Polyaniline/oxide-based core-shell like structured composites for reduction in electromagnetic pollution

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Abstract

Polyaniline (PANI) based composites with manganese dioxide (MnO_2, 30 wt.%) and vanadium pentaoxide (V_2O_5, 30 wt.%) have been synthesized using the *in-situ* polymerization synthesis route, whereas both the oxides used as filler materials in the polyaniline matrix. The amalgamated composites have been analyzed for morphological investigation and shielding the incident electromagnetic (EM) waves in the frequency range 8.2-12.4 GHz (X-band). PANI/MnO_2 and PANI/V_2O_5 composites are synthesized in core-shell like morphology, whereas PANI act as core while oxide act as the shell. The shielding of EM waves has been investigated in terms of shielding effectiveness (SE). PANI/MnO_2 composite exhibits the efficient SE value i.e. ~50 dB as shown in the figure. This higher value of SE is due to the ferromagnetic character of MnO_2 particles which increases the dielectric losses in the specimen. Whereas, PANI/V_2O_5 composite attain the smaller value of SE i.e. ~9 dB, because V_2O_5 particles are diamagnetic in nature, thus dielectric losses decrease. Moreover, SE decreases with an increase in frequency due to a decrease in dielectric losses. PANI/MnO_2 composite has an SE value greater than the minimum requirement for industrial application i.e. 30 dB, thus, PANI/MnO_2 composite can be used as EM shielding material, whereas, PANI/V_2O_5 composite can't fulfill this requirement.

Keywords: *EMI shielding, electromagnetic pollution, PANI, core-shell*

1. Introduction

The ubiquitous electronic devices used in navigation, satellite communication systems, cellular technology, microwave heating, radar detection, data security system, communication system, medical science and in security systems [1–5], etc., have brought great accessibility to our life with the evolution of information age, they have led to explosive growth in electromagnetic radiations [6,7]. Moreover, in the advanced technology life, the development and use of portable and wireless devices are increasing rapidly which can be dangerous for human being as well as a living organism in future because these devices create electromagnetic pollution, thus the reduction 'or' stop this kind of pollution become more important. Electromagnetic pollution will also increase in the future because as population increases, the use of these devices will also increase. Thus, to protect the environment and health of living bodies, exactitude of sensitive equipment from the influence of EM radiations, the shielding from electromagnetic radiations is essentially mandatory [8]. So, it is a big challenge in front of researchers and scientists to synthesize the appropriate sample and fabrication of suitable devices which can be utilized as a shield for reducing 'or' stop the electromagnetic pollution. Electromagnetic pollution also reduces the performance of electronic gazettes/devices as well as their average life which are already working in the science and technology community. Thus, the reduction of electromagnetic pollution from the atmosphere becomes more important for exiting or upcoming technologies as well as for living organisms. Also, after the fabrication of shielding devices and material, the performance and its average life create a question. So, we have to need to fabricate the device and synthesize the sample for shielding from electromagnetic pollution which exhibits good shielding performance and also having enough average life.

The shielding from electromagnetic waves can be accomplished by the reflection, absorption and internal multiple reflections processes on/in shielding materials, and these processes can contribute significantly if these shielding materials have enough either magnetic or dielectric losses. The magnetic losses in shielding materials are occurred due to magnetic characters of magnetic materials such as iron, nickel and manganese, etc., whereas dielectric losses are occurred due to conducting the nature of materials such as graphene, CNTs, etc. [9]. But the problem with these materials is their heavyweight, corrosion vulnerability, complex and time-consuming synthesis approach. So, these problems can be overcome by using conducting polymers doped with highly magnetic 'or' conducting materials a shielding material because composites of conducting polymers are generally easy to synthesized, lightweight, anti-rusting. Moreover, the properties of conjugated polymers can be changed on the basis of the synthesis process and incorporation of foreign impurities [10,11] in the polymer matrix. Also, the properties and applications of conjugated polymers can be altered by using various types of dopants and the pristine form and composite samples of conjugated polymers successfully utilized for various applications including EMI shielding [12] such as supercapacitor [13], sensor [14], cancer cell imaging [15], fuel cells [16], water purifying materials [17], etc. Therefore, in the present research work, we have been synthesized the Polyaniline and metal oxides based composites and utilized for EMI shielding effectiveness investigation.

2. Experimental details

2.1 Synthesis of PANI/MnO_2 and PANI/V_2O_5 Composites

The chemicals used in the synthesis of PANI composites with MnO_2 (30 wt.%) and V_2O_5 (30wt.%) were purchased from the Sigma Aldrich company. The aniline hydrochloride, ammonium persulphate, and MnO_2 (30 wt.%) used as the monomer, oxidant, and loadings in 25mM, 15mM, and 0.1M concentrations, respectively. All the chemicals were dissolved in distilled water separately, and cooling for one hour in the refrigerator. After the cooling, the oxidant solution was placed in an ice bath with maintaining the temperature between ~0-4 ^oC under continuous stirring, and loading solution added dropwise in it after that monomer solution added dropwise. On the addition of few drops of monomer solutions, the polymerization gets started, and the resultant solution was left in the refrigerator for 24 hrs to complete the polymerization reaction. Then, the precipitates of prepared materials were filtered out using the filter paper, and the prepared yield was washed with a sufficient amount of HCl, methanol, and distilled water till the filtrate become colorless. Thereafter, prepared samples dried in air and then in vacuum at 55 ^oC temperature. Finally, prepared sample crushed in fine powder using pestle mortar. A similar synthesis route was followed for the synthesis of the PANI/V_2O_5 (30 wt.%) composite.

2.2 Sample Characterizations

The morphological study of the prepared samples was investigated using the Field Emission Scanning Electron Microscope (FE-SEM) (FEI NOVA NANO SEM 450 model, Made in USA) under vacuum circumstances. The electromagnetic shielding measurements in the X-band (8.2-12.4 GHz) of the microwave region were investigated using the vector network analyzer (Model-PNA-L N5230C Agilent Technologies) having a cavity of dimensions ~22.86x10.16x2 mm^3 at room temperature.

3. Result and Discussions

3.1 Morphological Investigation

Figure 1(a,b) shows the morphological investigations of the prepared composite samples. The FESEM images of the prepared samples reveal the core-shell like structure of the prepared samples because particles of metal oxide materials are not clearly shown in figures that means the polyaniline wrapped over the metal oxide particles, and core-shell like structures are formed. Here, the metal oxide particles act as the core, and PANI act as the shell [18].

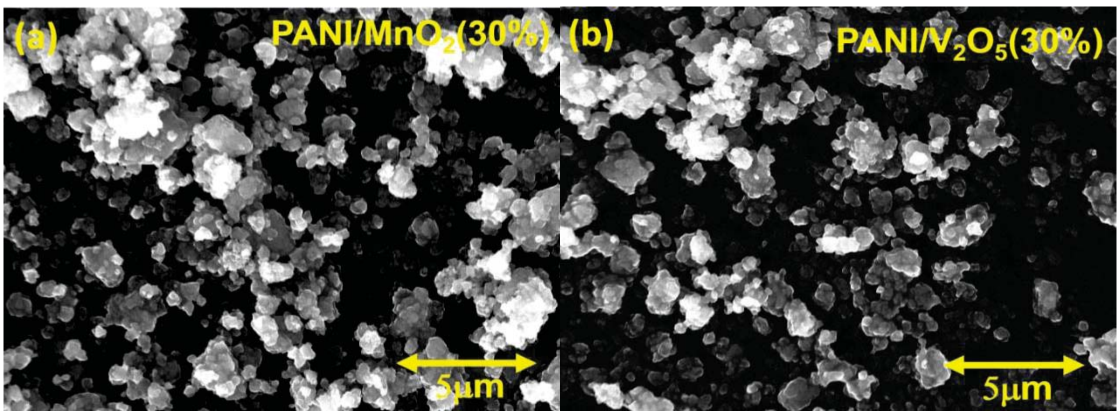

FIG 1.FESEM images of the prepared (a) PANI/MnO_2 (30%), (b) PANI/V_2O_5 (30%) composite samples.

3.2 EMI Shielding Properties Investigation of PANI/Metal Oxide Composites

The electromagnetic interference shielding effectiveness (EMI SE) are the properties of materials to shield the incident electromagnetic waves, and measured in decibel (dB). The attenuation of the incident electromagnetic waves depends upon the electric and magnetic dipoles available inside the shielding materials. The incident EM waves are split out into three components i.e. absorption, reflection, and transmission components during the interaction with a barrier material. The total shielding effectiveness (SE_T) of the materials is taking place due to reflection from the interface of air and shielding material, absorption inside the material, and multiple reflections. The remaining part of incident EM waves transmitted through the sample. Moreover, the contribution of electric and magnetic dipoles in attenuation of incident EM waves are due to conducting nature of graphene, MWCNTs, activated charcoal, and magnetic character of manganese, cobalt, iron. So, the conducting polymer PANI can be the better option for shielding EM waves due to the availability of a large number of electric dipoles. However, the shielding properties can be further enhanced by introducing highly conducting and magnetic materials in the PANI matrix.

The total shielding effectiveness is defined as the ratio of incident to transmitted wave powers and described as the sum of shielding effectiveness through the absorption (SE_a), reflection (SE_r) and multiple reflections (SE_m). The total shielding effectiveness (SE_T) can be given by [19-21]

$$SE_T = -10log_{10}\left(\frac{P_i}{P_T}\right) = SE_a + SE_r + SE_m \quad (1)$$

Here, P_i is the total incident power and P_T is the transmitted power of incident EM waves. When SE_T is greater than 15 dB, the SE_m can be neglected, and SE_T can be defined as

$$SE_T \approx SE_a + SE_r \quad (2)$$

SE_a depends upon the conducting nature of shielding materials in the bulk, and the attenuation of EM waves takes place in form of heat, whereas, the SE_r depends upon the mismatching in impedance at the air to barrier interface. At the interface, the available charge carriers at the surface interact with the incident EM waves and reflect them.

The SE properties of synthesized samples are measured from the scattering parameters S_{11}, S_{22}, S_{12}, and S_{21}, where S_{11} and S_{22} are related with the reflection, and S_{12} and S_{21} are related to the transmission of EM wave through the barrier material. Thus the reflection (R) and transmission (T) of incident EM wave can be expressed [18] as

$$R = \left(\frac{P_r}{P_i}\right)^2 = |S_{11}\, or S_{22}|^2 \quad (3)$$

$$T = \left(\frac{P_T}{P_i}\right)^2 = |S_{12}\, or S_{21}|^2 \quad (4)$$

And, the absorption (A) can be calculated using equations (3) and (4)

$$A = 1 - \left(\frac{P_r}{P_i}\right)^2 - \left(\frac{P_T}{P_i}\right)^2 = 1 - |S_{11}\, or S_{22}|^2 - |S_{12}\, or S_{21}|^2 \quad (5)$$

Through analyzing the scattering parameters, the shielding effectiveness can be calculated [22,23] as

$$SE_a = 10\, log\left(\frac{1-|S_{11}|^2}{|S_{12}|^2}\right) \quad (6)$$

$$SE_r = 10\, log\left(\frac{1}{1-|S_{11}|^2}\right) \quad (7)$$

$$SE_T = SE_a + SE_r \quad (8)$$

The calculated total shielding effectiveness has been plotted in Fig.2a as a function of frequency and different types of loadings. From the figure, it is observed that the total shielding effectiveness depends upon the applied frequency and types of loading concentration. PANI/MnO_2 composite has total shielding effectiveness of value ~50 dB, whereas, PANI/V_2O_5 composite have ~9 dB at 8.2 GHz frequency. The higher value of SE_T for PANI/MnO_2 composite may be due to the higher conductivity of PANI and magnetic character of MnO_2 particles. But the lower value of SE_T for PANI/V_2O_5 composite is due to the non-conducting and non-magnetic nature of V_2O_5 particles, and V_2O_5 particles having dominating behavior over PANI. Moreover, the SE_T decreases with the increase in the frequency of incident EM waves, this may be due to a decrease in types of polarizations with the increase in applied frequency.

The higher value of total shielding effectiveness for PANI/MnO_2 composite suggests the more than 99% blockage of incident EM waves but it is not expected for PANI/V_2O_5 composite due to the lower value of shielding effectiveness. The total transmitted power (%) can be calculated using the relation [24]

$$T(\%) = \left(\frac{P_T}{P_i}\right) x\ 100 \quad (9)$$

Where, P_T and P_i are transmitted and incident power of incident EM waves, respectively. Fig.2b shows T(%) as a function of applied frequency and loadings concentration. The PANI/MnO_2 composite exhibit the ability to block more than 99.9% of incident EM wave, whereas, in case of PANI/V_2O_5 composite, approximately 6 to 9% power of incident EM waves transmitted through the sample. This investigation suggests that PANI/MnO_2 composite can be suitable for shielding material at the industrial level but PANI/V_2O_5 composite doesn't fulfill this condition.

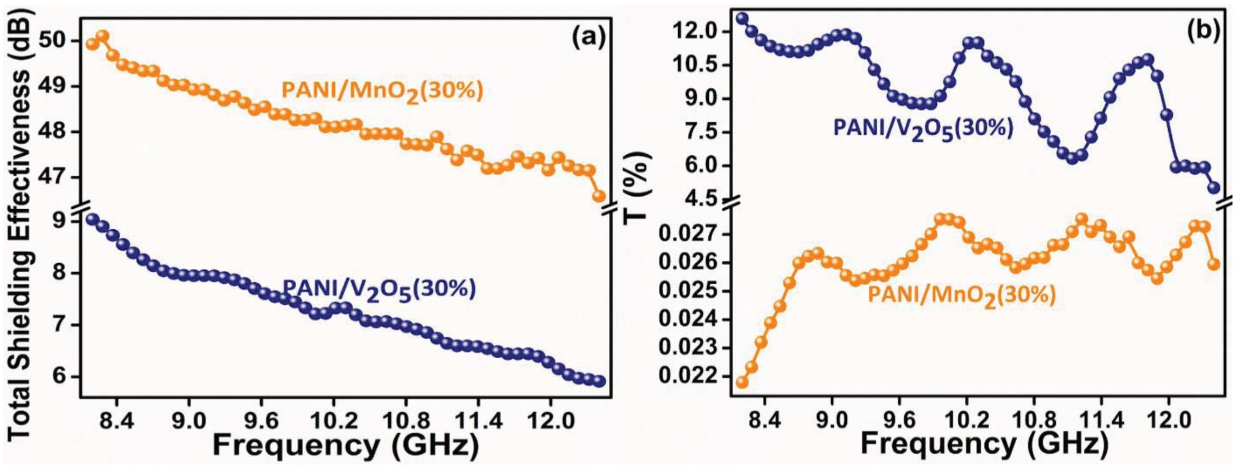

FIG 2.(a) Total shielding effectiveness, and (b) T(%) for PANI/MnO_2 and PANI/V_2O_5 composites as a function of applied frequency.

The analysis of total ac conductivity (σ_m) and skin depth (δ) are also important for shielding measurements. The total ac conductivity is sum of ac and dc conductivities due to availability of both free and bound charges in conjugated polymer system. The dielectric loss governs the pure ac conductivity, whereas, energy loss governs by pure dc conductivity. The total measured conductivity (σ_m) can be determined by the following expression [25]

$$\sigma_m = \varepsilon'' \varepsilon_o \omega \quad (10)$$

Here, ε_o is the permittivity of free space, and ω is applied frequency. Figure 3a shows the relation between measured ac conductivity with the applied frequency, and it is observed that the PANI/MnO_2 composite have higher value of (σ_m) as compared to PANI/V_2O_5 composite. The σ_m value are approximately three ordered greater for PANI/MnO_2 composite as compared to PANI/V_2O_5 composite. The $\sigma_m$almost increases with the increase in applied frequency.

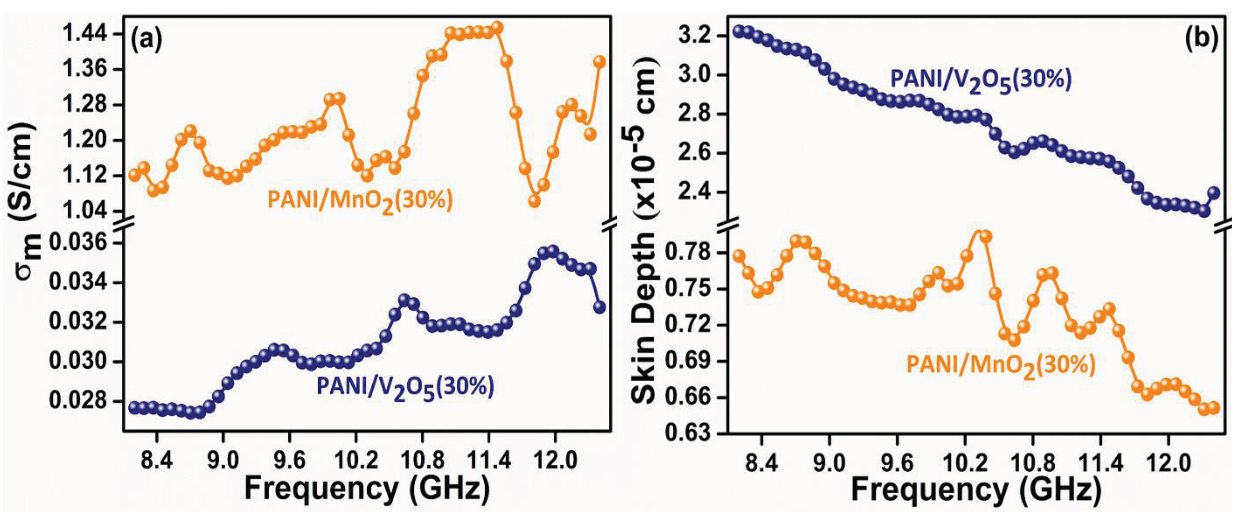

FIG 3.(a) Total ac conductivity and (b) skin depth for PANI/MnO_2 and PANI/V_2O_5 composites.

Another important electrical parameter for electrical measurement skin depth is defined as depth inside of material at which incident EM wave becomes 1/e of incident power of EM wave and can be expressed as [26]

$$\delta = \left(\frac{1}{\sqrt{\pi\mu\sigma f}}\right) \tag{11}$$

Where, μ, f and σ is the permeability, applied frequency and conductivity, respectively, and π is constant. Figure 3b shows the variation in skin depth as function of loading concentration and applied frequency. From the figure it is observed that the PANI/MnO_2 composite have less skin depth as compared to PANI/V_2O_5 composite, this may be due to magnetic nature of MnO_2 particles while non-magnetic and non-conducting nature of V_2O_5 particles.

4. Conclusion

Polyaniline and metal oxides based composites have been synthesized using the chemical oxidative polymerization with 30 wt.% loading concentration of MnO_2 and V_2O_5 particles. The prepared samples were synthesized in the core-shell like structure which is confirmed by FESEM, and metal oxide particles behave core, whereas, PANI act as shell. The prepared samples were utilized for EMI shielding material in X-band of microwave region, and the PANI/MnO_2 composite exhibit higher value of total shielding effectiveness i.e. ~50 dB, whereas, PANI/V_2O_5 composite have very small value of shielding effectiveness i.e. ~9 dB at 8.2 GHz frequency, this may be due to magnetic character of MnO_2 particles, and non-magnetic and insulating character of V_2O_5 particles. Moreover, PANI/MnO_2 composite have higher value of total ac conductivity and lesser skin depth.

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