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MICROWAVE SHIELDING, DIELECTRIC AND MAGNETIC BEHAVIOUR OF MWCNT/Fe_3O_4 PRO-HYBRID NANO OXIDES REINFORCED NATURAL RUBBER COMPOSITE IN E, F, I & J BAND FREQUENCIES

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In this research work a flexible shielding material for blocking microwaves with variable frequencies. The principal aim of this work is to improve the microwave shielding behaviour of natural rubber by reinforcing compound form of MWCNT and magnetite pro-hybrid nano particles. Compound form of nano particles have produced by ball milling method. The particles morphology has been analyzed using HRTEM. The particles dispersion morphology in matrix was revelled by SEM analysis. The natural rubber composites have been prepared by two roll mill method with varying particles volume percentages of 5, 10 &15. The magnetic properties were studied with VSM whereas the microwave shielding behaviour was analysed using typical microwave test bench. The magnetization of 15vol.% of compound particles reinforced natural rubber composite shows 587E^{-6}. Maximum microwave attenuation of 64dB was observed for 15vol.% of particles reinforced natural rubber composite in J band frequency.

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*Keywords:*PMC, MWCNT-Fe_3O_4, VSM, Microwave shielding, SEM, TEM

1. Introduction

Natural rubber reinforced with typical nano particles have attractive applications in engineering based on their typical properties [1]. The versatile nature of natural rubber woos their applications in most of engineering application based industries. Electromagnetic shielding is a prolonged problem in electronic gadgets where interference play crucial role [2]. Many researchers all over the world have trying to create best shielding material to avoid interference problem between telecommunication devices to improve their efficiency. The compound form of conductive and magnetic particles could be a best blocking elements in rubber matrix. The conductive particles may block the electric component and magnetic particles may block the magnetic component of incoming waves. The MWCNT and magnetite could be ball milled for several hours to produce compound form of particles to ensure homogeneous mixture of atoms. Two roll mill could be easy and cheapest method to produced these kind of particles reinforced natural rubber composites [3]. Some of authors concluded that additions of compound particles of Cu-Magnetite mixture in to epoxy resin improved the microwave attenuation behaviour of epoxy shield up to 38%. They have produced the compound form of particles by ball milling the particles up to 8 hours. They reported that milling time of 2 hours fetched better particle compatibility than other milling times. Another author concluded that additions surface treated MWCNTs in to epoxy matrix increased microwave attenuation behaviour up to 84dB. The semi-conductive MWCNTs observed most of the incoming microwaves and attenuate them by absorbing wave phenomenon [4]. Similarly many researchers have attended their ideas to improve the shielding efficiency in polymers and rubbers. On comparing the polymers rubber matrix could be more suitable matrix medium since it may have highly versatile nature. Many shielding products of their own designs could be possible in rubber matrix whereas polymers are so rigid and non recyclable. In this aspect the natural rubber and MWCNT-magnetite particles were selected to prepare a suitable shielding material. The compound particles of 5, 10 and 15vol% were utilized to produced

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the shielding materials. The dispersion morphology of compound particles may enforce maximum effect on the attenuation behaviour. The morphology could be analyzed using a scanning electron microscopy. The shape and size of MWCNT could be evaluated by a high resolution transmission electron microscope. The microwave attenuation behaviour could be evaluated by a microwave test bench having variable frequency setter.

2. Experimental procedure

2.1.Materials

The natural rubber matrix used here was procured from Elastoplast India pvt.ltd, Chennai. The MWCNTs of diameter 30nm and length 110nm were procured from Sigma Aldrich, USA. Metallic salts of Ferric chloride and NaOH were purchased from Merck India Ltd. All the chemicals were used in as-received condition without any post treatment processes.

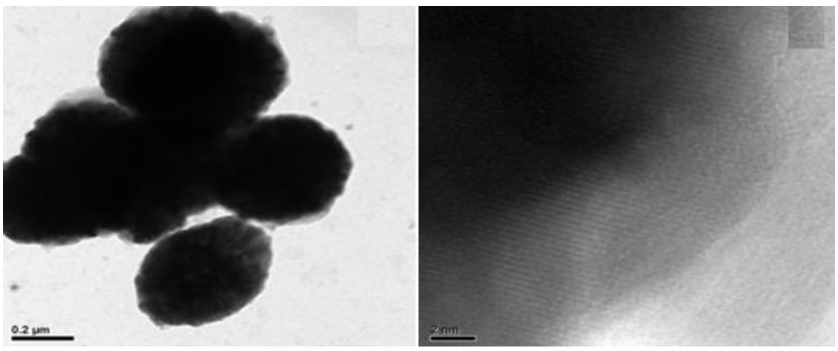
2.2 Particle preparation

2.2.1 Sol-Gel method

Sol-gel is one of the low temperature particle preparation chemical routes. Ferric Chloride (FeCl3) of 1Mol and NaOH of 2 mol was taken for sol-gel process. The sol of two metal atoms were prepared after constant stirring up to 1 h with 60^0C raising the temperature of sol up to 80◦C produced a brown gel at the final. The gel was kept in a silica crucible at 400^0C in a hot oven for 4 h and then furnace cooled to room temperature finally produced nano scaled iron(III) oxide particles [5]. Equations (1) and (2) gives the iron(IV)oxide formation. Fig. 1 shows the TEM images of sol-gel prepared magnetite particles. The TEM morphological analysis was performed using a High resolution Transmission Electron Microscopy JEOL JEM with standard testing procedure. The particles show circular morphology and crystalline pattern. Fig. 2 shows the XRD plot of sol-gel prepared magnetite particles [6]. The diffraction analysis was performed using a diffractometer Match phase analyzer, Germany.The strong peak at (111), (311) and (200) 2θ confirms the presence of FCC cubic Fe_3O_4 particles.

$$FeCl_3 + 3Na(OH)_3 \rightarrow Fe(OH)_3 + 3NaCl \quad (1)$$

$$2Fe(OH)_3 \rightarrow Fe_3O_4 + FeO + H_2 \quad (2)$$
$$2H_2O$$



(a) *(b)*

Fig. 1. TEM images of (a) spherical Fe_3O_4 and (b) HRM image of atomic layers.

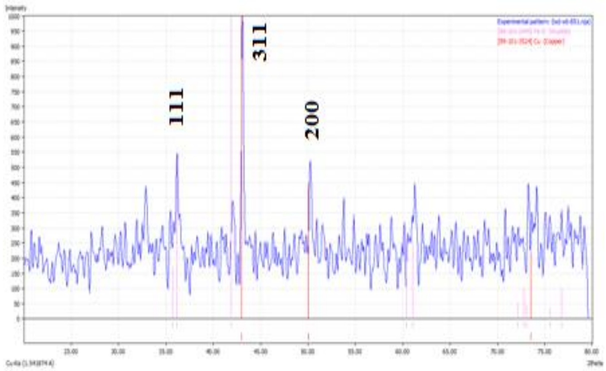
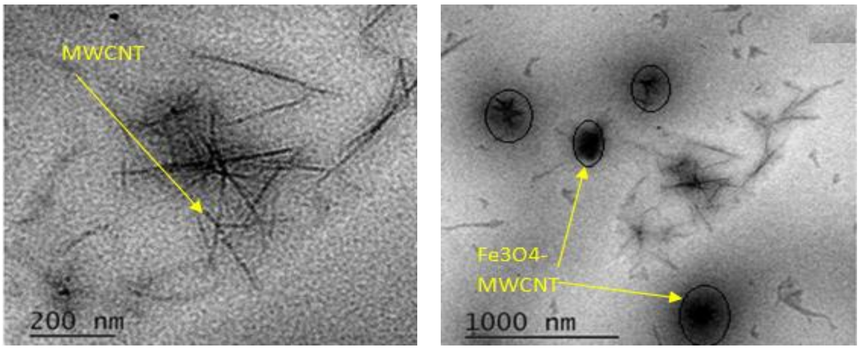


Fig. 2. XRD plots of Sol-Gel prepared Fe_3O_4 particles.

2.2.2. Ball milling process

The sol–gel-prepared Fe_3O_4 magnetic particles were mixed with as-received MWCNT with 1:1 volume ratio. The mix was taken in a ball mill jar and milled for 2 h. The ball material used was tungsten carbide. The ball to powder ration was maintained as 15:1. Number of balls used was 10 numbers and each ball is having diameter of 10mm. The Fig. 3 shows the TEM images of MWCNTs with compound magnetite [7].



(a) *(b)*

Fig. 3. TEM images of (a) MWCNT and (b) MWCNT-Fe_3O_4 compound.

2.3. Composite making

A fixed quantity of natural rubber and 5, 10 & 15vol% of compound particles were mixed and rolled in a two roll mill. More passes were done to ensure homogeneous mixture of natural rubber and MWCNT-magnetite particles [8]. The rolled NR- MWCNT/Fe_3O_4 compound was then fixed in a mould for curing process. MBTS (Dibenzothiazole disulphide) of 10g, TMT (Tetra methyl thiruramdisulfide) of 5g, Sulphur of 20g and Zinc oxide of 25g were added to the mix of rubber and compound particles separately. After 2 hours of curing with applied pressure and temperature thin 3mm sheets were made [9]. The prepared NR-Compound particles reinforced composite sheets were inspected for visual defects and cleaned for further study.

2.4. Specimen preparation

The prepared NR-MWCNT/Fe_3O_4 compound particles reinforced composite sheets were cut from moulded sheets by shearing process. Test specimens based on ASTM dimensions were prepared carefully using abrasive water jet Maxium water jets 1515, Kent, USA. The water jet was maintained at the pressure of 250MPa, abrasive flow is of 0.35Kg/min, grain size of 80mesh and nozzle diameter of 1.1mm. The compositedesignations and composition was given in Table 1 [10].

Table 1.Composite designation.

Composite Designation	Natural rubber vol%	Compound particle vol%
R	-	-
RF_1	95	5
RF_2	90	10
RF_3	85	15

R-Rubber; F-Filler

3. Results and discussion

3.1. Dielectric analysis

The dielectric behavior, which is important for the microwave shielding was analyzed using a LCR Hi-tester with variable frequencies from 50Hz to 500Hz.Figure 4 shows the graph of dielectric constant versus composites in difference frequencies. It is observed that the additions of compound MWCNT with magnetite increased the relative permittivity of natural rubber from 2.8 to 6.6. This massive increase is because of additions of conductive MWCNTs into natural rubber. It is noted that at lower frequencies the permittivity is very less compare than 100Hz. This phenomenon is because of improved polarization of conductive particles in the matrix [11]. The improvedpolarization at 100Hz leads electron flow across the conductor. The improved dielectric constant of 15%, 31% and 57% were observed for RF_1, RF_2 and RF_3 composite designations respectively. It is observed that the dielectric constant shows the decreased sign when the frequency increased. This is because of increased frequency deplete the polarization effect. Compare than 5vol% of filler particles in to natural rubber the 15vol% of fillers reinforces natural rubber gives better results in relative permittivity [12]. This is because of improved dipoles on the conductive particles.These improvements in conductivity of natural rubber remarkable wave absorption effect will be increased [13].

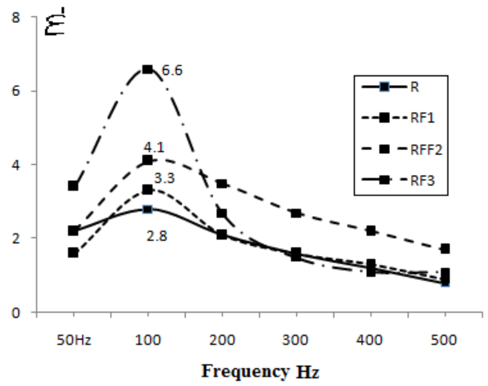


Fig. 4.Dielectric constant (vs) Frequency.

Fig. 5 shows the dielectric loss which occurs when the microwave is passing through the shielding material. It is noted that the dielectric loss is increased with particle content and frequency. These phenomenon get happed due to the change in polarization which will affect the charge carrier. The immobilized electrons converted as heat due to joule’s effect [14].

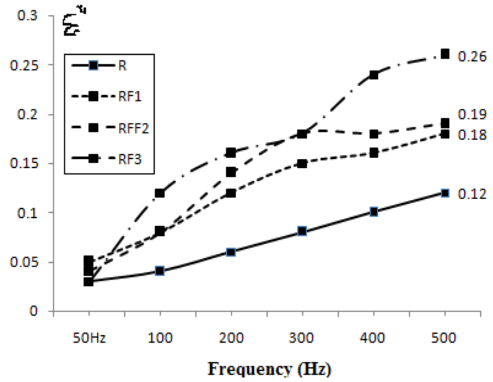


Fig. 5.Dielectric loss (vs) Frequency.

It is observed that the dielectric loss of 0.26 was observed for composite designation RF_3 which contains 15vol.% of MWCNT-Fe_3O_4 particles. It is also noted that when frequency increases the dielectric loss also increases. This is because of additions of MWCNTs increased the charge transfer thus increasing frequency could increased the loss factor [15]. Hence from the above analysis the permittivity of natural rubber was increased drastically by adding MWCNTs with Fe_3O_4 particles.

3.2. Hysteresis analysis

The accrued magnetic behavior of natural rubber composite which is loaded with magnetic particles was inspected using a vibrato sample Magnetometer (VSM), Lakshore, USA. The samples were carefully separated using a knife and loaded in testing chamber. The input magnetic flux was given from 5000G to 15000G. The induced magnetic moments were recorded in y axis as the unit of emu.

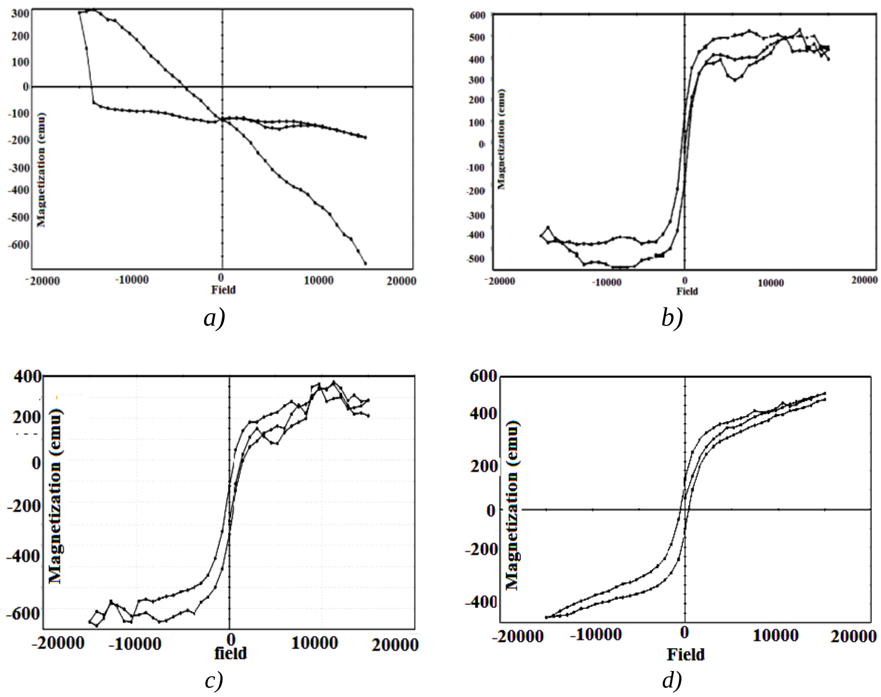


Fig. 6. Hysteresis loops of composites

Fig.6 shows the hysteresis loops of prepared natural rubber composites. It is observed that there is a negative magnetic loop in pure natural rubber whereas the reinforced natural rubber composites show much improved magnetic moments in positive trend. This is because of enforced magnetite into natural rubber. The improved magnetization of $212E^{-6}$ (Fig. 6B) $232E^{-6}$(Fig. 6C) and $584E^{-6}$(Fig. 6D) were observed for composites designations RF_1, RF_2& RF_3. Similarly the improved retentivity of $22E^{-6}$, $32E^{-6}$ and $130E^{-6}$ were observed for RF_1, RF_2& RF_3 composite designation. Hence from the above study it is very clear that the addition of magnetic particles into natural rubber increased the magnetic moments and retentive properties of natural rubber. The magnetically and electrically strengthened natural rubber composites are now capable of attenuating the incoming magnetic and electrical components of incoming microwaves [16].

3.3. Microwave shielding analysis.

Fig. 7 shows the microwave attenuation percentages of MWCNT-Fe_3O_4 particles reinforced natural rubber composite. The wave attenuation behavior was analyzed using a microwave test bench with variable frequency setup. The additions of MWCNT and Fe_3O_4 increased the electrical and mechanical wave components. The attenuation percentage of 15vol% of filler particles reinforced natural rubber composites shows maximum attenuation value of 42% equal to 62dB. This maximum attenuation is the cause of wave attenuation by magnetic and electrical components present in the shielding material.

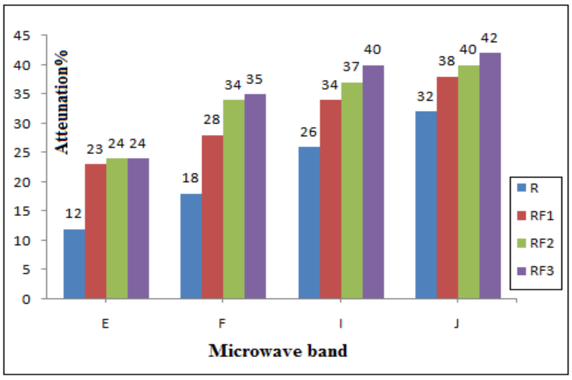
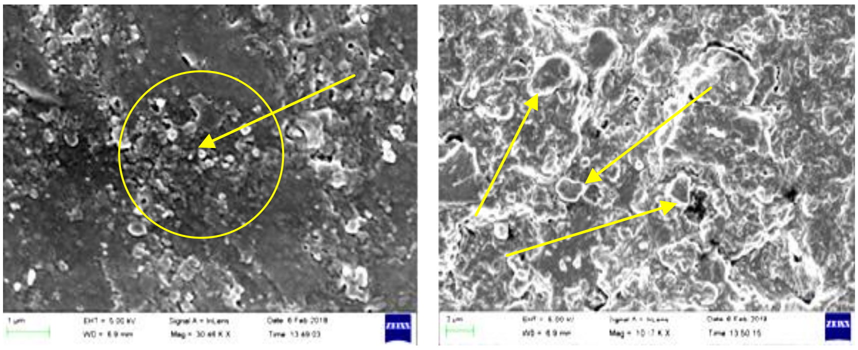


Fig. 7.Microwave attenuation of natural rubber composites.

It is observed from the Fig. 7 that the microwave attenuation was increased rapidly followed by additions of MWCNT and Fe_3O_4 particles. When these waves are hitting the shielding material absorbance and reflection of microwaves getting taking place by the presence of magnetic and electrical fields thereby leading to attenuation of waves get happened [17, 18, 19]. It is noted clearly that at lower microwave band the attenuation is minimum due to low amplitude of incoming wave whereas in high microwave bands the attenuation percentage is maximum. This is because of high amplitude of incident wave with in skin depth. The wave get attain more trough and crest within the skin depth thus leads large attenuation. Fig. 8 shows the compound particles in natural rubber matrix [20, 21].



a) b)

Fig. 8. (a & b) SEM images of MWCNT with Fe_3O_4 in rubber matrix.

4. Conclusions

The magnetic and electric way of strengthening the natural rubber was done by adding MWCNT and Fe_3O_4nano particles. Highly homogeneous mixture of conductive and magnetic particles into natural rubber composites was prepared using two roll-mill successfully. The dielectric constant of 15vol.% of MWCNT-Fe_3O_4 particles gives maximum value of 6.6 at 1KHz. Similarly the maximum magnetization of 584E^{-6} was observed for composite which consist of 15vol.% of particles.

The maximum microwave attenuation of 42% equal to 64dB was achieved for composite which may have 15vol% of compound particles. Finally the produced composite could be used as a shielding material where blocking of microwaves are essential.

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