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Research Article

Electromagnetic Wave Absorption Performance of Carbon Nanocoils by Using Mixed Ferrites as Catalyst

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Abstract

Rapid development of electronic devices and advanced technology creates more electromagnetic wave interference that is harmful to human health as well as equipment. Thus, the use of electromagnetic (EM) wave absorber becomes more focused among researchers and attracted more public attention. Carbon nanocoils (CNs) have been introduced due to its chemical, physical and mechanical properties that can produce lightweight, wide absorption range and strong absorption. This research highlights the use of mixed ferrites (Fe_3O_4 and $CoFe_2O_4$) as catalyst to grow carbon nanocoils. Different weight percentages of Fe_3O_4 and $CoFe_2O_4$ were mixed to grow carbon nanocoils and further used as fillers to be incorporated into epoxy matrix. The morphological study of synthesized carbon nanocoils and reflection loss of the prepared polymer composites were studied in the range of X-band and Ku-band at thickness 1 mm, 2 mm, and 3 mm. The reflection loss achieved shows that mixed ferrites as catalyst to grow carbon nanocoils have great potential to be used as an excellent EM wave absorbers at low thickness.

Keywords: Catalyst, mixed ferrites, EM wave absorber, lightweight, reflection loss.

Katalizör Olarak Karışık Ferrit Kullanımıyla Üretilen Karbon Nanobobinlerin Elektromanyetik Dalga Soğurma Performansı

Öz

Elektronik cihazların ve ileri teknolojinin hızlı gelişimi, insan sağlığına ve ekipmana zarar veren daha fazla elektromanyetik dalga girişimi oluşturmaktadır**.** Böylece, elektromanyetik (EM) dalga soğurucu kullanımına araştırmacılar arasında daha fazla odaklanılmış ve toplumun daha fazla ilgisini çekmiştir. Hafif, geniş absorpsiyon aralığı ve güçlü absorpsiyon üretebilen kimyasal, fiziksel ve mekanik özellikleri nedeniyle karbon nanobobinler (CNs) piyasaya sürülmüştür. Bu araştırma, karbon nanobobinleri geliştirmek için katalizör olarak karışık ferritlerin (Fe_3O_4 ve $CoFe_2O_4$) kullanımını ortaya koymaktadır. Fe_3O_4 ve $CoFe_2O_4$'ün farklı ağırlık yüzdeleri karbon nanosarmalları geliştirmek amacıyla karıştırılmış ve ayrıca epoksi matrisine dahil edilmek üzere dolgu maddeleri olarak kullanılmıştır. Sentezlenen karbon nanosarmalların morfolojik incelenmesi ve hazırlanan polimer kompozitlerin yansıma kayıpları 1 mm, 2 mm ve 3 mm kalınlıklarda X-bandı ve Ku-bandı aralığında incelenmiştir. Elde edilen yansıma kaybı, karbon nanobobinleri geliştirmek için katalizör olarak karışık ferritlerin, düşük kalınlıkta mükemmel bir EM dalga soğurucu olarak kullanılma potansiyeline sahip olduğunu göstermektedir.

Keywords: Katalizör, karışık ferritler, EM dalga emici, hafif, yansıma kaybı

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1 Introduction

Rapid development of technology creates more advanced electronic devices that produces more electromagnetic wave interference that is harmful to human and other equipment. Therefore, the increased in the applications of electromagnetic (EM) wave absorption in both commercial and military fields become a focus of current research interest among researchers. Carbon nanocoils (CNs) with peculiar helical morphologies are well known with their unique chemical, physical and mechanical properties that can have a great potential to be used as an excellent EM wave absorbers through certain modifications that have been made. The modifications need to be made to obtain EM wave absorber that is lightweight, have strong EM wave absorption, absorb in a wide frequency range with thin thickness. Other than being used as electromagnetic wave absorbers, the high-performance composites based CNs can be used for other application such as field emission devices, micro- or nano-electromechanical systems such as nano-sized springs, generator for electromagnetic waves etc.

The mixture of active catalysts such as Ni, Fe and Co are frequently used and display higher activity than the individual elements. Moreover, Fe, Co, Ni, Titanium and Tungsten are also found to be relatively effective for the growth of CNs [1, 2]. Thus, it results in materials having higher percentage yield and better quality of carbon nanotubes. Ref. [3] reported on using a mixture of Co and Ni as catalyst to synthesized Co/Ni attached SWCNTs by the dc-arc discharge technique. Ref. [4] have synthesized high yield of CNs by using iron-coated indium tin oxide as the catalyst although this method is not suitable for large amount of synthesis because it is expensive and time-consuming vacuum evaporation to prepare the iron film. On the other hand, Ref. [5] have synthesized helical carbon nanotubes by using combined sol-gel/reduction method. Ref. [6] reported that their research has synthesized plait-like CNCs by using sol-gel /reduction method. However, the coil pitch of CNs produced is too short to exhibit spring property.

In this paper, mixture of effective catalyst has been used as catalyst in the growth of helical and unique properties of CNs. This research also aimed to study the properties of synthesized CNs that helps in increase the performance of electromagnetic wave absorbing ability at higher frequency range.

2 Materials and Method

2.1 Preparation of polymer composite

The polymer composites were prepared by three different stages: i) synthesis of ferrite sample, ii) synthesis of carbon nanocoils as filler and iii) preparation of carbon nanocoils loaded into epoxy matrix. The ferrite nano powders were prepared by using solid state method and high energy ball milling was used to crush the powder into nanometer size range. Iron (II, III) Oxide (Fe_3O_4) 99.997% was purchased from Alfa Aesar and milled for 3 hours and cobalt ferrite ($CoFe_2O_4$) was synthesized using Cobalt Oxide (Co_3O_4)99.80% and Iron Oxide (Fe_2O_3) 99.5% from Alfa Aesar and milled for 10 hours. Both milled Fe_3O_4 and $CoFe_2O_4$ were sintered for 10 hours at temperature 1100^0C and 900^0C respectively. The synthesized powder was further mixed with different percentages and use as catalyst in synthesizing carbon nanocoils (CNs); S1 (20% Fe_3O_4+80% $CoFe_2O_4$), S2 (50% Fe_3O_4+50% $CoFe_2O_4$), and S3 (80% Fe_3O_4+20% $CoFe_2O_4$). However, synthesizing CNs by using pure Fe_3O_4 and $CoFe_2O_4$ as catalyst are

assigned as SF and SC respectively. The CNs were prepared via Chemical Vapor Deposition (CVD) method at 700^0C for 30 minutes by using ethanol as carbon source and Argon gas as the carrier gas. The synthesized CNs as shown in Figure 1 were then used as filler to be loaded into epoxy matrix.

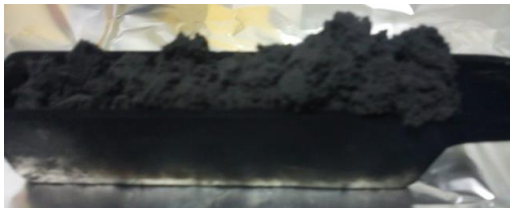

Figure 1. Synthesized Carbon Nanocoils.

The CNs loaded into epoxy resin as matrix was fixed to 8wt% since loading amount beyond that could not homogeneously dispersed in polymer matrix. The mixture was dispersed by using high-speed mixer at 3000 rpm for 20 minutes to improve the dispersion quality and avoid aggregation. The prepared mixture was further poured into customized dimension of sample holder by using solution casting method and cured overnight at room temperature. The polymer composites samples are assigned as SF/E, SC/E, S1/E, S2/E and S3/E. The sample holder was customized by following the exact dimension of X-band (22.860 mm x 10.160 mm) and Ku-band (15.799 mm x 7.899 mm) waveguide that can directly be measured using vector network analyzer (VNA). The thickness was fixed at 1 mm, 2 mm and 3 mm since thicker sample was not suitable for certain application.

2.2 Samples' Characterization

The phase analysis was carried out using an X-ray diffraction (XRD) spectra in the 2θ range of 20^0 to 80^0 using an X-Pert PANalytical diffractometer (PW3050/60) with a step size of 0.03^0 operating at 40 kV and 30 mA. The starting diameter size were measured using an LEO 912AB Energy Filter Transmission Electron Microscope (TEM) while the surface morphology was obtained from Field Emission Scanning Electron Microscope (FeSEM) micrographs using an FEI NOVA NanoSEM230 machine. The distribution of the diameter size was obtained by estimating a mean diameter of at least 200 different diameter images using intercept method. The vibrational phonon modes were determined by Raman Spectroscopy using a WITec Alpha 300R 532 nm excitation laser. The electromagnetic wave absorption properties of the samples were analyzed in the frequency range of 8 – 18 GHz using a Vector Network Analyzer (VNA) with one port option and was short using metal back.

3 Results and Discussion

3.1 CNs diameter size analysis

Figure 2 shows the TEM micrograph of different samples with the outer walls of CNs were smooth, slippery and most of it are hollow, curved, spiral and twisted together. There is also aggregation of the sample which attributed to the aggregation growth happened when the

repulsive interactions were not high enough to block their access due to Van der Waals interaction. The average diameter size of SC, SF, S1, S2 and S3 are 36.2 nm, 133.6 nm, 56.7 nm, 64 nm and 75.4 nm respectively. The average diameter size increased as the percentage of Fe_3O_4 increased from 20 wt% to 80 wt% (S1 to S3) attributed to larger particle size of Fe_3O_4 as starting particle size use as catalyst.

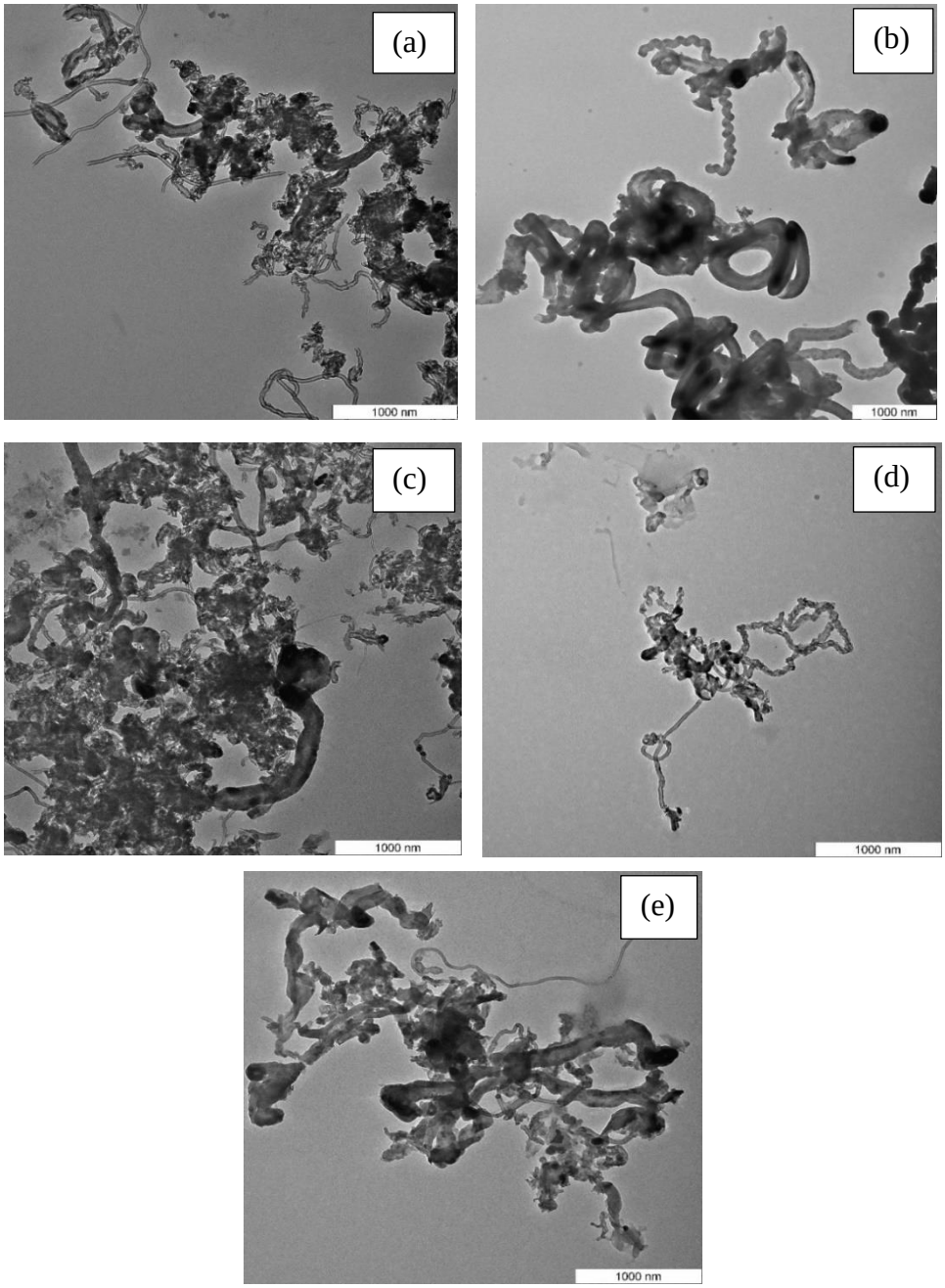

Figure 2. TEM micrograph of a) SC, b) SF, c) S1, d) S2 and e) S3.

Particle size would influence the diameter of synthesized CNs. Smaller particle size of catalyst results in smaller diameter of synthesized CNs. There are two growth mechanisms related to CVD method: i) tip growth mode and ii) base growth mode. Tip growth mode happens when the catalyst particles is at the tip of the growing nanocoils. On the other hand, base growth mode is when the particles remain at the nanocoils base, and it depends on the adhesion between the

catalyst and substrate. Catalyst particles size of more than 5 nm, results in formation of multiwalled carbon nanocoils (MWCNs) with more than 10 walls. However, for base related growth with less than 5 nm produces SWCNs with typically less than seven walls. The formation of MWCNs is suitable for EM wave absorption at microwave frequency range. Figure 3 shows diameter size distribution histogram of SC, SF, S1, S2 and S3.

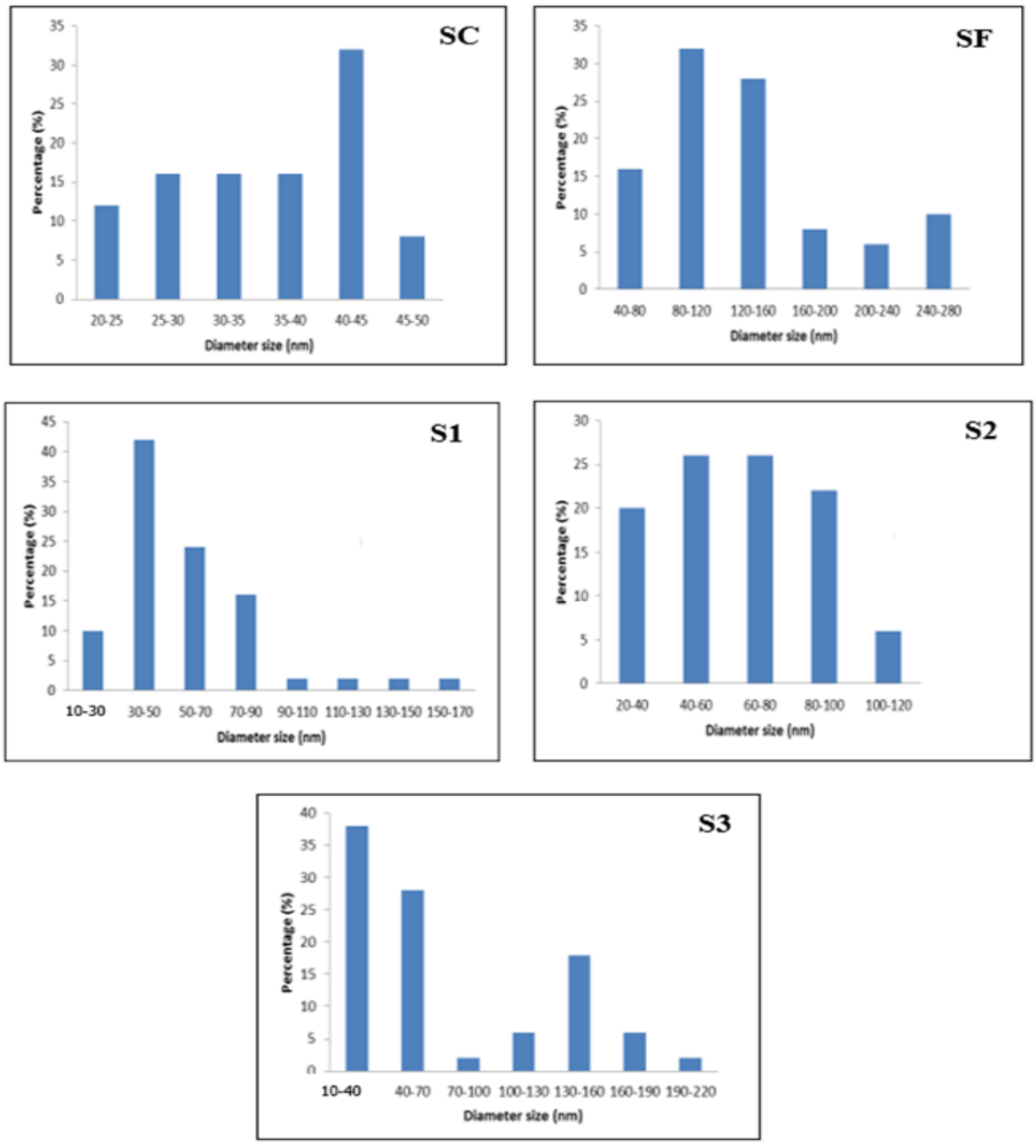

Figure 3. Diameter size histogram of SC, SF, S1, S2 and S3.

3.2 Microstructural analysis

Figure 4 shows FESEM image of SC, SF, S1, S2 and S3 with average dimeter size of are 49.8 nm, 105.9 nm, 21.2 nm, 22.4 nm, and 94.4 nm respectively. The CNs formation are in the form of bundles and entanglements that consists 50 to a few hundred individual CNs by strong Van der Waals Force. The aggregated CNs can be overcome by loading 8 wt% of CNs into epoxy matrix and homogeneously dispersed it by using high speed mixer. The composite samples forming a nearly interconnected network with small distance between CNs end. This individual and bundles MWCNs can attenuate the radiation through the interaction between interior and exterior microwave radiation.

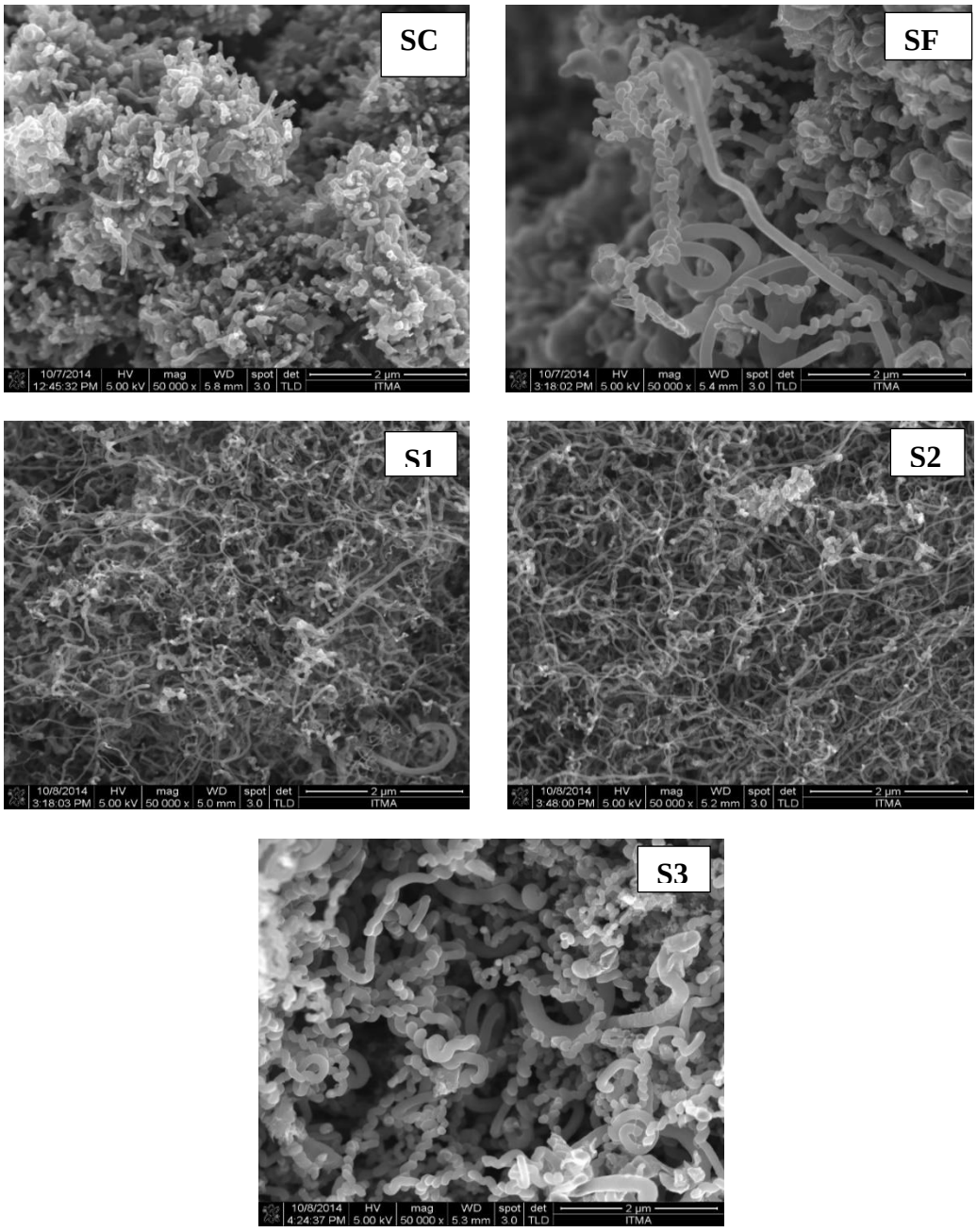

Figure 4. FESEM image of SC, SF, S1, S2 and S3.

The formation of carbon structures was mostly straight, netlike fibers and twisted. It is also worth noticing that the carbon structures favored to be in the spiral coil form. Basically, carbon coil like structures may results in having wide applications for example as an EM absorbing material [7]. Moreover, carbon nanocoils results in good EM wave absorber performance compared to conventional ferrites [8, 9]. The reason for the formation of coil structure is attributed to the regular insertion of pentagon-heptagon pairs at the junctions. Ref. [10] reported on the detail's explanation on the formation of various types of coiled fibers. Comparing between short fibers and microparticles, short fibers can improve the EM wave absorber performance because of their high surface-to-volume ratio, quantum size effects and the network structure effect of the composite's material.

3.3 Phase analysis

Figure 5 shows an X-ray diffraction pattern of SF, SC, S1, S2 and S3. Based on the diffraction pattern, the results consist of two phases; carbon (G) and Iron Carbide (Fe_3C) and the peaks were matched with the standard reference code data for carbon graphite (98-001-7175) and iron carbide (98-009-1656). The main highest carbon graphite peak and iron carbide peak were observed at angle $2\theta = 26.5^0$ and $2\theta = 45^0$ respectively. Ref. [11] reported that the reflections from basal hexagonal carbon atomic networks and parallel nanotube stacking layers are results from the hexagonal graphitic phase of carbon. Moreover, there are five remaining weak peaks of carbon graphite presence at different 2θ angle. Other peaks of iron carbide (Fe_3C) occurred at different 2θ angle because of the presence of iron (Fe) and carbon graphite (G) during CVD process. The formation of iron carbide phase presence for all condition regardless the type of CNs that was emanating from the catalyst particle or the amount of carbon deposited. The iron carbide form onto the active catalyst phase and it replace all the iron-based catalyst during the synthesizing process.

The XRD pattern of CNs has shown some similarities to graphite probably because of their similar intrinsic graphene properties. However, CNs have different chiralities and consist of different layers that differ CNs produce form this research with other reported research although the highest diffracted carbon peak (002) was similar to others. Therefore, the formation of peaks depends on the morphological orientation. The details review on the XRD pattern of CNs was reported by Ref. [12].

An X-ray beam that strikes single wall of CNTs produces (002) peaks, while beam that pass through an empty central core will produce an extra hexagonal peak array. This may occur multiple times at different azimuths that depends on the number of helix present. Moreover, there are few suppressed reflections peaks attributed to peak shifting and broadening that cause most of the carbon peak could not be obtained. This is also cause by different sizes and shapes with curved graphene layers. The shifting and peak broadening is also related to defects presence in the sample that was discussed in details in other analysis of this research work.

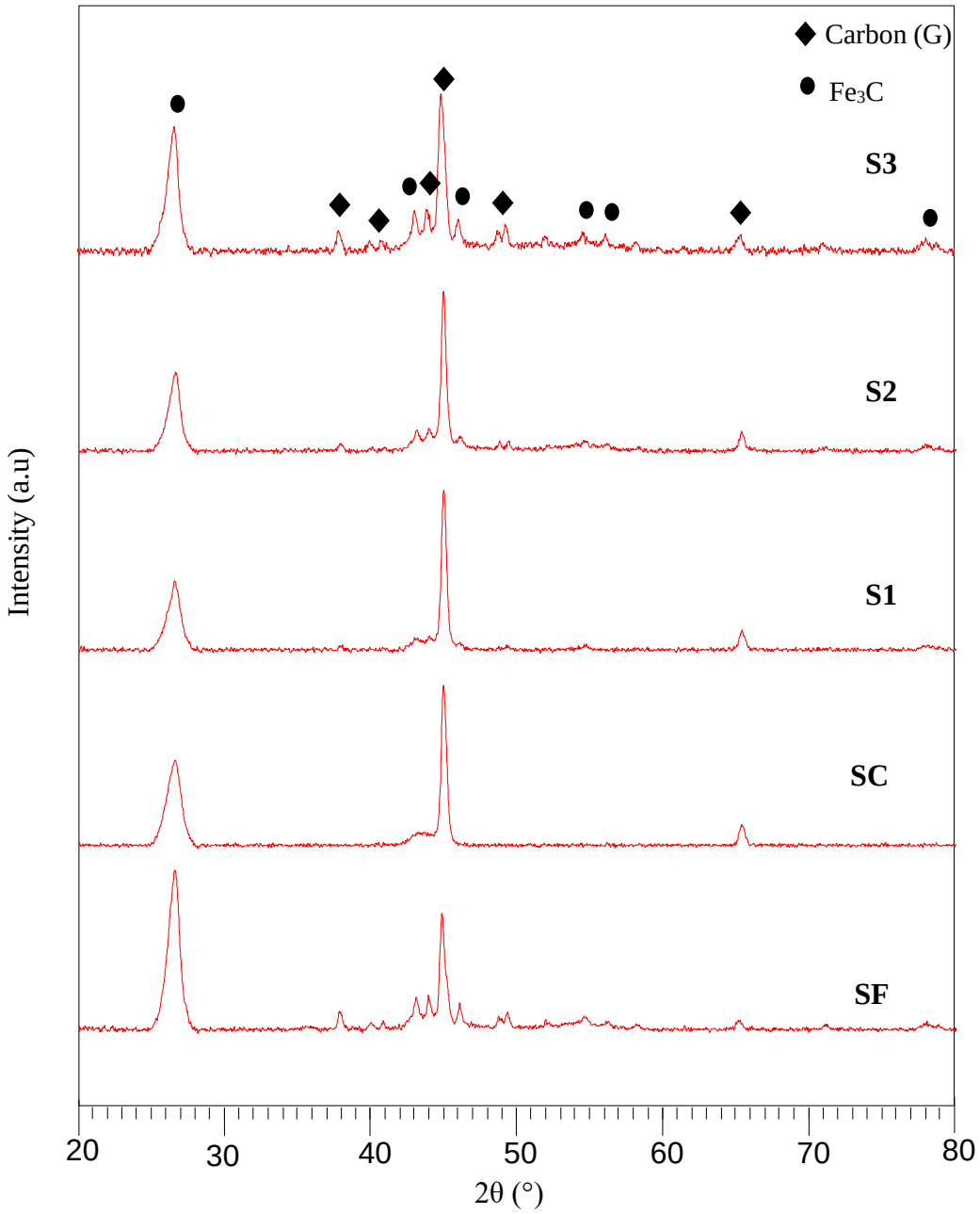

Figure 5. X-ray diffraction pattern of SF, SC, S1, S2 and S3.

3.4 Structural analysis (RAMAN spectroscopy)

Raman scattering of the composite shown in Figure 6 was measured to further validate the presence of CNT. High intensity Raman scattering of D and G bands for CNs are observed in between 1342.138 cm^{-1} to 1348.665 cm^{-1} and 1567.143 cm^{-1} to 1585.526 cm^{-1}, respectively. D-peak corresponds to the defects and disordered carbon or defective graphitic structures, and the G-peak is associated with the signal from crystalline graphitic layer. The I_D/I_G values of the CNs formation is depend on the structural characteristics of CNs and it determine the quality of CNs. The ratio of the intensities of these peaks (I_D/I_G) are 0.874 (SF), 1.201 (SC) and constant around 1.1 (S1,S2,S3) as shown in Table 1. This suggest that there are many formations of defects and the CNs contain long range disordered graphitic carbon which is consistent with

weak and broad diffraction peak at 26.5^0 in the XRD patterns. The formation of higher D-peak is also attributed to defects in the tube ends, staging disorders and curved graphene layers [13]. Large peaks of D-band and the broad peak of G-band indicate low graphitization of CNs. Moreover, there is also a splitting of G-peak at 1609.638 cm^{-1}. Since the samples prepared were MWCNs, thus, it is in good agreement with Raman spectra with the presence of more defects. The complicated structures indicate better EM wave absorption performance which was mainly attributed to the dielectric relaxation [14].

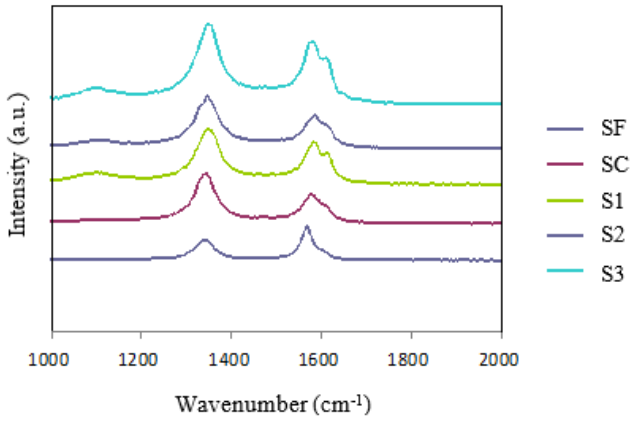

Figure 6. RAMAN spectra of SF, SC, S1, S2 and S3.

Table 1. Corresponding peak frequencies (Raman shift) for CNs sample in Raman spectra.

Sample name	D-band (cm^{-1})	G-band (cm^{-1})	I_D/I_G
SF	1342.138	1567.143	0.874
SC	1342.138	1575.208	1.210
S1	1348.665	1581.501	1.100
S2	1344.520	1585.526	1.182
S3	1344.520	1577.473	1.121

3.5 Microwave Characterization

Figure 7 shows the reflection loss (RL) of S1/E, S2/E and S3/E composite samples showing the influence of MWCNs on the EM wave absorption property. All composite samples showed a trend of reflection loss peak shift to lower frequency region as the thickness increased because of shift in the matching frequency. The reflection loss value obtained was below -10 dB for all samples especially for thickness of 3 mm. Note that for "10 dB absorbing bandwidth" as also marked by dotted line, it indicates that the frequency bandwidth having RL characteristics of over 90 %. The bandwidth of reflection loss less than -10 dB with thickness 3 mm for S1, S2 and S3 are 5.5 GHz (9.5 – 15 GHz), 6.3 GHz (11.7 – 18 GHz) and > 3GHz (< 8 GHz – 11 GHz) respectively. The reflection loss of samples of thickness 1 mm could not be observed since the formation of peak is at much higher frequency range. On the other hand, the reflection loss peak for sample of thickness 2 mm starts to be observed for S1/E, S2/E and the full resonance peak only observed for sample S3/E. Furthermore, the reflection loss peak between S1/E, S2/E and

S3/E of thickness 3 mm, are observed at 12 GHz, 14 GHz and 9.5 GHz respectively. However, it shows not so much improvement on the RL peak values that is around -23 dB. Ref. [15] reported that the reflection loss of pure CNTs and $CoFe_2O_4$ nanoparticles prepared by CVD method and measured by metal back method is low and the peak values were 6 and 8.3 dB respectively (within 2-18 GHz frequency range).

Therefore, the formation of resonance peak of the composites sample plays the role by absorbing the microwave energy and attenuating the radiation via the interaction between interior electron and exterior microwave radiation. The formation of defects can also act as polarization centers that can contribute to strong microwave absorption and it was attributed mainly to the dielectric relaxation [14].

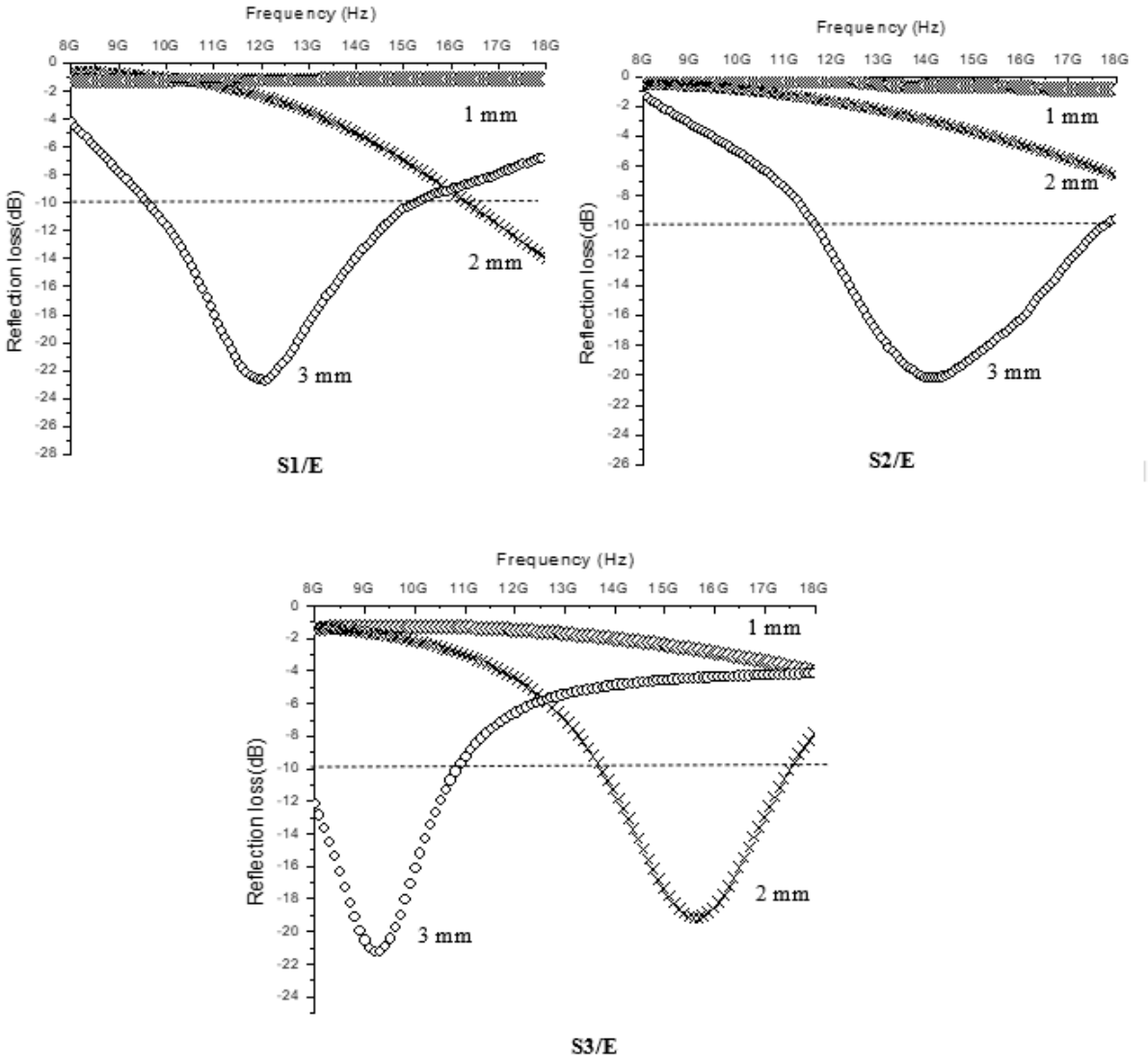

Figure 7. Reflection loss of S1/E, S2/E and S3/E at different thickness (1 mm, 2 mm, 3 mm).

4 Conclusion

In conclusion, the use of nanometers starting particle sized as catalyst to synthesized CNs enhanced the EM absorption capability. Moreover, the carbon structures forms were mostly

straight, spiral, hollow tube, netlike and twisted fiber. The formation of sufficient defects and spiral like structure can enhance the multiple reflection route and contribute to better performance of EM wave absorber. In addition, well-dispersion of CNs into epoxy resin helps in enhance the internetwork structure of the polymer composite as signal passes through the materials, thus, low conductivity and proper dielectric loss created are also advantageous for EM wave absorption. Furthermore, thickness of the samples affects the reflection loss peak as it will shifts towards lower frequency range due to shift of matching frequency. CNs catalyzed by mixed ferrite helps in better EM absorbing performance with only 8wt% filler being added and reflection loss can reach until -23 dB with appropriate bandwidth. Thus, it may help in having lightweight material and the result obtained in this research shows that it may be promising material for electromagnetic applications at higher EM wave gigahertz frequency range depends on the applications needed.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

Author Contributions

Writing-original draft preparation: Fadzidah Mohd Idris

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Writing-review and editing: Hatika Kaco, Siti Munirah Mohd, Nurhidaya Mohamad Jan, Zanariah Mohd Idris, Haslinawati Mohd Mustapha

Funding acquisition: Fadzidah Mohd Idris

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