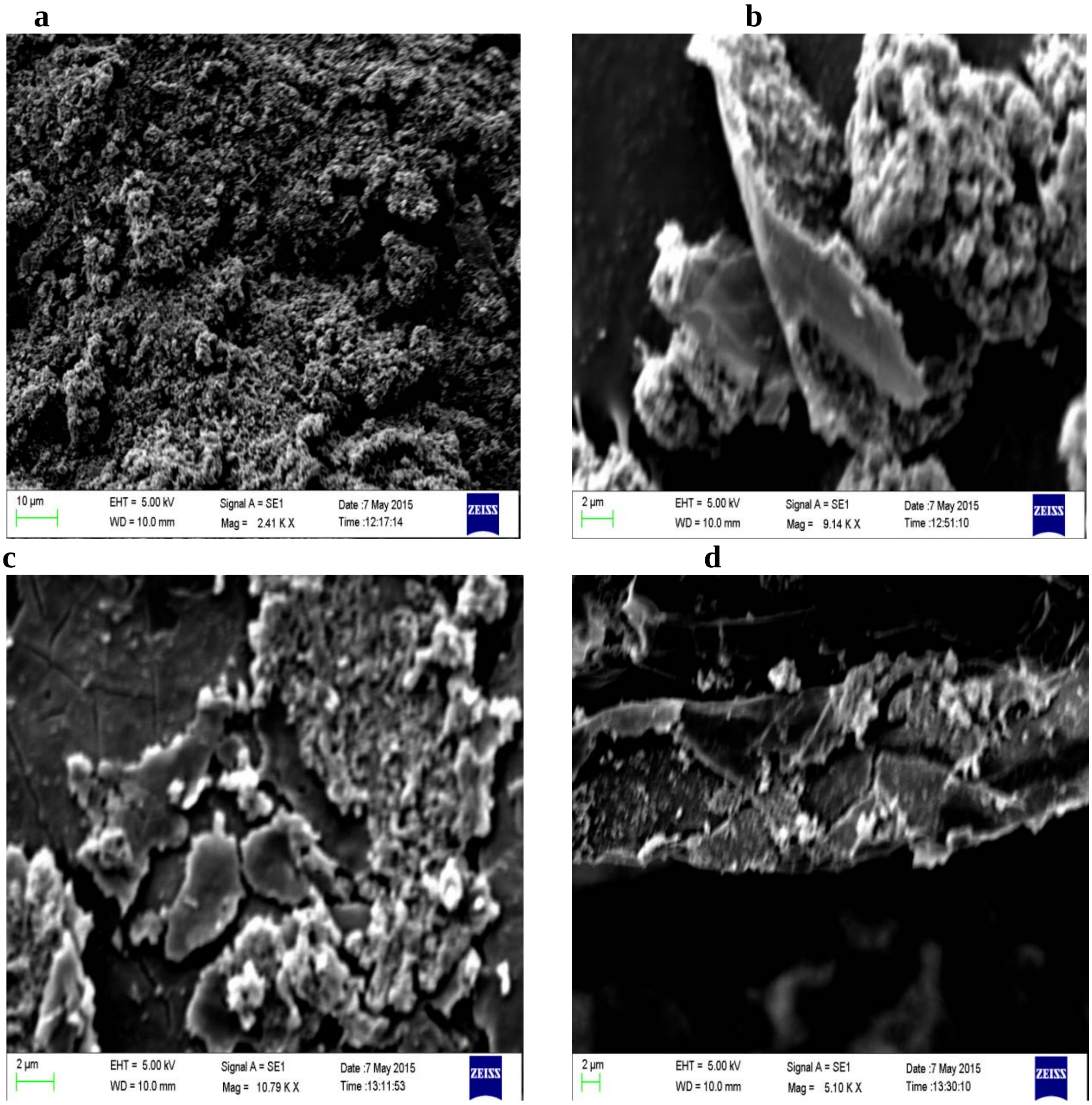

Fig. 1-SEM images of (a) pure PANI and for (b)1%,(c) 3% and (d) 5% GNS in PANI

3.2. FTIR spectroscopy

Fourier transforms infrared spectra were recorded by KBr pellet technique in the wavelength range 400-4000 cm^{-1} by Thermo Nicolet, Avatar 370. FTIR spectra of pure PANI and PANI/GNS nanocomposites are shown in the Fig. 2. For pure PANI, the absorption bands at 1552.23 and 1487.56 cm^{-1} are assigned to the C=C stretching of quinone rings and benzene rings. (Verdejo, Bernal, Romasanta, & Lopez-Manchado, 2011).A significant peak at 1107.41 cm^{-1} (C-N stretching) for PANI was found due to the charge delocalization over the polymeric backbone. The shift of characteristic peaks of PANI indicated strong interaction between PANI and GNS fillers and facilitates effective degree of electron delocalization which enhances the conductivity of polymer chains (Chen, Dung, Li, Yip, Hsu, Tai, 2011).

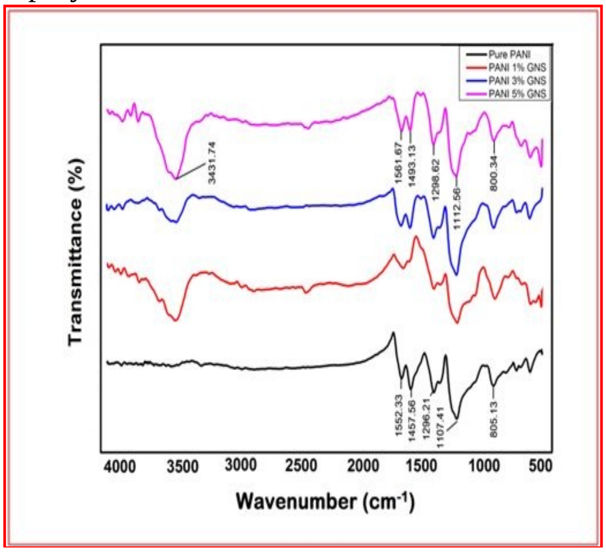

Fig. 2- FTIR of PANI/GNS composites

3.3. Electrical Conductivity

The electrical conductivity was measured by four probe method. The samples were prepared as round shaped pellets at room temperature. It is observed in Figure 3, that the electrical conductivity of GNS/PANI composites increased with the increased in weight percent of GNS in PANI matrix. The remarkable enhancement of electrical conductivity potentially endows the lightweight GNS/ PANI with good electromagnetic interference (EMI) shielding property.

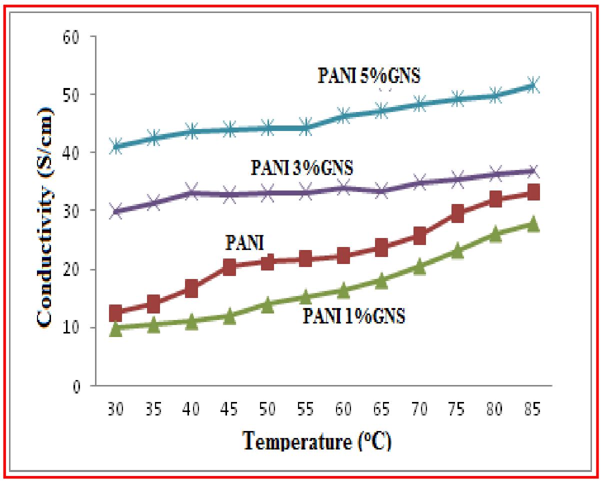

Fig. 3- Electrical Conductivity of PANI/GNS composites

3.4. Permittivity and Permeability

Electromagnetic interference shielding, permittivity and dielectric loss measurements were carried out on vector network analyzer in the microwave range of 12.4–18 GHz (Ku band) using Agilent Technologies, E8362B.Complex permittivity and the permeability of composites as well as te EMI shielding effectiveness were calculated using scattering parameters (S_{11} and S_{21}) based on the theoretical calculations given by Nicholson, Ross and Weir (Singh, Ohlan, Pham, Balasubramaniyan, Varshney, Jang, Hur, Choi, Kumar, Dhawan, Kongd, Chung, 2013).The frequency dependence of relative dielectric constant, dielectric loss, permeability, and magnetic loss of nanocomposites respectively are shown in Fig. 4(a), (b), (c) and (d). The dielectric constant exhibited decreasing trend with frequency. This can be attributed to the decreasing ability of the dipoles (present in the system). The dielectric constant (ε′) as well as dielectric loss (ε″) of the nanocomposites exhibit measurably improved values as the concentration of GNS in PANI matrix increases. The increase in the permittivity value is ascribed to the motion of free charge carriers. Also, the enhanced electromagnetic absorption properties can be attributed to charge transfer from polyaniline to graphene. The permeability of higher concentration of GNS was found to be higher. This may be due to the improvement of the magnetic properties along with the reduction of eddy current losses. The results show that the magnetic loss is in negative region for 1% GNS concentration which means radiation passes through it without any absorption. It is cleared that dielectric loss is the most important contributing part than the magnetic loss and the composites has the magnetic property also.

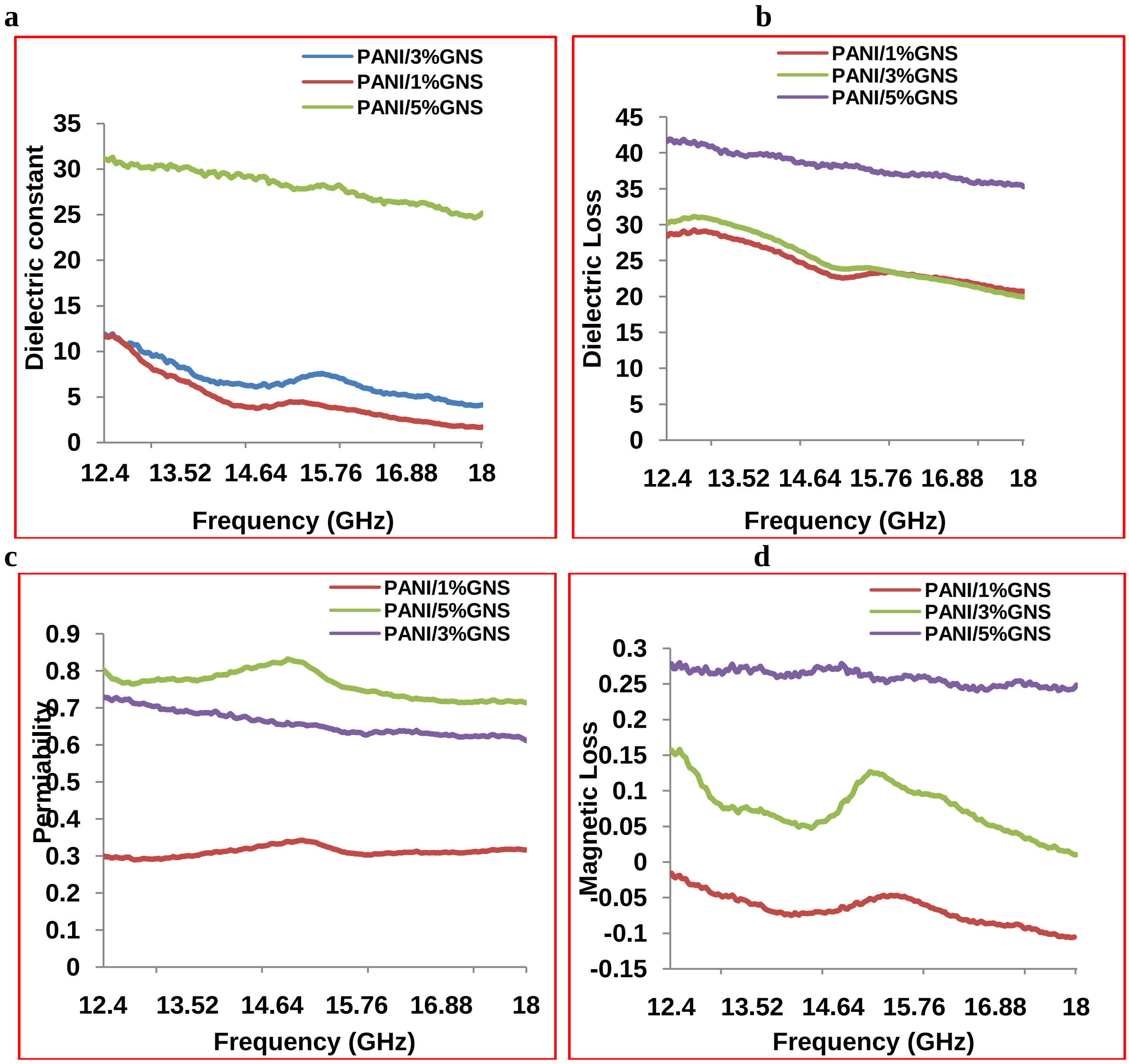

Fig.4- (a) dielectric constant of PANI/ GNS composite; (b) dielectric loss of PANI/ GNS composite;(c) permiability of PANI/ GNS composite;(d) magnetic loss in PANI/ GNS composite.

3.5. Electromagnetic Interference (EMI) Shielding

The EMI SE was found to be increased with increase in GNS content. The increase in GNS from 1% to 5%, the volume resistivity of composites decrease and SE increase. With increasing amount of GNS, the number of percolating networks increases. The shielding effectiveness for reflection (SE_R), absorption (SE_A) and total (SE_T) of PANI/1%GNS, PANI/3%GNS, and PANI/5%GNS as a function of frequency are shown in Fig. 5(a), (b) and (c) respectively. The SE_R is nearly linear in nature for each composition in the entire frequency range of measurement and shows a negligible change even with the increase in GNS loading. The SE_A is increased from 20 to 30 dB with increase in GNS loading from 1 to 3 wt%. The experimental results show that absorption is the primary shielding mechanism and reflection is the secondary shielding mechanism. The SE_T of nanocomposite as a function of frequency Shows that, the nature of SE_T for each composition is nearly linear with frequency, but the SE_T of composite is found to increase with the increase in GNS loading. Total Electromagnetic Interference Shielding Effectiveness of 1, 3, and 5 wt% GNS loading is 28, 30, and 40 dB, respectively.

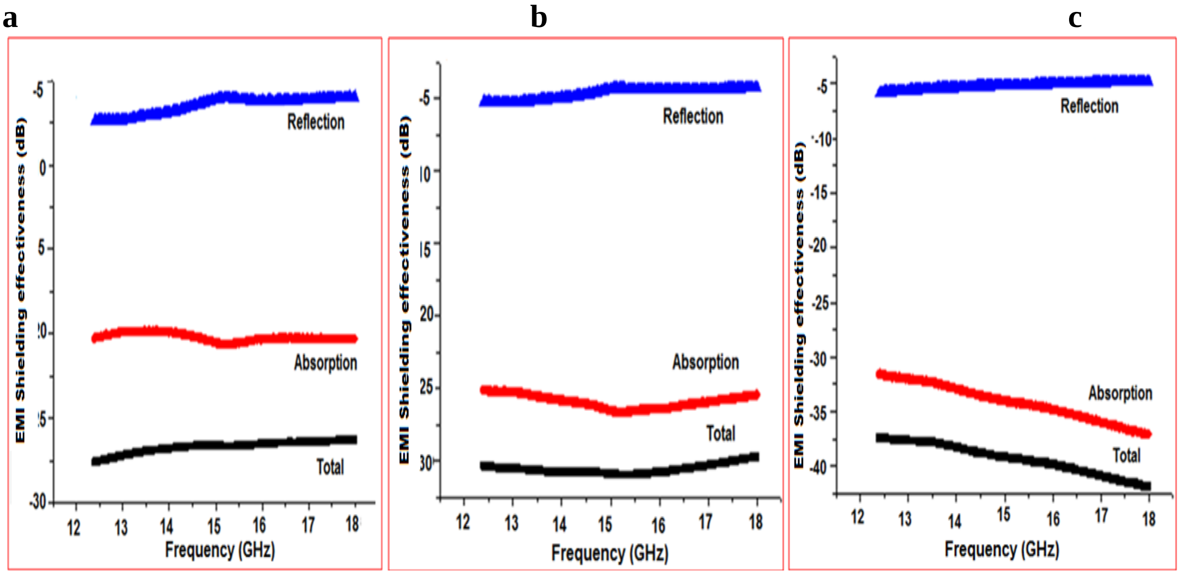

Fig. 5- EMI Shielding effectiveness for (b) 1%; (c) 3% ;(d) 5% GNS in PANI

4. Conclusion

GNS/PANI nanocomposites were successfully synthesized by in-situ chemical oxidative polymerization. Nanocomposites showed semiconducting nature as that of PANI with improved properties for EMI shielding. The EMI shielding effectiveness (SE) of nanocomposites was found to be increased with increasing GNS content and it was found to be absorption dominated indicating GNS/PANI nanocomposites can be used as lightweight EMI shielding materials for electromagnetic radiations in Ku band. The composites shows high value of EMI SE obtained for composites indicating it is higher than the required value of EMI shielding effectiveness (20 dB) for commercial applications.

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