Comparative Study of Radar Reflection Losses of MWCNTS/Epoxy and SWCNTS/Epoxy Composites

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Abstract: Single-Wall Carbon Nanotubes (SWCNTs) and Multi-Wall Carbon Nanotubes (MWCNTs) possess excellent electromagnetic properties when SWCNTs and MWCNTs are separately embedded into host polymer such as epoxy. Even with low weight ratios ranging at about (0.1, 0.3, 0.5 and 1 wt.%) reflection losses are clearly increased after SWCNTs and MWCNTs were added because of the extraordinary properties of SWCNTs and MWCNTs. In this research many examinations have been carried out on the nanocomposite samples to evaluate the electromagnetic properties of these samples. Scanning Electron Microscopy (SEM), X-Ry Diffraction (XRD) and Raman spectroscopy are used to elaborate the hetero structure of the fabricated nanocomposite samples.

Key words: Single-wall carbon nanotubes, multi-wall carbon nanotubes, lectromagnetic, separately, epoxy, nanocomposite

INTRODUCTION

The aim of this study is to study the electromagnetic properties of nanocomposites material for polymer matrix reinforced by Single-Walled Carbon Nanotubes (SWCNTs) and Multi-Wall Carbon Nanotubes (MWCNTs) separately. Recently wide attention has been increasingly paid on multifunctional to obtain extraordinary electromagnetic properties. New multifunctional materials can be achieved by using polymer reinforced with Carbon Nanotubes (CNTs) which have important applications such as sensor, actuators and radars. Nanocomposites are synthesized by solution casting technique (CVD) (Gojny *et al.*, 2004; Ma *et al.*, 2010). Small amount of Carbon Nanotubes (CNTs) can be embedded into polymer matrix to improve the electromagnetic properties of the network manufactured nanocomposites. Because the CNTs are very small in size it is capable to diffuse and disperse into the polymer matrix. Nanocomposite materials with polymer such as epoxy as a matrix possess an attractive interest technology as it is attributed to their mechanical, electrical and thermal properties. Recently, many researches were done for epoxy reinforced with CNTs. It was found that small amount of CNTs extremely affect the properties of the epoxy and how it changes from insulator material to conductive material. However, it must be mentioned that the CNTs as a reinforced material of polymer (such as epoxy resin) depends on the ability to transfer load from the epoxy resin to the CNTs. Here there are two factorsthat could be affected. First is the homogeneity dispersion of CNTs and second is the interfacial bonding between the epoxy resin and CNTs (Zhou *et al.*, 2012a, b). Different polymers have been used as a matrix to produce nanocomposite materials such as polyimides, polyamides, elastomers, polyurethane polyaniline and epoxy. Each of the polymers gives properties that is different from the others. However, epoxy is preferred to achieve excellent mechanical, electrical and thermal properties, especially when it is reinforced by CNTs to synthesize advanced nanocomposites for numerous applications (Koerner *et al.*, 2005). The weight percentage of CNTs is considered the key factor to manufacture ultra-nanocomposite. Previous studies emphasize that the suitable amount of carbon nanotubes should be <1 wt.% (Liao *et al.*, 2004; Che *et al.*, 2014). As an important factor to enhance the mechanical and electrical properties of fabricated nanocomposites, the CNTs must be dispersed and distributed homogeneously in the polymer matrix. Carbon nanotube tend to agglomerate when embedded into polymer whereby, increasing the weight percentage of carbon leads to increase in the size of agglomeration of CNTs and thus create a network which in turn decreases the mechanical and electrical conductivity. To achieve high mechanical and electrical properties of nanocomposites with polymer matrix it is demanded that the reinforcement elements should have high mechanical properties such as strength, impact strength and high electrical conductivity. On the other hand, they must be a high binding between the reinforcement materials and polymer matrix and the reinforcement materials should have a high surface area (Zhao *et al.*, 2013; Nemaa *et al.*, 2014).

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MATERIALS AND METHODS

Experimental work: Two types of carbon nanotubes used in this study (Single Wall Carbon Nanotubes (SWCNTs) and Multi-Wall Carbon Nanotubes (MWCNTs) are obtained from manufacturer/supplier; Cheap Tube Inc., (USA) 3229 Rte 121E, Ste3. Table 1 shows the characteristics of single-wall carbon nanotubes and multi-wall carbon nanotubes.

Epoxy Sikadur© 52 LP as a polymer matrix. The component of epoxy is Bisphenol A (epichlorohydrin) oxiraine [(C-12-14 alkyloxy) methyl] derives. Epoxy and hardener were mixed by mixing ratio component (A: component B = 2:1 by volume). Table 2 shows the properties of epoxy and hardener.

Nanocomposite preparation: The specimens of each nanocomposites of SWCNTs/Epoxy and MWCNTs/ Epoxy are synthesized using solution casting method. Firstly, the epoxy and hardener (Sika Paddle) in the ratio of 2:1 wt.% are mixed together for 5 min. Then, the mixture is poured in plastic mould (Teflon) with dimensions $10 \times 4.3 \times 1$ cm to achieve total volume of 43 cm². Mixing process is done at ordinary condition of room temperature and atmospheric pressure. The density of mixture can be calculated with the Eq. 1:

$$\rho = \frac{W}{V}\left(\frac{g}{cm^3}\right) \qquad (1)$$

Where:

ρ = 1.1 g/cm³
W = 50 g
V = 43 cm³

The first specimen is prepared with epoxy using 33.33 g and 16.66 g hardener, however, each of SWCNTs and MWCNTs is added to the epoxy with 0.1, 0.3, 0.5 and 1 wt. %, respectively and then hardener has been added. The solution is stirred in electromagnetic stirrer type (hot plate magnetic stirrer) rotating at 1400 rpm for 15 min. Figure 1 shows the magnetic stirrer which is used in this study.

After this process the hardener has been added to the solution of epoxy and CNTs, then the mixture is stirred in same device for 5 min.

The mixture should be subjected to the sonication process for 10 min to achieve a good dispersion of CNTs in epoxy because the ultrasonic method has high level of energy (40 kHz 70 W) that helps the CNTs to disperse in the epoxy through a bunch of created bubbles and collapse process. This can be done by sonicator type (popular 2500 mL heatable ultrasonic cleaner JP-4820 cheap cleaner) as shown in Fig. 2.

Table 1: The characteristics of single-wall carbon nanotubes and multi-wall carbon nanotubes

Property	MWCNTs	SWCNTs
Diameter	40-80 nm	<30 nm
Length	1-12 μm	0.5-2 μm
Purity	>99 wt.%	>90 wt.%
Ash	0 wt.%	<1.5 wt.%
SSA	>233 m²/g	>407 m²/g
Electrical conductivity	>10^2 S/cm	<1.5^{*102}S/cm
Density	1.75 g/cm²	1.4 g/cm²

Table 2: The properties of epoxy and hardener

Property	Epoxy	Hardener
Colour	Pale yellow	Clear color
Density	1.1-1.15 g/cm²	1-1.05 g/cm²
Viscosity	600-900 mPa.s	370-470 MP.s
Tensile strength	54 MPa	
Elongation at break	3.1%	
Shear strength	29.6 MPa	
Modulus elasticity	1400 MPa	

Fig. 1: Magnetic stirrer

Fig. 2: Sonicator

The mixture of CNTs/Epoxy is poured in a Teflon mould and cured at room temperature for 24 h, then the specimens are post heated in an oven type (JRAD Model: 05) at 75°C for 1.5 h to degas the air after that the mixture is cooled inside the furnace reaching to the room temperature. Figure 3 shows the oven that is used for heating process.

Examinations of nanocomposite
Scanning Electron Microscopy (SEM): A Tescan Vega III (Czech Republic) SEM has been used to inspect the SWCNTs powder, MWCNTS powder and the pristine nanocomposites of each SWCNTs/Epoxy and MWCNTs/Epoxy. Small amount of SWCNTs and MWCNTs samples were fixed on the stub of SEM by using a tab of silver. Small size of specimens was used for this examination and is mounted on the stub of SEM by using carbon tape and coated by the gold to preventing the charging through the analysis. There are many parameters to be considered for SEM examination of nanocomposite specimens such as acceleration voltage (30-200 kV), size of the spot (1 nm-10 μm) and working distance (4-11 mm). Many photomicrographs were taken to reveal the dispersion of CNTs into epoxy, homogeneity and the possibility of forming aggregation of CNTs.

Raman spectroscopy: Raman spectroscopy was used to know Raman band shift of SWCNTs and MWCNTs powder. The spectra of Raman were collected through the Sentera Raman scope which is connected to the Olympus BH-2 microscopy at 180° of geometrical scattering. Laser

Fig. 3: Oven type (Jrad Model:05)

A CVL Melles Groit He-Ne with wave length 632 nm was used for excitation throughout the work distance length of the object which gave a spot at the surface of the specimen about 5 μm in size.

X-Ray Diffraction Analysis (XRDA): X-ray diffraction analysis was used to assess the phases of nanocomposites by calculating their crystal structure. This examination gives a high accuracy to define the arrangement of atoms in the crystal cell by scattering beam of X-ray. Bragg law enable us to determine the crystallographic structure for the specific nanocomposite through the Eq. 2:

$$2dSin\,\theta = n\lambda \qquad (2)$$

Where:
n = Order of reflection 1, 2, 3
λ = Wave length of X-ray = 1.54050 A°
d = Interplaner distance (A°)
θ = Angle of incidence or reflection of X-ray beam

The nanocomposite specimen was held on the glass substrate with dimensions at about 3×2 cm. This examination is done via. XRD-6000 device, Japanese manufactured by Shimadzu Company. The angle of Bragg range 2θ is ranging between (10-80°) with working voltage at 40 kV and current at 30 mA. The interplaner distance (d) was calculated using Bragg law.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM): Scanning Electron Microscopy (SEM) is the most powerful tool for obtaining the nanostructure characteristics, shape and homogeneity (Silva *et al.*, 2013). The images of SEM show the morphology of fractured nanocomposite of SWCNTs and MWCNTs. Figure 4 shows distinctly a good dispersion of CNTs into epoxy and uniformly homogeneous. SWCNTs and MWCNTs configure a clearly expansive nanostructure networks into the host matrix. These networks have a greatly significant features because it aperient paths to transport the electrons through the CNTs particles. Consequently, the electromagnetic properties can be affected by this network structure and can be improved according to the desired applications.

Raman spectroscopy: Raman spectrum is considered as one of the most effective techniques that is applied to analyse an extensive fundamental characteristics of carbon nanotube structures (Bai and Allaoui, 2003). Also it ensures a little time (fast), non-destructive evaluation and no need for preparation of samples. Figure 5 shows SWCNTs and MWCNTs Raman spectroscopic it can be
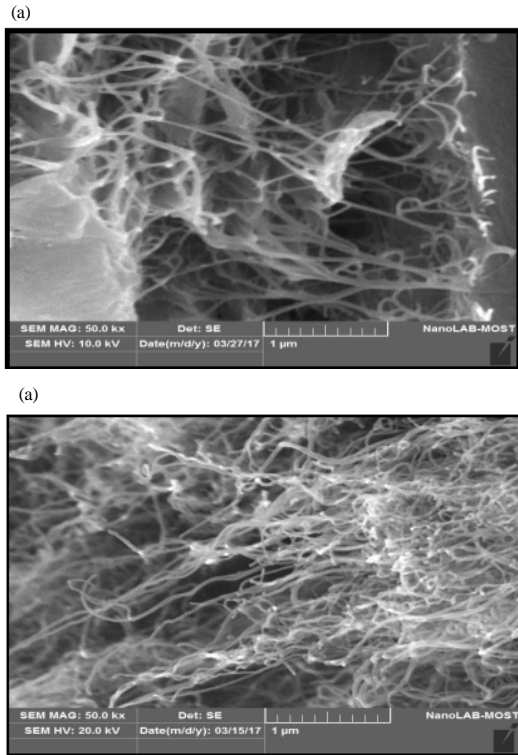
Fig. 4: a) SWCNTs/Epoxy nanocomposites and b) MWCNTs/Epoxy nanocomposites

Fig. 5: Raman spectra for: a) MWCNTs and b) SWCNTs
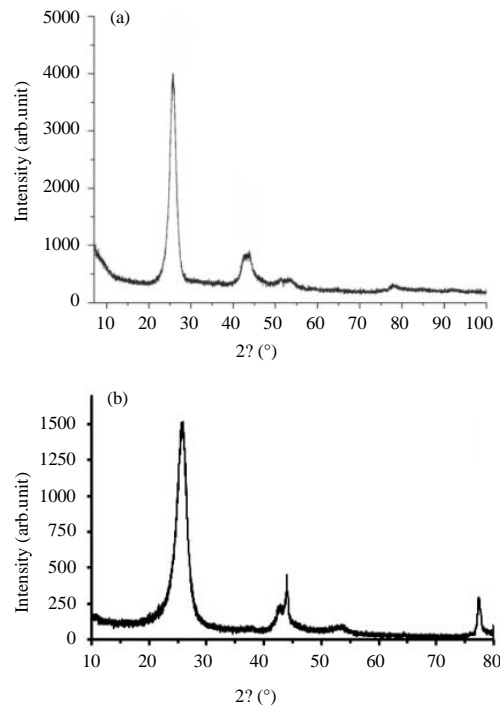
Fig. 6: XRD pattern of pure sample of: a) SWCNTs; b) MWCNTs

seen clearly that the G band for SWCNTs located at 1589.79 and 1582.56 cm^{-1} for MWCNTs which are virtually consistent with the theoretical standards position and intensity of CNTs. Also, the difference between them can be noted from their intensity, despite their similarity in vibration structure which are related to carbon lattice vibration. The G band is widely used as a measure of quality of carbon nanotubes where the more narrowing of G band mean good purified material which is compatible with the results of this research.

The D band refers to disorder or defects of carbon structure which appear prominently at 1350.72 cm^{-1} for MWCNTs and less prominent for SWCNTs at 1344.4 cm^{-1}. Another band by which SWCNTs and MWCNTs can be distinguished is called Radial Breathing Mode (RBM) which is located at low frequencies (266.62 cm^{-1}). This band has a distinct feature that commonly relate with SWCNTs more than MWCNTs. From Fig. 5 the RBM is obviously appearing for SWCNTs and disappearing for MWCNTs. The explanation of this behaviour is attributed to multiple wall of carbon in case of MWCNTs, therefore, the peak with low energy become too weak to be discovered.
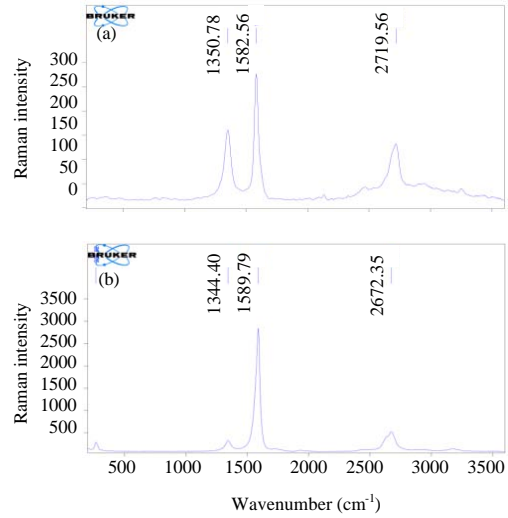
X-Ray Diffraction (XRD): The X-ray diffraction results revealed some information about nanomaterial such as purity, distribution of chirality, interlayer space and diameter (Ajayan *et al.*, 2013). Figure 6 shows a mainly XRD pattern peaks of pure SWCNTs and MWCNTs at 2 which almost ranged between (25.6-26°). From this peak pattern it can bedefined that the reinforcement materials are CNTs.
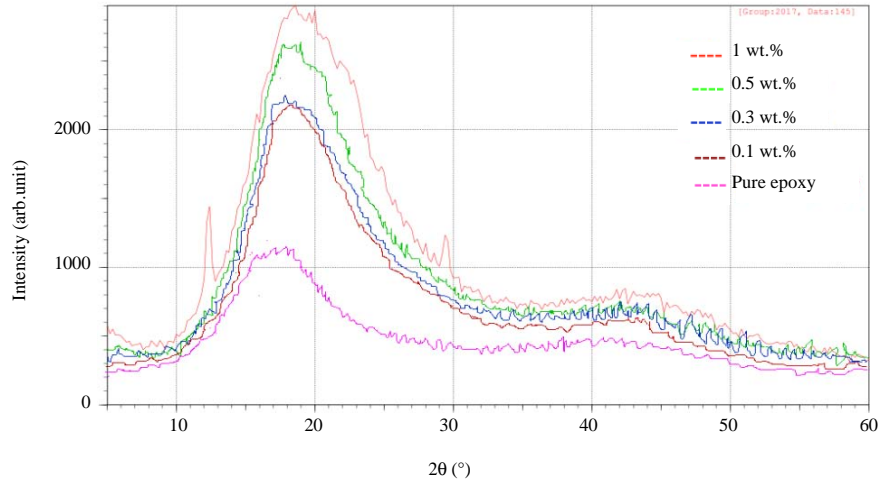
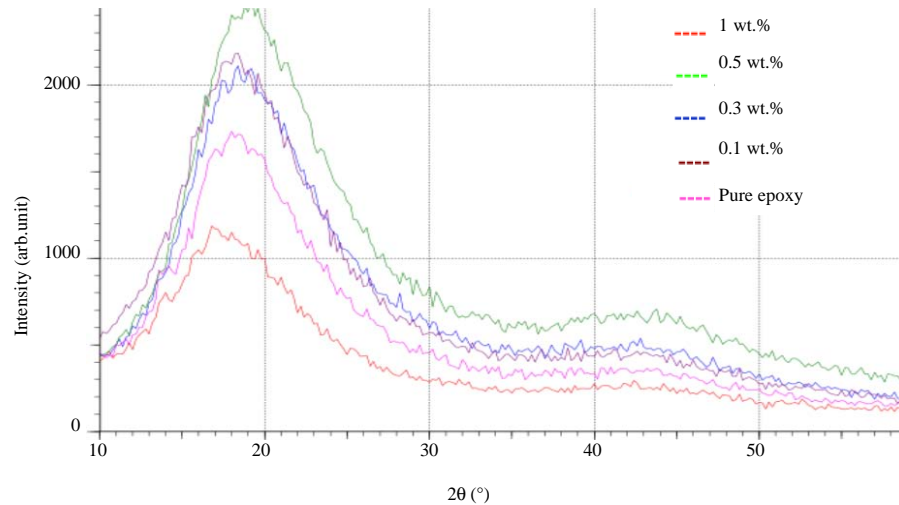Fig. 7: XRD pattern of SWCNTs/Epoxy nanocomposites

Fig. 8: XRD pattern of MWCNTs/Epoxy nanocomposites

By applying Bragg law, the interplaner space is found out at 3.430 and 3.485 Å for MWCNTs and SWCNTs, respectively, which are a little larger than graphite interplaner space distance (3.353 Å). The expansion of interplaner space of MWCNTs and SWCNTs refers that the graphite structure inter-layer in MWCNTs and SWCNTs are extended during the preparation synthesis. The most important property of XRD pattern of multiwall carbon nanotubes is approach to graphite characteristics which is attributed to their innate nature. For the samples of pure epoxy it can be observed that an amorphous peak is located at $2\theta = 17.1°$. By adding SWCNTs or MWCNTs with different weight fractions into epoxy, all peaks are shifted toward more degree values of 2θ reaching to 19°. So, the increasing of 2θ will continue as long as weight fraction of CNT increasing as shown in Fig. 7 and 8.

Unfortunately, the XRD method has a slightly benefit to distinguish between nanostructural details of SWCNTs and MWCNTs because of non-crystalline atoms arrangement of carbon and their special vibrations. Hence, the spectroscopy is more compatible with carbon atomic structure (Fig. 9).

Measurements of reflection losses in X-band: The VNA system was used to measure the reflection losses of SWCNTs nanocomposite. The increasing values of dB of S-parameters in negative part refers to the decreasing reflection or insertion losses. The minus sign of S parameter represents that the value isn't gain (loss). The S11 parameter represents the Reflection Losses (RL). Figure 10 shows the reflection losses of MWCNTs nanocomposite samples against frequency at X-band
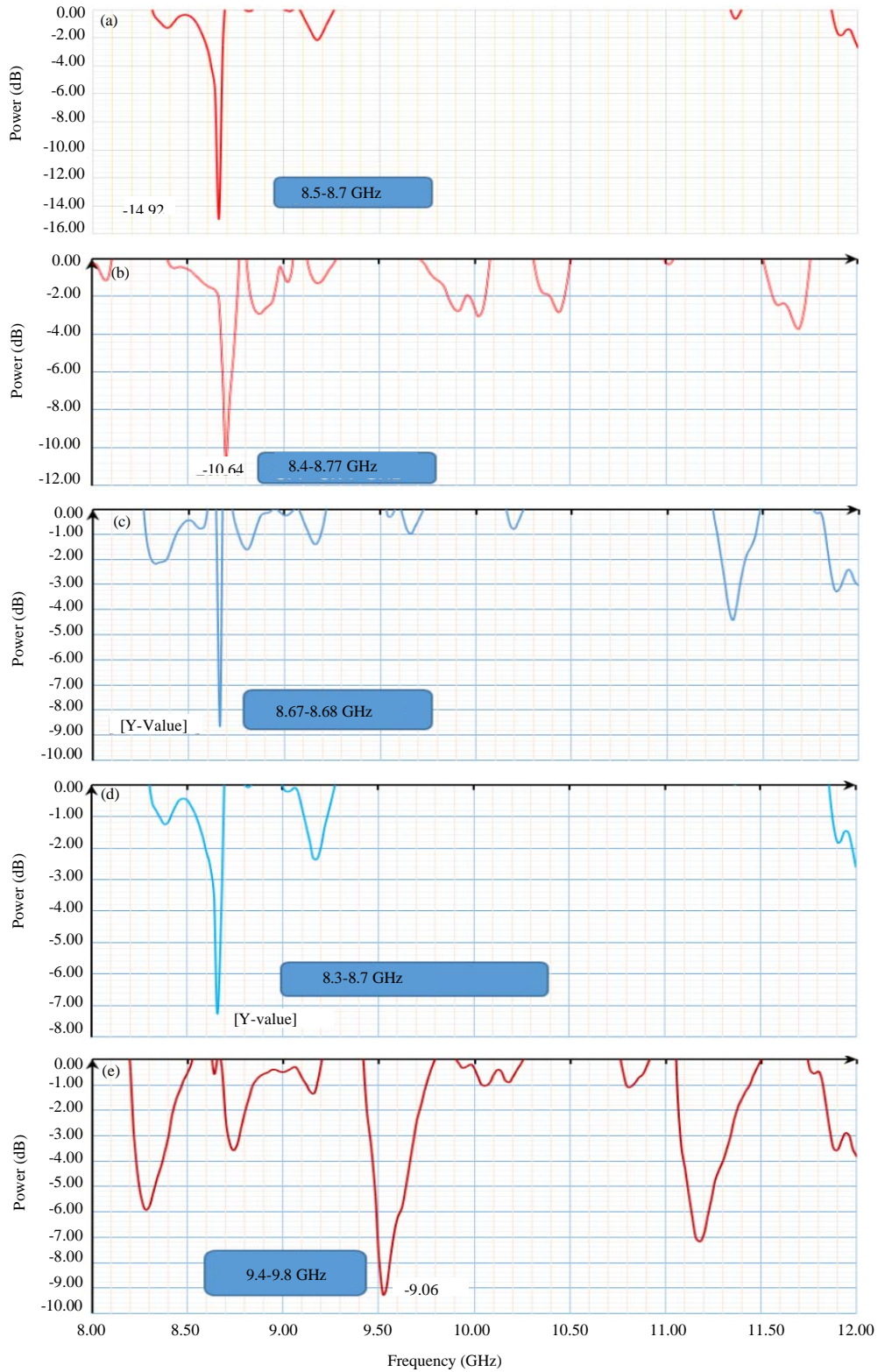
Fig. 9: The reflection losses of MWCNTs nanocomposite samples against frequency at X-band range with different content of wt.% of CNTs: a) 0 wt.% CNTs; b) 0.1 wt.% CNTs; c) 0.3 wt.% CNTs; d) 0.5 wt.% CNTs and e) 1 wt.% CNTs
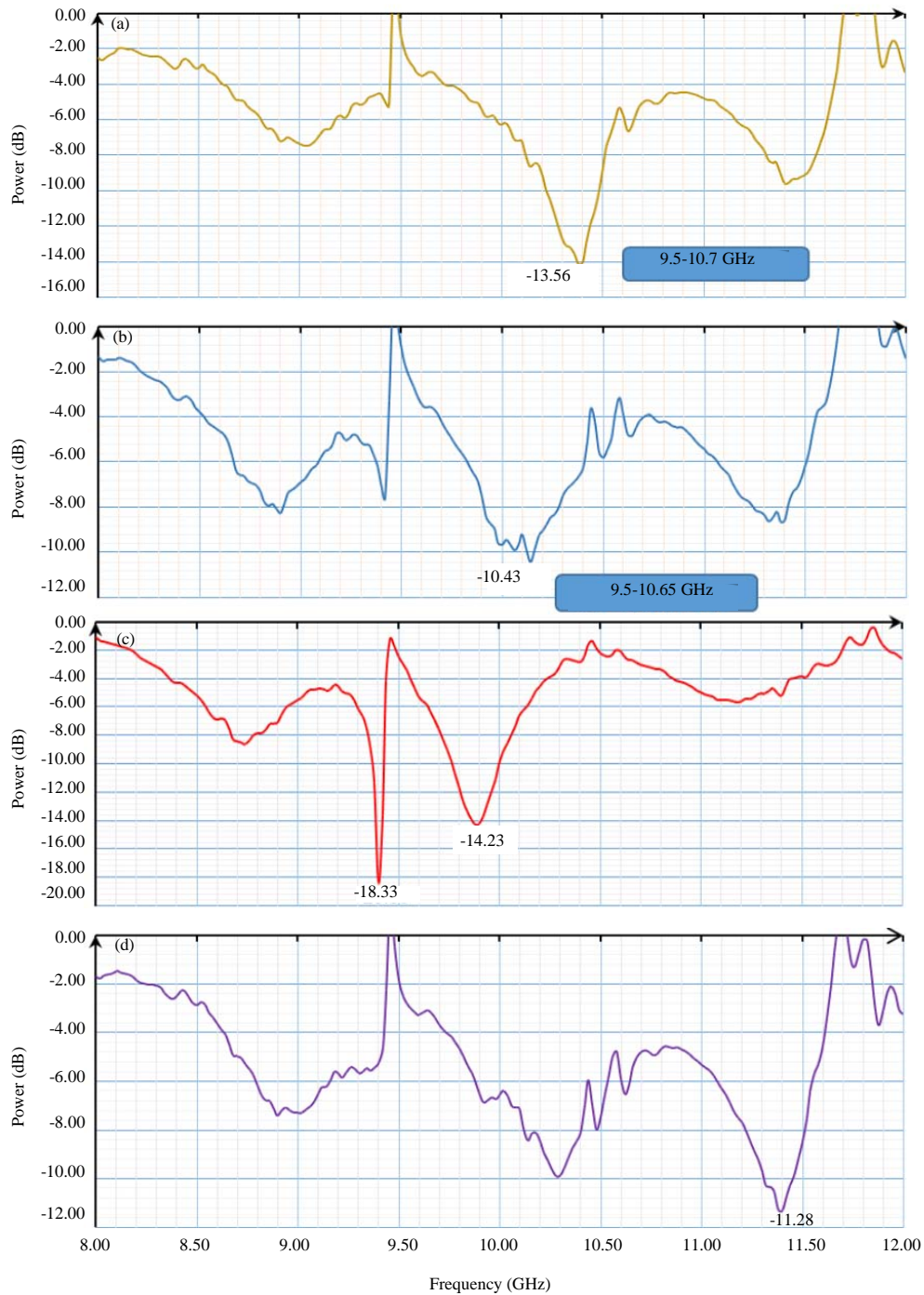
Fig. 10: The reflection losses of SWCNTs nanocomposite samples against frequency at X-B and range with different content of wt.% of CNTs: a) 0.1 wt.% CNTs; b) 0.3 wt.% CNTs; c) 0.5 wt.% CNTs and d) 1 wt.% CNTs

range. It can be noted that the maximum reflection losses appear at 1 wt.% of MWCNTs at clearly three bands frequency ranges, the main one of them is between 9.4-9.8 GHz as shown in Fig. 9e. The content ratio of MWCNTs is concerned with reflection extent because of the absorption of magnetization which is greatly relative with the magnetic saturation, therefore, the reflection strength can be affected subsequently (Lafta, 2016). The successive increasing of content of CNTs do not ensure the reflection minimization but can gives random behaviours.

Obviously, the SWCNTs have an extreme disparity between two nanomaterials. The result reveals a great difference and wide scope between them. This belongs to the extraordinary properties of the network structure which SWCNTs own. The maximum reflection losses are apparent at 0.5 wt.% content of SWCNTs throughout the X-band which range between (8-12 GHz) with maximum peak reaching up to 18.33 dB as shown Fig. 10c. It's good to indicate that the small grain size leads to more double inner reflections and that cause a multiple deformation in the nanocomposites material. In general, the comparison between two nanocomposites samples demonstrate that SWCNTs can be used as an absorber for incident electromagnetic waves more than MWCNTs.

CONCLUSION

The fabricated nanocomposite characteristics are directly influenced with weight fractions of each SWCNTs and MWCNTs whereby, increasing the weight concentrations of SWCNTs and MWCNTs will improve the electromagnetic properties.

SEM, Raman spectroscopy and XRD analysis emphasize that uniform dispersion of SWCNTs and MWCNTs are into epoxy matrix. Increase the reflection losses for SWCNTs/Epoxy nanocomposite about (67%) more than MWCNTs/Epoxy nanocomposite.

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