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# **Carbon Nanotubes Composites for Microwave Applications**

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# Carbon Nanotubes Composites for Microwave Applications

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## ABSTRACT OF THESIS

Carbon nanotubes have become a focus of study due to the great applications you can have and its excellent properties. In this thesis the compounds formed by a host and a percentage of carbon nanotubes are modelled. The models used are the Debye model, the Maxwell Garnett model and McLachlan model. These models have been implemented in several scripts with the mathematical program Matlab. The purpose is to solve or approximate the unknown parameters of these models of a fast and accurate way because solving these models manually can become very complicated. On the other hand this thesis explains how to obtain statistical calculations with the program Graphpad Prism.

**KEYWORDS:** Carbon nanotubes (CNTs), multiwalled carbon nanotubes (MWCNTs), Debye, Maxwell Garnet (MG), Modelling.

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## INTRODUCTION

Carbon nanotubes have become the last two decades in elements of great interest for both theoretical research and technological developments. Carbon nanotubes are an allotrope of carbon (i.e., having different chemical structures), like diamond, graphite and fullerenes. The Japanese physicist Sumio Iijima discovered them in 1991 [a]. Since the first observation, they have generated great expectations thanks to their extraordinary mechanical, thermal and electrical properties [b]. They are 200 times stronger than steel, the best known thermal conductors and they can carry electric currents one hundred times larger than the copper. Thus, they can be considered excellent candidates for a wide range of technological applications in different areas of impact, as flexible electronic sensors, biomedicine, construction and automotive. [c]

With these carbon nanostructures is possible create nanomaterials based polymer matrices reinforced with carbon nanotubos that have proven to be of great interest. With this type of nanomaterial have improved mechanical, electrical and optical properties, according of those requirements in the industry today, there have been several studies regarding the generation of these nanomaterials, but much remains to be studied as the effects of the concentration of the nanostructures and the size and distribution of the polymer particles.

From a theoretical point of view, their study requires a model that best describes their physical properties. In this thesis, several models that can be used to study the physical properties of the nanocomposites are described and implemented with Matbal scripts.

The objective of this thesis is to model equations that describe the behavior of a compound that contains inclusions of carbon nanotubes. To model this behavior some equations that are too complicated to solve manually are presented so it is necessary to find a suitable mathematical method and solve it computationally in an effective manner.



The thesis is divided into sorted chapters that provide the information necessary to the resolution of our problem at the end of the thesis. Starting with the chapter 2 that explains some basic knowledge about carbon nanotubes and applications that have in the existing industry.

The chapter 3 details the models that help us to study the host or composite. The permittivity measurements from a host or composite were obtained with measuring instruments. For the host, the Debye model allows us to obtain a more linear and less noisy curve from the measured permittivity host. In the case of composite in which there is a host and a certain percentage of inclusions MWCNTs (Multiwalled nanotubes) must be used Maxwell Garnett model or McLachlan model depending if the percentage of inclusions is above or below the percolation threshold. Specifically, for the Maxwell Garnett model there are different equations depending on the type of inclusions (cylindrical, ellipsoidal, spherical...). This will allow us to know the permittivity of the inclusions if the permittivity of the compound and the host are known.

The chapter 4 shows the utilization of a statistical calculation program called GraphPad Prism. Graphics and advanced statistics can be obtained from the measurements of the permittivity of the material.

In the last chapter of this thesis the functioning of each script is explained, and results from many runs of the scripts are shown to demonstrate the correct operation of each script with different samples of hosts, inclusions and composites.

To better understand this thesis where the problem is solved through mathematical environment Matlab, where the necessary scripts were created to model these equations, it is advisable to examine the attached scripts while a reading of the thesis is done to understand the equivalence between the explanation and the commands used.

## 1. FUNDAMENTAL KNOWLEDGE

To better understand the goals of this thesis is necessary to have some basic knowledge about carbon nanotubes composites. This information can be found in several articles and books that are detailed throughout the thesis as references.

### 1.1. CARBON NANOTUBES

Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties. Carbon nanotubes are added as conductive fillers in the electrically conductive adhesive (ECA) allowing reach the percolation threshold with small volume fraction loading compared to silver filled adhesives. They are among the stiffest and strongest fibers known, and have remarkable electronic properties. They are chemically stable, mechanically very strong and conduct electricity [3].

There are two main types of nanotubes [3], single walled nanotubes (SWNTs) that are one layer of carbon hexagons and multiwalled nanotubes (MWCNTs) wherein one single tube is encased inside several larger tubes (See figure 1)

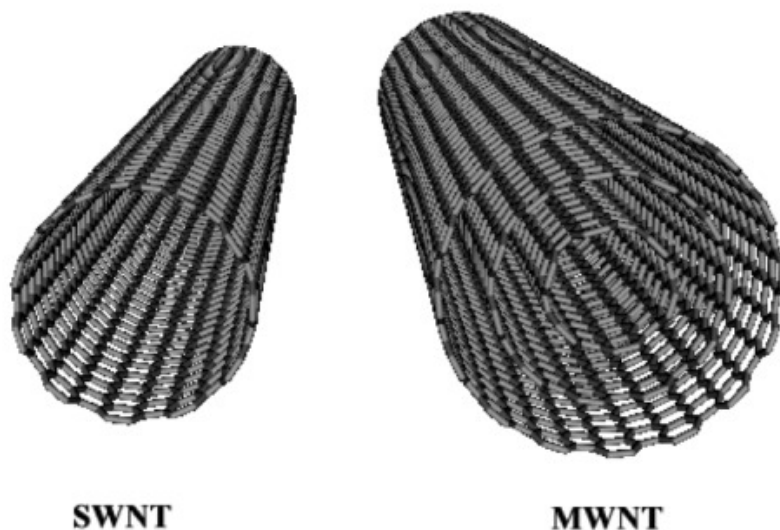


Figure B1. Single Wall (left panel) and multiwall (right panel) carbon nanotubes from [3]

Single walled nanotubes (SWNT) are the mostly likely candidate for miniaturizing electronics past the micro electromechanical scale that is currently the basis of modern electronics but SWNT are still very expensive to produce [3].

MWCNT are electrically conductive independent of synthesis method and have extremely high strength to weight ratio offering the potential to improve the stiffness of the polymer matrix. The unique mechanical and electronic properties of multiwall nanotubes are proving to be a rich source of new physics and could also lead to new applications in materials and devices [3].

Multiwall carbon nanotubes (MWCNT) are metallic, whereas single wall carbon nanotubes (SWCNT) may be metallic or semiconducting depending on the chirality of the graphene walls.

## **1.2. APPLICATIONS**

These composites have applications that offer greater advantages and better characteristics than other materials. This section describes several applications of these composites.

### **1.2.1. CONDUCTIVE ADHESIVES**

There are alternatives to solder technology like electrically conductive adhesive (ECA) technology that consist of a polymer binder and conductive filler [3]. This polymer is used as insulator in the technology industry because it has very good dielectric properties. It can be thermoplastic or thermosetting. The thermoplastic have a long linear molecular structure allowing heating up to the melting point without losing the intrinsic characteristics and its has a unlimited shelf life at room temperature. One disadvantage of the thermoplastic adhesives is that they have a longer curing time compared with thermosetting adhesives. The main classifications of ECAs are isotropic conductive adhesive (ICA) and anisotropic conductive adhesive (ACA).

### 1.2.1.1. ISOTROPIC CONDUCTIVE ADHESIVE (ICA)

The most common is athermosetting resin and it consists of polymer resin such as epoxy and conductive fillers particles [3]. Generally, conductive fillers are silver flakes because of their high conductivity, simple fabrication process and maximum contact with flakes. There are other conductive filler as nickel and copper but they get worse under high temperature and conditions.

The conductive fillers in the ICA composite make contact with other and form a conductive path to provide electrical conductivity. To ensure good electrical conductivity the volume fraction loading of the conductive filler particles must be higher than the percolation threshold. The percolation threshold determines if the adhesive is conductive or insulating if the amount of conductive filler is larger or smaller than the threshold. The typical volume fraction of conductive fillers is about 25% to 30% volume fraction to overcome the percolation threshold and ensure electrical conductivity [3]. For silver the weight percentage is 78% to 82% [3]. However for less than 1% volume fraction of carbon black in the resin can cause electrical conduction. The largest reduction in volume resistivity is observed at 0.25 wt.%, which means the percolation threshold is less than 0.25 wt.% [3].

There are two conductive pathways in ICA [3]. One is caused by particle-to-particle contact within the polymer matrix (Figure 2). The other is percolation, the electron transport brought about by quantum-mechanical electron tunnelling between particles close enough to allow dielectric breakdown of the matrix (Figure 3).

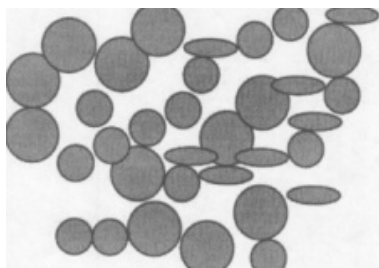


Figure B2. Particle-to-particle from [3]

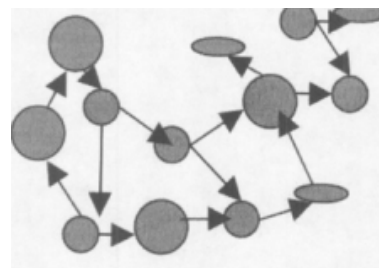


Figure B3. Tunnelling from [3]

#### **1.2.1.2. ANISOTROPIC CONDUCTIVE ADHESIVE (ACA)**

These adhesives are pastes or films of thermoplastics and the volume fraction of filler is below the percolation threshold, close to 0.5% to 5% [3]. Thus, there is no continuous electrically conductive path in ACAs before bonding. The component terminations are pressed against the corresponding pads on the substrate in order to compress the conductive particles trapped between the component terminations and substrate pads in order to form the electrically conductive path during bonding. After bonding the ACAs become electrically conductive in one direction and remain insulating the other direction.

## 2. MODELLING OF COMPOSITES WITH AN ISOTROPIC DIELECTRIC BASE

The percolation threshold shows the limit for composite with concentration of conducting inclusion to know if the composite is conductive or insulating. If the concentration of conducting inclusion is below percolation threshold the composite is insulating and if it is above percolation threshold is conductive composite. In order to model both cases there are different mathematical models. When the composite is below the percolation threshold, the Maxwell Garnett model and Bruggeman model can be applied while above the percolation threshold is valid the McLachlan's equation.

### 2.1. DEBYE MODEL

Before discussing these models is important to talk about Debye model to calculate the effective permittivity of the constituents (host or inclusion). The result of this equation is the permittivity of the constituent, so it is necessary for models that have spoken at the beginning of the chapter.

The Debye model for a dispersive dielectric material [2] [4][5] is:

$$\epsilon_D = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)}{1 + j\omega\tau} \quad (1a)$$

And a conductive inclusion material can be described with the Debye model [2][5]:

$$\epsilon_D = \epsilon_\infty + \frac{\sigma}{j\omega\epsilon_0} \quad (1b)$$

Where:

$\epsilon_s$  and  $\epsilon_\infty$ : Static and "optic" limit permittivity values

$\tau$  : Relaxation time

$\omega$  : Angular frequency

$\sigma$  : Material conductivity

$\epsilon_0$  : Permittivity in free space

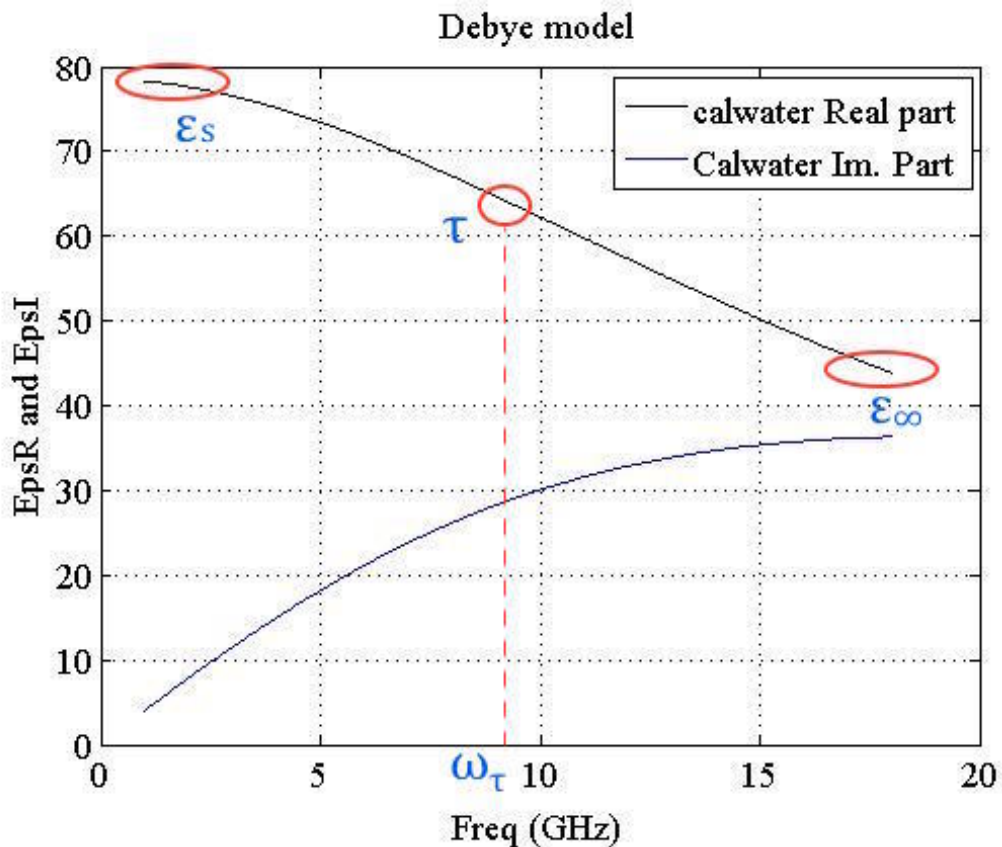


Figure B4. Description of the curve Debye model

To better understand the Debye model each parameter must be explained. The  $\epsilon_s$  term is the value that tends permittivity when the frequencies are close to 0. The term  $\epsilon_\infty$  is the value that has the permittivity when it tends to high frequencies. In the frequency where the curve has a higher derivative is the relaxation frequency and  $\tau$  is the inverse of this frequency.

Typically know the effective permittivity of the material through the measuring equipment in a frequency range. So it is necessary to estimate the values to find the parameters of the curve and have a minor mistake in the following models.

## 2.2. MAXWELL GARNETT (MG) MODEL

As was said at the beginning of the chapter, there are different models depending on whether the inclusion concentration is above or below the percolation threshold. When the concentration of conducting inclusion will be below

percolation threshold, the Maxwell Garnett (MG) model [1][2][4][5] is the simplest and the most widely used for description of composite media at comparatively low concentrations of inclusions. One important property of the MG formulation is its linearity with respect to frequency for a multiphase mixture.

To use the MG formulation several conditions are assumed [1]:

- The mixture is electro-dynamically isotropic
- The mixture is linear (none of constitutive parameters depends on the intensity of electromagnetic field)
- The characteristic size of inclusion is small compared to the wavelength in the effective medium
- The concentration of conducting inclusions should be lower than the percolation threshold.

The Maxwell Garnett equation [1] for multiphase mixtures with randomly oriented ellipsoidal inclusions:

$$\varepsilon_{eff} = \varepsilon_b + \frac{\frac{1}{3} \sum_{i=1}^n v_i (\varepsilon_i - \varepsilon_b) \sum_{k=1}^3 \frac{\varepsilon_b}{\varepsilon_b + N_{ik} (\varepsilon_i - \varepsilon_b)}}{1 - \frac{1}{3} \sum_{i=1}^n v_i (\varepsilon_i - \varepsilon_b) \sum_{k=1}^3 \frac{N_{ik}}{\varepsilon_b + N_{ik} (\varepsilon_i - \varepsilon_b)}} \quad (2)$$

Where:

$\varepsilon_b$ : relative permittivity of a bases dielectric

$\varepsilon_i$ : relative permittivity of the i-th type of inclusion

$N_{ik}$ : depolarization correspond to x, y and z Cartesians coordinates.

$V_i$ : fractional volume of the inclusion in the mixture

The  $N_{ik}$  are the depolarization factors of the i-th sort of inclusions and the index  $k=1, 2$  and  $3$  correspond to X, Y, and Z Cartesians coordinates.



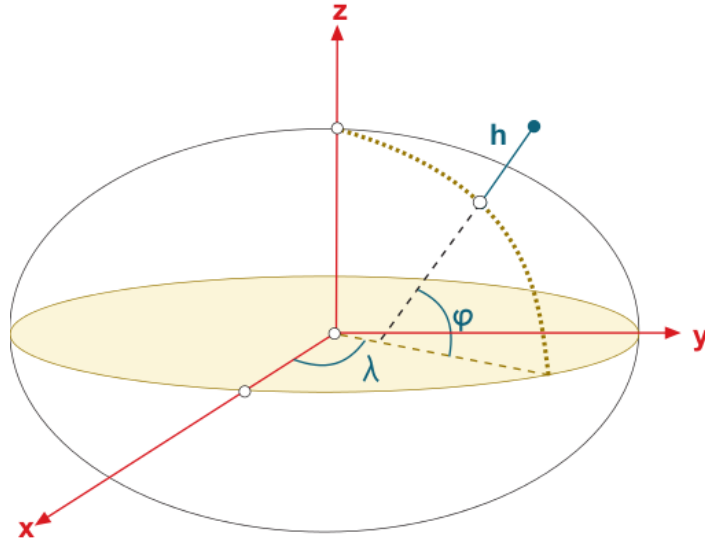


Figure B5. Cartesian coordinates of ellipsoid

Two depolarization factors  $N_{ik}$  of ellipsoidal inclusions [1] are close to 1/2, and the third can be calculated from physical measures of diameter  $d$  and length  $l$  as:

$$N \approx \left(\frac{d}{l}\right)^2 \ln\left(\frac{l}{d}\right) \quad (3)$$

The Maxwell Garnett mixing rule is applicable when the concentration of the conducting particles in the mixture is below the percolation threshold  $p_c \approx 4.5/a \ll 1$ , where  $a$  is an aspect ratio for the inclusions.

Although for our study, the cylindrical inclusions are more remarkable than ellipsoidal. This implies another Maxwell Garnett equation [5] with cylindrical inclusion:

$$\varepsilon_{eff} = \varepsilon_b + \frac{\left(\frac{1}{3}\right)V(\varepsilon_i - \varepsilon_b) \sum_{k=1}^3 \left(\frac{\varepsilon_b}{\varepsilon_b} + N_{ik}(\varepsilon_i - \varepsilon_b)\right)}{1 - \left(\frac{1}{3}\right)V(\varepsilon_i - \varepsilon_b) \sum_{k=1}^3 (N_{ik}(\varepsilon_i - \varepsilon_b))} \quad (4)$$

Where:

$\varepsilon_b$ : relative permittivity of a bases dielectric

$\varepsilon_i$ : relative permittivity of inclusion

$N_{ik}$ : depolarization correspond to x, y and z Cartesians coordinates.

V: fractional volume of the inclusion in the mixture

Just as for the previous case, the index  $k=1, 2$  and  $3$  of  $N_{ik}$  correspond to X, Y, and Z Cartesians coordinates.

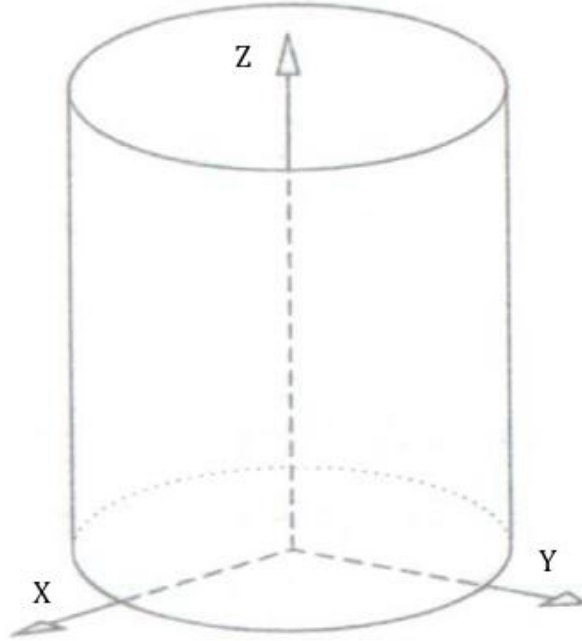


Figure B6. Cartesian coordinates of cylinder

Depolarization factors  $N_{ik}$  of elongated cylindrical inclusions [5], in the assumption that their diameter  $d$  is much less than its length  $l$ , are calculated through their aspect ratio  $a = l/d$  as:

$$N_{i3} = \frac{1}{2} \frac{\ln \left( a + \frac{\sqrt{a^2 - 1}}{a} - \sqrt{a^2 - 1} \right) a - 2\sqrt{a^2 - 1}}{(\sqrt{a^2 - 1})^3} \quad (5a)$$

$$N_{i1} = N_{i2} = \frac{1 - N_{i3}}{2} \quad (5b)$$

These MG equations allow express the permittivities of the base and inclusions as complex functions of frequency [1]:

$$\boldsymbol{\varepsilon}_b(\boldsymbol{j}\boldsymbol{\omega}) = \boldsymbol{\varepsilon}_{\infty b} + \boldsymbol{\chi}_b(\boldsymbol{j}\boldsymbol{\omega}); \quad (6a)$$

$$\boldsymbol{\varepsilon}_i(\boldsymbol{j}\boldsymbol{\omega}) = \boldsymbol{\varepsilon}_{\infty i} + \boldsymbol{\chi}_i(\boldsymbol{j}\boldsymbol{\omega}); \quad (6b)$$

Where:

$\boldsymbol{\varepsilon}_{\infty b,i}$  : High-frequency permittivity values for the base material and for inclusion of the i-th type.

$\boldsymbol{\chi}_{b,i}(\boldsymbol{j}\boldsymbol{\omega})$  : dielectric susceptibility functions.

By this and because the MG formula is linear, the resultant effective permittivity of the mixture can be also represented through effective high-frequency permittivity and susceptibility function [1]:

$$\boldsymbol{\varepsilon}_{eff}(\boldsymbol{j}\boldsymbol{\omega}) = \boldsymbol{\varepsilon}_{\infty eff} + \boldsymbol{\chi}_{eff}(\boldsymbol{j}\boldsymbol{\omega}) \quad (7)$$

This means that mathematical modelling bases on equation 2 and 4 will provide an efficient tool for the analysis of the frequency behaviour of a composite depending on the physical properties and geometry of its constituents.

A Debye or Lorentzian dependence can approximate the effective susceptibility function of mixture [1]:

$$\boldsymbol{\chi}_{eff}(\boldsymbol{j}\boldsymbol{\omega}) = \sum_{k=1}^N \frac{A_k}{\mathbf{1} + \boldsymbol{j}\boldsymbol{\omega}\boldsymbol{\tau}_k} \quad (8)$$

And if the inclusions are conducting particles (metallic) their frequency characteristic in term of relative permittivity [1] is

$$\boldsymbol{\varepsilon}_i(\boldsymbol{j}\boldsymbol{\omega}) = \boldsymbol{\varepsilon}' - \boldsymbol{j}\boldsymbol{\varepsilon}'' = \boldsymbol{\varepsilon}' - \boldsymbol{j} \frac{\boldsymbol{\sigma}}{\boldsymbol{\omega}\boldsymbol{\varepsilon}_0} \quad (9)$$

### 2.3. BRUGGEMAN MODEL

Another option, known as the Bruggeman model, treats the binary mixture as being composed of repeated units cells composed of the matrix phase with spherical inclusions in the center. The equation model [6] to calculate the effective dielectric constant is:

$$V_b \left( \frac{\epsilon_b - \epsilon_{eff}}{\epsilon_b - 2\epsilon_{eff}} \right) + V_i \left( \frac{\epsilon_i - \epsilon_{eff}}{\epsilon_i - 2\epsilon_{eff}} \right) = 0 \quad (10)$$

Where:

$\epsilon_b$ : relative permittivity of a bases dielectric

$\epsilon_i$ : relative permittivity of inclusion

$V_b, V_i$ : fractional volume of the constituents in the mixture

#### 2.3.1. COMPARISON WITH MAXWELL GARNETT

To see an example this method is compared with Maxwell Garnett for a blend of inorganic spheres with  $\epsilon_2 = 1,000$  dispersed in a polymer matrix with  $\epsilon_1 = 2.3$  [6]. The effective dielectric constant predicted by the Bruggeman equation increases sharply for filler volume fractions above 20% and can be very high for ceramic particle loadings higher than 50% by volume.

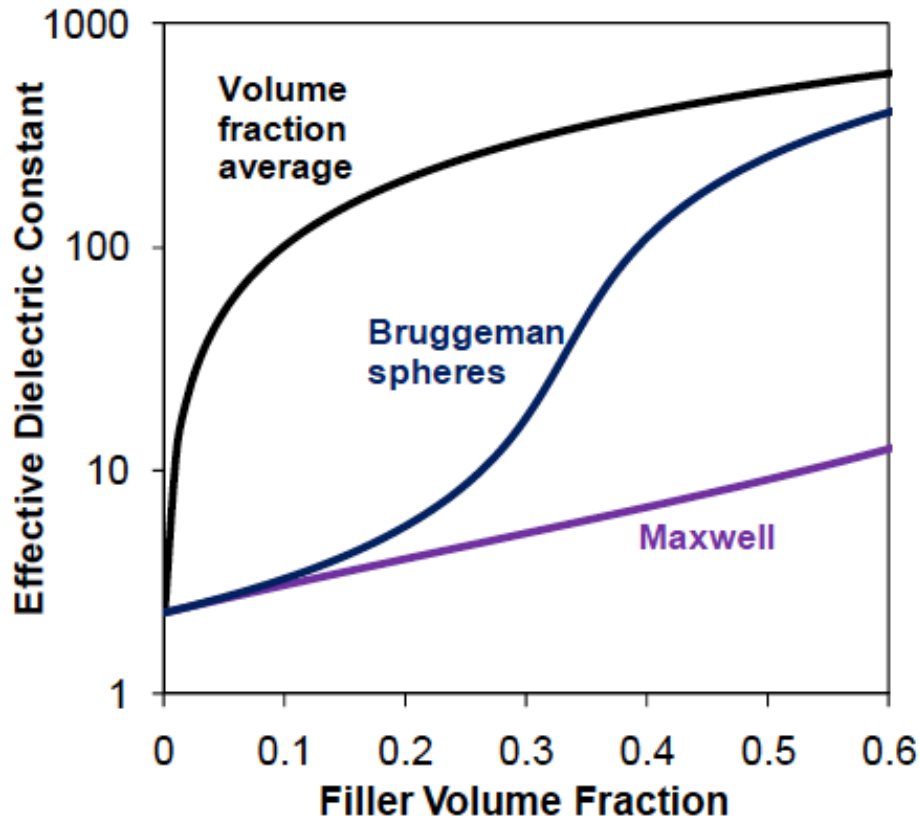


Figure B7. The dielectric constant predicted by Maxwell and Bruggeman

The effective-medium theory (EMT) proposed that when the particle size of the ceramic filler is small compared to that of the composite, the dielectric permittivity of the composite could be calculated in terms of an effective medium whose dielectric permittivity can be obtained by averaging over the dielectric permittivity of the two constituents. They introduced an arbitrary fitting parameter in their model to account for the irregular morphology of the ceramic particles.

Myroshnychenko et al. used the finite element modelling method for prediction of the complex effective permittivity of two-phase random statistically isotropic heterostructures [6]. They assumed the composite to be a distribution of one dielectric phase randomly dispersed in a continuous matrix of another dielectric phase. The numerical values for the effective complex permittivity were found to lie between the curves corresponding to the Maxwell and Bruggeman equations.

## 2.4. MCLACHLAN'S MODEL

Otherwise, when the concentration of the conducting particles in the mixture is above the percolation threshold, the McLachlan's equation [2] should be used. This equation is the following:

$$\frac{(1 - v_i)(\epsilon_b^{1/s} - \epsilon_{eff}^{1/s})}{\epsilon_b^{1/s} + \left(\frac{1 - p_c}{p_c}\right)\epsilon_{eff}^{1/s}} + \frac{v_i(\epsilon_i^{1/t} - \epsilon_{eff}^{1/t})}{\epsilon_i^{1/t} + \left(\frac{1 - p_c}{p_c}\right)\epsilon_{eff}^{1/t}} = 0 \quad (11)$$

Where:

$\epsilon_b$ : relative permittivity of a bases dielectric

$\epsilon_i$ : relative permittivity of inclusion

$V_i$ : fractional volume of the inclusion in the mixture

$s, t$ : process exponents

$p_c$ : percolation threshold ( $p_c \propto 1/a$ )

The ratio of the exponents  $s/t$  indicates the symmetry of the real and imaginary part of the permittivity around the percolation threshold  $p_c$ . The percolations threshold for long fibers with an aspect ratio  $a=l/d \gg 1$  where  $l$  is the length of fibers and  $d$  is de diameter, is inverse proportional to the aspect ratio of inclusion  $p_c \propto 1/a$  [2]. The measurement results showed on carbon-fiber-filler composites the similar behaviour  $p_c \approx 1/a$ .

### 3. GRAPHPAD PRISM

To modelling additional programs are also used to obtain more data and statistical calculations from the samples of the relative permittivity of the material. In this case the program, which has been used, is GraphPad Prism. This program is not free, but you can try it for 30 days. As this project does not focus on the use of this program, this chapter only talks about the most basic and important aspects for our study during the day trial. GraphPad Prism combines scientific graphing in 2D, comprehensive curve fitting (nonlinear regression), understandable statistics, and data organization.

#### 3.1. PREVIOUS SETTINGS

GraphPad Prism offers two ways to enter data. One way is to enter the data manually in the program table. This method is useful when there are not many data but when you have a large amount of data is very laborious. Furthermore the program can open files with the extension .PZF, .PZFX .PZM .PZT and .XML. These extensions are not common and the Matlab program does not provide data on these extensions. Therefore, there is another way to enter data. There is an option called "import data" that works quite well with .txt files, so this is the option chosen to enter the data, but to have the data in a text file from Matlab must create a script you convert us these data to .txt and place each vector data as columns in the file.

*Conversion .m to .txt – Script A1 – conversionToGraphpadPrismE16.m*

The operation of this script is simple; loads the data obtained from the measurements of the materials and store this data in a matrix by placing each vector as a column. After proper commands are used to store the data in those variables in a text file. Two output files are obtained.

*epsRtoGraphpad.txt*

This file contain the real data of permittivity of the loaded measures

*epsItoGraphpad.txt*

This file contain the imaginary data of permittivity of the loaded measures

Once these files are created, GraphPad Prism can import these data.

### **3.2. EXAMPLE OF UTILIZATION**

To see how it works this program, nine measures of different samples are imported, where three of these samples will have an inclusion rate of 1wt.%, other three will have a rate of 3wt.% and the other three will have a rate of 5wt.%.

The samples used in this example are shown in the graphic with the mean values depending on the frequency in the figure 8 and 9. These data will introduce a program for our example.



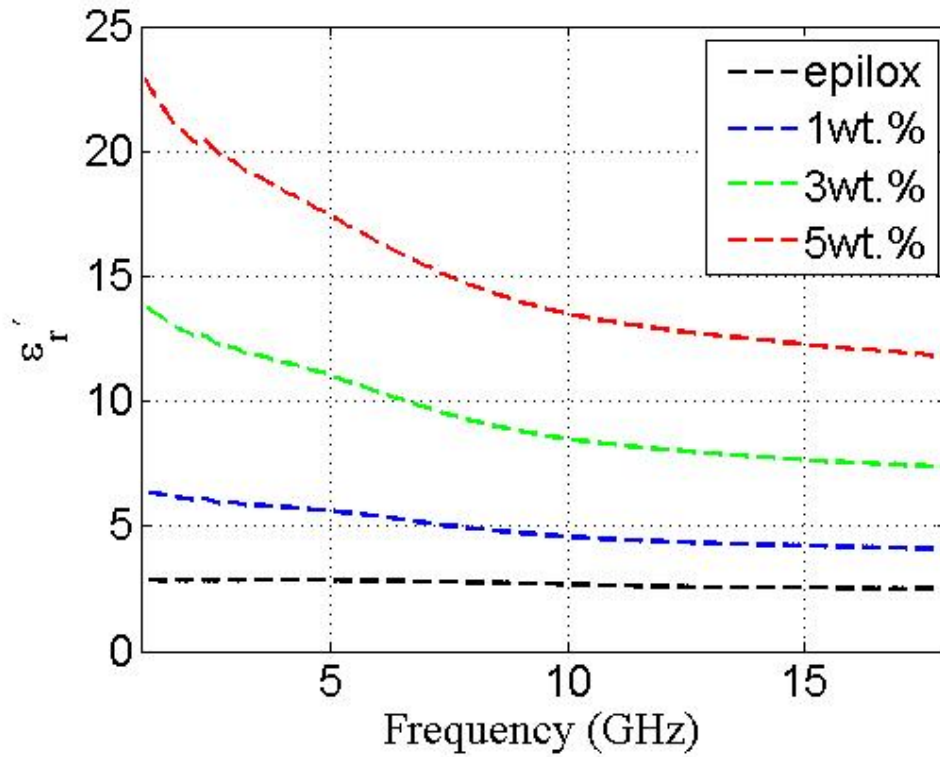


Figure B8. Real part relative permittivity with different wt.% - Example

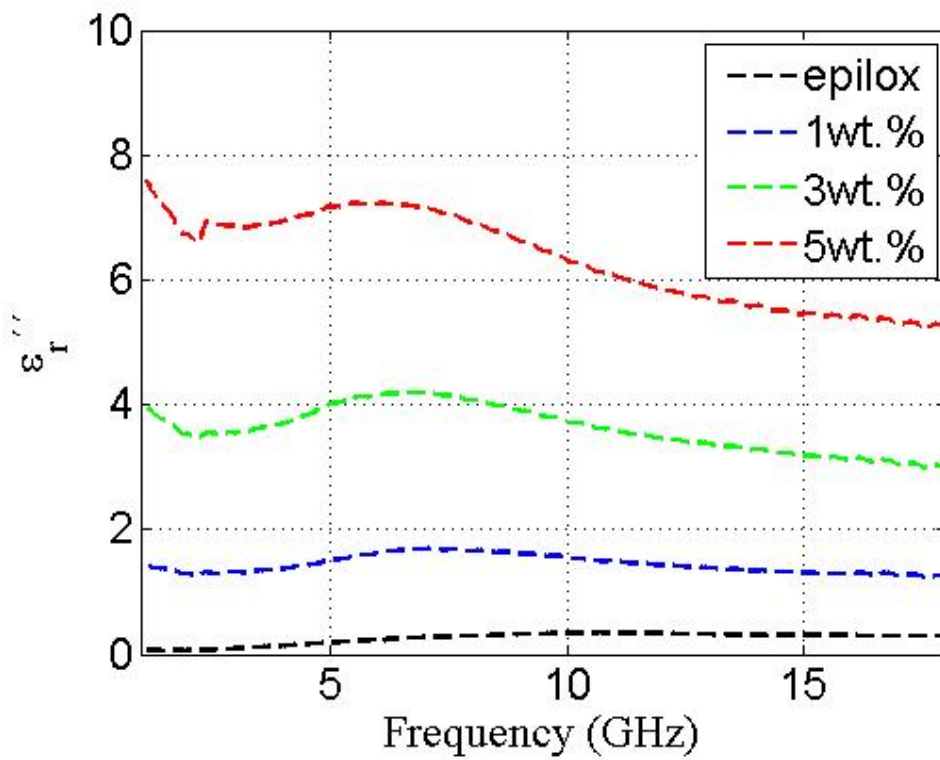


Figure B9. Im. part relative permittivity with different wt.% - Example

When the program is open, the first option the first option should be chosen is how the data is realed, if individually with the XY axis, columns, column groups, contingency, survival or parts of whole. Also an existing project can be loaded.

For this project the most important is the grouping of columns, also called TWO-WAY ANOVA. As for this example, there are 3 samples for each group, so the 3-column option must be chosen.

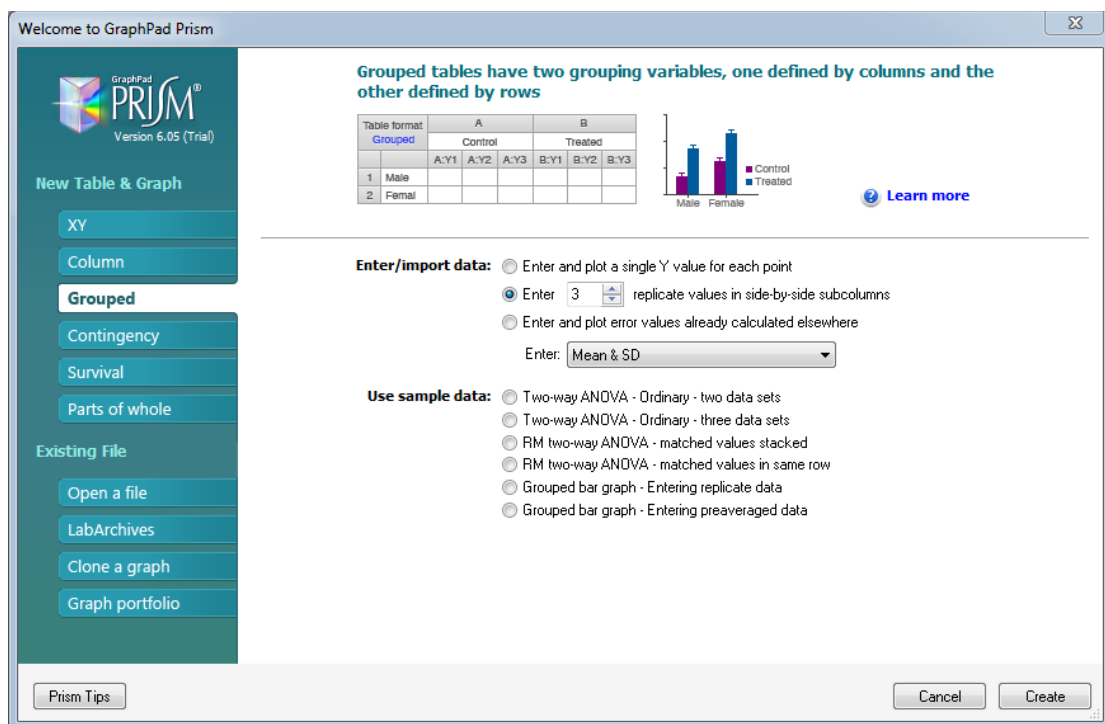


Figure B10. Choose graph – Example

The aspect of the program is similar to Microsoft Excel program. As the program is configured with 3 column groups, The screen is divided into 3 groups of columns.

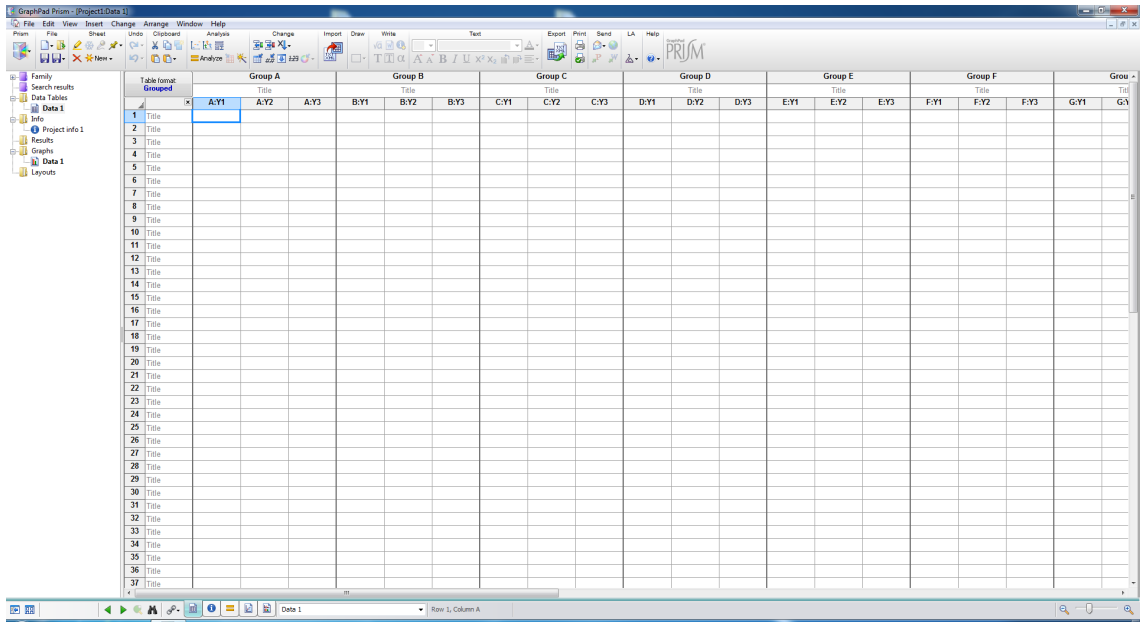


Figure B11. Principal view Graphpad Prism– Example

The first thing to do is import the data contained into a text file selecting "insert" and then choose "import data". The text file with the data must be chosen and the program shows some options to distribute the data imported into the cells. Thus the data appear in the text file in the program.

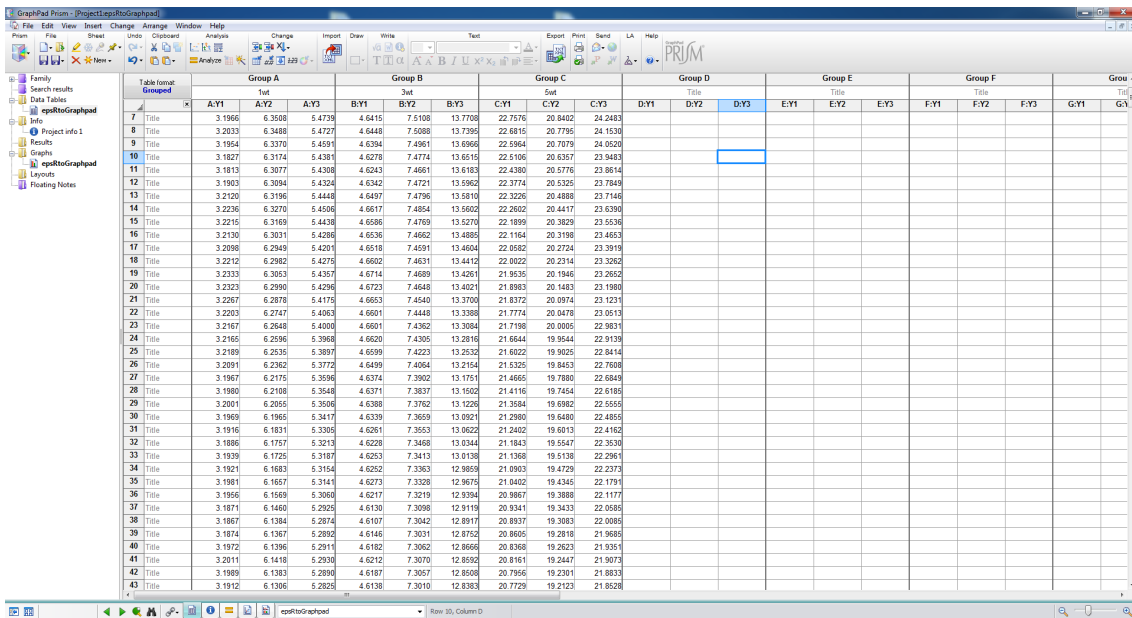


Figure B12. Principal view with data– Example

Now, the data is entered into the program and several options appear on the left side of the program. The most important statistical process and view the results of our data are "Results" and "Graphs".

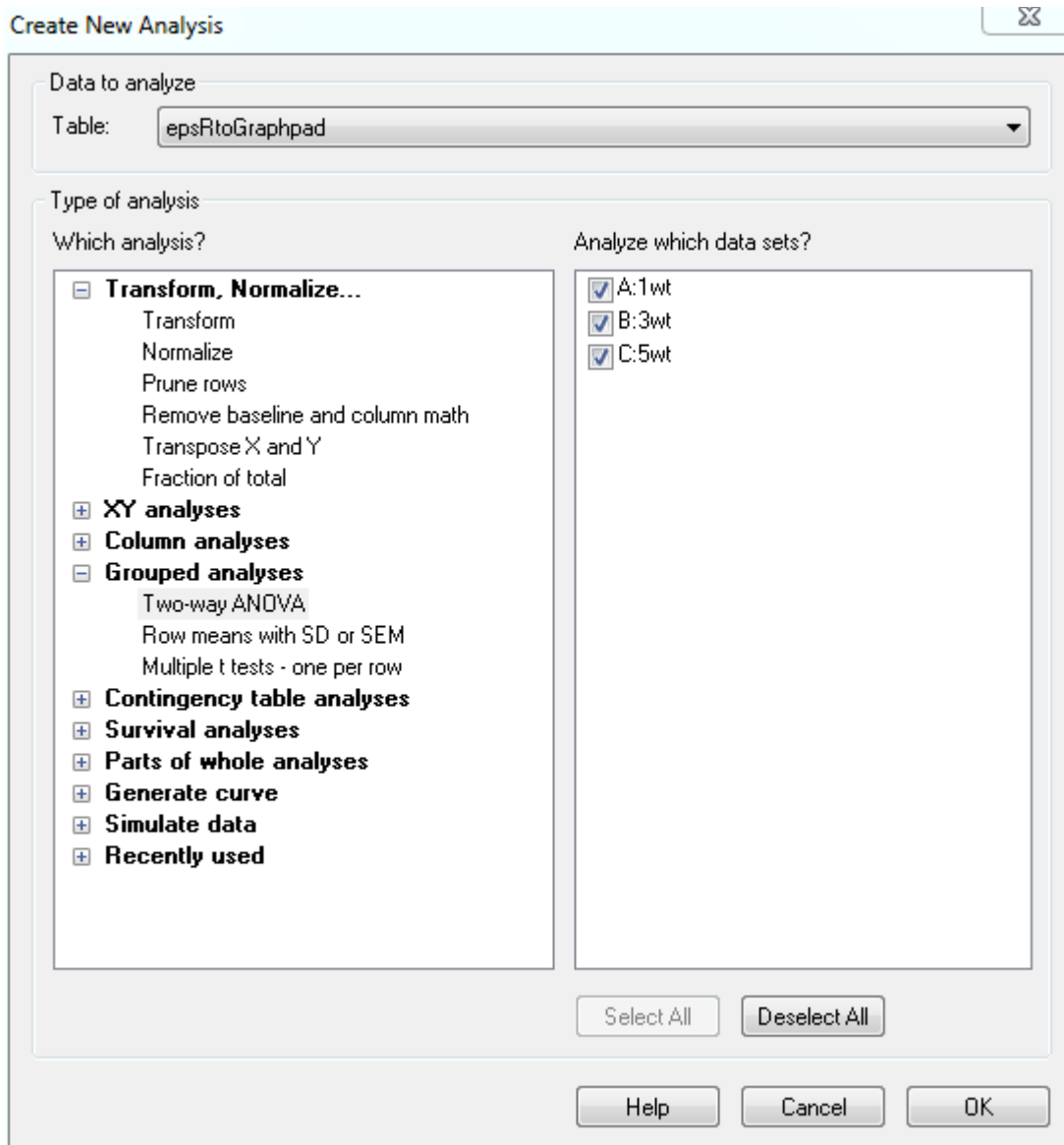


Figure B13. Result option view- Example

The "results" option allows us to perform many statistical analyses of our data and shows us the numerical form. For our project is important to the mean and standard deviation, which although they have created scripts to perform these calculations, let's see how these calculations is obtained GraphPad Prism. As the entered data is fairly long vectors, the better to see it is by the graphics.

The “graph” option allows us to show different types of graphs a simple statistical analysis of our data. The different types of graphs can all show the following calculations:

- Means
- Means with standard deviation
- Mean with SEM
- Mean with 95% CI
- Mean with range
- Geometric mean
- Geometric mean with 95% CI
- Median
- Median with range
- Median with interquartile range

The most useful for this thesis is a graph with the mean of each group of samples with the standard deviation. The graph shows the mean in each column and can see drawn above the standard deviation of each group.

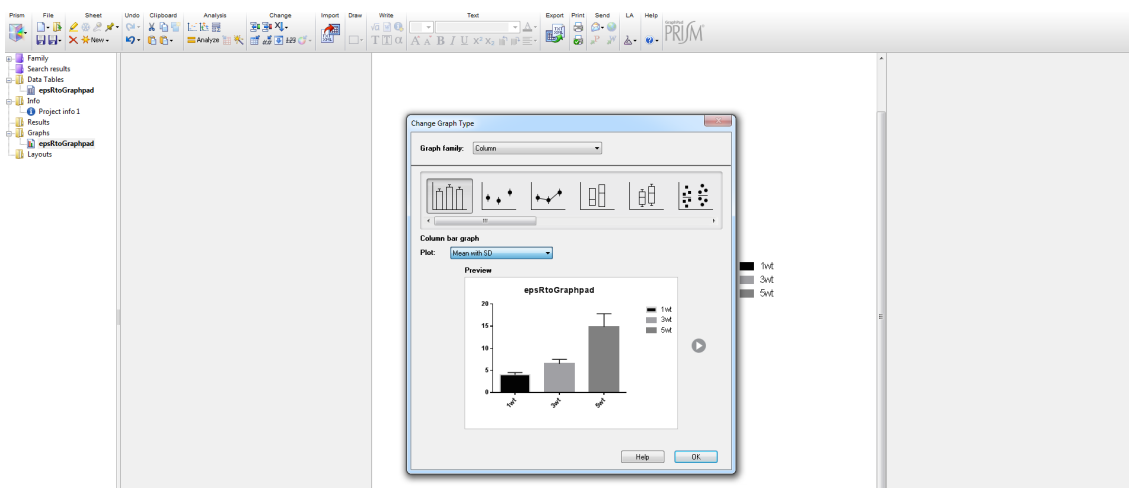


Figure B14. Graph option view– Example

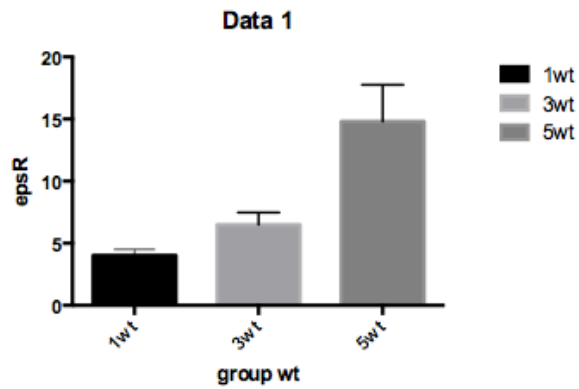


Figure B15. Graph means and SD – Real part- Example

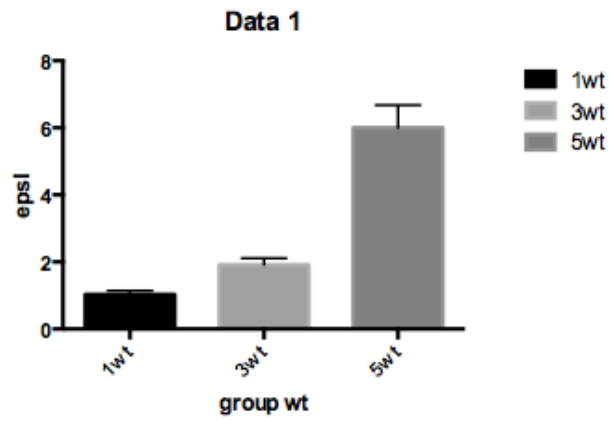


Figure B16. Graph means and SD – Im. part- Example

This is the way to select different samples in groups and perform simple graphs with statistical calculations. With the graphics much work is simplified because it is faster to see the results graphically.

#### 4. RESULTS

In this chapter the description of the script have been used for modelling of composite is presented. Along with his description a number of examples will be shown to see which is the result of the implementation of these script.

For the realization of these scripts there are some initial data that are obtained from the measurements of the constituents or mixtures, and these are called samples. These samples are detailed in Chapter 5.1.

Below are presented some script that if necessary used for make some pre-sets to the samples obtained with the measuring instruments. These scripts are to calculate the average and standard deviation of a set of several samples. This helps to reduce the error averaging the measurements and discard samples that are totally different to most samples. These scripts are detailed in Chapter 5.2.

Along with the script of Chapter 5.2, the script Debye help us obtain approximations of the parameters of the effective permittivity of a material, which is usually the host used in the mixtures of compound. This script is detailed in Chapter 5.3.

At the end of chapter, the modelling scripts of composite are presented and these are divided into two categories in function of the percolation threshold. The one hand if the concentration of conducting inclusions in the composite is less than the percolation threshold, Maxwell Garnett model is used. On the other hand if the concentration is higher, McLachlan model is used. These scripts are detailed in Chapter 5.4 and 5.5 respectively.

The measurements obtained from measuring devices are obtained in files with extension .prn. The script made in this thesis need to have .mat data files, so it is necessary to use a script that converts those files into .mat data files. With this script the information of the complex effective permittivity of the measured material is obtained, the frequency range that has been used, and in some cases

also includes the sensitivity of the meter. (See Appendix A2 *LoadAgilent.m* and A3 *LoadAgilentSens.m*)

Measures only provide us information of the complex effective permittivity, but other parameters can be obtained with this data. These data can be the conductivity, Tan Delta or graphics Cole Cole. The way to get the conductivity is using equation (12).

$$\sigma = \epsilon_i * 2 * \pi * freq * \epsilon_0 \quad (12)$$

Where:

$\epsilon_i$ : Relative permittivity – Imaginary part

freq: Frecuencia (Hz)

$\epsilon_0$ :  $8.854187/10^{12}$ ;

Similarly can be calculated Tan Delta with the equation (13).

$$\tan \delta = \frac{\epsilon_i}{\epsilon_r} \quad (13)$$

Where:

$\epsilon_r$ : Relative permittivity – Real part

$\epsilon_i$ : Relative permittivity – Imaginary part

For the graph Cole-Cole is not necessary to use any equation, it is just making the graph where the real part of the effective permittivity faced with the imaginary part.

#### **4.1. SAMPLES PRODUCTION AND PERMITTIVITY MEASUREMENT**

This section describes the samples and measures available along with their characteristics. In addition, some technical details are indicated from the point of view chemical for the production of these samples.



#### 4.1.1. SAMPLE PRODUCTION

Samples used in this thesis were made in DISAT (Department of Applied Science and Technology) in Politecnico di Torino <http://www.polito.it/carbongroup>. There are four types of samples detailed in Table 1. These types are composite composed of a host and a variable amount of inclusion of MWCNTs.

Type	Resin host	Diameter (nm)	Length ( $\mu\text{m}$ )	Aspect ratio	Purity (%)	Producers	MWCNTs
1	Epoxy	30-50	0.5-2	30	>95	Cheaptubes	MW0
2	Epoxy	25-45	>10	325	>98	Grecia	E15
3	Epoxy	6-10	>10	1000	>90	Grecia	E16
4	RTM6	9.5-10	1.5	150	>90	Nanocyl NC7000	NC7

Tab. 1: Multi walled carbon nanotubes used

A commercial thermosetting resin (Epilox), produced from Leuna-Harze was used as polymer matrix. It is a bi-component system formed by a Resin and a Hardener. Resin (T-19-36/700) is a commercial modified, colorless, low viscosity (650-750 mPa•s at 25°C) epoxy resin with reduced crystallization tendency having a density 1.14 g•cm<sup>-3</sup>. The chemical composition of Epilox resin T19-36/700 is mainly Bisphenol A (30-60 wt.%), with addition of crystalline silica (quartz) (1-10 wt.%), Glycidyl ether (1-10 wt.%), inner fillers (10-60 wt.%). Hardener (H10-31) is a liquid, colorless, low viscosity (400-600 mPa•s at 25 °C) modified cycloaliphatic polyamine epoxy adduct having density 1 g•cm<sup>-3</sup>.

MWCNTs have been dispersed in Epilox in desired concentration using the following procedure:

1. MWCNTs and Epilox quantities are weighted via digital balance and preliminary mixed together with a metallic spatula

2. The mixture is dispersed using an UltraTurrax® mixer for 10 minutes in order to create a well dispersed solution
3. Curing agent (Epilox® Hardner H 10-31: liquid, colourless, modified cycloaliphatic polyamine apoxide adduct) is added to the mixture in 6:10 ratio and a 10 minutes mechanical stirring performed
4. The mixture is slowly poured in 27 mm in diameter cylindrical moulds
5. Nanocomposite is degassed in a vacuum chamber for 20 minutes
6. Final product is dried in oven for 3 hours at 70°C

The shape and thickness of the samples (see Fig. 17) were chosen in order to fulfill the requirements of the setup for complex permittivity measurements. The mould filled with the composite was placed in a vacuum chamber to remove all the presented air bubbles in the samples due to mixing process.

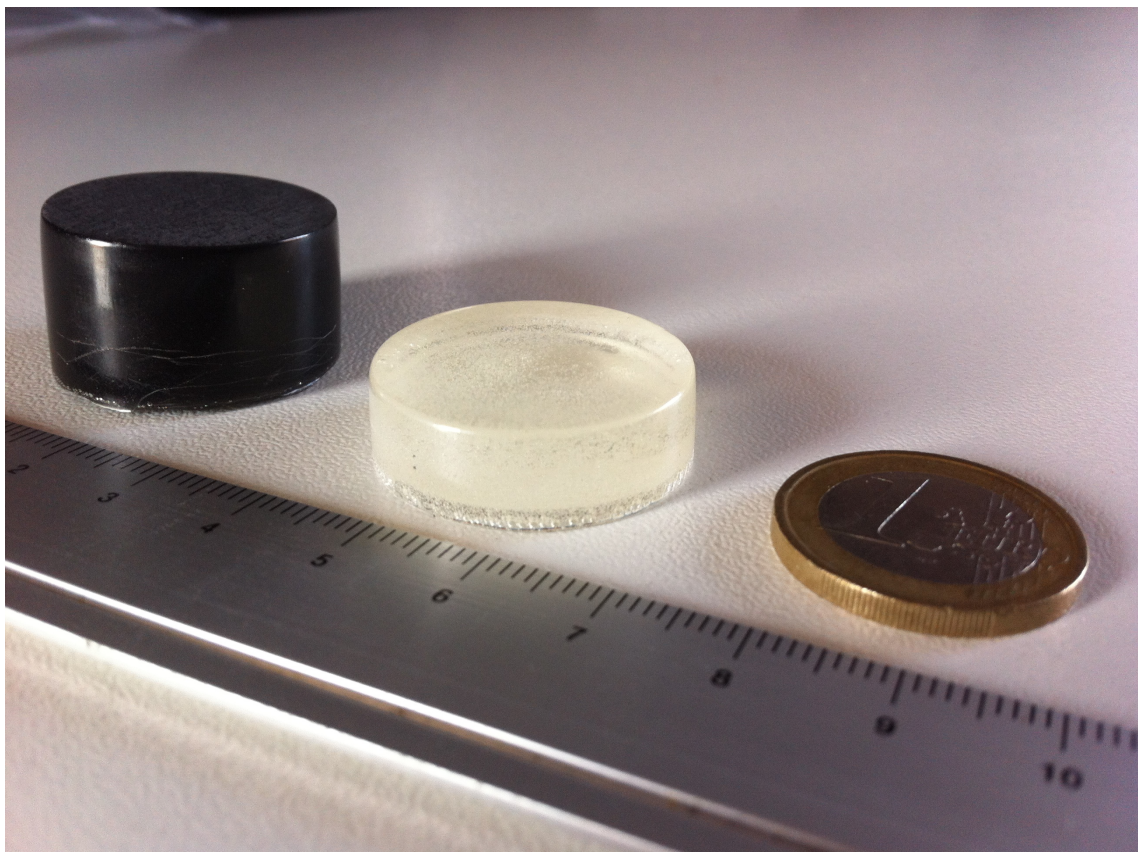


Figure 17. Real scale images of samples with 1 wt.% of MWCNTs NC (black specimen) and pristine epoxy (transparent specimen) are shown.

#### 4.1.2. FESEM ANALYSIS

As the dispersion of MWCNTs inside the resin is a crucial point, it was checked using FESEM (Field Emission Scanning Electron Microscopy, Zeiss Supra 40) analysis. Samples were crio-fractured and exposed surfaces analyzed. This procedure (breaking the specimen into two pieces after flash freezing in liquid nitrogen) guarantees that the internal structure is not affected by fracture avoiding internal resin elongation with subsequent MWCNTs reorientation.

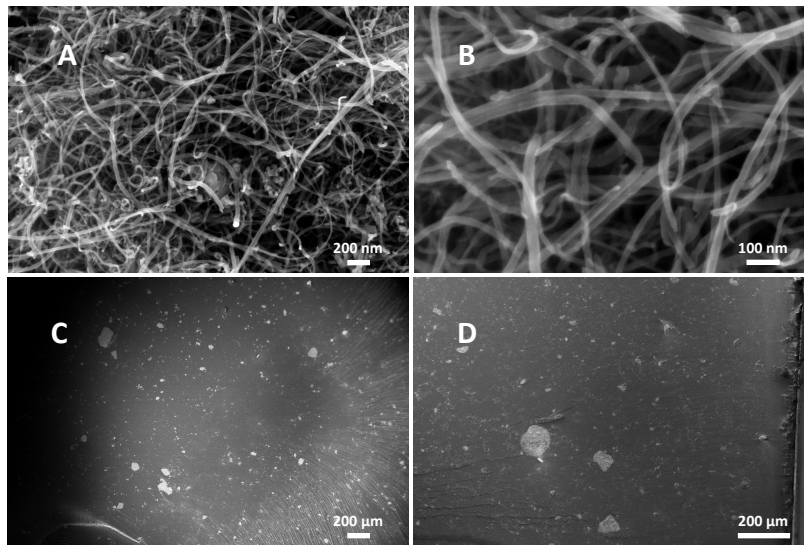


Figure 18. FESEM images of MWCNTs used (A and B) and crio-fractured area for the NC at 1 wt.% (C) and 3 wt.% (D) wt. of filler

#### 4.1.3. COMPLEX PERMITTIVITY MEASUREMENTS

The complex permittivity of pure Epoxy resin and composites with 1 wt.% and 3 wt.% MWCNTs was measured in the frequency range 3-18 GHz, therefore the wavelength is between 0.1 m - 0.0166 m, using the relationship  $c = \lambda * f$  where  $c = 3 * 10^8$  m/s. Samples were measured using a commercial dielectric probe (Agilent 85070D) and a Network Analyzer (E8361A). A standard calibration short/air/water was adopted. These types of measurements were chosen because of its wider-band feasibility (200 MHz-20 GHz) with respect to waveguide measurements or free-space measurements. Moreover, the samples can be of

relatively small dimensions. The drawback is that the samples should have a very smooth, flat surface in order to avoid the presence of an air-gap at the probe face.

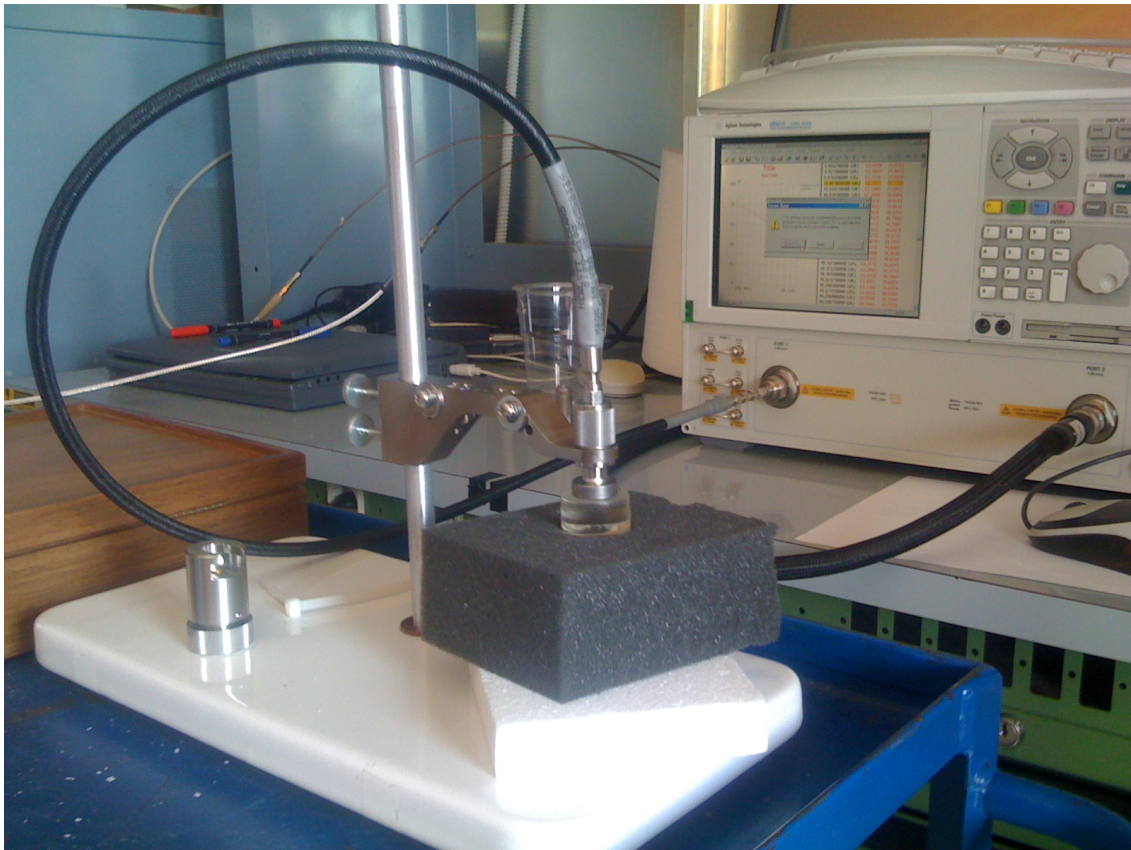


Figure 19. Measurement Setup

#### **4.2. BASIC STATISTICAL ANALYSIS**

Normally, the measurement of a sample is not achieved with a single measurement, it is necessary to make several measurements to the same sample, obtaining very similar results to each other but not identical, due to measurement errors that may exist.

To reduce measurement error and reduce all measurements to a single measurement, it should be the average of all measurements, and if necessary, discard measurements have very different values to the majority of measurements

To do the average, a script that realises a simple processing of the measures was created. In each measure done in a same material, different results are obtained

with many similarities because is the same material but with measurement error. So, the script allows us to upload as many measures as there are, and the average obtained is shown along with the measures in one graph. In this manner, the measurement error probably will be less than with a single measurement. (See *Appendix A4 PlotAvgv1dh.m and A5 PlotAvgAllv1dh.m*)

Besides of obtain the average of the measures obtained, is useful calculate a range whose result can oscillate due of mistakes. Calculating the standard deviation, and adding and subtracting the standard deviation to the average value this range is obtained. So, this range shows us how much is the deviation of the measures obtained and this deviation is different for each frequency. If a new measurement of the material is obtained, probably it will be inside the range calculated of the standard deviation. (See *Appendix A6 PlotStdv1dh.m*)

#### **4.2.1. RESULTS FOR PURE EPOXY**

In this section the average and standard deviation analysis is applied to pure epoxy samples. If all the existent measurements are loaded, a result as shown in the figures 20-24 is obtained. The graphics allow us to see how the sample s1 has values that are not similar to the other measures. This sample s1 can be discarded and run the script again with the remaining samples.

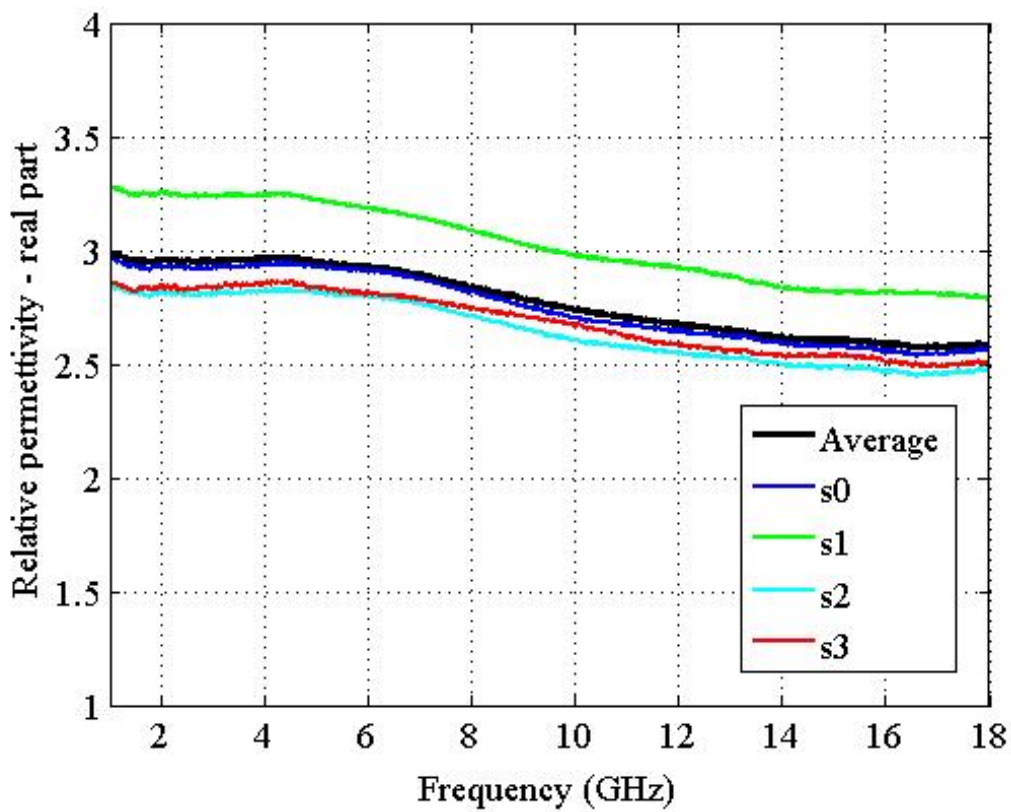


Figure B20. Average real part

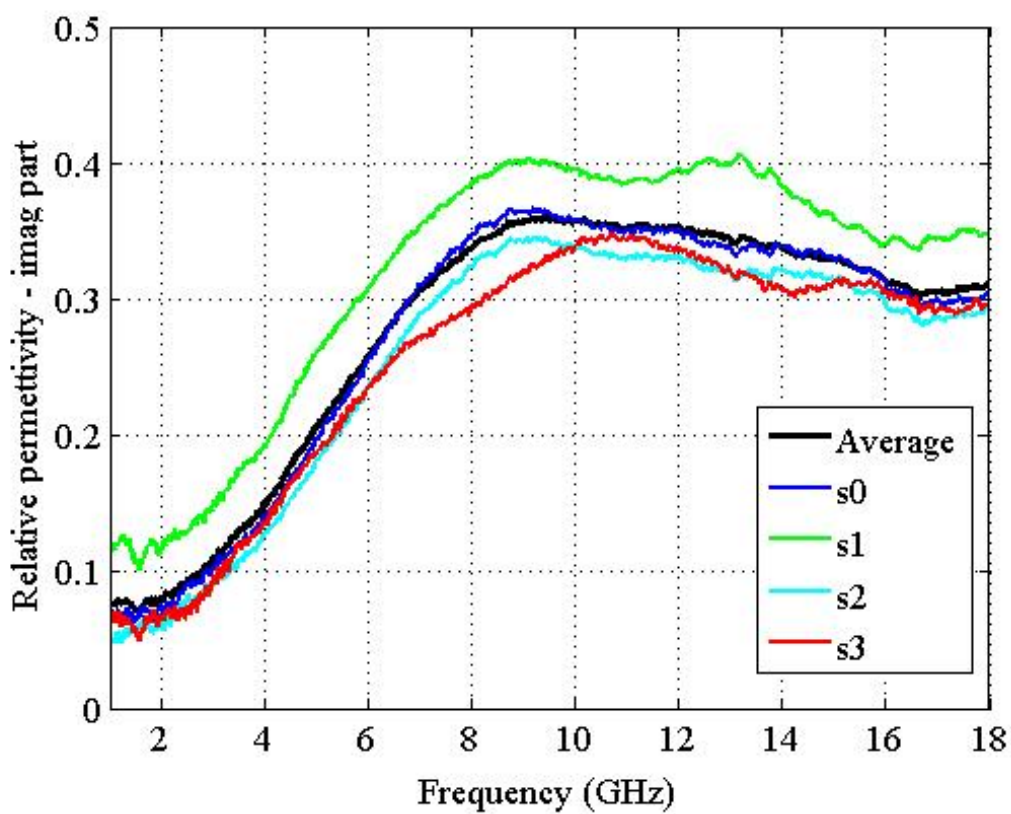


Figure B21. Average imaginary part

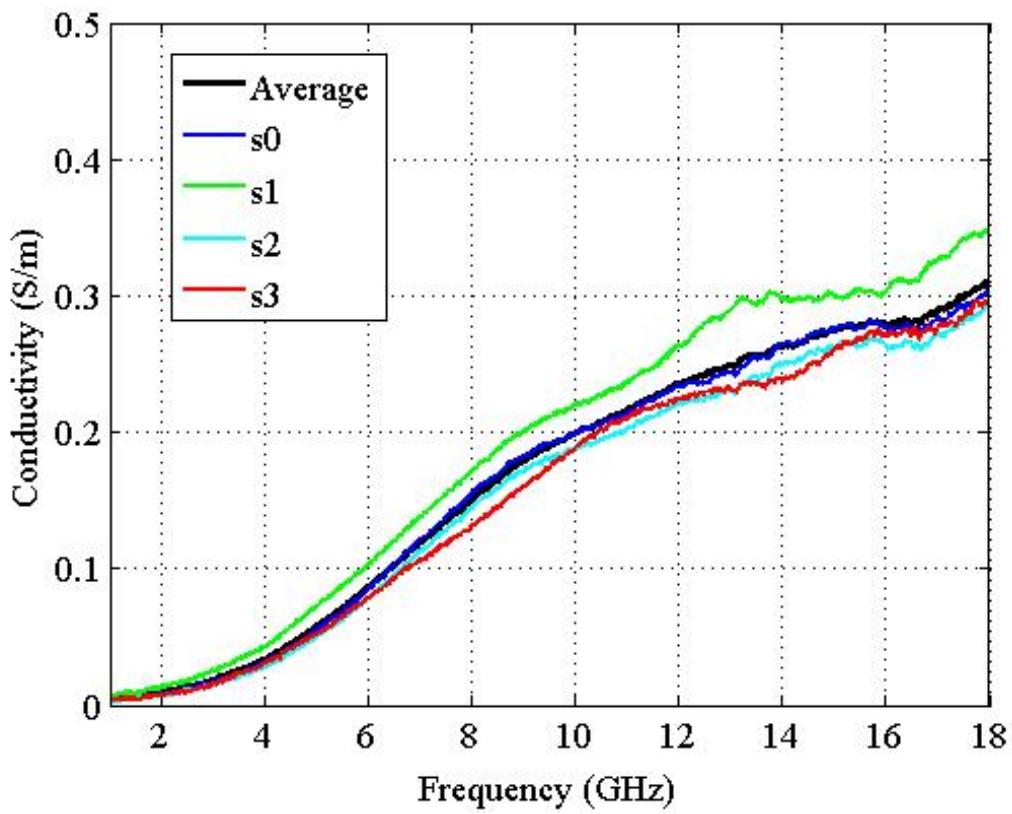


Figure B22. Average conductivity

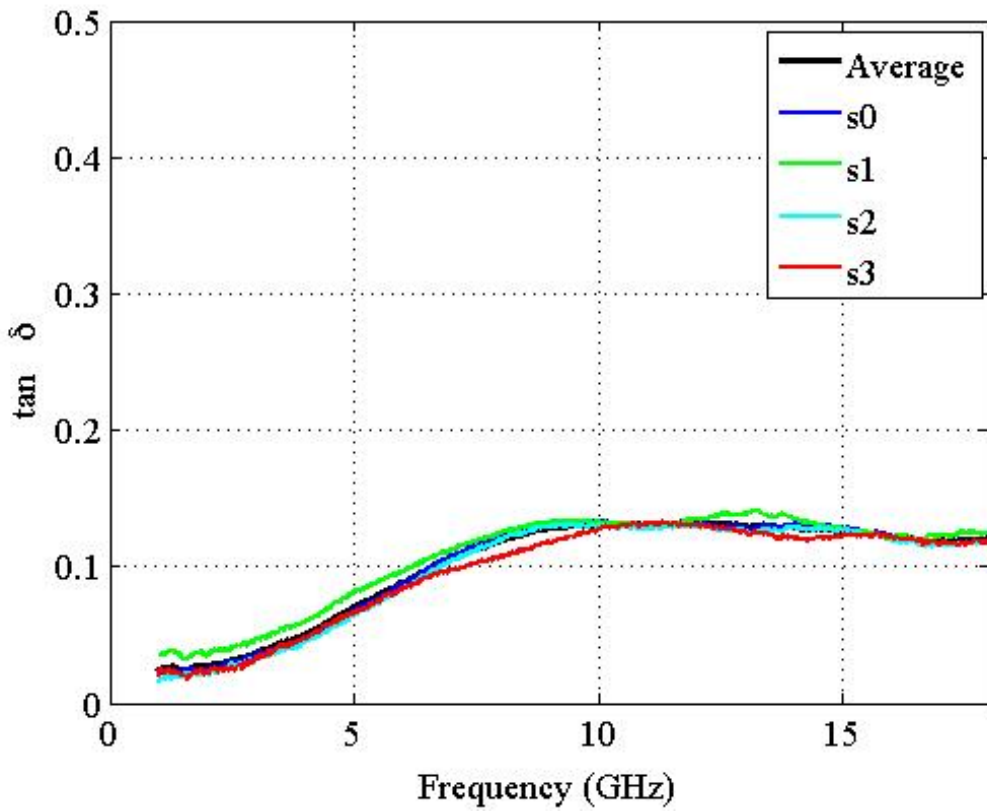


Figure B23. Average tan delta

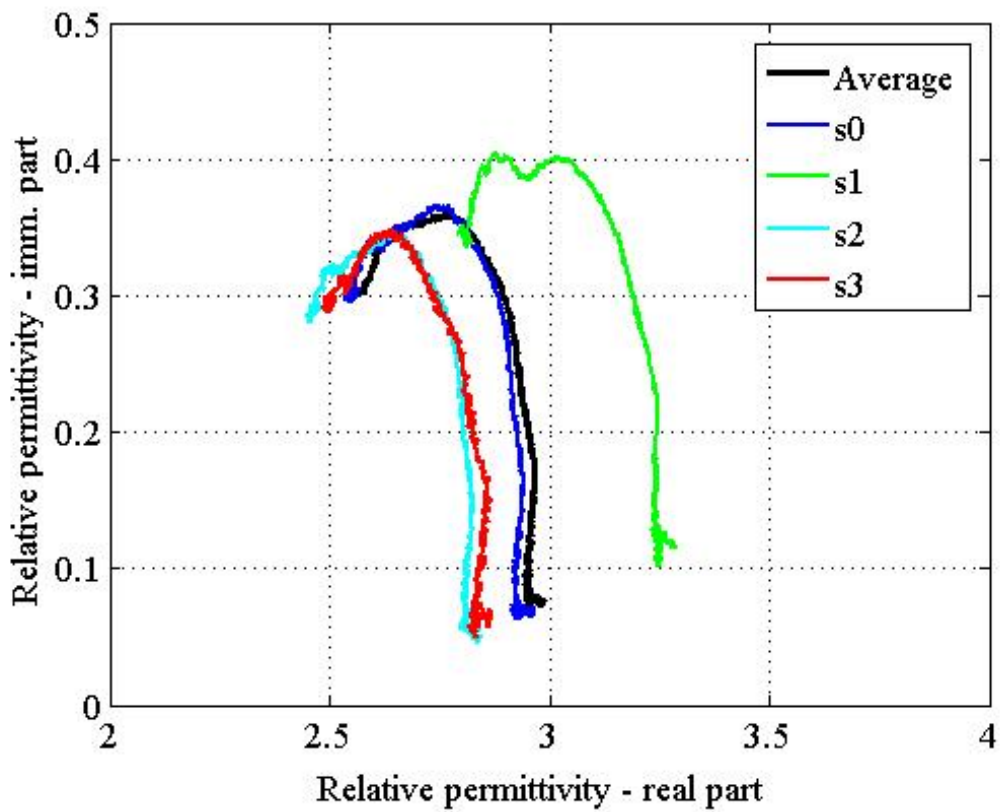


Figure B24. Average cole cole

However, if the sample s1 is discarded, the result of the script shows a more accurate result, as the figures 24-29 are shown. This is a simple calculation but reduces considerable error of measurement, that later they can become large errors of inaccuracy.



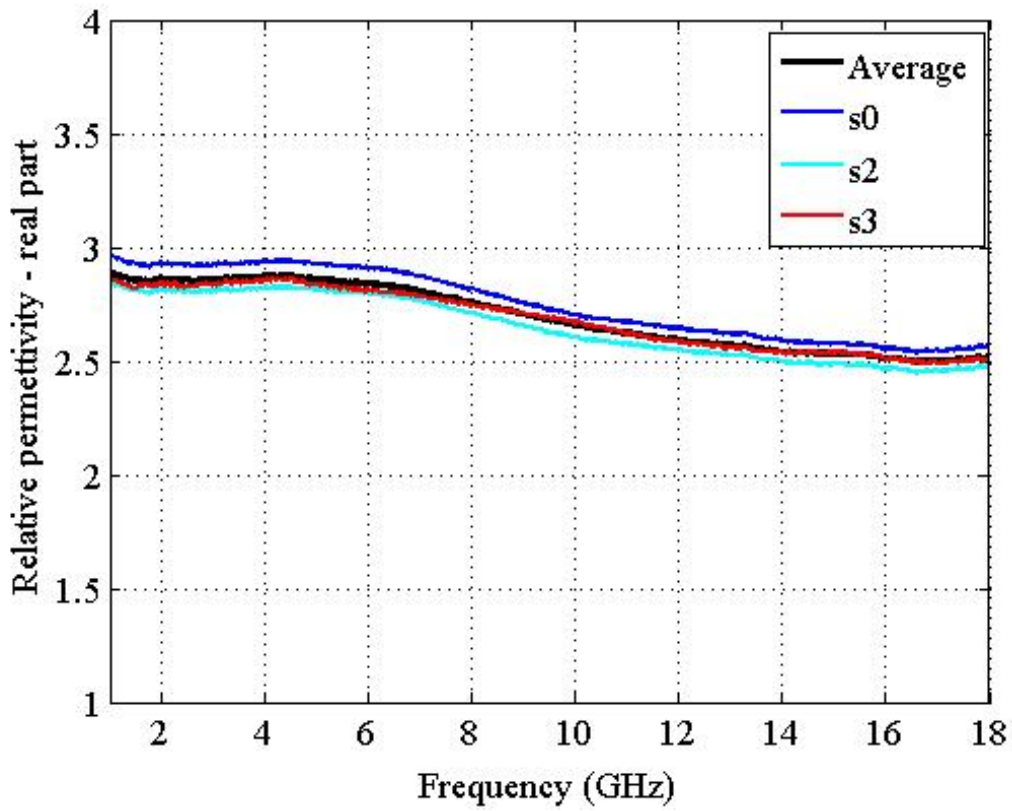


Figure B25. Average real part without s1

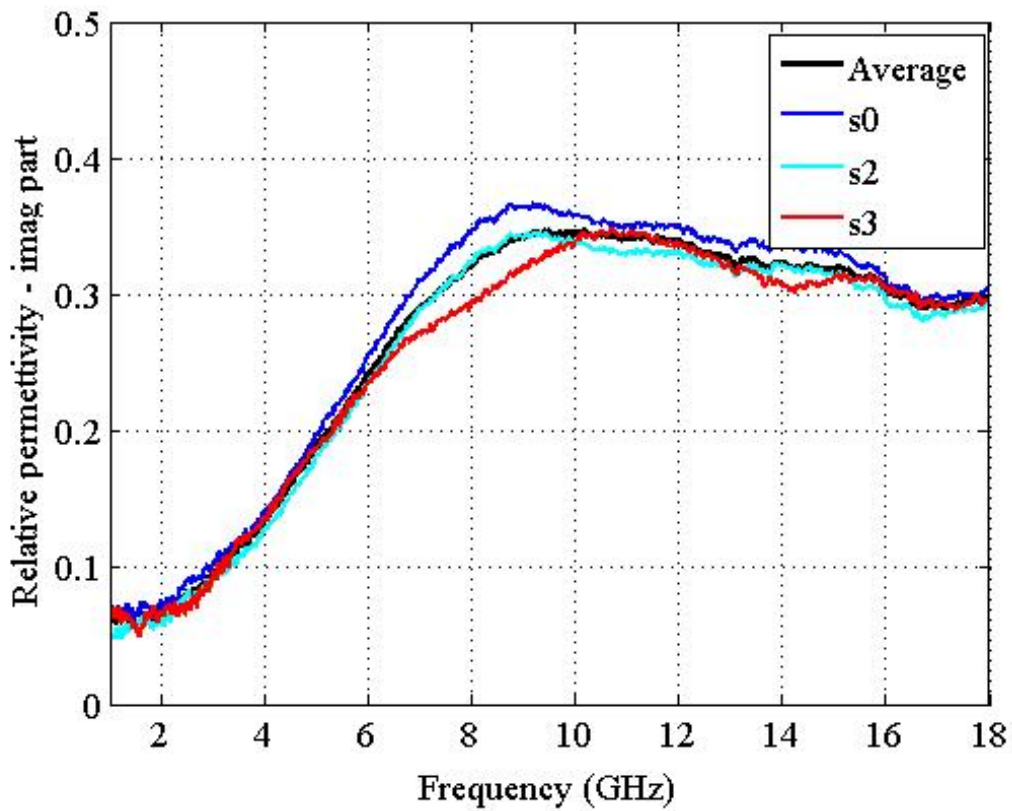


Figure B26 Average imaginary part without s1

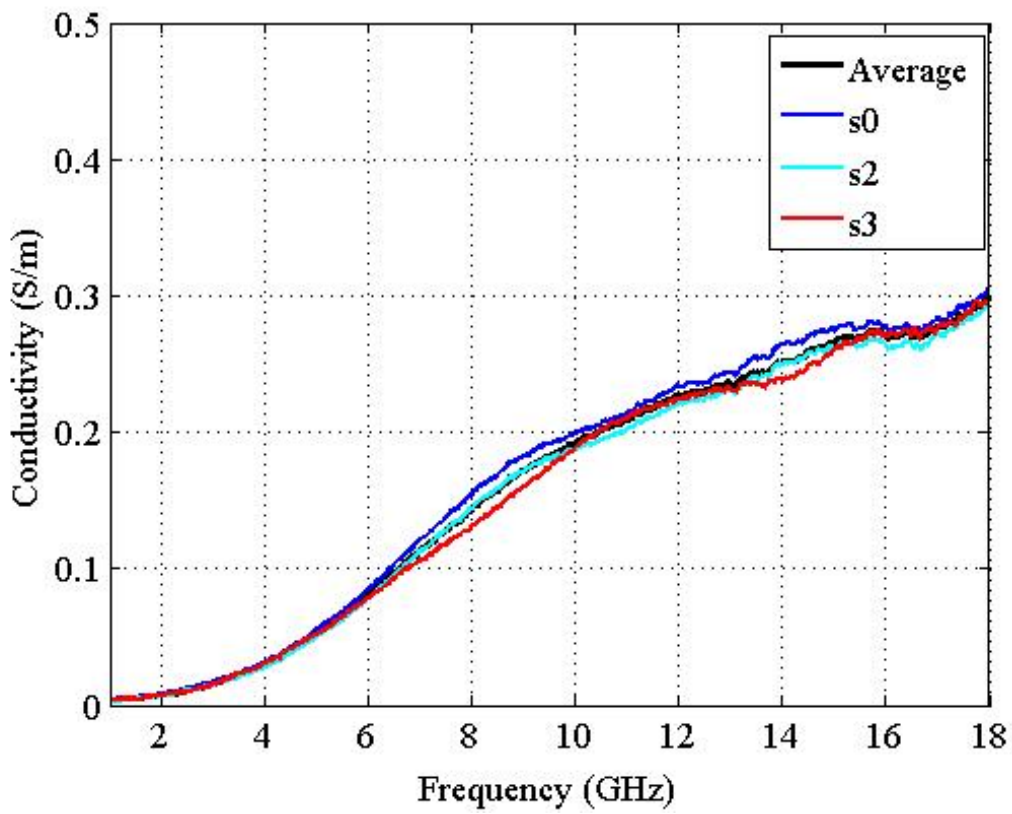


Figure B27. Average conductivity without s1

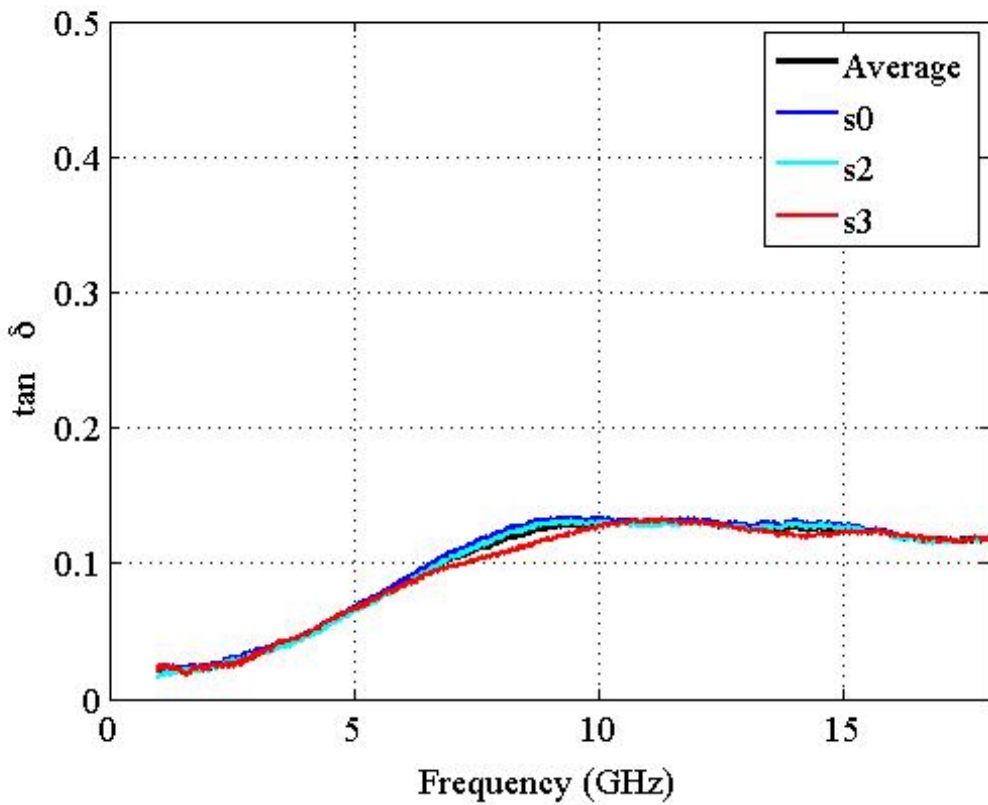


Figure B28. Average tan delta without s1

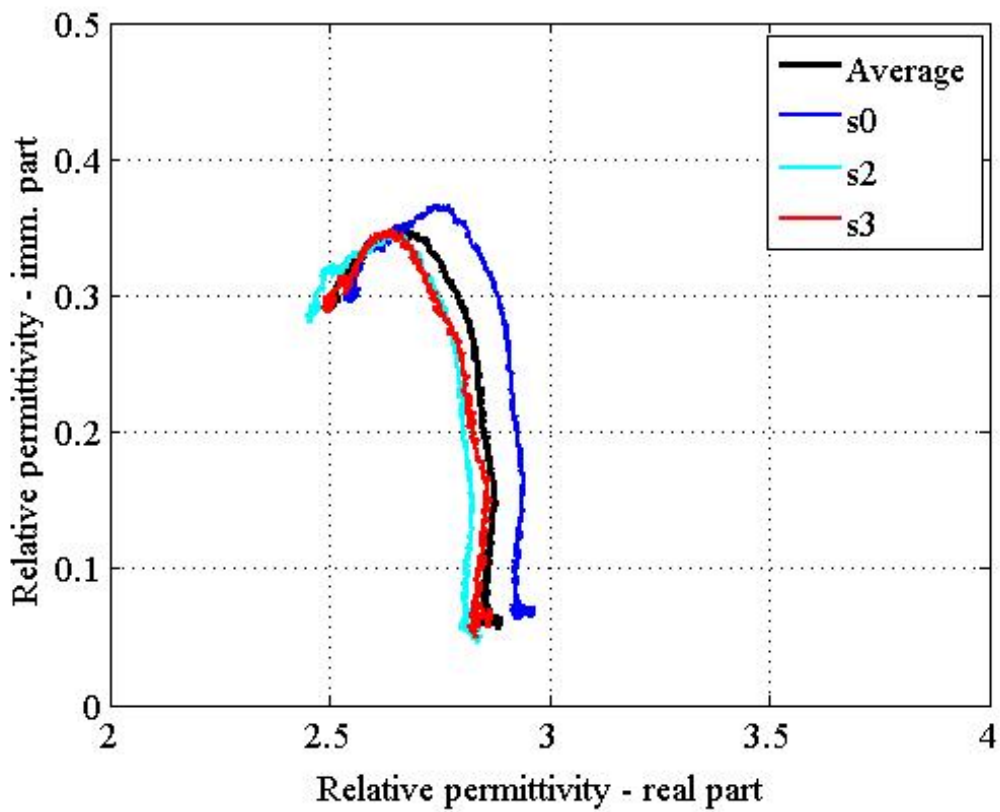


Figure B29. Average cole cole without s1

The same way as the calculation of the average, the results obtained of script A2 to know the range of standard deviation is shown in figure 30-33. Similarly as in the previous script, the range of the standard deviation is reduced considerably due to discard the sample s1.

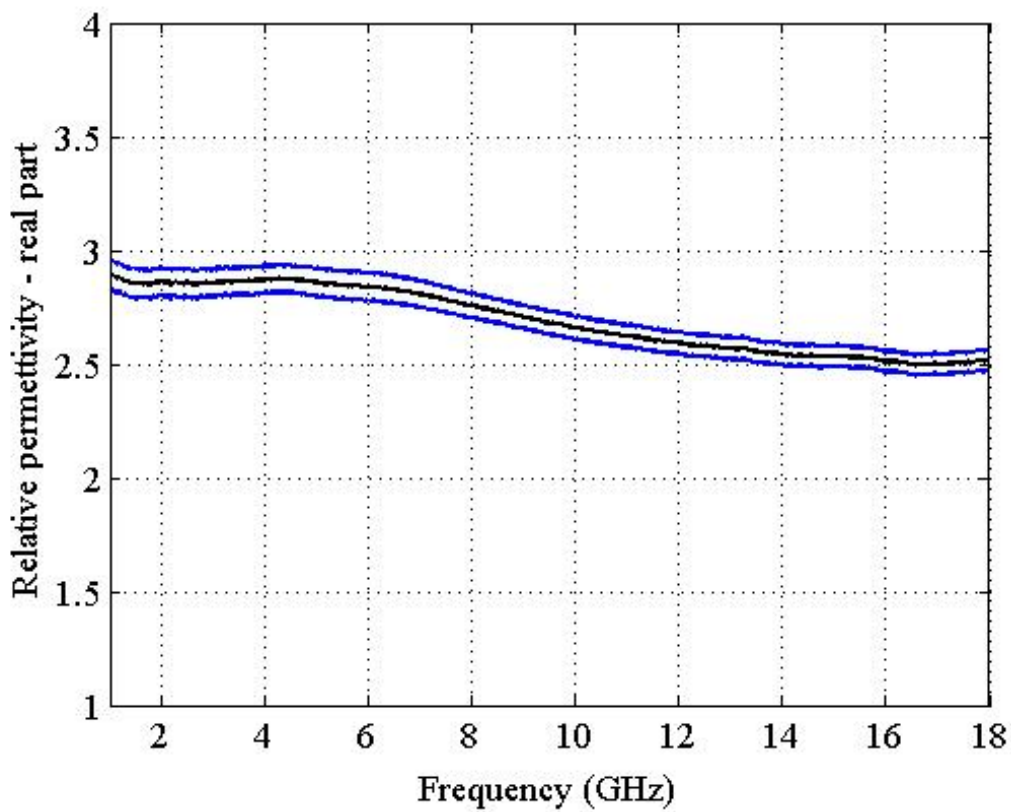


Figure B30. Standard deviation permittivity real part

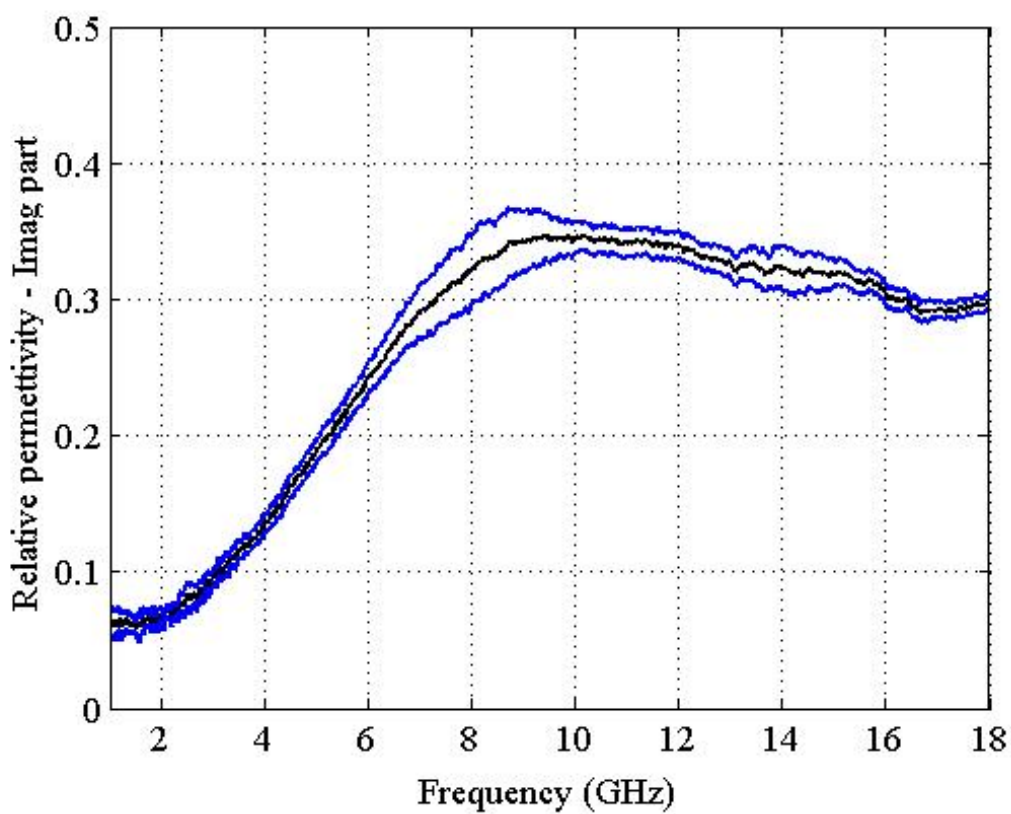


Figure B31. Standard deviation permittivity imaginary part

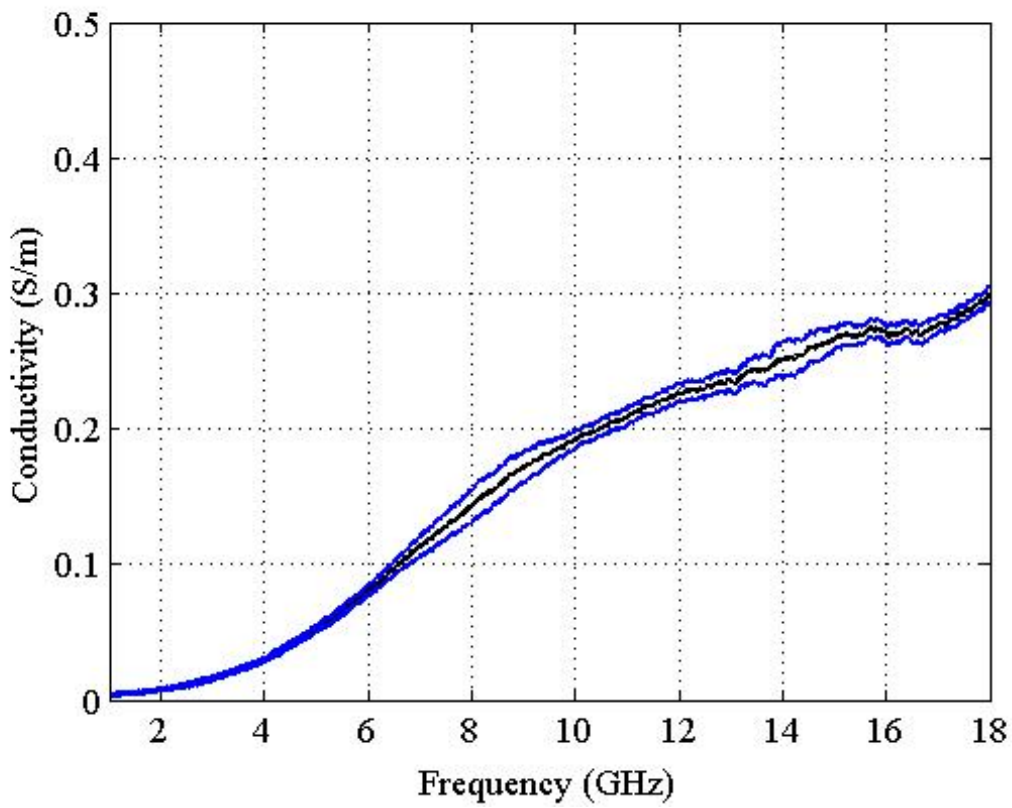


Figure B32. Standard deviation conductivity

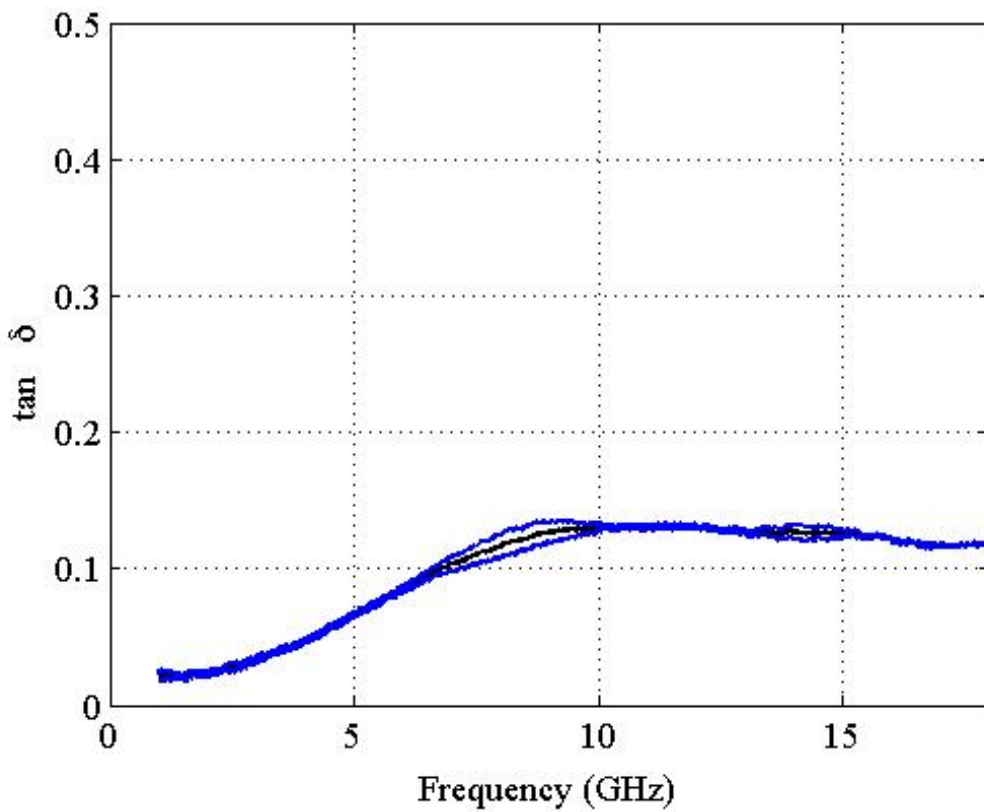


Figure B33. Standard deviation tan delta

### 4.3. DEBYE MODEL

It takes a script that helps us to find unknown values of Debye equation model from the result, which it is obtained from the measure of different materials. This result will not be completely perfect, because the result comes from measures that have a measurement error compared with the completely perfect result.

If necessary, the previously script A1 to obtain the average value of several measurements should be used. After doing these previous calculations, the script should find an approximation of the unknown values of the Debye equation.

Recalling previous chapters, the Debye equation is:

$$\epsilon_D = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)}{1 + j\omega\tau} \quad (14)$$

Where:

$\epsilon_s$  and  $\epsilon_\infty$ : Static and "optic" limit permittivity values

$\tau$  : Relaxation time

$\omega$  : Angular frequency

$\epsilon_D$ : Permittivity of the material

The result  $\epsilon_D$  is a complex term, therefore has real and imaginary part, and the fit should be done so that the approximations of the unknown values match the real relative permittivity and imaginary relative permittivity.

Therefore, the problem is the following:

Known values:  $\epsilon_D = \epsilon_{Dreal} + \epsilon_{Dimm}, freq$

Unknown values:  $\epsilon_\infty, \epsilon_s, \tau$

Given this situation, it has built a script in matlab to obtain the unknown values from known values. There are 3 unknowns against a single equation, the values will get an estimate approaching totally correct values.

To learn more about the functioning of the script, you must go to see the code of the script. In this thesis, a summary of script steps is explained to reach the solution, the approximate values of the unknown values.

First, the known values are loaded, in this case  $\varepsilon_D = \varepsilon_{Dreal} + \varepsilon_{Dimm}$  and  $freq$ . Later, several guidance values are necessary to approach the correct value of unknown values.  $\varepsilon_S$  is the value at which tends the permittivity when it is working at frequencies near to zero. Therefore several values of the permittivity of the lower frequencies are selected and their average is calculated.

Likewise for  $\varepsilon_\infty$ , but this time does it with the permittivity of the highest-frequency. Thus, an approximate value of permittivity when tends to zero and infinity is obtained.

For the term  $\tau$  the derivative of the permittivity is calculated and the maximum of the derivative corresponds to one frequency. This frequency is the point of greatest variation of the permittivity.

With these initial values, with the help of the Nelder-Mead method [7] thanking that MatLab has incorporated this method in their commands and it is extremely useful for this case. The command is `fminsearch` [8].

The method looks so rough a local optimal solution to a problem with N variables when the function to minimize varies smoothly. Introducing the Debye (9) formulates and indicating the known terms and unknown term, the script returns an approximate value of the unknown variables, which are the values that are looking. As the term permittivity is a complex term with real and imaginary part, first fit with the real part, after the imaginary part and finally making the average of the two results obtained, which are very similar to each other, the unknown values are obtained and it will presumably be very close to the correct values.

With these values, the equation Debye is calculated and the result is compared with the sample loaded at the beginning of the script. Both results are very similar. *(See Appendix A7 FitDebyeModelv6dh.m)*

### 4.3.1. RESULTS

In this section the script is tested considering deionized water whose characteristics are well known. An example to the theory Debye curve with known values of deionized water to see that the results are correct, and another example with a sample of deionized water measurement.

#### 4.3.1.1. TEST EXAMPLE: DEIONIZED WATER

First, the script calculates the ideal curve created with Debye equation and the well known parameters of deionized water.

```
Freq. range : 1Ghz - 18Ghz
εs: 78.6583
ε∞: 4.9
τ : 5.243838e-11
Freq. relaxation : 1.9070e10
```

After running the script, the values obtained are:

```
εs: "78.6613".
ε∞: 4.9030".
τ : "5.243838e-11".
Freq. relaxation : "1.9070e+10".
```

The values obtained are practically the same as the original, and the curve calculated with the approximations values are practically equal to the original curve. (See Fig. 34, 35)



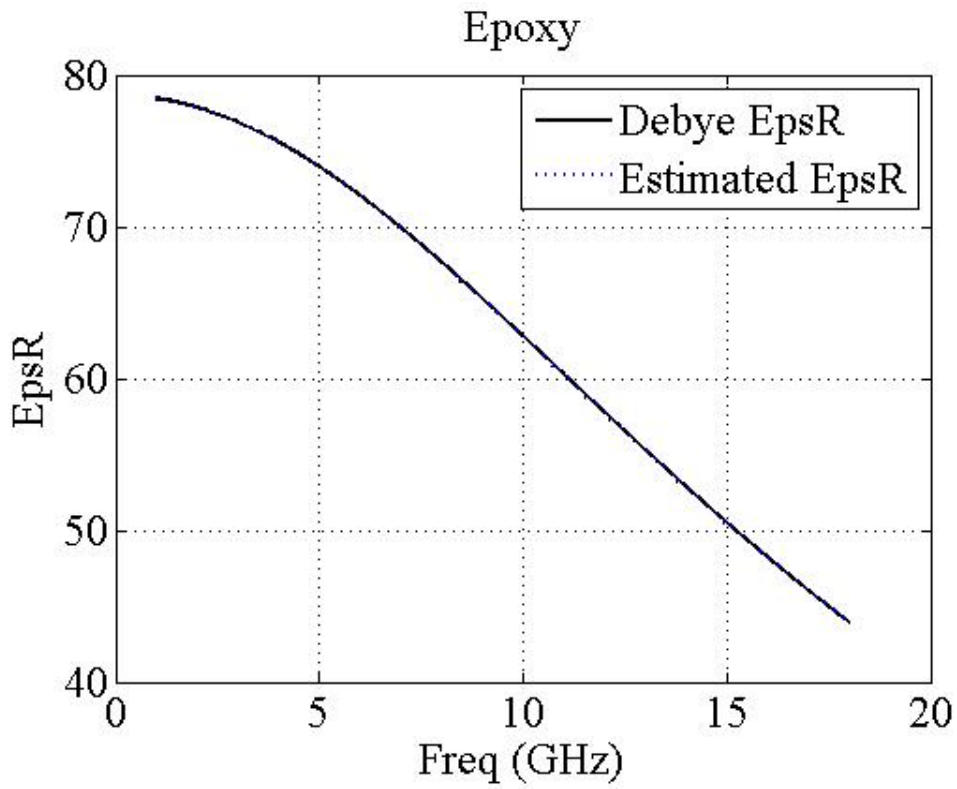


Figure B34. Fit Debye real part with ideal curve of deionized water

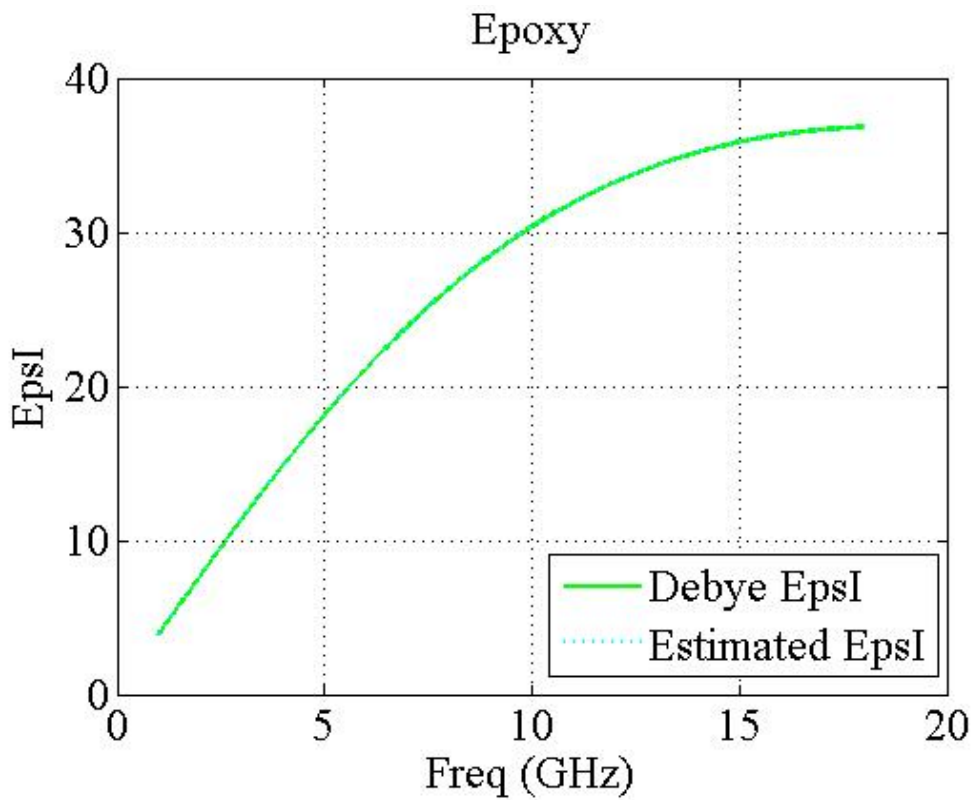


Figure B35. Fit Debye imaginary part with ideal curve of deionized water

#### 4.3.1.2. EXAMPLE: DEIONIZED WATER MEASUREMENT

In this second example the script load the real and complex permittivity of water (file: calwater.mat). This is a simple example because the curve is quite ideal. It is not totally perfect as the previous case because the permittivity of water is a measurement, which has measurement errors.

In this case, the correct values are not known to compare with the approximations obtained, so it is necessary to compare the results with the graphics 36 y 37.

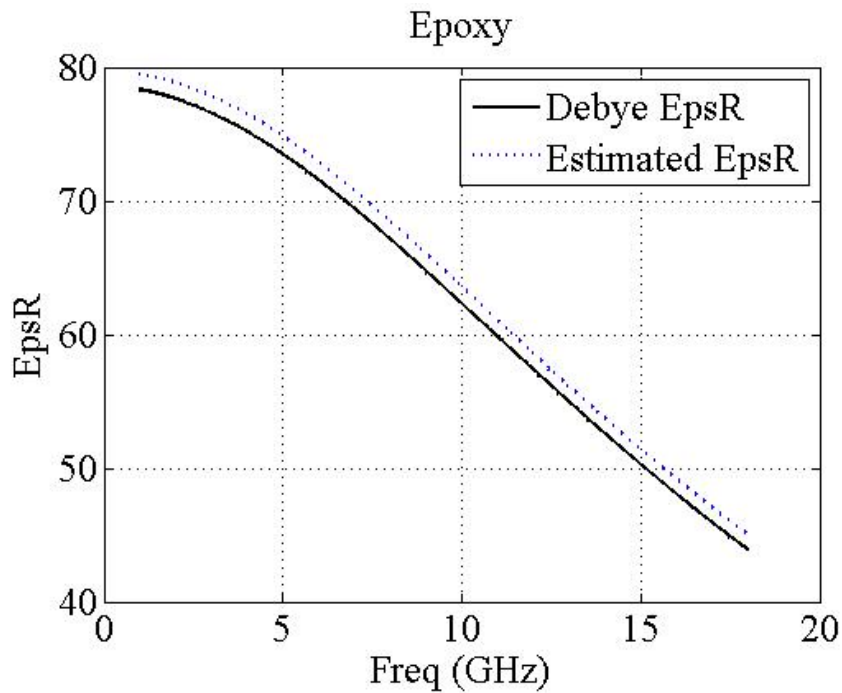


Figure B36. Fit Debye real part with calwater curve

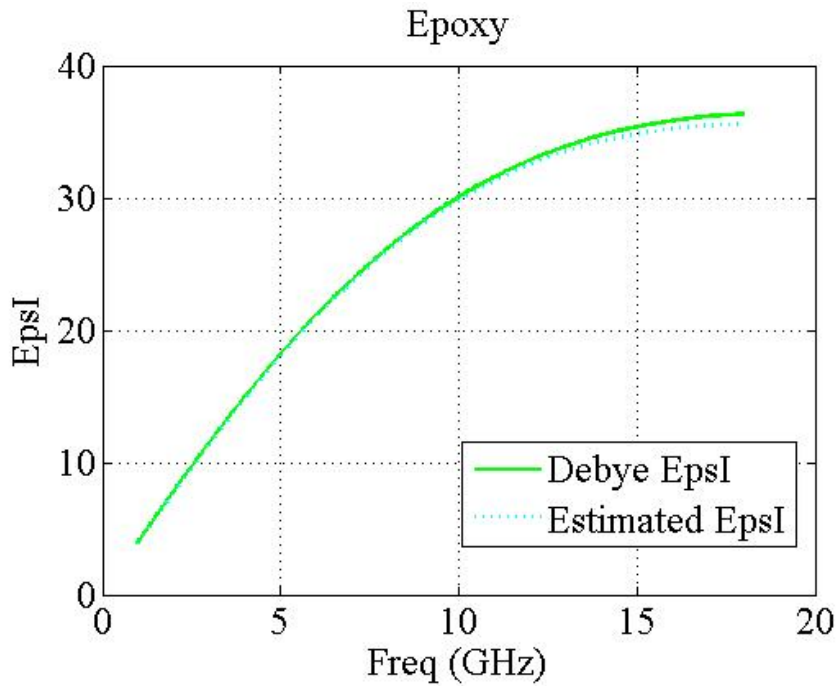


Figure B37. Fit Debye imaginary part with calwater curve

The curves in this case are not as perfect as the previous section, but the curve obtained is a good approximation to the original curve.

#### 4.3.1.3. EPOXY SAMPLE

In this final example for the equation Debye show the average permittivity of epiloX where the curve is not perfect and it have measurement errors. The estimated curve is near to the measurement permittivity and the approximation curve is more lineal. It is concluded that the approximation is highly accurate for both the real part and for the imaginary part in the figure 38 and 39.

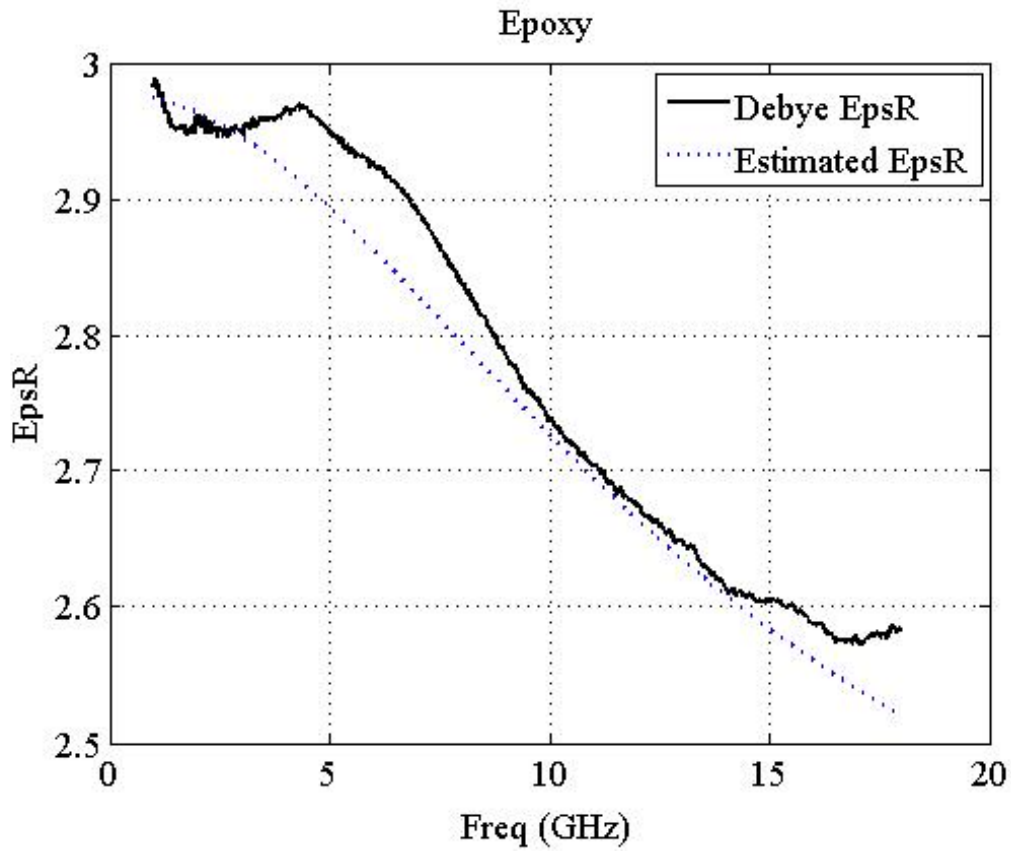


Figure B38. Fit Debye real part of Epilox

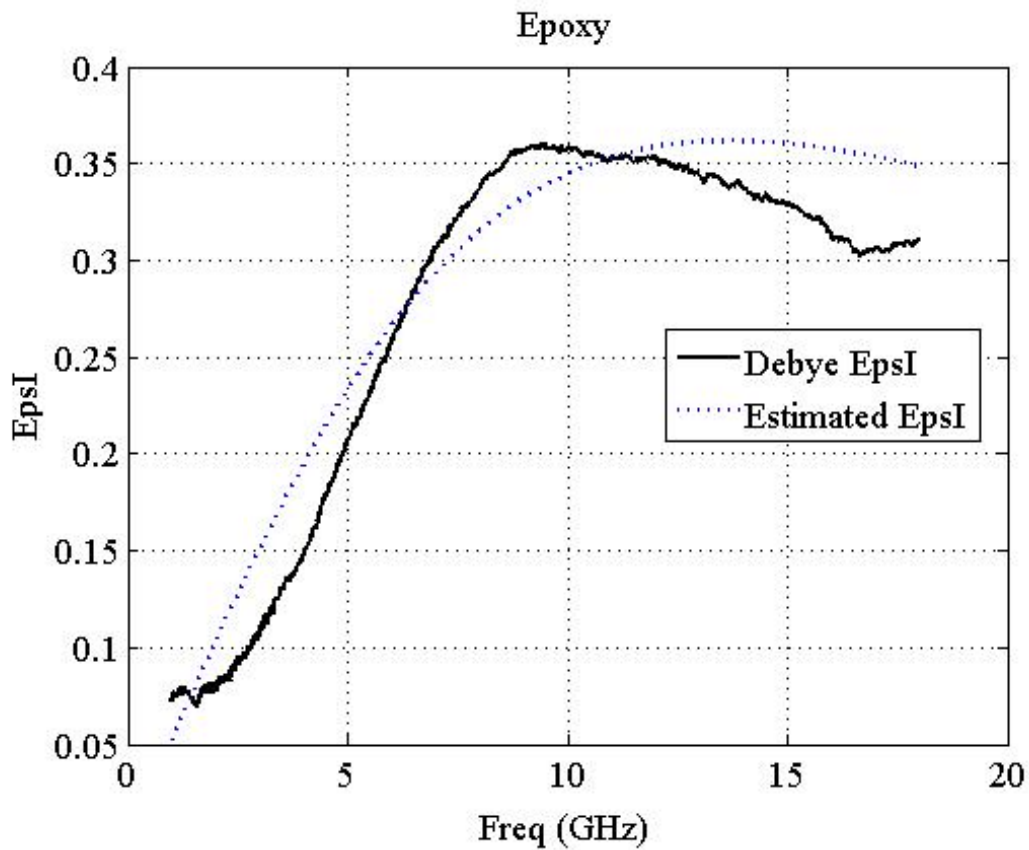


Figure B39. Fit Debye imaginary part of Epilox

#### 4.4. MAXWELL GARNET EQUATION

Now that the relative permittivity of the individual materials is obtain with Debye equation, the Maxwell Garnett equation relates two permittivities of two materials that are in a mixture. A material is the host and the other constituent is the inclusion. The amount of inclusion to be present in the mixture is given in weight percentage. These data will allow us to obtain the result of the relative permittivity of the mixture with the Maxwell Garnet equation.

Remember that the equation of Maxwell Garnet with cylindrical inclusion is:

$$\varepsilon_{eff} = \varepsilon_b + \frac{\left(\frac{1}{3}\right)V(\varepsilon_i - \varepsilon_b) \sum_{k=1}^3 \left(\frac{\varepsilon_b}{\varepsilon_b} + N_{ik}(\varepsilon_i - \varepsilon_b)\right)}{1 - \left(\frac{1}{3}\right)V(\varepsilon_i - \varepsilon_b) \sum_{k=1}^3 (N_{ik}(\varepsilon_i - \varepsilon_b))} \quad (15)$$

Where:

$\varepsilon_b$ : relative permittivity of a bases dielectric (host)

$\varepsilon_i$ : relative permittivity of inclusion

$N_{ik}$ : depolarization correspond to x, y and z Cartesians coordinates.

V: fractional volume of the inclusion in the mixture

This equation has the values of depolarization of cylindrical inclusions, which can be obtained from measuring the physical mixture with its diameter and length. The relative permittivity of the host usually known because the base is not a composite, and their values can be found in books and publications. The relative permittivity of the mixture can be obtained from the measurement of the mixture directly, and the weight percentage of inclusion is known in the composite. The situation is the following:

Known values:  $\varepsilon_b$ ,  $N_{i1}$ ,  $N_{i2}$ ,  $N_{i3}$ , V and  $\varepsilon_{eff}$

Unknown values:  $\varepsilon_i$

This is an equation with a single unknown variable. Solving this equation manually can be very laborious. Besides this, the  $\varepsilon_{eff}$  and  $\varepsilon_b$  can be vectors containing the relative permittivity according to frequency that has been measured. So the  $\varepsilon_i$  result can be a vector of solutions corresponding to each frequency. The vector  $\varepsilon_i$  will contain the relative permittivity of the inclusions.

The operation of this script uses the method to solve [9] equation Matlab integrated but adapted to resolve as many equations as values are in the vector. First load or enter the known variables, the length of the  $\varepsilon_b$  and  $\varepsilon_{eff}$  vectors is checked and the length of these vectors must match. The permittivity of the host and the permittivity of the composite is necessary to solve the permittivity of the inclusion. The solution will have so many results that the length of these vectors.

Once done, the script enters a loop with as many interactions as the length of the vectors. In the iterations the script will resolve the MG equation for each value of the vectors. As an equation of the second degree, the script chooses only the positive solution and stores it in other vector. This vector contains the solutions, and hence the relative permittivity of inclusions for each frequency. This vector contains the solutions that are relative permittivity of inclusions. *(See Appendix A7 solveMGequationv4.m)*

It is also usual to have several measures of the compound with different percentage of inclusion in the compound. By this, there is another script that allows that loads host material measurement and the number of samples with different weights of the compound. Maxwell Garnett equation is solved for each sample, and as the results are very similar, the script calculates the average of all results. This average is the final result, which indicates the relative permittivity of the inclusions in the composite. *(See Appendix A8 solveMGplus.m)*

#### 4.4.1. EVALUATION OF THE $\epsilon_i$ WITH SAMPLE TYPE 3 - E16

After understanding how our script works, this chapter presents how are the results of the script *solveMGequationv4.m* with one sample of our composite as input data. The details of this example are:

```
Freq. range : 1Ghz - 18Ghz
 $\epsilon_b$  : epiloX-old.mat (vector)
 $\epsilon_{eff}$ : E16-e163p0101013.mat (vector)
V (weight of inclusion): 1,863
AR: 1000
```

With this data, the vector of solutions shown in Figure 40 is the permittivity of inclusion obtained.

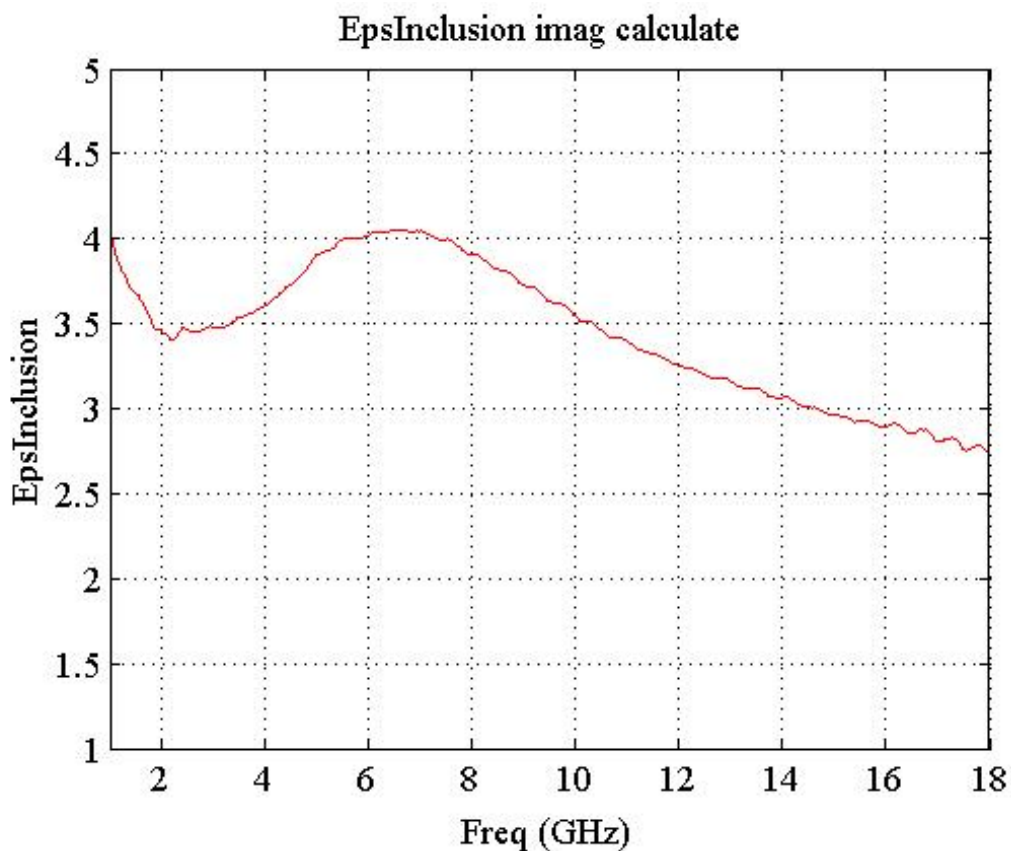


Figure B40. Epsilon inclusion calculate with MG script – Example 1

As the figure 30 shown, there are vector with a solution to the equation of Maxwell garnet for each different frequency. To check the result, this result is introducing into the equation MG along with relative permittivity of the host and other data, and the result of the equation must match the permittivity of the composite. In this case the permittivity of the composite of E16 with 3% of inclusion is used and this curve matches with the calculated result.

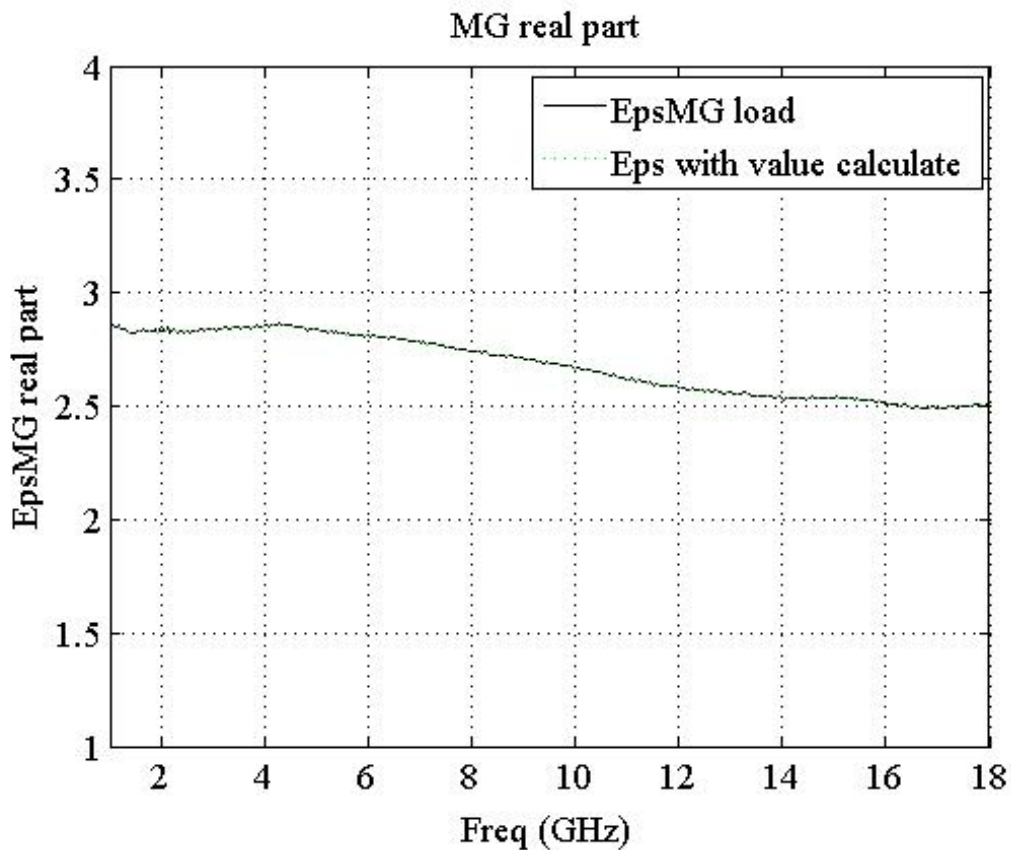


Figure B41. The result matches with the permittivity of the composite- real part



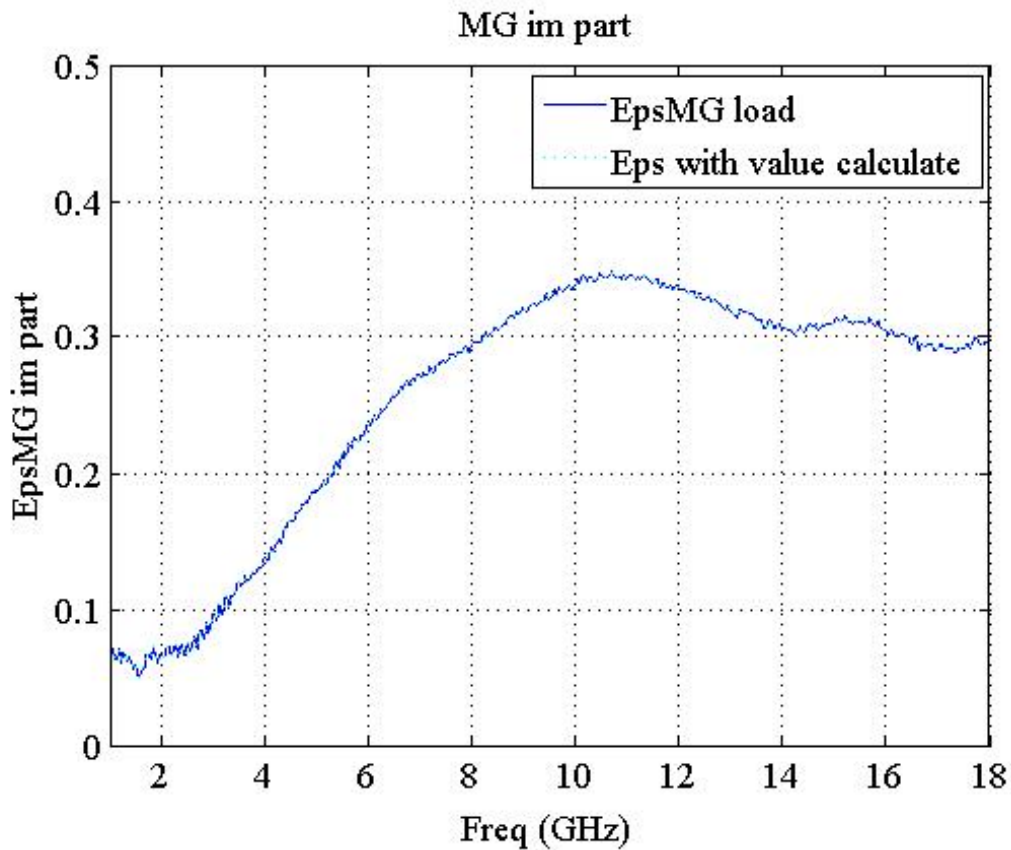


Figure 42. The result matches with the permittivity of the composite- Im. part

This check is useful to know that the script solves the equation correctly, once verified, do not need to do it again for the following samples.

#### 4.4.2. EVALUATION OF THE $\epsilon_1$ WITH SEVERAL SAMPLES OF DIFFERENT WEIGHT TYPE 4 – NC7

Now the script solveMGplus.m will be used to obtain the mean of the permittivity of MWCNTs calculated from samples of composite with different percentage of inclusion.

Specifically these inputs are used:

```
Freq. range : 1Ghz - 18Ghz
εb : resina-a.mat (vector)
Num. samples: 5
εeff,1: resina0p5.mat (vector)
V1 : 0.3
εeff,2: resina1p0.mat (vector)
V2 : 0.616
εeff,3: resina1p5.mat (vector)
V3 : 0.926
εeff,4: resina1p8.mat (vector)
V4 : 1.113
εeff,5: resina2p0.mat (vector)
V5 : 1,237
AR: 150
```

After loading these data, the script processes and calculates the relative permittivity of the MWCNTs for each of the composite introduced. When the script has these results, which should be the same theoretically, the script calculates the average of these result and the approximate values of the relative permittivity of the MWCNTs used in this composite is obtained.

In the figure B43 the results of the permittivity of the MWCNTs calculated for each compound are shown together the average of these results.

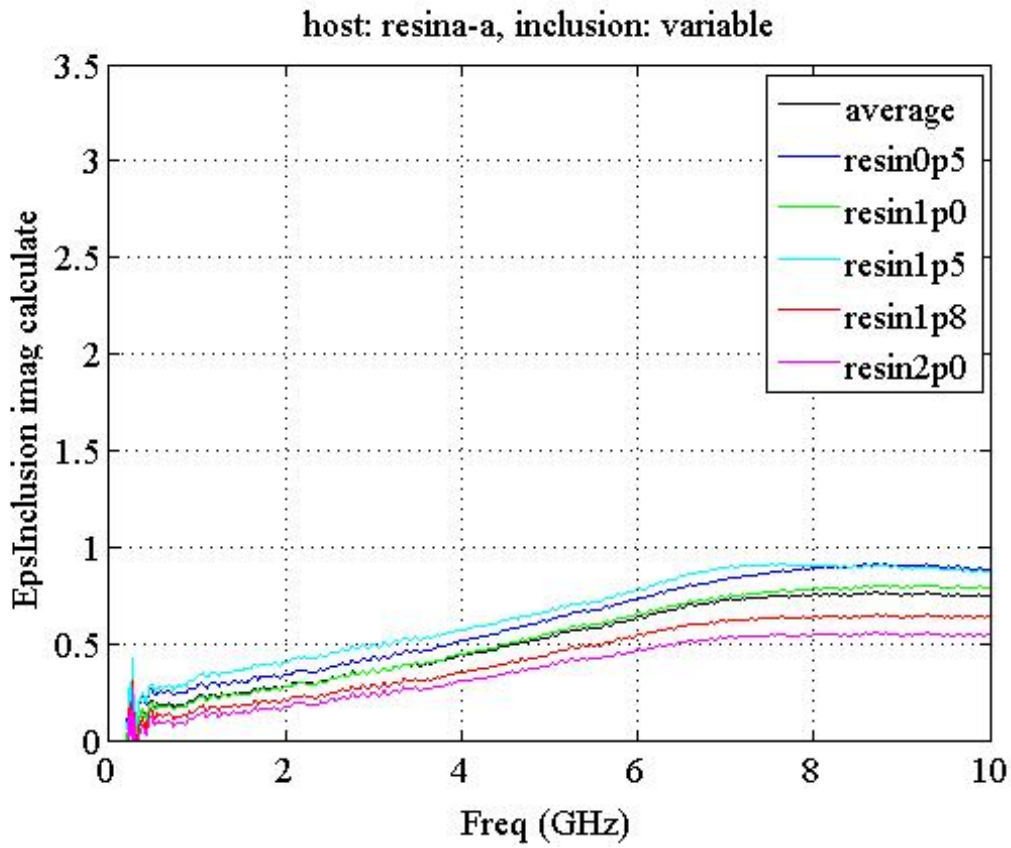


Figure B43. Permittivity imaginary of MWCNTs for each composite and average

Now, the permittivity of the inclusions is known, the conductivity can be calculated from the permittivity of the imaginary part, with the formula (12). Obtaining and representing the conductivity in a graph the results are shown in Figure B44.

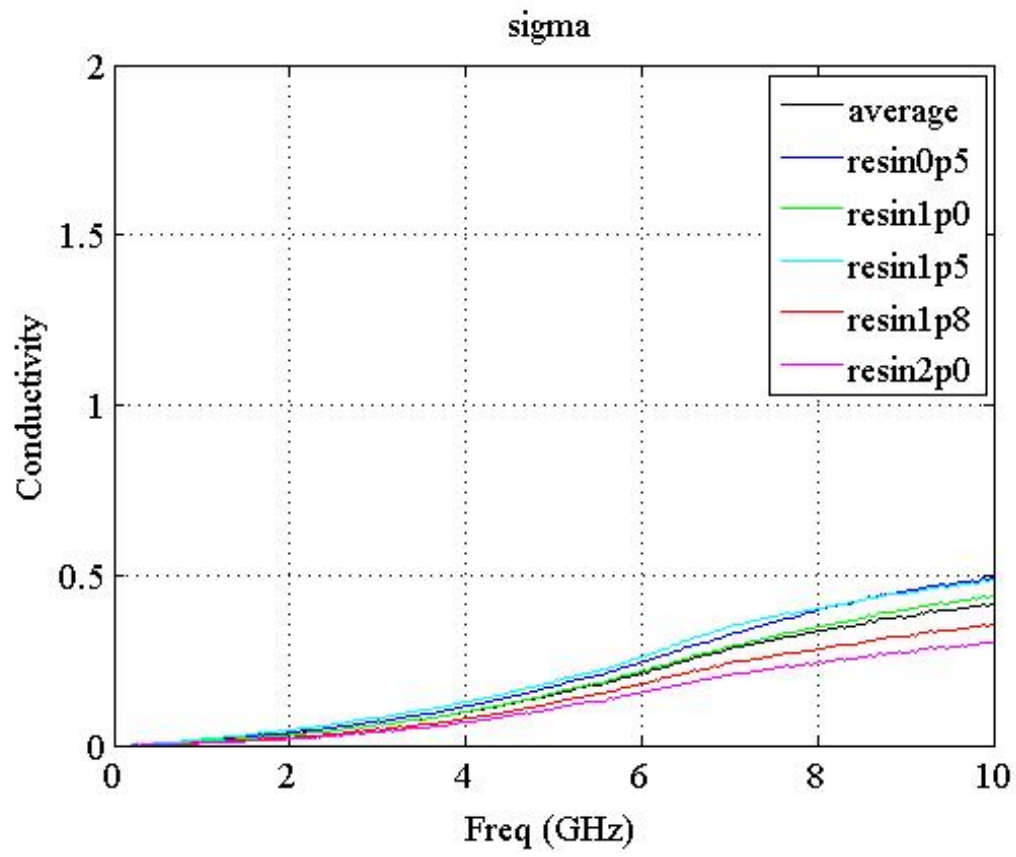


Figure B44. Conductivity for each composite and average

## 5. CONCLUSIONS

The objective of this thesis was to model equations that describe the behaviour of these carbon nanotubes in conjunction with a host, i.e., a compound that contains inclusions of carbon nanotubes. Model these equations manually can be a very laborious and time-consuming job, so it was necessary to use mathematical programs that help us solve our problem more effectively.

The program chosen to develop this modelling was Matlab because it is a tool of mathematical software that offers integrated development environment (IDE) with its own programming language (language M) and it offers countless techniques, toolbox and implementations that make the job easier.

The initial data of the materials are measurements that contain errors of measurement. Therefore it was necessary to study the different mathematical methods of estimation, approximation and resolution of multiple equations to make proper and effective modelling.

After several months of work, the result of the study applied to equations is shown in the attached script to this thesis. These scripts are presumably able to model the behaviour of materials in an efficient and correct way, which was the objective of this thesis.

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