공학석사학위논문

Study on Electromagnetic Properties of Sendust/MWCNTs/Polymer Composites

센더스트/다중벽 탄소나노튜브/폴리머 복합체의 전자기적 특성에 대한 연구

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ABSTRACT

Study on Electromagnetic Properties of Sendust/MWCNTs/Polymer Composites

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This dissertation is about a study of making an electromagnetic wave absorption material that has high permeability and high permittivity. As a first step to make a hybrid composite that satisfy these two properties, a magnetic absorber (mixing Sendust with polymer) and a dielectric absorber (mixing MWCNTs with polymer) was made through melt mixing and solution mixing process. And to measure the permeability and permittivity of each absorber, vector network analyzer was used as a measurement tool.

The measurement results showed that the complex permeability and the electromagnetic wave absorption ability of a magnetic absorber increased in two conditions: when more amount of Sendsut was mixed and by using flake shape Sendust instead of bulk shape. While the complex permittivity and the electromagnetic wave absorption ability of a dielectric absorber proportionated to the weight ratio of MWCNTs.

Sendust/MWCNTs/polymer composites were created in order to make an electromagnetic wave absorption material as initially planned. We challenged to make the best hybrid composite that could gratify the conditions of preserving high permeability and high permittivity by changing the proportion of filler. In order to get a fixed permeability value contain of Sudust was fixed to 100 phr and 3 composites were made by adjusting the amount of MWCNTs to 5 phr, 10 phr and 15 phr. The result showed that the complex permittivity and the power loss increases as more filler was mixed but this was not promising because there was great reduction of reflection loss. The most realistic and effective hybrid composite was the composite with 5 phr of MWCNTs which was lighter and had excellent electromagnetic wave absorption with only 16 dB at a 4.6 GHz frequency.

Key words : Sendust, Multi-walled carbon nanotube, Electromagnetic wave, EMI absorber, Electromagnetic properties

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Contents

List of Tables

List of Figures

Chapter I

Introduction

I-1. Electromagnetic interference (EMI) shielding

Recent development of electronic and information technology has brought astonishing levels of change. Electronic devices, such as personal computers and mobile phones have become more highly integrated, miniaturized and lighter. The rapid progress of high-speed processing has increased the operating frequency range to GHz to tens of GHz frequency band. One of the most important factors that influence the reliabilities of electronic devices is EMI (Electromagnetic interference). EMI is a disturbance caused by electromagnetic noise which not only affects the performance of the electric devices, but are also harmful to humans by increasing the temperatures of living tissues and weakening the immune function [1-4]. For this reason, using shielding materials to control EMI has arisen as a crucial issue in many nations around the world. Korea is not an exception, and therefore employing new shielding materials and developing new measurement techniques can be keys to tackle EMI shielding and suppression.

As you can see in fig. I-1, electromagnetic waves are formed when an electric field couples with a magnetic field. As illustrated in fig. I-2, these electromagnetic waves can be classified in terms of frequency range. EMI is carried in RF (radio frequency) field which is approximately between 3 kHz to 300 GHz frequency range.

Electromagnetic noise is a phenomenon when electrical signal introduces undesirable and unavoidable noise. Noise can be generated in many ways and affects electronic frequency and radio frequency. As fig. I-3 shows, noises can be classified into two categories. Conducting noise is a noise delivered through electric current [5]. Radiation noise refers to a noise that is radiated internally or externally through the air in a form of electromagnetic wave. Conducting noise can be avoided by using filter which blocks electronic transmission paths. Electromagnetic shielding is a commonly used effective manner to minimize and in some instance to eliminate radiation noise [1, 2]. However, when electromagnetic shielding reflects or scatters electromagnetic waves it increases noises and moreover causes malfunction, inefficiency and transmission errors. In terms of radiation noise, absorption loss can be incurred as electromagnetic wave penetrates the shield and interferences. For this reason, there has been a significant attention for the best candidate materials that can not only reduce the level of electromagnetic radiation but also absorb transmitted signal noise [6, 7].

General conditions that are required for materials to absorb electromagnetic wave are ones which are thin-walled, light-weighted and which can cover wide range of frequency [8, 9].

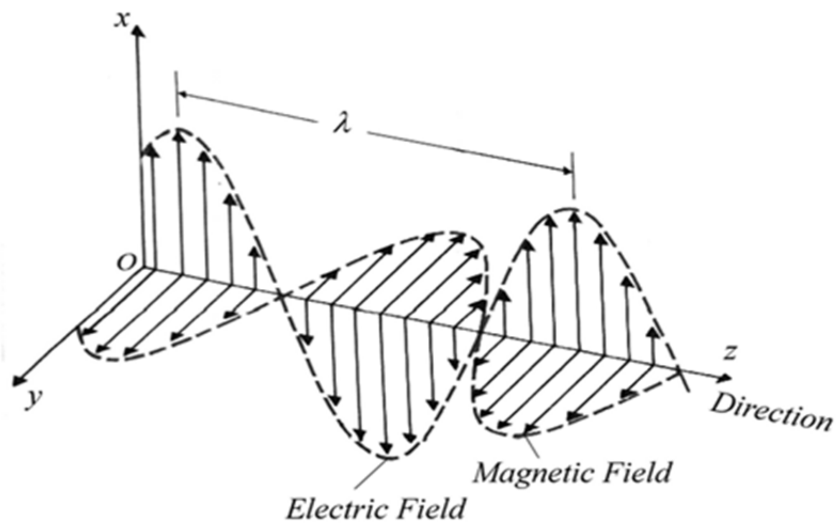

Figure. I-1. Illustration of an electromagnetic wave

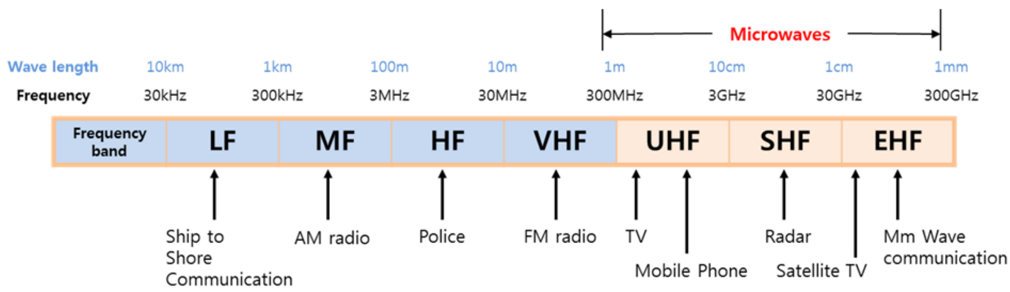

Figure. I-2. Illustration of electromagnetic spectrum

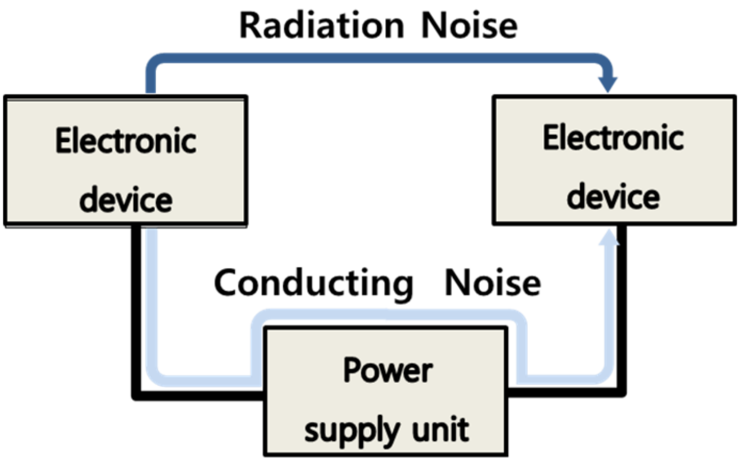

Figure. I-3. Diagram of electromagnetic noise

I-2. Materials for absorption of electromagnetic waves

In general absorber, when incident electromagnetic waves is absorbed, the energy of the waves converts to heat. In many cases, electromagnetic waves incident on the interface to be partially reflected due to the differences of impedance of media. However with good electromagnetic waves absorber we can not only reduce the amount of waves being reflected but also increase the heat attenuation into the maximum value and decrease the amount of waves being transmitted. The following explains the two attenuation materials

I-2.1. Dielectric Absorption Material

When an external electric field is applied to a dielectric material the material becomes polarized. The total effect of an electric field on a dielectric material is called ‘dielectric polarization’. When a dielectric is placed in an external electric field, electric charge shifts in the opposite direction of the electric field and reduces the total electric field inside the material. Permittivity is determined by the ability of a material to polarize in response to the electric field. Formula $\varepsilon=\varepsilon'-j\varepsilon''$ is used to determine complex permittivity of a material. In this formula real part (ε') is associated with propagation, and the imaginary part (ε'') corresponds to the dielectric loss factor and electrical conductivity σ

[10]. The equation of σ is:

$$\sigma = 2\pi f \varepsilon_0 \varepsilon''$$

where ε_0 is the permittivity of free space [11, 12].

Diffusional process plays a significant role in dielectric polarization and frequency at which a dielectric material is used effects dielectric polarization. When frequency increases and the speed of dielectric polarization can no longer follow the change of an external electric field, the real part ε' decreases and the imaginary part ε" increases.

Dielectric absorption materials can be categorized into two classes; materials in which are made by compounding dialectic powder ($BaTiO_3$, $SrBi_2Ta_2O_5$, $Bi_4Ti_4O_{12}$ etc.) with polymer and materials made by compounding conducting powder (MWCNTs, grapheme, carbon black etc.) with insulating polymer. In the latter case, interface-charge polarization occurs within the interface between conductive filler and insulating polymer matrix. This dissertation will describe the process of making dielectric absorption materials by compounding insulating polymer with MWCNTs[13]. MWCNTs were chosen for this study because it enables higher electrical conductivity and is light-weighted [14].

I-2. 2. Magnetic Absorption Materials

While some atoms are bounded with pairs of electrons, magnetic materials have unpaired electron spins. Magnetic occurs when spins of unpaired electrons are aligned in same orientation. A region of this aligned unpaired electron spins is called a ‘domain’. Each domaiwn is separated by a transition region called ‘domain wall’. Domains which are randomly oriented can become aligned under the influence of an externally applied magnetic field. When the strength of an external magnetic field (H) is applied to a magnetic substance, the response of the material to H is called magnetic flux density (B). The ratio of magnetic flux density to magnetic field strength is called permeability (μ). This means that when permeability increases the magnetic flux that passes through a substance also increases, enhancing the strength as a magnet. Even when the applied external magnetic field strength is weak if the permeability is high the substances can be easily magnetized. Therefore, in all compositions, the main contribution to the initial permeability is due to domain wall motion. Magnetic impurities and void can act as impediments to domain wall motion, this disturbance which is also known as the ‘pinning effect’ affects the permeability and moreover become the cause of hysteresis [15].

The permeability of magnetic materials can be expressed as $\mu=\mu'-j\mu''$, where μ' and μ'' are the real and imaginary part of the relative permeability. The real part μ' is associated with magnetization of a material and the imaginary part μ" refers to energy loss. There are several possible factors that cause energy loss, such as eddy current, hysteresis and other undiscovered residual losses. Since the move of a domain wall itself is a diffusional process it needs relaxation time. In normal conditions when frequency increases, less time is needed to change the external electric field. When the relaxation time and the period of the applied electric field differs greatly, energy loss increases and permeability decreases. To a certain extent when frequency increases the velocity of a domain wall cannot follow the change of an external electric field and so the real part of the permeability decreases and the imaginary part increases. However, when frequency increases above a certain degree, there comes a moment when both the real part of the permeability and the energy loss reaches nearly zero. Since magnetic absorption materials are designed to absorb and consume energy, we need to find an ideal condition where much energy is lost as possible.

The greatest disadvantages of using bulk of magnetic material is that, although it has high permeability value much over thousand, it can only can maintain the permeability at frequencies below 1 Hz. Since energy loss is an important aspect of an electromagnetic absorber, developing a magnetic absorption material that works in higher frequency range is worthwhile [16].

Magnetic material is that, although it has remarkably high permeability value, it can only was conventionally used to make polymer composite because it can maintain high permeability at high frequency.

In order to make a polymer composite that can maintain high permeability in high frequency range, the bulk shape magnetic powder were transformed into flake shape through ball-milling process. This process was crucial firstly, because the flake shape magnetic materials were capable of restraining the eddy current loss that declines the magnetic property. The eddy current losses P_e can be expressed as below.

$$P_e \propto \frac{f^2 {B_M}^2 d^2}{\rho}$$

In this formula d stands for thickness of the sample, B_M the maximum magnetic flux density, f the frequency and ρ stands for electrical resistivity. Since eddy current loss is proportional to the square of the thickness, it can be reduced by reducing the thickness of the magnetic filler [17]. Secondly, the reason for transforming the shape is to increase the real permeability using magnetic anisotropy [18]. Shape-anisotropy is a dipolar interaction which contribution is depended on the shape of the material. The permeability increases with accordance to the direction of the thickness of a material and decreases with accordance to the direction of the length. Since there is an extreme difference in the length and the thickness in flake shape, thus permeability remains high.

Although ferrite is a popularly used magnetic absorber, due to the reason that it is difficult to transform its shape, Sendust was selected as a magnetic absorber in this study. Sendust, as a soft magnetic material, has high permeability and can be easily transformed into flake shape through ball milling process.

I-3. The Purpose of the Experiment

The permeability of magnetic absorption materials that are conventionally used to absorb electromagnetic wave has severe limits because these materials cannot be maintained over 1 GHz frequency range. The permeability can be maintained in a much higher frequency range when it is processed into a flake-shape. However, still this frequency range is not high enough compare to wireless LAN, Bluetooth, mobile phone and wireless Local Loop. Moreover materials made through the process are heavy because high-density metallic materials are used. Electromagnetic wave absorption materials made with MWCNTs, in contrast, is lighter and can work in higher frequency range. However this method is barely suitable because it is far too expensive to afford and produces narrow bandwidth usage. The purpose of this dissertation is to make absorption materials which combine both the permeability of magnetic absorption materials and permittivity of dielectric absorption material by using hybrid system. The ultimate goal through this method is to make electromagnetic absorption materials with low-density, high absorption rate and that can work in abroad frequency range.

Chapter II

Experimental Section

II-1. Materials

Two pellet shape polymer resins, polyolefin elastomer (POE, LC-170, LG chem) and ethyl vinyl acetate (EVA, 45% VA) were used as polymer matrix. Two kinds of Sendust (83.9% Fe, 9.6% Si and 6.5% Al, Chansung) in bulk and flake types were used as magnetic filler. Multiwalled carbon nanotubes (MWCNTs, HANOS CM-250, 95 wt.% purity, Hanwha Chem) was selected as conducting filler. Stearic acid (Aldrich) and NAUGARD-445(Uniroyal) were used as lubricant and antioxidant respectively. P-Xylene (Daejung) was used as an organic solvent to produce MWCNTs/Polymer suspension and Ethanol (Daejung) was used as an organic solvent to precipitate MWCNTs/Polymer suspension.

II-2. Sample preparation Process

All the samples that were made through the following procedure (II-2.1., II-2.2., II-2.3.) were shaped into thin sheets (50 mm × 50 mm × 1 mm).

Toroidal shape samples in size 7 mm outer diameter 3 mm inner diameter were later made of these composite sheets. Table II-1 presents constituent absorber materials for each sample.

Table.II-1. Constituent absorber materials for each sample

Chapter	Sample numbering	Sendust shape & contents	MWCNTs contents
II-2.1.	1-1	Bulk 100 phr	-
	1-2	Bulk 200 phr	-
	1-3	Bulk 300 phr	-
	1-4	Bulk 400 phr	-
	2-1	Flake 100 phr	-
	2-2	Flake 200 phr	-
	2-3	Flake 300 phr	-
	2-4	Flake 400 phr	-
II-2.2.	3-1	-	-
	3-2	-	5 phr
	3-3	-	10 phr
	3-4	-	15 phr
II-2.3.	4-1	Flake 100 phr	5 phr
	4-2	Flake 100 phr	10 phr
	4-3	Flake 100 phr	15 phr

II-2.1. Fabrication of Sendust/polymer composites

Two mixed polymer resins (EVA and POE in the 3:7 ratio) were mixed with both bulk shape and flake shape Sendust for 10 minutes in a twin screw internal mixer (Haake Rheomix model 600p) heated to 100℃ at 100 rpm. Once they are heated, only the composite mixed with flake shape Sendust was processed by a laboratory scale roll press machine at 90℃ for 10 minutes to make the Sendust particles aligned in the same direction. Finally the two mixed samples were processed by a laboratory scale hot press machine at 80℃ for 3 minutes and annealed to room temperature for 3 minutes.

II-2.2. MWCNTs/Polymer Composites

p-Xylene was used as organic solvent for both polymer solution and MWCNTs suspension. MWCNTs were first suspended in p-xylene in sonication at 60℃ for 1 hour in a condition where MWCNTs content were fixed at 0.5 wt% and later stirred at 60℃ for 1 hour/300 rpm. After this process is made, MWCNTs suspension was poured to p-xylene/ polymer solution (EVA and POE in the ratio 3:7). These mixtures were again sonicated at 60℃ for 1 hour and were stirred at 60℃ for 1 hour/300 rpm. Once this process was done, the mixtures were stirred at 500 rpm to room temperature with little drops of ethanol added to make it precipitate. The precipitates were filtered and dried in a vacuum oven at 80℃ for 24 hours. To achieve better experiment result, the mixture was again mixed for 10 minutes in a twin screw internal mixer heated to 100℃ at 100 rpm. Finally the composite was pressed by a hot press machine at 80℃ for 3 minutes and annealed to room temperature for 3 minutes.

II-2.3. MWCNTs/Sendust/Polymer Composite

MWCNTs were first suspended in p-xylene in sonication at 60℃ for 1 hour in a condition where MWCNTs content were fixed at 0.5 wt% and then stirred at 60℃ for 1 hour/300 rpm. After this, MWCNTs suspension was poured to p-xylene/ polymer solution (EVA and POE in the ratio 3:7). For the next step, the mixture was sonicated at 60℃ for 1 hour and then stirred at 60℃ for 1 hour/300 rpm. After this stage, the mixture was stirred at 500 rpm to room temperature with little drops of ethanol added to make it precipitate. The precipitates were filtered and dried in a vacuum oven at 80℃ for 24 hours. The material was then mixed with flake shape Sendust for 10 minutes in twin screw internal mixer heated to 100℃ at 100 rpm. To make the Sendust particles aligned in same direction, mixture was processed by a roll mill machine at 90℃ for 10 minutes. Finally the mixture composite was both pressed by a hot press machine at 80℃ for 3 minutes and annealed to room temperature for 3 minutes

II-3. Measurement of Electromagnetic Properties

S (scattering)-parameter measures the ratio of the incident and reflected signal. In this experiment, VNA (vector network analyzer, E8364A, Agilent) was used to measure the s-parameters of the material in the frequency range of 45 MHz to 6 GHz. The measurement was made by inserting the toroidal samples into a coaxial measurement unit which is connected to VNA with two ports. Fig. II-2 shows the induction effect of an electromagnetic wave carried by the ports to the waveguide that was measured by VNA. Then, the scale and phase response of the sample under test to the incident stimulus of electromagnetic wave was evaluated and noted from 45 MHz to 6 GHz. As fig. II-1 the measured s-parameters includes S_{11} (forward reflection coefficient), S_{21} (forward transmission coefficient), S_{22} (reverse reflection coefficient) and S_{12} (reverse transmission coefficient).

Scattering coefficient S_{11} and S_{21} is both related to reflection coefficient(Γ) and transmission coefficient(T), and for this reason can be written as follows.

$$S_{11} = \frac{(1 - T^2)\Gamma}{1 - T^2\Gamma^2}$$

$$S_{21} = \frac{(1 - \Gamma^2)T}{1 - T^2\Gamma^2}$$

The impedance Z_{in} is related to the permeability (μ_r) and permittivity (ε_r) of a sample in a coaxial airline and can be written as follows.

$$Z_s = Z_0 \frac{\mu_r}{\varepsilon_r}$$

Using these equation, reflection coefficient (Γ) and transmission coefficient (T) can be expressed as:

$$\Gamma = \frac{Z_{in} - Z_0}{Z_{in} + Z_0} = \frac{\frac{\mu_r}{\varepsilon_r} - 1}{\frac{\mu_r}{\varepsilon_r} + 1}$$

$$T = \exp\left[-j\left(\frac{\omega}{c}\right)\sqrt{\varepsilon_r \mu_r} \cdot d\right]$$

when ω refers to the 'angular frequency', d the 'thickness' and c the 'velocity of light'. Hence, the permeability and the permittivity can be expressed as follows.

$$\frac{\mu_r}{\varepsilon_r} = \frac{(1 + \Gamma)^2}{(1 - \Gamma)^2} = a_1$$

$$\mu_r \varepsilon_r = -\left(\frac{c}{\omega d}\right) \ln\left(\frac{1}{T}\right)^2 = a_2$$

$$\mu_r = a_1 a_2, \ \varepsilon_r = a_2/a_1$$

According to transmission line theory, the RL (reflection loss) of an electromagnetic wave in normal incidence of a single-layer material which is backed by a perfect electrical conductor (PEC) or a metal can be defined as:

$$\mathrm{RL} = 20\log_{10}\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right|$$

where Z_0 is the characteristic impedance of free space,

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} = 377\,\Omega$$

Z_{in} refers to the input impedance at free space and material interface, and its equation is usually written as:

$$Z_{in} = Z_0\left(\sqrt{\frac{\mu_r}{\varepsilon_r}}\right)\tanh\left[i\left(\frac{2\pi \cdot f \cdot d}{c}\right)\left(\sqrt{\mu_r \varepsilon_r}\right)\right]$$

Where the μ_r and ε_r are the complex permeability and complex permittivity of the substance and, i denotes $\sqrt{-1}$, f the input frequency, d the thickness of a sample and c the velocity of electromagnetic wave in free space [19]. Normally the reflection loss (RL) is obtained by measuring the S_{11} (forward reflection coefficient) as shown in the fig. II-3.

In order to measure the near-field power loss, the 50 mm×50 mm×1 mm size sample was attached to a microstrip line sample holder and the holder was connected to VNA in a frequency range from 45 MHz to 6 GHz as shown in the fig. II-4. Below is the formula that was used to infer the transmission loss power [20].

$$\text{power loss}\left(\frac{P_{loss}}{P_{in}}\right) = 1 - (|S_{11}|^2 + |S_{21}|^2)$$

The Power loss corresponds to the electromagnetic absorption loss at near-field and can be measured by the formula given below

$$\text{Power loss} \propto \mathrm{d}\sqrt{\mu_r \cdot f \cdot \sigma_r}$$

where μ_r is the relative permittivity, f the frequent, d the thickness of the sample and σ_r the relative conductivity, respectively [20].

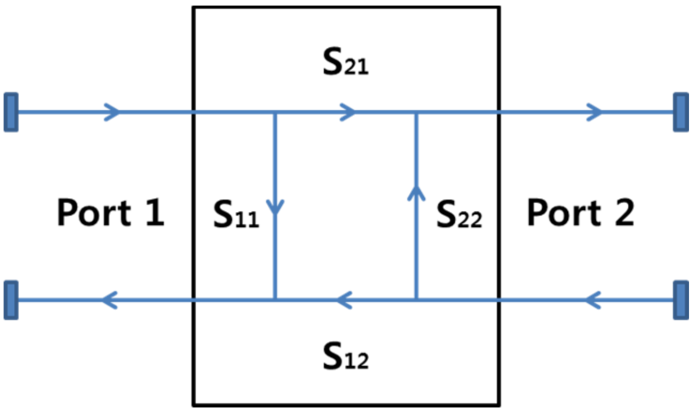

Figure. II-1. Vector network analyzer system setup for measuring scattering parametes

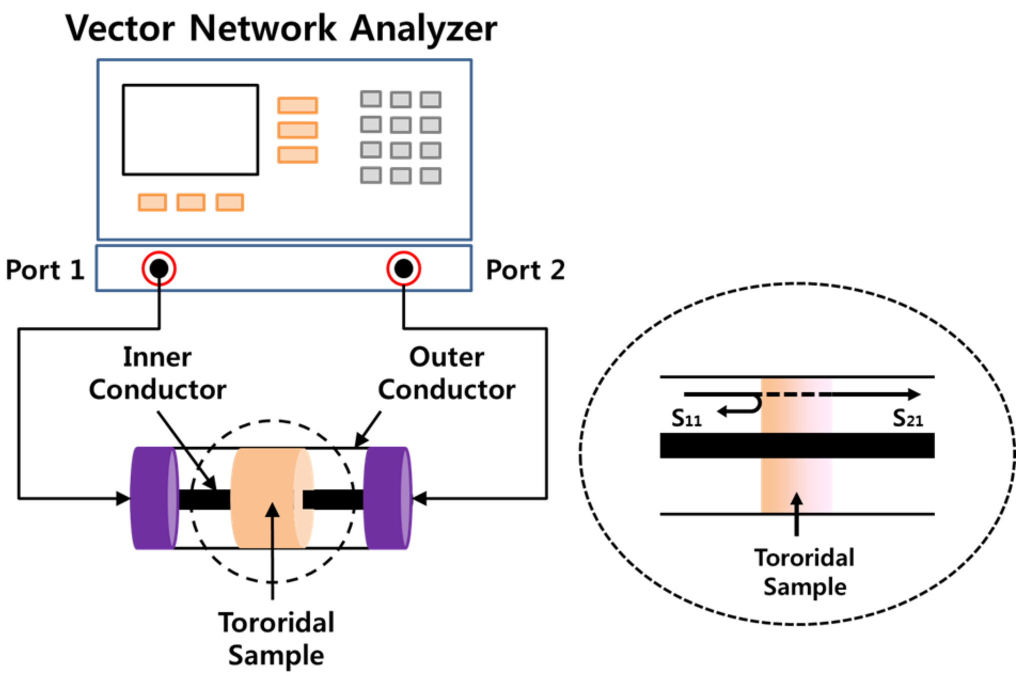

Figure. II-2. Two-port coaxial jig used in measuring the reflection (S_{11}) and transmission (S_{21}) scattering parameter

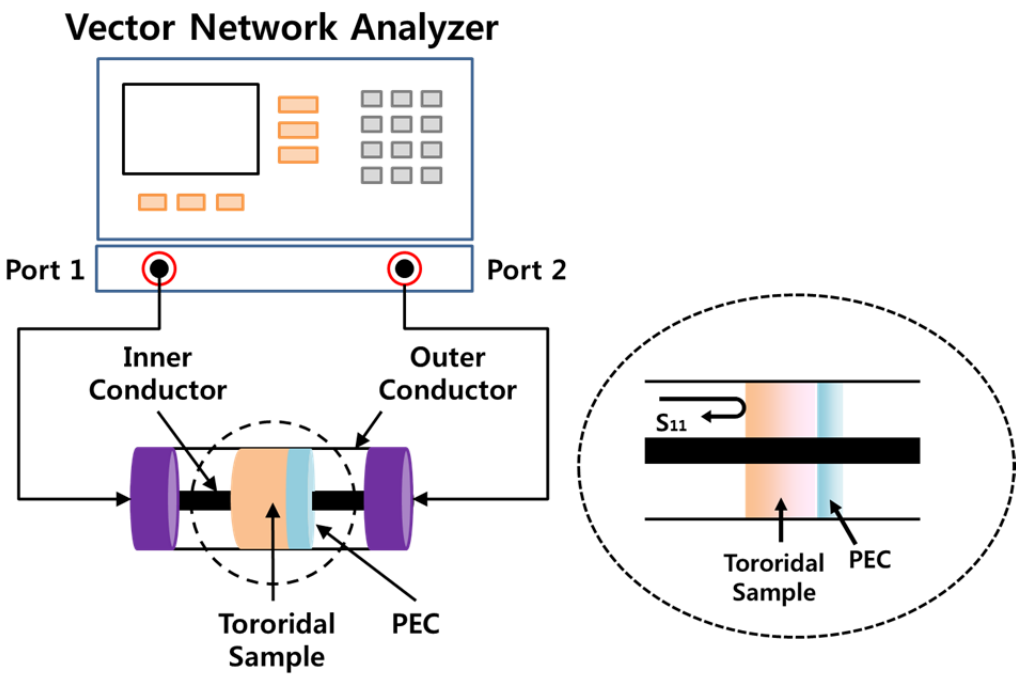

Figure. II-3. Two-port coaxial jig used in measuring the reflection (S_{11}) scattering parameter of material back by a perfect electrical conductor (metal plate)

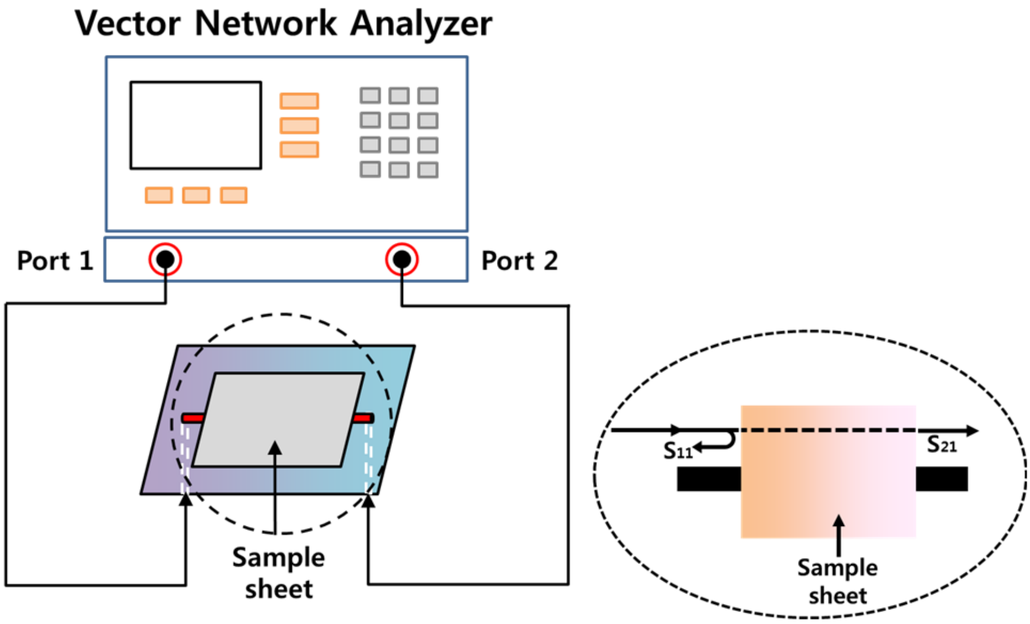

Figure. II-4. Two-port coplanar jig used in measuring the reflection (S_{11}) and transmission (S_{21}) scattering parameter

Chapter III

Results and Discussion

III-1. Electromagnetic Properties of Sendust/Polymer Composites

Fig. III-1 indicates the SEM (Scanning Electron Microscope) images of Sendust powder to determinate the shape and sizes of fillers (bulk shape and flake shape). Ball milling process was used to effectively transform the bulk shape filler into a flake shape. The figure shows that both bulk and flake shape filler were approximately the same in size but different in thickness. The thickness of bulk shape filler was measured around 50-80 ㎛ while the thickness of a flake type filler was less than 3 ㎛. The result proves that flake shape Sendust has higher aspect ratio than the bulk.

Fig. III-2 displays the SEM images of the fracture section of absorber materials that contains 400 phr of both bulk and flake shape Sendust. The results show that both Sendust filler were well dispersed with polymer matrix without leaving empty spaces. Distinctively, after being pressed in a roll press the flake shape powder was well oriented in the rolling direction.

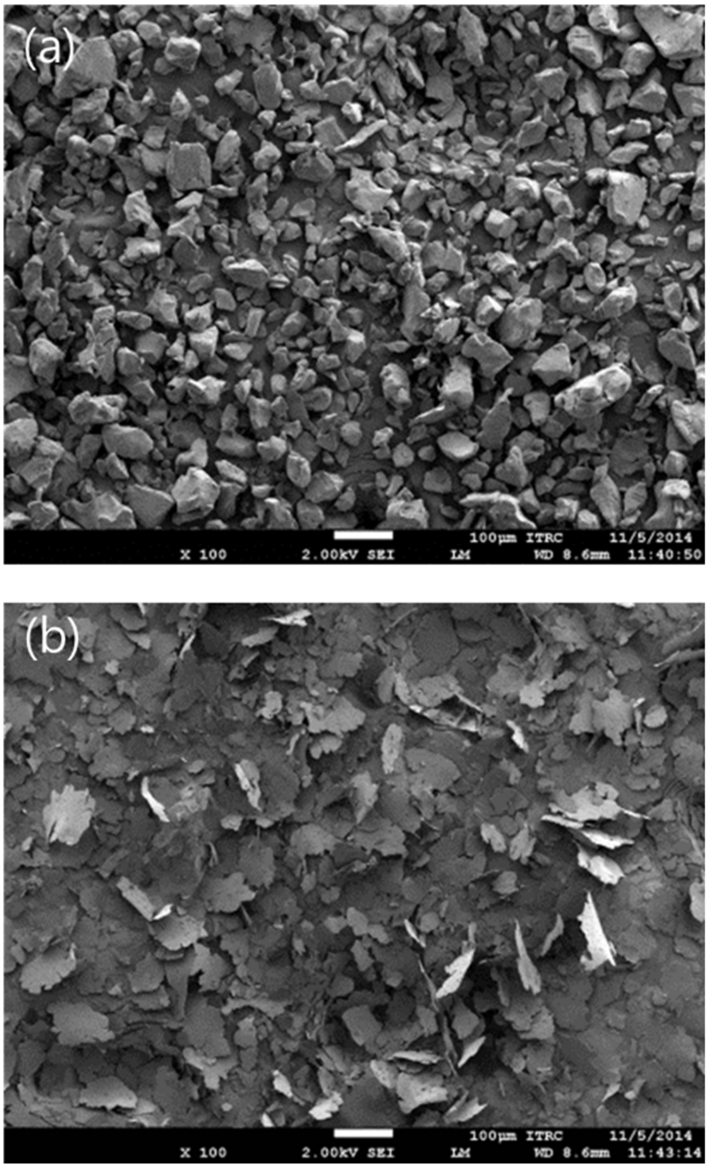

Figure. III-1. SEM image of Sendust powder, (a) bulk shape, (b) flake shape

(at × 100 magnification)

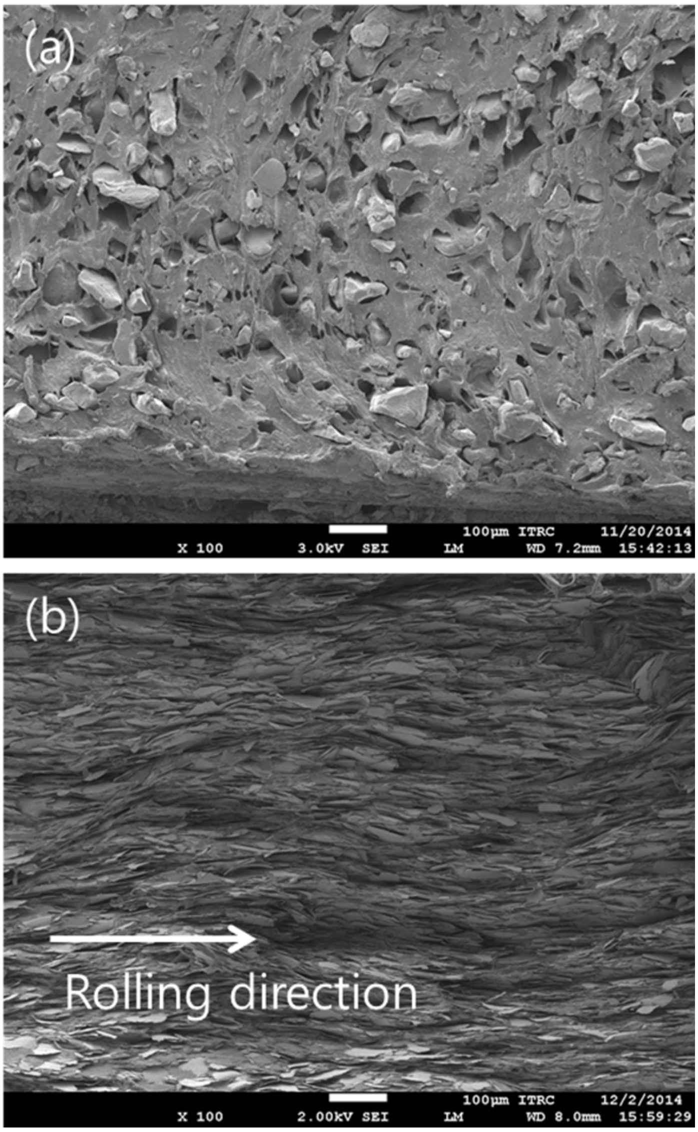

Figure. III-2. SEM image of Sendust/polymer composites, (a) 400 phr bulk shape, (b) 400 phr flake shape (at × 100 magnification)

In this study, complex permeability, reflection loss and power loss were measured in order to demonstrate how effectively Sendust/ polymer composites can absorb electromagnetic wave according to the shape and content of Sendust. Each result are graphed to observe the highest and lowest to value in the frequency range from 45 MHz to 6 GHz,

In order to measure the complex permeability of the composites, VNA was used as a measurement tool. The results of both real part of the complex permeability (real permeability) and imaginary part of the complex permeability (imaginary permeability) are described in fig. III-3. The real permeability is showed in the straight-line graph in upper graph. At the frequency range from 45 MHz to 6 GHz, the real permeability of bulk type filler was to the nearest 1, as if it were in free space. The permeability of composite that contain 400 phr and 100 phr of flake type filler also dropped to nearly 1 from 30 and 8 respectively. The graph also showed that the frequency range also have dominant influence in the value of real permeability. That is to say, when the frequency of alternative magnetic field increases, the velocity of the domain wall exceeds the maximum value and for that reason can cause a condition where the time for domain wall motion can no longer follow the frequency change [21]. Hence, it affects the real permeability to reduce.

The result of the imaginary permeability is shown in the curve graph below side. Similar to real permeability, the flake shape Sendust showed higher imaginary permeability than the bulk type. The absorber material that contained 400 phr of flake shape Sendust reached the maximum value 12 at 400 MHz frequency range, while the maximum value of material that contained 100 phr of flake shape Sendust was only 3 at 800 MHz. The two graphs shows: first, the more flake type filler was mixed the higher value of complex permeability was gained. And second, the more filler was contained the maximum value were showed in lower frequency range. Consequently, as explained in I-2.2., transforming the bulk shape filler into flake shape can be an effective method to increase the magnetic shape anisotropy and reduce eddy current loss.

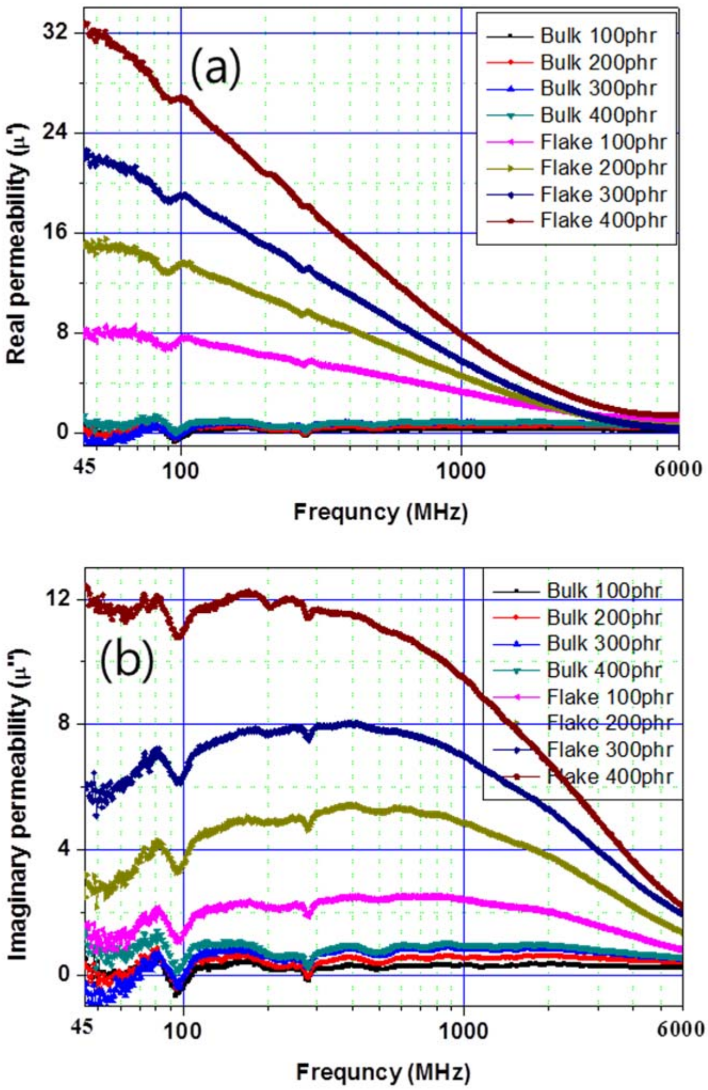

Figure. III-3. Complex permeability for different Sendust shape and concentration versus frequency, (a) real permeability, (b) imaginary permeability

Fig. III-4 and fig. III-5 shows the measured result of RL (Reflection Loss) and power loss of materials with different filler shapes and concentration ratio of Sendust. RL results are deeply related to the ability to absorb electromagnetic waves. That is to say, higher RL value refers to stronger ability to cope with electromagnetic waves. Materials that contained 400 phr of flake shape filler absorbed 6.3 dB of electromagnetic wave at 2 GHz while the bulk shape filler only absorbed 2 dB at 6 GHz. Similarly when materials that contained 100 phr of flack shape filler absorbed 3.7 dB of electromagnetic wave at 3 GHz the bulk shape filler only managed to absorb 0.4 dB at the same frequency range.

This brought us two conclusions: first, as it has been approved by many researchers in related fields [22,23], when the filler shape is transformed into flake shape and the filler contents increases the maximum value of RL is likely to be observed at lower frequency range. Second, as the filler shape is transformed into flake shape and the filler contents increases the intensity of RL increases.

Fig. III-5 indicates that the power loss is proportionated to the amount of filler included in the composites, and flake shape filler had bigger value than the bulk shape. Which prove that permeability is relevant to the shape and concentrations of Sendust. The grape shows that materials that contain 400 phr of flake shape filler absorbs 50% of energy in 1 GHz and 25% of energy in bulk shape. While material that contains 400 phr of flake shape filler was capable to absorb almost 90% of energy in 2.5 GHz, the bulk shape was able to absorb 90% of energy in 6 GHz. To sum up, we can say that when more power is lost the materials tend to have better absorption ability.

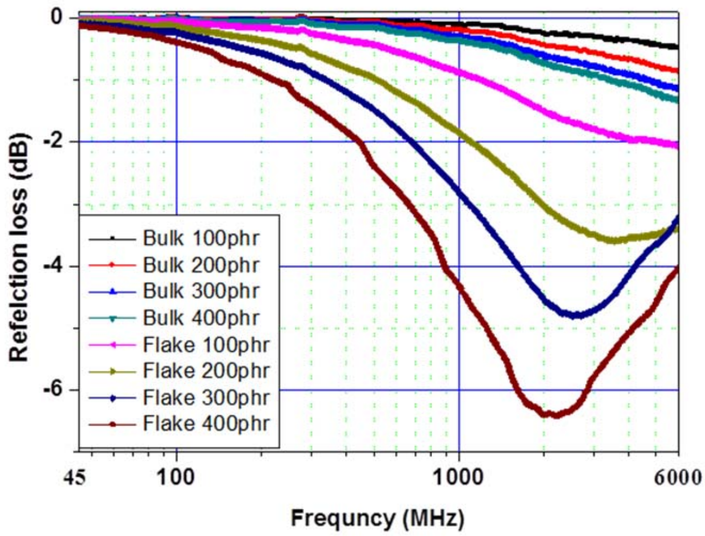

Figure. III-4. Reflection loss for different Sendust shape and concentration versus frequency

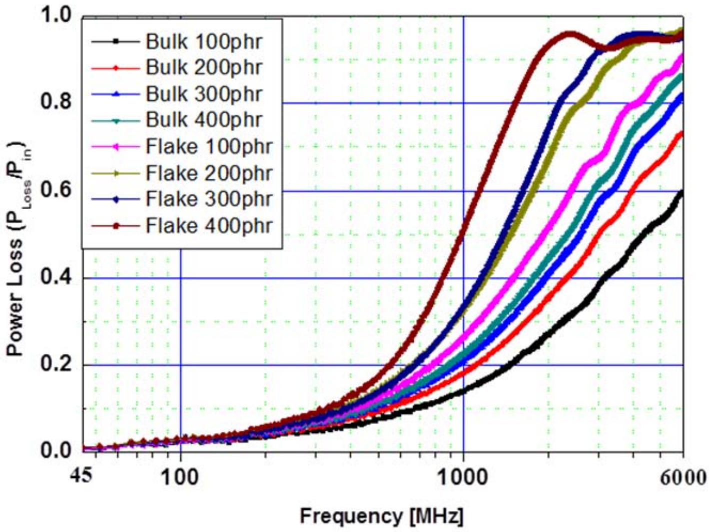

Figure. III-5. Power loss for different Sendust shape and concentration versus frequency

III-2. Electromagnetic Properties of MWCNTs/Polymer Composites

Fig. III-6 indicates the SEM images of 15 phr MWCNTs/polymer composites. In both images you can see thin white wires. These thin wires are MWCNTs. The MWCNTs are in white because of its high conductivity and for this reason, they are evenly split without leaving any empty space.

Fig. III-7 graphs show the complex permittivity of MWCNTs/polymer composite according to the MWCNTs content within the frequency range from 45 MHz to 6 GHz. Four MWCNTs/polymer composites were used in this experiment. The composite which did not contain any of MWCNTs was named 'neat polymer' and other composites contained 5 phr, 10 phr, 15 phr of MWCNTs respectively. The graph showed that the real part of relative permittivity increased as the MWCNTs content increased. The permittivity value of the samples that contained none of the MWCNTs, 5phr, and 10phr slowly decreased from 5, 20, and 50 respectively, while the sample that contained 15 phr of MWCNTs made a remarkable decrease from 60. It is know that MWCNTs have higher interfacial bonding strength. As more MWCNTs are mixed the interfacial electric polarization among the polymer and MWCNTs gets amplified [24]. Moreover, such phenomenon as electric polarization or atomic polarization was not observed during the measurement, because these phenomenon only happen at much higher frequency range [25].

As you can see in the SEM images in Fig. III-6, the material that contained 15 phr of filler had much higher real part of permittivity (real permittivity) than the material that contained 10 phr of filler due to continues path of MWCNTs formed by conductive filler. 'Percolation threshold' is an important phenomenon for the composites because it refers to the minimum weight of the filler to increase conductivity of the composite. Therefore, percolation threshold can be a reliable reason for filler concentration seen in the SEM images [26]. External electric wave needs relaxation time to cause interfacial electric polarization but when frequency increases above a certain degree and dipole can no longer follow the change it consequently decreases the real permittivity. Similar to real permittivity, the imaginary permittivity increases as the content of filler increases. This is because when the content of filler increases the conductivity of the composite.

Since neat polymer does not carry any elements that can react with the external electromagnetic wave. The neat polymer showed very low complex permittivity in both real and imaginary part.

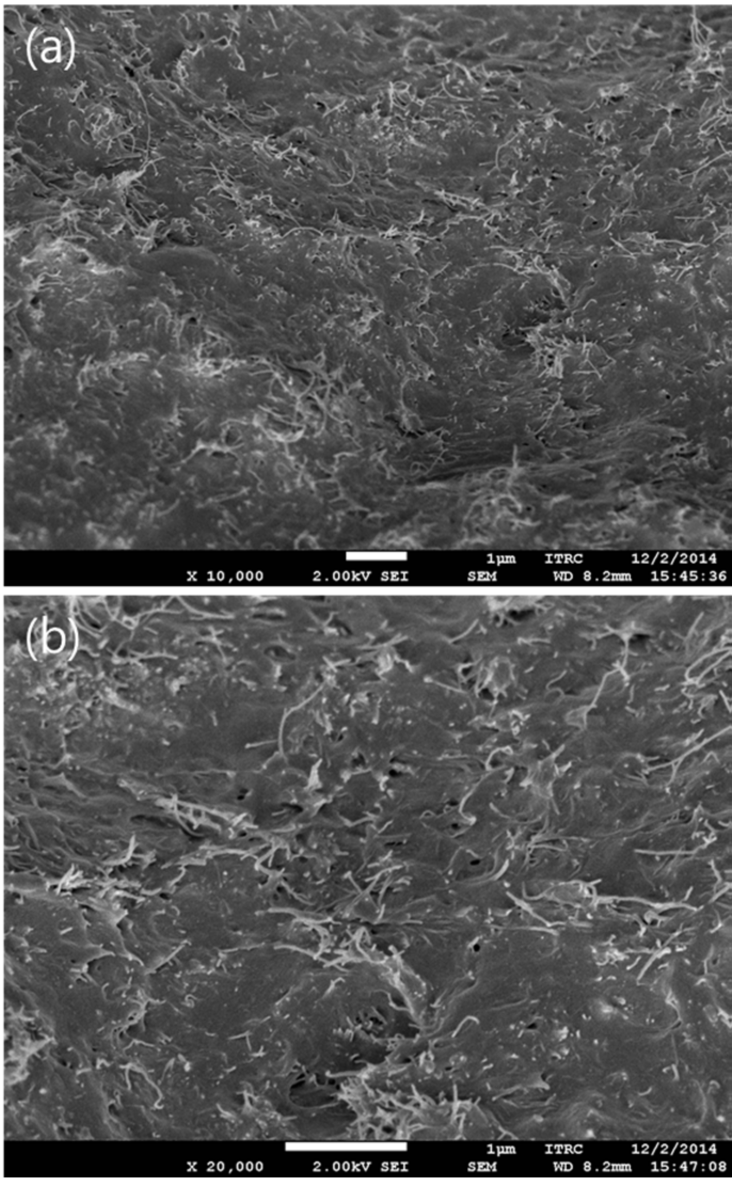

Figure. III-6. SEM image of 15phr MWCNTs/polymer composites, (a) magnification × 10000, (b) magnification × 20000

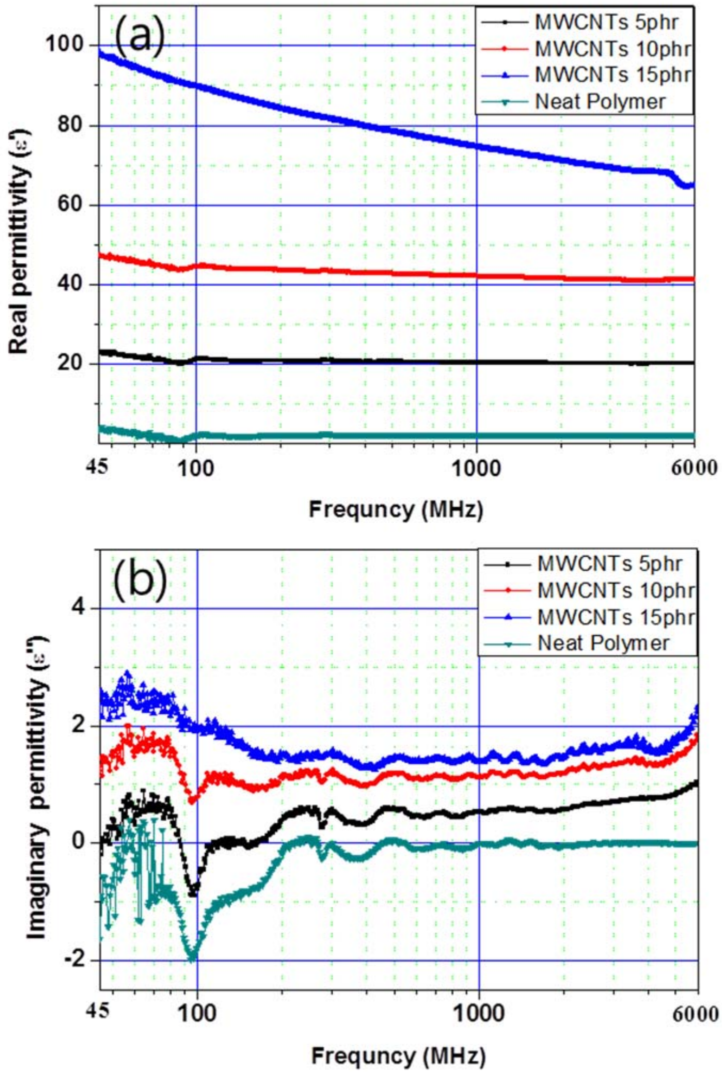

Figure. III-7. Complex permittivity for different MWCNTs concentration versus frequency, (a) real permittivity, (b) imaginary permittivity

Fig. III-8 and fig. III-9 shows the figure of reflection loss and power loss of MWCNTs/Polymer Composites. The figure shows that the maximum value of reflection loss is observed in lower frequency ranges as MWCNTs contain increases. For example, the maximum value of a composite that contained 15 phr of filler reached 17 dB at 4.5 GHz while the composite that contained 10 phr of filler only reached 7.5 dB of power loss at 5.1 GHz. The maximum value for materials that contained 5 phr of filler was not monitored in the experiment because of limited frequency range. However judging from the fact that the relaxation process of interfacial electric polarization is affected by the amount of filler mixed in the composite and by comparing the data of other composites, the maximum value of the composite that contains 5 phr of filler is presumed to be lower than 7.5 dB at frequency range higher than 6 GHz.

Fig. III-9 shows the microstrip line power loss is dominated only by magnetic wave but not electromagnetic wave, and therefore, when applying the equation described in section II-3. we can draw a conclusion that increasing the content of MWCNTs contributes to increase the conductivity of composites and eventually increases the power loss.

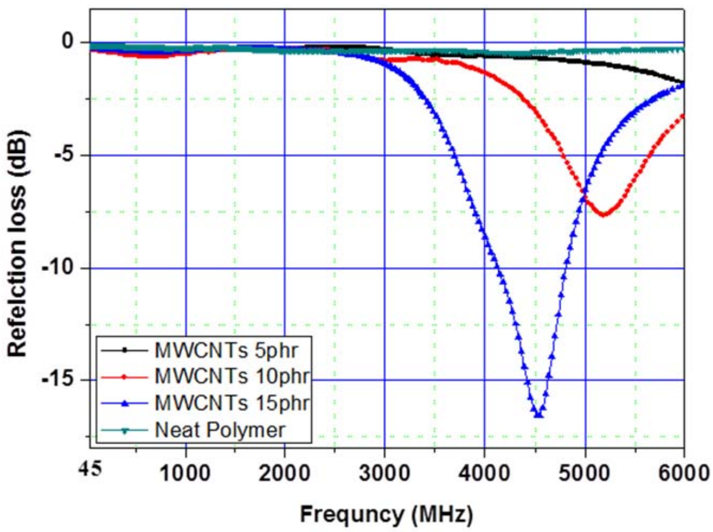

Figure. III-8. Reflection loss for different MWCNTs concentration versus frequency

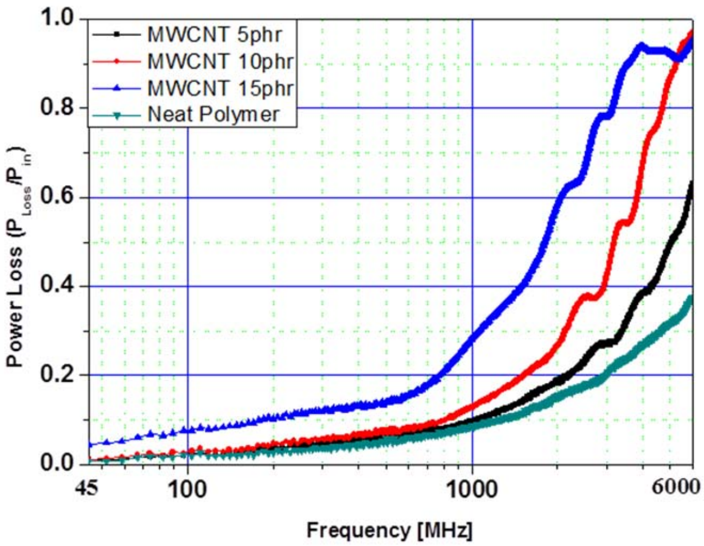

Figure. III-9. Power loss for different MWCNTs concentration versus frequency

III-3. Electromagnetic Properties of Sendust/MWCNTs/Polymer Composites

In order to make a lighter electromagnetic absorption material, Sendust/WMCNTs hybrid system was created by using the results from III-1. and III-2. Three Samples were made to be a candidate by mixing Sendust and MWCNTs in different proportion.

Flake shape Sendust was selected due to its excellent absorption property at low frequency range. The content ratio of Sendust was fixed to 100phr in order to reduce weight and was mixed with 5, 10, 15 phr of MWCNTs respectively. A hypotheses was set up that since the contain contents of Sendust is fixed, the complex permeability will also have constant value and the complex permittivity will change according to the amount of MWCNTs mixed in each samples.

Reflection is observed in many types of electromagnetic wave and the difference in impedance for the medium is the major cause of reflection. When the difference in impedance is big the reflection value also increases. When the impedance of an absorber (Z_{in}) matches with free space impedance (Z_0 = 377 Ω) the incident electromagnetic wave penetrates 100% of the energy without causing any reflections. This phenomenon is called 'impedance matching' and in order to attain the condition of zero reflection Z_0 needs to be similar to Z_{in}

[26]. In a condition that contain ratio of Sendust is fixed to 100 phr, the following experiment will focus on finding the most ideal condition that matched the impedance by controlling the permittivity. MWCNTs have excellent conductivity while Sendust as a metal-alloy is also a conductor. Since both Sendust and MWCNTs are conductive, the permittivity of the mixed composite is hard to predict due to the synergy effect of the two materials. Unlike complex permeability values which are relatively easy to predict, permittivity values are hard to predict and it is thus why this experiment is a necessary process to grad accurate date in order to measure permittivity values.

The top SEM image in fig. III-10 is a composite that is magnified 500 times. The composite is made by mixing 15 phr of MWCNTs and 100 phr of Sendust. The image shows that the flake shape Sendust is well oriented in the direction of the roll press without leaving any free space. While, as indicated in fig. III-2 (find p32), it is impossible to distinguish polymer and Sendust in the composite that contained 400 phr of flake shape Sendust. On the other hand, both polymer and Sendust was observable in composites that have low content of Sendust and moreover, we were able to confirm that there was no empty space. In the 500 times magnified image, MWCNTs were not observed due to low expulsion. However, Sendust and MWCNTs were observed together through 10000 times magnified image. These thin wires are MWCNTs.

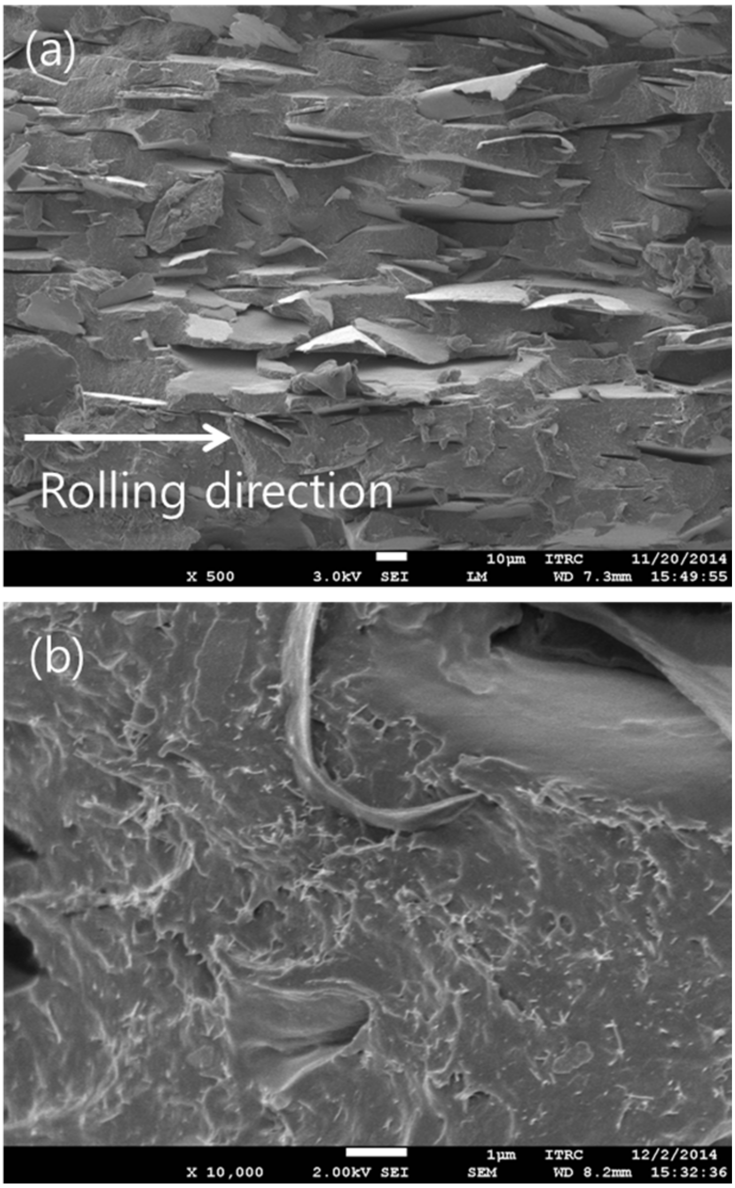

Figure. III-10. SEM image of 100 phr Sendust flake / 15 phr MWCNTs/polymer composites, (a) at × 500 magnification, (b) at × 10000 magnification

Fig III-11. indicates the complex permeability of absorbers at frequency range from 45 MHz to 6 GHz. Since MWCNTs themselves does not have permeability the permeability of the composites are totally depended on the amount of Sendust contained in the composites. The samples used in this experiment were produced by mixing 100 phr of Sendust and 5, 10, 15 of MWCNTs respectively. The figures showed that the amount of MWCNTs have nothing to do with the value of real and imaginary permeability. The value of real permeability of the samples decreased consistently from 7 to 1 and the value of Imaginary permeability increased constantly from 1 until they reached the maximum vale 2,4 at 800 MHz and then gradually decreased to 0.8. The complex permeability value of a composite that contains 100phr of Sendsut described in fig. III-11 shows the same value of that in fig. III-3 (find p38).

Fig. III-12 indicates the complex permittivity of absorbers that were made by mixing polymer with MWCNTs and Sendust at frequency range from 45 MHz to 6 GHz. By consulting the graph shown in fig. III-7, we were able to compare the complex permittivity of two absorption materials: Sendust/MWCNTs/polymer composites and MWCNTs/polymer composites. The real permittivity value of Sendust/MWCNTs/polymer composites showed higher value than MWCNTs/polymer composites in overall. For example the real permittivity value of a composite that contained 15 phr of MWCNTs and

100 phr of Sendust had 120 higher values than the composite without Sendust. When Sendust was mixed with MWCNTs/polymer composites with 10 phr and 5 phr of MWCNTs the value increased by 50 and 40 respectively. The reduction ratio of Sendust/MWCNTs/polymer composites and MWCNTs/polymer composites showed very similar pattern. With the composites that had 5 phr and 10 phr of MWCNTs the reduction ratio did not make remarkable change, while in the other hand the composite that contained 15 phr of MWCNTs showed rapid decrease. This tendency is likely to be shown when MWCNTs and Sendust inside the insulating polymer matrix are mixed together and thus, increases interfacial electric polarization.

Imaginary permittivity which refers to the energy loss is relevant to the conductivity of a composite. MWCNTs have excellent conductivity, and for this reason the conductivity of a Sendust/MWCNTs/polymer composites increase when the weight ratio of MWCNTs increases. This fact is determinable by comparing the fig. III-12 with fig. III-7 (find p46). For example the imaginary permittivity value of a composite that contained 15 phr of MWCNTs and 100 phr of Sendust had 35 higher values than the composite without Sendust. By the same token, the real permittivity value of composites that contained 10phr and 5 phr of MWCNTs only (fig. III-7) increased by 5 and 2 respectively when mixed with Sendust (fig. III-12). To sum up both real and imaginary permittivity had highest value with the composite that contained 15 phr of MWCNTs and this phenomenon is estimated to happen because the filler content has exceeded percolation threshold [11].

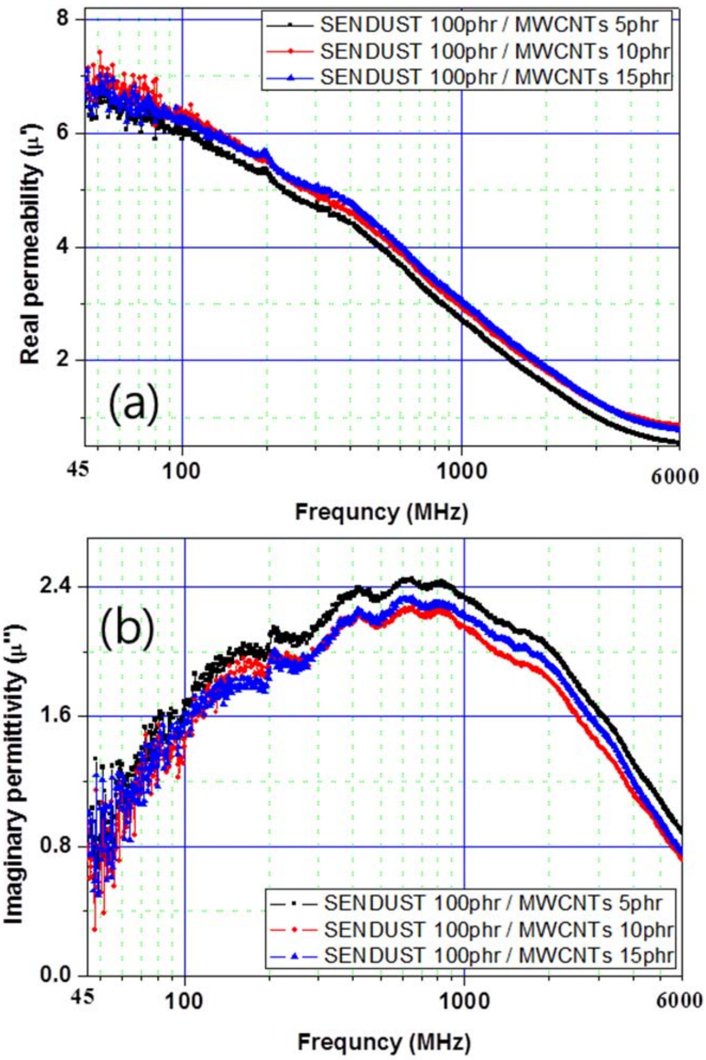

Figure. III-11. Complex permeability for different ratio of MWCNTs concentration versus frequency with fixed ratio of Sendust flake, (a) real permeability, (b) imaginary permeability

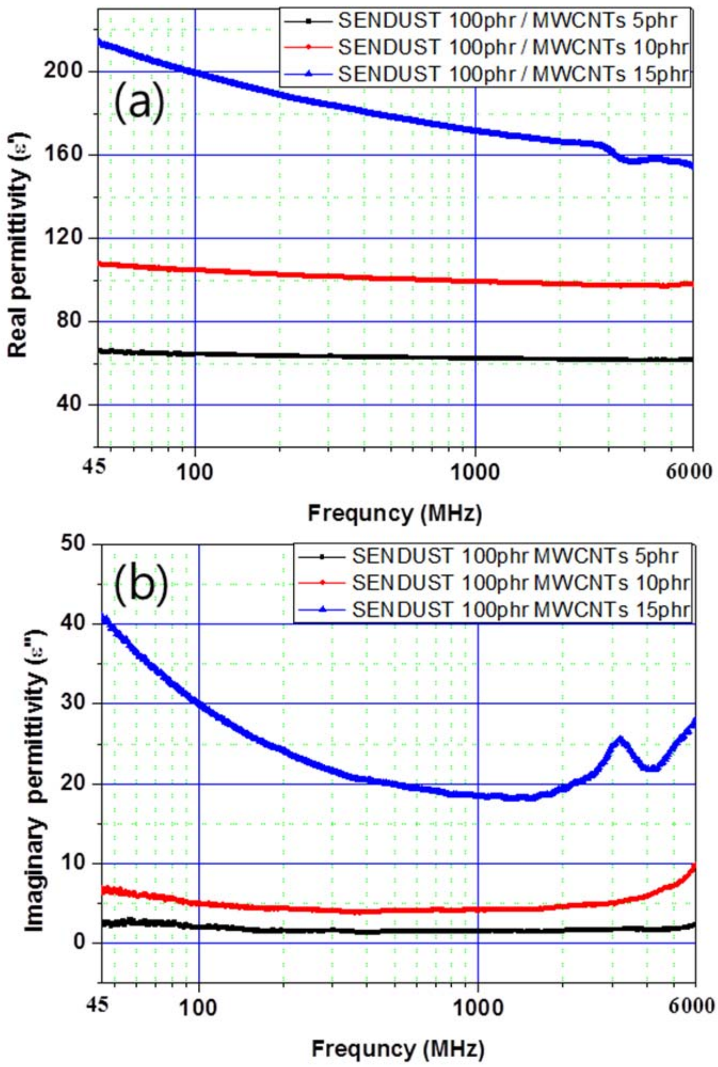

Figure. III-12. Complex permittivity for different ratio of MWCNTs concentration versus frequency with fixed ratio of Sendust flake, (a) real permittivity, (b) imaginary permittivity

Fig. III-13 and fig. III-14 shows reflection loss and power loss of Sendust/MWCNTs/polymer composites at the frequency range 45 MHz to 6 GHz. The maximum reflection loss value of Sendust/MWCNTs/ polymer composite that contained 5 phr MWCNTs was 17 dB at 4.6 GHz. While the maximum value of composites with 10 phr and 15 phr of filler was 7 dB at 4.3 GHz and 4 dB at 2.5 GHz respectively. The results brought us a conclusion that as more conductive fillers are mixed the peak value is found in lower frequency range.

Contrastively to the previous results, high intensity values are gain from composites that contain less MWCNTs filler due to the phenomenon of impedance matching. By using electromagnetic characteristic parameter map that are made by previous studies, we were able to find the best conditions that matches zero-reflection[27]. Complex permittivity for impedance-matching can be calculated if the values of complex permeability at each frequency range are known. The composite that contains 100 phr of Sendust and 5 phr of MWCNTs was able to meet the necessary and closest conditions for zero-reflection. Meanwhile, Sendust/MWCNTs/polymer composites with 10 phr and 15 phr of MWCNTs failed to meet the requirements to satisfy the condition for zero-reflection. In general conditions, when the amount of MWCNTs increases more dipoles are formed. The increase of dipoles as a consequence contributes to the increase of dielectric loss. Despite this fact when reflection occurs, electromagnetic wave cannot penetrate through the absorption material and therefore, reflection loss decrease [28, 29].

Power loss, as seen in fig. III-14, is proportionate to permeability and conductivity, therefore when the amount of MWCNTs mixed in the composite increases the conductivity also increases resulting high power loss. Materials that contain 100 phr of Sendust and 5 phr of MWCNTs lost 30% of power in 1 GHz and for composites that contain 10 phr and 15 phr lost 40% and 60% of power at the same frequency range. In short, power loss value of Sendust/MWCNTs/polymer composite had higher result value than using Sendust and MWCNTs respectively. Table III-1 is made to compare the density and power loss of 3 materials: Sendust flake, MWCNTs and Sendust/MWCNTs/polymer composite, which were made through experiment III-1, III-2, and III-3. The density of 400phr Sendust flake was 4.65 g/cm^3 which managed to absorb 40% of the energy at 1GHz. The density of 15 phr MWCNTs was 1.05 g/cm^3 and this filler could absorb 30% of energy at 1 GHz. Astonishingly the density of Sendust/MWCNTs polymer composite with 100phr of Sendust flake and 15 phr of MWCNTs was only 1.75 g/cm^3 but it could absorbed 60% of energy at the same frequency range. Through all these procedures we eventually succeeded in making an absorber that is light weighted and has excellent electromagnetic wave absorbing property.

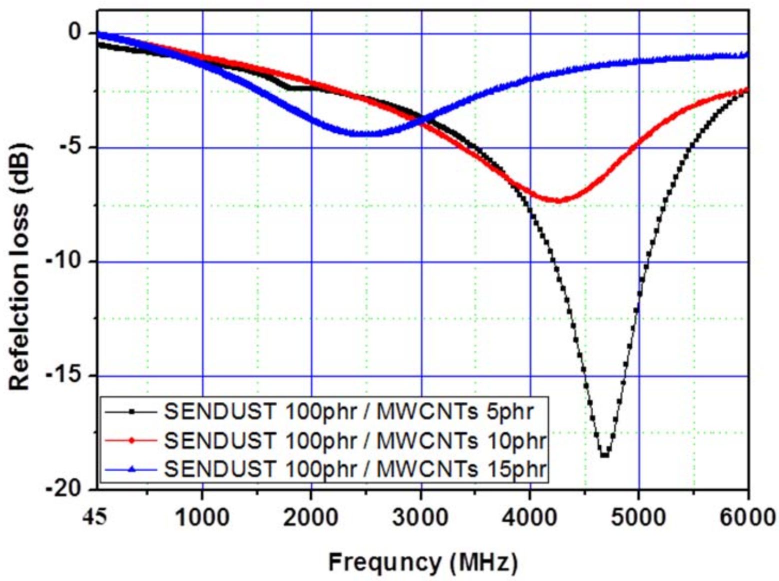

Figure. III-13. Reflection loss for different ratio of MWCNTs concentration versus frequency with fixed ratio of Sendust flake

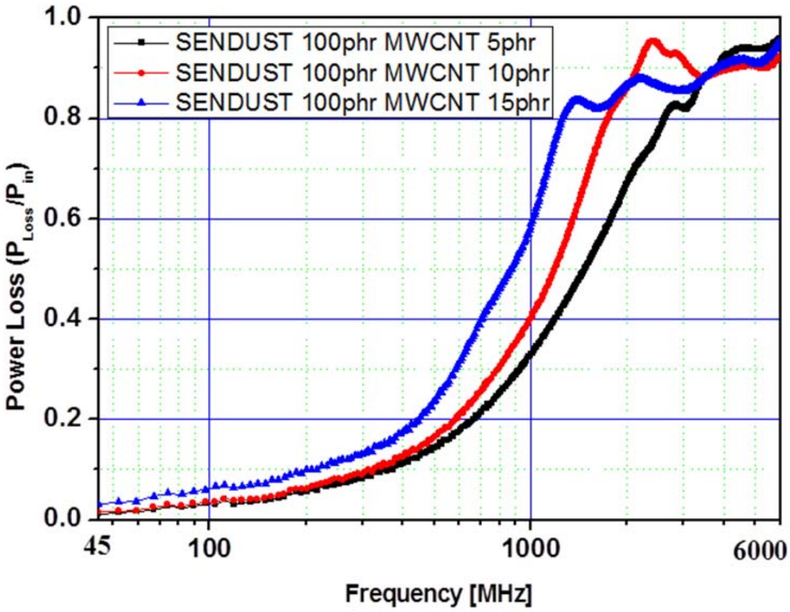

Figure. III-14. Power loss for different ratio of MWCNTs concentration versus frequency with fixed ratio of Sendust flake

Table III-1. Power loss and density of magnetic, dielectric and hybrid absorbers

	SENDUST0 flake 400 phr	MWCNTs 15 phr	SENDUST 100 phr MWCNTs 15 phr
Density	4.65 g/cm^3	1.05 g/cm^3	1.75 g/cm^3
Power loss at 1 GHz	0.5	0.3	0.6

Chapter IV

Conclusion

This dissertation describes the process of developing a hybrid system that has high level of permeability and permittivity by compounding magnetic absorber and dielectric absorber.

In case of magnetic absorber, properties of electromagnetic were significantly influenced by the shape and the weight ratio of Sendust powder. Through the observation, two methods were found to increase both the real and imaginary part of complex permeability: first, by transforming a bulk type Sendust into a flake type, and second by increasing the content of filler. The shape of a Sendust was an important factor to increase permeability because it contributes to increase magnetic shape anisotropy and reduce eddy current loss. The study found out that as the amount of filler in the composite increases, it also affects the intensity to increases making the reflection loss value reaches its peak in low frequency range. As if filler shape and weight ratio of filler influences the permeability of a composite, these two factors were also the two major conditions that greatly influence power loss. That is to say, changing the Sendust shape into a flake type and mixing more Sendust filler into the composite contributed to increase power loss value. The increases in power loss values are attributable to the increases in the permeability of composites.

As for dielectric absorber made by mixing MWCNTs filler, properties of electromagnetic changed in accordance with the amount of filler. Both real part and imaginary part of complex permittivity increased as the content of filler increased. Increase of interfacial electric polarization between polymer and MWCNTs can be explained as the main reason to cause such changes. The maximum value of reflection loss was observed in low frequency as the content of filler in the composite increases. Through the experiment, we found out that the weight ratio of filler had core influence in changing the value of power loss. This result can be explained as the amount of filler mixed in the composite increases the conductivity increases.

The permeability of a Sendust/MWCNTs/polymer composite was able to maintain the same value because the amount of Sendust filler was fixed to 100phr. In this way we could focus on observing the permittivity of the composite by adjusting the amount of MWCNTs. And as a result we found out that as more MWCNTs was mixed the permittivity also increased. By applying the impedance matching theory, we were able to find the optimum promotion of complex permeability to complex permittivity. By analyzing the data we got from the measurement we found out that the reflection loss intensity reached the maximum value when 5 phr of MWCNTs was mixed with 100 phr of Sendust. In other word, we find the ideal condition to make an effective absorber using less filler. Through the process of measuring power loss, we found that as more MWCNTs were used the conductivity of an absorber increased. That is the amount of filler was proportionate to the level of conductivity. As a conclusion the Sendus/MWCNTs/polymer had lighter density than using only Sendust and had better electromagnetic wave absorption ability than using only MWCNTs.

References

[1] D. Park, Y. Lee, S. Park, C. Lee, S. Kim, W. Kim, *Macromol Res*. 2013, 21, 905-910.

[2] N. Joseph, S. Singh, R. Sirugudu, V. Murhy, S. Ananthakumar, M. Sebastian, *Maters. Res. Bull.* 2013, 48, 1681–1687.

[3] D. Adang, C, Remacle, A. Vorst, *IEEE Trans. Microw. Theory Tech*., 1998, 57, 2488-2497.

[4] Z. Chen, C. Xu, C. Ma, W. Ren, H. Cheng, *Adv. Mater*. 2013, 25, 1296–1300.

[5] X. Gong, I. josifovic, J. Felrreira, *IEEE T. Power Electr*., 2013, 28, 3138-3146.

[6] O. Akman, H. Kavas, A. Baykal, M. Toprak, A. Coruh, B. Aktas *J. Mag. Mag. Mat.* 2013, 327, 151–158.

[7] J. Liu, M. Itoh, K. Machida, *Appl. Phys. Lett*., 2003, 83, 4017-4022.

[8] H. Jia, W. LI, Y. Haojie, *J. Mater. Sci*., 2009, 44, 3917-3927.

[9] B. Wen, M. Cao, M. Lu, W. Cao, H. Shi, J. Liu, X. Wang, H. Jin, X. Fang, W. Wang, J. Yuan, *Adv. Mater*. 2014, 26, 3484–3489.

[10] Olivier Gallot-Lavallee, eBook, ISTE Ltd/John Wiley and Sons Inc, Hoboken, NJ, 2013.

[11] R. Yang, W. Kuo, H. Lai, *J. APPL. POLYM. SCI*. 2014, 131, 40963.

[12] K. Moon, H. Choi, A. Lee, K. Cho, H Yoon, K. Suh, *J. Appl. Polym. Sci.* 2000, 77, 1294-1302.

[13] Z. Fan, G. Luo, Z. Zhang, L. Zhou, F. Wei, *Mat. Sci. Eng. B*, 2006, 132, 85-89.

[14] E.T. Thostenson, Z. Ren, T.W. Chou. *Compos. Sci. Technol*. 2001, 61, 1899-1912.

[15] Nicola A. Spaldin, 2nd ed., Cambridge University Press, New York, 2011.

[16] H. S. Cho, A. S. Kim, S. M. Kim, J. Namgung, M. C. Kim, G. A. Lee *Phys. Stat. Sol. A*, 2004, 201, 1942-1945.

[17] X Wang, R Gonga, P Li, L Liu, W Cheng, Mat. Sci. Eng. A, 2007, 466, 178-182.

[18] A. García-Arribas, E. Fernández, A. Svalov, G. Kurlyandskaya, A. Barrainkua, D. Navas, J. Barandiaran, *Eur. Phys. J. B*. 2013. 86. 136-142.

[19] E. Michielssen, J. Sajer, S. Ranjithan, R. Mittra, *IEEE Trans. Microwave Theory Tech*., 1993, 41, 1024-1030.

[20] S. Kim, Y. Yoon, S. Lee, G. Kim, Y. Kim, Y. Chun, K. Lee, *J. Mag. Mag. Mat*., 2007, 316, 472-474.

[21] K. Sakai, N. Asano, Y. Wada, S. Yoshikado, *J. Eur. Ceram. Soc*., 2010, 30, 347-353.

[22] J. Gogoi, N. Bhattacharyya, S. Bhattacharyya, *Composites: Park B*, 2014, 58, 518-523.

[23] S. Kim, S. Kim, Y. Yoon, K. Lee, *J. App. Phys*., 2005, 97, 10F905.

[24] Y. Chen, M. Cao, T. Wang, Q. Wan, *Appl. Phys. Lett.,* 2004, 84, 3367-3370.

[25] S. Abbas, M. Chadra, A. Verma, R. Chatterjee, T. Goel, *Composites: Part A,* 2006, 37, 2148-2154.

[26] K. Park, S. Lee, C. Kim, J. Han, *Compos. Sci. Technol*., 2006, 66, 576-584.

[27] H. M. Musal, H. T. Hanan, *IEEE Trans. Magn.,* 1989, 25, 3851-3853.

[28] M. H. Al-Saleh, U. Sundararaj, *Carbon*, 2009, 47, 1738-1746.

[29] Y. Feng, T. Qiu, C. Shen, *J. Mag. Mag. Mat*., 2007, 418, 8-13.

국문요약

본 논문에서는 높은 투자율과 유전율을 모두 지니는 전자기파 흡수체에 대해 연구하였다. 두가지 특성을 모두 가지는 하이브리드 흡수체를 만들기 위해 자성 흡수체와 유전성 흡수체를 각각 용융 혼합법과 용액 혼합법으로 제조하여 그 전자기적 특성을 먼저 확인하였다. 모든 샘플의 전자기적 특성은 벡터 네트워크 분석기를 이용해 측정하였다.

자성체인 센더스트와 폴리머를 혼합하여 만든 흡수체의 경우 센더스트 함량의 증가와, 판상화를 통해 복소수 투자율과 전자파 흡수능이 크게 증가 하는 것을 확인 할 수 있었다. 전도체인 다중벽 탄소나노튜브와 폴리머를 혼합하여 만든 유전성 흡수체의 경우에도 충전제 함량 증가에 따라 복소수 유전율과 전자파 흡수능이 크게 증가 하는 것을 확인 하였다.

하이브리드 전자파 흡수체의 경우 복소수 투자율은 고정하기 위해 센더스트 양은 100phr로 고정하고, 다중벽 탄소나노튜브의 함량만 5, 10, 15 phr로 조절하였다. 충전제의 증가에 따라 복소수 유전율과 전력손실은 증가하였지만 반사손실은 감소하는 결과가 나왔다.

결과적으로 센더스트 100phr, 다중벽 탄소나노튜브 5phr일 때 반사손실이 4.6GHz에서 16dB인 가볍고 우수한 전자파 흡수체를 만들 수 있다.

주요어: 전자파 흡수, 센더스트, 다중벽 탄소나노튜브, 전자기적 특성
학 번 : 2011-20642