Electrical and microwave characteristics of silver nanoparticle composites

Research on non-linear DC and RF reflection and transmission behaviour

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Cover: TEM images of clusters of silver nanoparticles. Particles are about 50-100nm in size.
Abstract

Research has been carried out on the electrical and microwave characterization of silver nanoparticles composite material. Main focus has been the investigation of the presence of non linear resistive and reflective behaviour. This behaviour is most likely to occur in composites with a filler ratio near the percolation threshold. Therefore, research focusses on fabrication and characterization of composite material in which silver nanoparticles are used, coated with an insulating shell.

Electrical characterization has shown non linear resistive behaviour for composite material with a filler ratio well above the percolation threshold. This verifies the functionality of an insulating coating, were a composite material which is relatively easy to fabricate will show remarkable non linear resistive behaviour. The increase in conductivity with increasing applied voltage strongly indicates a tunneling mechanism between particles.

Microwave response measurements showed a transition in the composite material at around 20% filler ratio up to were the composite theoretically can be described as a dielectric. Reversible power dependent reflectivity has not been observed, though for high power microwaves the composite showed an irreversible alteration in reflective response. Furthermore, due to a layered structure with different loss, significant asymmetrical reflective response is observed.
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Preface

After my internship at Stanford University, California, USA, I started in April 2008 with the final stage of the master program Applied Physics, my graduation project. After a period of orientation, I was offered the possibility to carry out research in collaboration with Thales BV. For me this was a great opportunity. Where my internship was mainly a great personal experience, it lacked an inspirational scientific experience. The idea of the collaboration between physics with a potential commercial application appealed to me. What we didn’t know, was the wideness of the field of research we entered in our first meetings. It took quite some time to determine the actual focus of the research, which finally has resulted in a report which makes first steps towards more extensive research on the investigated materials, which have great potential in showing interesting behaviour. Overall, this period of graduation was a very learningful experience where I rediscovered my fascination for physics and research.

First, I would like to thank Guus Rijnders en Simon van den Berg for the fruitful discussions we had in this field, where we could not only rely on knowledge in research fields familiar to us, but where we were challenged to take leaps into the unknown. Where at first it was a challenge for me to stay motivated in this process, I learned to appreciate this, the beauty of research in its purest form. Also always relaxing were our discussions about music and guitars, for me as a musician the confirmation that, although seemingly contradictory, the creative side of music and the abstract side in physics complement eachother tremendously.

Next, I would like to thank de BRAK and Heerendispuut Bracque for its beautiful friendships, inspirational discussions about all facets in life, the wednesday evenings and the fun weekends. Furthermore, my band, Duck4Cover, the musical inspiration it brings me and all the amazing adventures we had on the road. Then of course, my roommates from Studentenpaleis de Handige Jongens, with whom I lived together for six years. I would like to thank my parents, my brother and his wife for their loving support and Nadya for her love and care!

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Chapter 1

Introduction

In 1888, the German scientist Heinrich Rudolf Hertz physicist clarified and expanded the electromagnetic theory of light that had been put forth by Maxwell and the famous Maxwell equations. Not long after this scientific breakthrough, he was the first to satisfactorily demonstrate the existence of electromagnetic waves by building an apparatus to produce and detect VHF or UHF radio waves. The path towards the development of radar was created. The first to use radio waves to detect "the presence of distant metallic objects" was Christian Hülsmeyer, who in 1904 demonstrated the feasibility of detecting the presence of a ship in dense fog.

Now, more then hundred year after the first demonstration of the use of electromagnetic waves in object detection, RADAR has become a concept which basics are familiar to many. In fact, the word RADAR is actually an acronym for RAdio Detection And Ranging, abbreviated by the U.S. Navy to RADAR. The term has since entered the English language as a standard word, radar, losing the capitalization.

The basic principle of a radar system is as follows. A transmitter emits electromagnetic waves. When the waves come into contact with an object the wave is scattered in all directions. The signal is thus partly reflected back and it has a slight change of wavelength if the target is moving. The receiver is usually, but not always, in the same location as the transmitter. Although the signal returned is usually very weak, the signal can be amplified through use of electronic techniques in the receiver and in the antenna configuration. This enables radar to detect objects at ranges where other emissions, such as sound or visible light, would be too weak to detect. Radar finds its use in a wide range of applications, meteorological detection of precipitation, measuring ocean surface waves, air traffic control, police detection of speeding traffic, military applications, or to simply determine the speed of a baseball.

Figure 1.1 shows a schematic representation of a basic pulsed radar system, which can transmit and receive a microwave pulse. [1]. Behind the antenna a circulator functions as a switch between transmitting and receiving. A circulator has multiple channels, in which the electromagnetic waves propagate from one channel to another only in a particular order. It is a passive junction of in this case three ports in which the ports can be listed in such an order that when power is applied to any port it is transferred to the next on
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Figure 1.1: A schematic representation of a basic radar system. The system contains two ports for transmitting and receiving. The circulator allows a single antenna to both transmit and receive. A limiter 'protects' the receiving electronics by attenuating signals above a certain threshold.

In the transmission line, a high power amplifier amplifies the signal to be send. In the receiving line, after the circulator, a limiter lets signals of low power pass, while attenuating signals above a certain threshold. These limiters make use of diodes. A diode is a component which allows an electric current to flow though it in one direction while blocking current in the opposite direction. A modern semiconductor diode is made of a crystal of semiconductor like silicon that has impurities added to it to create a region on one side that contains negative charge carriers, or electrons, called n-type semiconductor, and a region on the other side that contains positive charge carriers, holes, called p-type semiconductor. The boundary within the crystal between these two regions is called a PN junction. The exact principle behind the asymmetric resistive behaviour of a diode is not of interest in this report. Nonetheless, the behaviour of a diode itself is of interest and is schematically shown in figure 1.2.

Figure 1.2: The current voltage characteristic of a diode. At positive bias current is allowed to flow. At negative bias the diode is resistive up to the breakdown voltage.
The figure shows the non symmetrical behaviour of a common diode. At a forward voltage, the diode is conducting. At backward voltage the diode is resistive up to a certain point, were dielectric breakdown occurs and current is also flowing in the backward direction. This is the physical limit were the diode is permanently damaged.

Summarizing, diode based limiters have an important role in a radar system. The limiter makes sure the signal is weakened such that a signal is formed which can be analyzed by the electronics behind this ‘protective wall’. Still, since limiters are based on diodes, there is a limit to its capacities. At a certain power, dielectric breakdown will occur, likely causing irreversible damage to electronics behind the limiter in the receiving line.

Therefore, in collaboration with Thales Nederland BV, the following research field is proposed:

*In the field of material science and nanotechnology, is it possible to develop materials which intrinsically have a power dependence in their electrical and microwave response? More specific, a material, which on macroscopic scale would show power dependent response in its resistivity, and a power dependent reflective and transmissive response, increasing in reflection, decreasing in transmission, when subjected to microwaves.*

A material which would fulfill these properties is a material, in which an intrinsic transition from dielectric properties to metallic properties would occur, for an applied potential or an applied electromagnetic field. A dielectric material is obviously resistive, and for low values dielectric values very transmissive for microwaves. A metal on the other hand is obviously very conductive and highly reflective for microwaves.

In fact, in an ideal situation, this material should show ‘diode-like’ non linear behaviour. The material is resistive at low potential, but conducting for high potential. The same non linear behaviour for its response to microwaves. Transmissive at low power, reflective at high power. A material which shows these types of non linear behaviour would create new possibilities in limiters and controlling high electric fields and high power electromagnetic radiation.

With this in mind, a literature study has shown that a material of great interest and potential to show these non linear effect are based on percolative systems. Therefore, more specific, this research will focus on the electrical and microwave characterization of composite material of an insulating embedding medium with metal filler particles.

First, chapter 2 will elaborate in more detail on the theoretical aspects on these percolative composite materials and the theory behind non linear resistive behaviour, resulting in the research questions. Next, the structural characterization of the composite material will be outlined in chapter 3. Chapter 4 will subsequently discuss the sample preparation and experimental setup to carry out a electrical DC characterization of the material, followed by the outline of the sample preparation and experimental setup for the microwave characterization of the composite material in chapter 5. Finally, conclusions and recommendations will be presented in chapter 6.
Chapter 2

Theoretical background and research questions

As introduced, this research will focus on the electrical and microwave behaviour of composite material were conducting particles are embedded in an insulating epoxy matrix. The potential of these systems to show non linear effects when submitted to a potential or electromagnetic radiation is investigated.

These systems can be described as a percolative system described by percolation theories. First this chapter will elaborate more on these systems and their non linear resistive behaviour due to varying filler ratio. Furthermore, literature will be discussed were theory and measurements are compared, indicating field dependent resistive behaviour near the percolation threshold caused by tunneling effects.

Subsequently, the general microwave response of materials will be discussed shortly. Also, literature describing permittivity measurements on composite material of filler particles is discussed.

Last, from this theory, the focus of the research will be discussed by proposing the research goals.

2.1 Percolation theory

In general, a composite of a medium with filler particles can be described as a mathematical percolative system based on theory of percolation. This theory describes the behaviour of connected clusters in a random medium. The composite material focus of this research in particular consists of a insulating medium in which conducting metal particles are embedded. Hence, the resistivity of these models are described by this theory of the behaviour of connecting clusters.

The electrical conductivity and dielectric constant, of metal-insulator mixtures, discussed later on, are the most widely investigated physical properties of percolative systems [3]. As said, in general, a percolative system is described by the mathematical model of percolation...
The main concept of percolation theory is the existence of a percolation threshold $f_C$, the filler ratio of clusters when connected paths between clusters start to occur. In the case of a composite of an insulating medium with conducting particles representing the clusters, the resistance behaves very non-linear.

Namely, when a certain amount of conductive filler is spread in an insulating polymer matrix, the material transforms from an insulator to a conductor. As the concentration of the conducting additive is raised above $f_C$, the number of continuous paths through the compound increases allowing conduction of charge carriers [4] [5] [6]. This resistivity as function of volume ratio filler material is shown in figure 2.1.

![Figure 2.1: On the left, a schematic representation of the resistivity against volume fraction filler particles. At a certain volume particles tend to form linkages, resulting in a drastic drop in resistivity. The volume fraction at which this occurs is indicated by $f_C$. On the right, an actual resistivity measurement on a composite of silver micro particles composite as a function of the micro silver particle volume fraction [7].](image)

Percolation threshold values are usually in between 10-20% volume ratio filler particles, depending on the size of the filler particles [8] [7] [9].

### 2.2 Field dependent conductance

When the conductivity of a conductor-insulator composite is treated as a theoretical percolation problem, for the conductivity of the composite, the following scaling law applies [5]:

$$\sigma_{dc} \propto (f - f_C)^t,$$

with $\sigma_{dc}$ the DC conductivity, $f$ the filler ratio, $f_C$ the percolation threshold and $t$ and arbitrary positive constant. Monte Carlo calculations in simulations of three dimensions have shown that the value for $t$ is about 1.6-2.0 [10].

Several experimental values of $t$ measured in real systems like carbon black filled polymers, however, disagree with this theoretical value. When in a Monte Carlo experiment physical contact between conductive particles is needed to permit the conduction of the charge carriers through the compound, in real conductor-insulator composites the electrons are
allowed to tunnel from one conductive cluster to another separated by a thin insulating polymer layer. This is an indication that these materials, near percolation threshold, could show a conductivity dependent on the applied electric field.

This field dependence is verified in literature [11]. The relation between the resistance and the filler volume ratio of these composites, as shown in figure 2.1, can be divided into three regions. The first region shows a high resistivity at lower volume ratio. In the second region, the transition from insulator to metal occurs in a narrow span of increasing filler volume ratio, were in the third region, the material is fully conducting.

It has been shown that the electric field dependence of current in the first region is ohmic and changes into a non-ohmic behavior in the second region. The third region shows an ohmic current behavior again. The non-ohmic current behaviour and the sharp change in conductivity in the second region can be explained in terms of a tunneling conduction. It has to be noticed, that although the transition seems steep, there is a small span in filler ratio in which this transition occurs. At this filler ratio tunneling gaps exist, but a fully conducting path is still not present. Therefore, when the composite is fully conducting and shows ohmic behaviour, actual percolation occurs, were conducting particles form conducting paths between contacts.

Measurements that show this field dependence resulting in strong non linear behaviour are shown in figure 2.2 [12].

Figure 2.2: At above 21% volume ratio of coated silver nanoparticles, non-ohmic behaviour is observed. At a certain applied electric field, current density increases drastically caused by tunneling conduction. The field strength at which this occurs depends on the shell thickness.

Current-voltage measurements are shown for two types of composites, containing silver nanoparticles with ‘thick’ and ‘thin’ shells. These shells form a tunneling barrier between the particles. This ensures that even at high volume filler ratio, theoretically above the percolation threshold, particles still do not percolate. But particles are very close together,
were the composite shows the non-ohmic behaviour. It can be seen that the composite with particles with thin shell starts to conduct at 5kV/cm. For the thick shell, this obviously higher, since the spacing between particles is bigger. Here, the material starts to conduct at 10kV/cm. It is shown that this nonlinear behaviour is recoverable, which makes these composite very interesting. This system in particular, consisting of silver nanoparticles with a thin coating, has become focus of this research, which will be outlined in more detail later on.

### 2.3 Microwave response materials

Besides the interest in non-linear conductivity, focus of this research is also the microwave response of these composites. This includes the reflective and transmissive behaviour of the material. As introduced, the composite material will experience a transition between insulator and conductor. This obviously will affect its microwave response.

Measurements mainly have been carried out in a frequency span of 8-12GHz, or the X-band range, see appendix C. This because this is a commonly used frequency span in the microwave industry, were these frequencies correspond with wavelengths in the order of centimeters, which is from a practical point of view convenient in the construction of microwave components.

#### Microwave response in conductors

At high filler ratio, the material acts metallic and conductive. Therefore, it will be very reflective for microwaves. Basically, when an electromagnetic wave interacts with a conductive material, charges within the material are made to oscillate back and forth with the same frequency as the fields. The movement of these charges, usually electrons, forms an alternating electric current, from which the magnitude is greatest at the conductor’s surface. The decline in current density versus depth is known as the skin effect and the skin depth is a measure of the distance over which the current falls to 1/e of its original value.

The skin depth is defined as the depth below the surface of the conductor at which the current density decays to \( \frac{1}{e} \), about 0.37 of the current density at the surface, inducted by the electromagnetic wave interacting with the surface of the conductor. The skin depth can be calculated as follows:

\[
\delta = \sqrt{\frac{2\rho}{\omega \mu}},
\]

with \( \rho \) the resistivity of the conducting material, \( \omega \) the angular frequency of the currentflow and \( \mu \) the absolute magnetic permeability of the conductor. Permeability is the measure of the ability of a material to support the formation of a magnetic field within itself. In other words, it is the degree of magnetization that a material obtains in response to an applied magnetic field. Absolute permeability \( \mu \) is equal to \( \mu_0 \cdot \mu_r \), were \( \mu_0 \) is the permeability of free space equal to \( 4\pi \times 10^{-7} \, \text{N} \, \text{A}^{-2} \) and \( \mu_r \) the relative permeability of the conductor. At a frequency of 10GHz, typical skin depth for silver is 0.64\( \mu \text{m} \).
Microwave response in dielectrics

Different from conductors, dielectric or insulating materials do not only reflect electromagnetic waves, but partially will reflect, partially transmit waves, depending on the relative permittivity $\varepsilon_r$, relative permeability $\mu_r$, lossiness $\tan\delta$ of the material and the frequency of the electromagnetic waves.

Permittivity is the measure of how much resistance is encountered when forming an electric field in a vacuum. In other words, permittivity is a measure of how an electric field affects, and is affected by, a dielectric medium. Permittivity is determined by the ability of a material to polarize in response to the field, and thereby reduce the total electric field inside the material. Thus, permittivity relates to a material’s ability to transmit or ‘permit’ an electric field.

The relative permittivity of a homogeneous material is the permittivity relative to that of free space, also called dielectric constant, were $\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$, with $\varepsilon_0$ the permittivity of free space with a value of $\varepsilon_0 \approx 8.85 \cdot 10^{-12}$. The relative permittivity is frequency dependent and complex, were $\varepsilon_r(\omega) = \varepsilon'_r(\omega) + i\varepsilon''_r(\omega)$.

Most influential on the microwave reflective behaviour of materials is the difference of the relative permittivity between two interfaces. A bigger difference in permittivity will result in a higher reflection and less transmission. Since this research will examine the reflective and transmissive behavior of a thin sample in between air, with the main focus on its reflective response, for a dielectric layer in between air, the reflection is expressed as [13]:

$$R = \frac{R_1 + R_2e^{-2\gamma_m l}}{1 + R_1R_2e^{-2\gamma_m l}}, \quad \text{(2.3)}$$

with $\lambda_m$ is the complex propagation constant in the layer of thickness $l$. Reflection and transmission coefficients at the boundaries $z = 0$ and $z = l$ are calculated through the characteristic impedances or the corresponding media [1].
\[ R_1 = \frac{Z_m - Z_0}{Z_m + Z_0}, R_2 = \frac{Z_0 - Z_m}{Z_0 + Z_m} \] (2.4)

The characteristic impedance of air is \( Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} \), the characteristic impedance of the dielectric material is \( Z_m = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \). Loss of the material is defined as \( \tan \delta = \frac{\varepsilon''}{\varepsilon'} \). The propagation constant in the material is given as:

\[ \gamma_m = j\omega \sqrt{\frac{\mu_0 \varepsilon_0}{\varepsilon_r}} \sqrt{\varepsilon'_r} - j\varepsilon''_r \] (2.5)

Figure 2.4: Relation between the relative permittivity of a dielectric material and the reflection when subjected to electromagnetic radiation in the microwave range.

Figure 2.4 shows the relation between the relative permittivity and the reflection for a 1mm thick slab of lossless material, with the reflection in dB defined as \( R(dB) = 20 \log_{10}(|R|) \). This makes the reflection dimensionless and is simply the ratio between the reflected and incident microwave. It can be seen that up to -2dB, the permittivity gradually increases. Higher reflections lead to a drastic and more than exponential increase in the permittivity.

Microwave response of filler composites

Literature also describes permittivity measurement at microwave frequencies depending on filler ratio [14]. Figure 2.5 shows the measurements on composite material of two different epoxy resins with carbon black filler. These measurements were carried out at 9.5GHz, in the microwave range. The solid lines show three different proposed relations between permittivity and filler ratio shown in equation 2.6, 2.7 and 2.8 [15].

The proposed possible models in the literature to describe the permittivity of a composite containing metal particles are:

Bruggeman’s formula:

\[ \varepsilon^* = \frac{\varepsilon_m^*}{(1 - \Phi)^3} \] (2.6)
2.4. RESEARCH GOALS

Corkum's equation:

\[ \varepsilon^* = \varepsilon^*_m \frac{1 + 2\Phi}{(1 - \Phi)}, \]  
\[ (\varepsilon^*)^\alpha = \frac{(1 - \Phi)(\varepsilon^*_m)^\alpha}{(1 - \frac{\Phi}{\Phi_c})}, \]  

with \( \varepsilon^* = \varepsilon'_r - j\varepsilon''_r \) the relation between the relative permittivity and its real and complex part of the composite material, \( \varepsilon^*_m \) the complex relative permittivity of the embedding medium, \( \Phi \) the filler ratio, \( \alpha \) an arbitrary positive constant and \( \Phi_C \) the percolation threshold.

Clearly, all relations show a more or less exponential increase in permittivity with increasing filler ratio, were the percolation threshold is of influence. Especially the Shin model tends to increase dramatically near the percolation threshold. Therefore, research on the possible power dependence of the reflectivity of conducting filler composite material with increasing filler volume ratio up to the percolation threshold, which has not yet been carried out in literature, is of great interest.

2.4 Research goals

Considering the conductive characteristics of these composite materials: from theory, it is shown, that composite materials with conducting filler particles show interesting nonlinear conductive behaviour based on percolation theories. This non linearity is strictly connected to the filler ratio of conducting particles. It has also been shown that field dependent nonlinear conductive behaviour occurs around the percolation threshold, were particles are close together but do not yet form connected paths. Since conductivity does
not match percolation simulations, it is assumed that tunneling plays an important role in the conductive behaviour around the percolation threshold. This field dependent non linear conductive behaviour based on tunneling effects has also been measured.

Considering the microwave characteristics of these materials: All these measurements described in literature are carried out at a constant microwave power. As shown, modelling microwave response of composite materials is always based on fits and assumptions, but has never been very well understood. The power dependent microwave response systems also have never been investigated. Since these materials show interesting non linear field dependent resistive behaviour when potential is applied, it has become of interest how these materials would behave when subjected to various microwave powers. Possibly, due to tunneling effect at the surface, near percolative composites could show non linear reflective behaviour when subjected to certain high energy microwaves. This could be based on induced currents between particles, creating conductive behaviour which makes the material more reflective.

Considering the composite material itself: These field dependent non linear effects will only occur in non percolating systems. Non linear effect will very likely only be seen near the percolation threshold, were particles are close together, but do not form conducting paths. Therefore, the composite material of interest consists of coated silver nanoparticles embedded in an epoxy resin. The next chapter will elaborate more on this composite, from which the production and characterization is part of the research.

The following research goals have been formulated:

- The fabrication of a composite material of coated silver nanoparticles in an insulating epoxy resin. Analyzing particles for their composition and presence of a coating in the first place, then creating homogeneous composite material with a defined varying filler ratio.
- Electrical characterization of this composite material. This includes resistance measurements and field dependence measurements, to investigate possible non linear field dependent resistive behaviour.
- The microwave characterization of this composite material at varying conductive filler ratio. This includes measuring the power dependent reflective and transmissive behaviour of these composite materials, to investigate a possible power dependence in the reflective behaviour of the composite material. From these measurements the calculation of the material parameters, relative permittivity $\varepsilon_r$, relative permeability $\mu_r$ and loss tangent $\tan\delta$. 
Chapter 3

Structural characterization

As introduced, this research focuses on the electrical and microwave characteristics of silver nanoparticle composites. In general, a composite material is a material made from at least two or more materials with significantly different physical or chemical properties. Again, the composite material of interest in this research is a material in which metallic silver nanoparticles are spread in an insulating epoxy resin at varying volume ratios.

This chapter first will outline the characterization of the used silver nanoparticles with the use of Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Next the fabrication and characterization of the composite material will be discussed. This composite material will be used to construct various composite samples for DC and RF measurements outlined in the following chapters.

Main questions in the structural characterization of the used commercially available silver nanoparticles and the composite material are:

- What is the exact size distribution of the particles?
- Do these nanoparticles have a 'coating', and insulating thin shell around the metallic core?
- If so, what is the shell thickness?
- Do the particles tend to cluster together as powder/part of composite?
- How do nanoparticles behave as part of a composite material when embedded in a polymer matrix of an epoxy resin, will these particles drift to the bottom, or will they spread homogeneously?

3.1 Silver nanoparticles

As outlined in the previous chapter, the proposed ideal model for the composite consists of a insulating matrix for which an epoxy resin is chosen filled with conducting filler particles with an insulating coating resulting in an insulating defined barrier between the
CHAPTER 3. STRUCTURAL CHARACTERIZATION

conducting particles, which prevents the particles from percolating at any ratio. As filler material, silver nanoparticles are chosen, since silver is most conducting of all metals with a resistivity of $1.59 \times 10^{-8} \Omega \text{m}$ [16].

Silver nanoparticles instead of microparticles were chosen since from first test measurements on microparticles in epoxy resin, it turned out to be very difficult to form an even slightly homogeneous filled sample, as can be seen in figure 3.1, showing a section of a testsample. Particles clearly sink to the bottom and percolate. Even at very low filler fraction, the bottom side of the sample would fully conduct, very undesirable and not functional for this research.

![Figure 3.1: SEM images of a cut-through of resin with 40%wt silver micro particles with size 5-8µm](image)

Therefore, it is chosen to use commercially available silver nanoparticles. In the chemical synthesis and fabrication of these nanoparticles, a thin organic layer is constructed around the particles. Ideally, constructing this insulating shell around the silver particles would be part of this research, but this turned out not to be feasible, and is not chosen to be the focus of this research considering the difficulty and chemical focus of this process. In the next sections, a structural characterization is carried out by analyzing the particles with SEM, TEM and XPS. SEM and TEM will provide information about the size of the particles and will verify the presence of this shell coating around the silver particles. XPS will tell which elements are present in the powder. If more elements are present, this also will indicate the presence of a layer. This layer is likely to be organic, resulting in XPS peaks at for instance carbon, oxygen and nitrogen.

3.1.1 TEM characterization

Figures 3.2 and 3.3 show TEM images of the silver nanoparticle powder at two different scales. The particles can be seen as the darker regions, surround by greyisch amorph areas were vacuum is present. The particles seem to be partly transparent. This is inherent to the technique on which TEM is based, were imaging is based on the interaction of electrons transmitting through the sample [17]. Particles are about 50-100nm in size.

It can be seen that a thin coating around the nanoparticles with a thickness of about 1-3nm
3.1. SILVER NANOPARTICLES

Figure 3.2: TEM images show an average particle size of about 50-100nm. Furthermore, around the particles a thin amorph layer with a thickness of about 1-3nm can be seen.

Figure 3.3: Unlike figure 3.2, no coating seems to be present.

is present. But this does not seem to be the case for all the particles. As can be seen in Figure 3.3, this coating is not visible. The image clearly shows a periodic line structure mainly visible at the edges of the particle which is the direct result of the crystal structure of the silver. This periodic structure is present up until the edges unlike the images in figure 3.2. If a coating was presence, as in Figure 3.2, an amorph crystal 'structure' would be visible, between the edge of the silver particle and the vacuum. Still, as will be discussed and verified further on, it can be assumed that the bulk of particles is coated.

3.1.2 SEM characterization

Next, a SEM characterization is carried out on the silver nanoparticle powder, shown in figure 3.4. At an amplification of 100.000x, clearly the individual particles are visible. Average size distribution is about 50-100nm as expected. Also, the particles seem to cluster together. The image does not give any information about the presence of a coating
since the resolution is too low at these dimension, and the SEM technique itself only gives topographic information.

![SEM image of the silver nanoparticles](image)

**Figure 3.4:** SEM image of the silver nanoparticles. Clearly the particles tend to cluster together. Average size distribution is about 50-100nm.

### 3.1.3 XPS characterization

For the analysis of the elemental composition of the nanoparticles X-ray Photoelectron Spectroscopy (XPS) is used. This quantitative spectroscopic technique measures the elemental composition, chemical state and electronic state of the elements that exist within a material. By irradiating a material with a beam of X-rays XPS spectra are obtained. Simultaneously the kinetic energy and number of electrons that escape from the surface of the material are measured. This makes XPS a surface chemical analysis technique that can be used to analyze the surface chemistry of a material. X-rays penetrate the surface with a depth of about 1 to 10nm, so elemental information is obtained in this depth range.

![XPS spectrum](image)

**Figure 3.5:** Typical XPS spectrum for ordinary silver

If the silver nanoparticles are coated, this would clearly be visible in a XPS scan, as the first few nanometers of the particle, penetrated by X-rays, will consist of different elements then silver. This is then visualized in the the XPS spectrum by various peaks at different
3.1. SILVER NANOPARTICLES

elements. It is likely that the coating is organic, so peaks will be visible at carbon, and elements likely to be bonded on carbon, such as hydrogen, nitrogen and oxygen. If the particles are not coated, all these peaks will be much less present, and the silver peak will clearly dominate. This is visible in the reference XPS spectrum shown in Figure 3.5. The spectrum only shows peaks at various energies corresponding to the different electron bands of silver [18].

Figure 3.5: XPS spectrum of the nanoparticles. Clearly visible are peaks at C1s, N1s, and O1s, compared to Figure 3.5

Figure 3.6 shows the XPS spectrum of the nanoparticles. Significant peaks are visible for carbon, nitrogen and oxygen. Smaller peaks representing other elements are also present. The atomic concentrations of the four most present energies and corresponding elements are outlined in Table 3.1.

Table 3.1: Atomic Concentration Table

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>N1s</th>
<th>O1s</th>
<th>Ag3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values</td>
<td>0.314</td>
<td>0.499</td>
<td>0.733</td>
<td>6.277</td>
</tr>
<tr>
<td>Values</td>
<td>24.50</td>
<td>6.60</td>
<td>24.24</td>
<td>44.66</td>
</tr>
</tbody>
</table>

From this XPS measurements, the following conclusions can be drawn:

- The carbon content is much higher than expected from adventitious carbon, or in other words, 'carbon from the air' on powder material.
- The oxygen content is higher than expected from fully oxidized silver Ag2O.
- The nitrogen content is higher than what can be expected from air.
- The carbon spectrum does not look like adventitious carbon since it is too wide. The
high energy bands indicate carbon bound to oxygen.

- Zinc and Chlorine are found in small amounts. Maybe they are a part of the shell surrounding the nanoparticles.

From the XPS measurement, it can be concluded that it is very likely that the particles have an organic coating. The concentration of elements other than silver is much higher, than to be expected from contamination of the sample from elements in the air. One has to take into account that, as said earlier, these concentration ratios do not apply for the ‘bulk’ of coated silver particles, as obviously, in the first few nanometers that the x-rays penetrate the particle surface the beam only ‘see’ the coating and no silver.

3.2 Composite of nanoparticles in epoxy resin

After the structural characterization of the silver nanoparticles, next step is to characterize the behaviour of the silver particles embedded in an epoxy resin, with the goal to produce a composite material in which silver particles are spread as homogeneous as possible, at varying filler ratio.

Basically, constructing these composites is quite straightforward. A commercially available resin is used, consisting of two mixtures of an epoxy embedding medium based on EPON 812, the most widely used embedding resin for electron microscopy [19], with two different hardeners, 2-dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (NMA). Two mixtures are made, one containing 5ml medium with 8ml DDSA, the second with 8ml medium and 7ml NMA. After thorough magnetic stirring, these mixtures are poured together and subsequently, 16 drops of 2,4,6-tris(dimethylaminomethyl)phenol (DPM-30) accelerator is added. Changing the ratio between the two mixtures will influence the hardness and brittleness of the final product.

To make the final composite, a measured amount of silver particles is added to the epoxy resin mixture. This composite is then stirred by magnetic stirring. This gives the actual composite material with a certain volume ratio of silver particles.

To make samples, two types of molds that have been fabricated for the microwave measurements, more thoroughly discussed in chapter 5, are used. These molds are cured in an oven at an average temperature of 60°C, while turning, to prevent particles from sinking. The aim is to create a composite with the conducting silver filler particles homogeneously dispersed in the epoxy matrix. Therefore, it needs to be examined how the particles behave in the resin after the curing process. This includes:

- Particles drifting and settling on the bottom of the epoxy matrix
- Distribution of particles through the epoxy matrix
- Possible clustering of particles

Therefore, SEM images are taken from sections of test samples, discussed in the next section.
3.2. COMPOSITE OF NANOPARTICLES IN EPOXY RESIN

3.2.1 SEM characterization

First, test samples are created by filling a X-band mold with the liquid composite material, resulting in samples with a thickness of about 1mm. Again, the fabrication of this mold and samples will be discussed more thoroughly in section 5.2.1 and is not yet of interest in this section. To analyze possible sinking of particles, a low volume filler ratio of 5% silver particles is chosen. SEM images of sections of the sample are shown in figure 3.7.

![SEM images of a section of a test sample with a 5% silver particle filler volume ratio at two different scales.](image1)

Figure 3.7: SEM images of a section of a test sample with a 5% silver particle filler volume ratio at two different scales. Macroscopically, the particles seem to have spread homogeneously in the material, as can be seen on the left. No particle sinking is present, which would result in a clear visible gradient in contrast in the image. Microscopically, the particles cluster, as can be seen on the right.

![A film of the composite dropped and cured on a thin gold layer sputtered on a silicon substrate. Silver particles are spread microscopically.](image2)

Figure 3.8: A film of the composite dropped and cured on a thin gold layer sputtered on a silicon substrate. Silver particles are spread microscopically.

It can be seen that this sample fabrication method leads to macroscopically homogeneous samples, as no significant contrast gradient is present in the section of the samples. This indicates that particles did not sink to one side of the sample, but spread homogeneously through the sample. Microscopically, particles still tend to cluster.
For the DC measurements outlined in the next chapter, a drop of composite material with a high volume filler ratio of 25% is put on top of a substrate, resulting in a thin layer of composite material. To examine structural behaviour of this thin film of composite, a test sample is created were a drop of composite material with a filler ratio of 25% is put on top of a gold sputtered silicon substrate. After curing, the film is scratched to be able to make SEM images of a section of the composite thin film. The SEM images are shown in Figure 3.8. Clearly, also here, the macroscopically, the particles are spread homogeneously, but microscopically also cluster.

3.2.2 Conclusions structural characterization

This chapter outlined the structural characterization of commercially available silver nanoparticles and the composite material that has been constructed from these particles embedded in a commercially available epoxy embedding resin. The main questions proposed were the following:

- What is the exact size distribution of the particles?
- Do these nanoparticles have a 'coating', and insulating thin shell around the metallic core?
- If so, what is the shell thickness?
- Do the particles tend to cluster together as powder/part of composite?
- How do nanoparticles behave as part of a composite material when embedded in a polymer matrix of an epoxy resin, will these particles drift to the bottom, or will they spread homogeneously?

With the use of SEM, TEM and XPS it can be concluded that the average size of the particles is about 50-100nm. Also is very likely that these particles have some form of organic coating, with an average thickness of about 3nm. Considering the method in which these particles are made chemically, namely a synthesis in an organic solution, these characterization verifies the expected presence of a coating.

Still, it is questionable whether all particles are individually coated. TEM images also showed particles that very likely were not coated. But considering the XPS measurement and the synthesis of these powders, it may be assumed that the bulk of the particles is coated, which makes these particles useful in the suggested model of non percolating spaced metallic particles in an insulating matrix of epoxy resin.

Next, test samples from the composite material are constructed and examined with SEM. It is shown that with the proposed fabrication technique silver particles spread macroscopically homogeneous through the epoxy without sinking to one side. Also, for increasing filler ratio, the density of silver particles also increased homogeneously. Microscopically, the particles do tend to cluster, but again, are very likely to experience an average spacing due to the coating. This prevents clustering and makes the composite samples useful for the DC and microwave measurements, outlined in the next chapters.
Chapter 4

Electrical DC characterization

In this chapter the DC electrical properties of the composite material are examined. First, a basic setup is constructed to measure the resistance of bulk composite material at high volume ratio silver nanoparticle filler material. This will provide information about the presence of an insulating shell around the metal particles. Next, the electrical properties on microscopic scale are examined. Herefore, substrates are used on which gold contacts are sputtered with a spacing of only a few micrometer. By depositing the composite material on these contacts, a more quantitative approach can be used to describe the system, since a quantified amount of particles is positioned in between the contacts. By applying a potential sweep on the contacts, the current and resistance response of the composite material is examined and whether non linear behaviour as described in literature is observed.

4.1 Resistance measurements on bulk composite

As described in the theory, composite materials containing metallic particles show a distinct transition with increasing particle filler ratio, from an insulating to a conducting material. From theory, this transition occurs at a filler volume percentage of about roughly 10-20%. Above this filler ratio, particles percolate creating conducting paths which drastically increases conductivity of the material.

As introduced in the previous chapter, it is very likely that the used silver nanoparticles used in this research have an thin organic insulating shell. Theoretically this would mean, that a composite, with a volume filler particles higher then the volume at which theoretically percolation occurs, would still be insulating. Therefore, a rough resistance characterization is carried out on a composite with a volume filler ratio of 25%, above the percolation volume percentage.

To carry out this measurement, a drop of composite material is deposited on a thin gold layer of about 200nm sputtered on a silicon substrate. At various points on the composite layer conducting silver glue contacts are constructed, so resistance is measured at multiple spots. Also contacts are constructed on the gold layer. A schematic representation of the
setup is shown in figure 4.1. A section through a contact is shown in figure 4.2. Clearly, the 'blob' of silver glue can be seen on top of a layer of composite material with a thickness of about 200µm. The smooth dark region left from the layer of composite material is the gold layer. It has to be taken in mind that the whole sample is tilted slightly, were the SEM is actually looking on top of the gold layer, were there is a 90° angle between the gold and composite layer.

With a multimeter, initial resistance on all the contacts was measured. It immediately became clear that the composite was fully resistive. No value was measured, which indicates that the resistance of the composite is out of range of the multimeter which measures resistance up to $10^7$Ω. Considering the volume filler ratio of 25%, higher then the theoretical percolation volume, this is a clear indication of the presence of a insulating shell around the silver nanoparticles which prevents the particles from percolating.

Next, voltage sweep measurements have been carried out by connecting the contacts to a Keithley potentiometer. These sweep measurements started at an initial voltage of 5V, were resistance immediately irreversibly dropped to a few Ohms, very likely indicating an immediate dielectric breakdown. It can be concluded that the composite clearly responds on an applied voltage. Likely by heating, the material locally intrinsically changes, causing a percolating path, which results in a local drop of the resistance.

New measurements at better control of the voltage sweeps were not carried out by the
lack of new samples, this is a recommendation for further research to the electrical bulk behaviour of the composite.

Figure 4.2 shows the SEM images of sections of the sample taken after the voltage sweep measurements. No structural change is visible. But a dielectric breakdown could easily have taken place in a different part of the sample since the path for breakdown can be very local.

4.2 Microscopic electrical characterization composite

The measurements described above are very qualitative of nature. Possible non linear effects of these materials are better to be examined on a smaller scale, with a more quantitative approach. If conductivity is measured through a quantified amount of particles more quantitative information of the conductivity of the composite material is obtained. Therefore, a new setup is constructed to measure conductivity of the composite more locally. The following sections will describe the used substrate and measurements on the composite.

4.2.1 Sample preparation, experimental setup

To carry out conductivity measurements on a smaller scale, substrates are used on which gold microscopic structures are sputtered specific for carrying out two and four point measurements. These substrates have four contact points in the corners of the about 0.25cm$^2$ large Si with SiO$_2$ terminated substrates. These contacts are connected to a microscopic gold structure in the middle of the sample with a slight spacing of a few micrometer between each contact. A schematic example of the structure on a substrate is given in figure 4.3(a) and 4.4(c).

![Figure 4.3: The used substrate for the microscopic electrical measurements with dimensions given. A two-point voltage sweep is carried out over two connected contacts, as can be seen in the schematic figure on the right.](image)

On the substrate, a 'blob' of composite material with a 25% volume fraction of silver nanoparticles is dropped on the gold contacts, as indicated in Figure 4.3(b). The volume ratio of 25% is chosen since it is higher then the percolation volume ratio. Therefore, it is
ensured that particles are packed closely together, only spaced by the insulating shell that surrounds the particles.

For the actual measurement, copper wires are connected to the gold contact in the corners of the substrate using conducting silver glue. These copper wires are connected to bnc connectors, which are connected to the Keitley potentiometer setup.

The used and measured substrates and samples are shown in figure 4.3. Although a large area of the substrate is covered with composite material, current will eventually flow through a path with the least resistance. In a more or less homogeneous system, it can be assumed, that current will flow through the shortest path directly between the obviously highly conducting gold contacts, through only the composite material in between the contacts. This idea is visualized in figure 4.4(b), which shows a substrate (not the measured substrate) on which composite material is spincoated. Paths of composite material between the contact can be seen, which represents the basic idea and model of the measured sample in figure 4.3.

![SEM images of the used substrates for the micro measurements. On top of the electrodes the composite is spincoated. This schematically represents the basic model, were on a micrometer scale the electrical behaviour of the composite material is measured.](image)

With the substrate in figure 4.3 it is possible to carry out two point measurements at three different spots of the 'blob'. The distance over which a potential is applied on the composite material is 3µm, as can be seen in the schematic representation. Since the particles are about 100nm in size, only a small amount of nanoparticles form the insulating path between the contacts. Applying a potential could possibly lead to tunneling effects since only a small amount of particles 'connect' the contacts. These particles are closely packed together with only a nanometer spacing in between two particles. The next section will outline the actual voltage sweep measurements on the sample.

### 4.2.2 Conductivity measurements

Multiple samples were created by the method described in the previous section. Conductivity characteristics were measured by sweeping a voltage range over the contacts and simultaneously measuring current and voltage at the connected contacts. A well controlled sweep voltage range in these measurements turned out to be crucial for the measurements. In most cases at low voltage, resistance was very high. With increasing voltage resistance
tended to drop drastically, indicating a breakdown in the sample, similar to the macroscopic behaviour outlined in the previous section. When the same sweep was repeated, the resistance remained at low values, indicating a non reversible, non reproducible behaviour.

But in more controlled voltage sweeps it was achieved to measure non linear reversible behaviour. Figure 4.5 and 4.6 show a two point conductivity measurement on. Again, in this measurement, a composite with a silver particle filler ratio of 25% is deposited on a substrate as shown in Figure 4.3, where two of the four contacts are connected to a potentiometer.

The graphs shows two different voltage sweeps which were carried out in sequence. The first measurement shows a linear sweep from 0.01V to 1V and back, which is shown by the two red lines. The sweep starts at 0.01V, increases up to 1V, then decreases again to 0.01V. It can be seen that both paths do not overlap exactly, which indicates that the material is slightly altered in its non linear resistive response. After the sweep sample turns out to be a bit less resistive. But qualitatively, the material shows a clear voltage
dependent non linear response.

The second sweep, indicated in blue, is carried out subsequent to the first. Interesting is the fact that the initial resistance is a little bit higher again, than at the end of the first measurement. This means that the material ‘recovered’ over time. Instead of the first ‘two-way’ sweep, this measurement is just a ‘one-way’ sweep in a wider range of 0.001V to 15V. Again, a drop can be seen, only this time at a higher voltage. But again, qualitatively, the same non linear behaviour is observed.

A reference measurement on a clean substrate and a measurement in which the two contact are shorted with silver glue are also shown in figure 4.5. Since the measurements with the composite are in between these two measurements, it is clear that the composite material has a non linear influence on the conductivity between the contacts. And also, the behaviour is reversible, since qualitatively, this behaviour appears in two individual sweep measurements. Although the two sweeps don’t match perfectly, they roughly overlap showing qualitatively the same behaviour indicating that this behaviour is intrinsic to the material.

4.3 Conclusions electrical DC characterization

In this chapter the DC conductivity measurements on bulk scale and micro scale were outlined. On bulk scale no current voltage characteristics were determined due to lacking experience with the experimental setup. High voltages were applied on the sample which in all cases led to dielectric breakdown of the sample. Though, it was shown, that samples with high volume ratio filler material, well above the theoretical percolation threshold volume, were initially resistive. This indicates the presence of the insulating shell around the silver nanoparticles. Measurements on micro scale were carried out using substrates with a gold sputtered structure which can be used to do four point and two point measurement. After test runs to control the range of the voltage sweep interesting data was obtained in a two point measurement. In this setup, the current voltage characteristic of a composite with a volume fraction of silver nanoparticles of 25% was determined. This measurement qualitatively showed reproducible non linear behaviour of the material.

Basically at this point we can conclude:

• It can be assumed that the bulk of particles is coated as the samples in the macroscopic and microscopic measurements were insulating at first, even at a high volume ratio of silver particles were percolation is expected.

• In the microscopic measurements, reversible reproducible non linear behaviour intrinsic to the composite material is seen. This effect, considering literature, is very likely the result of tunnel effects between particles close together. It is shown that a rather simple fabrication method, were nanoparticles are stirred in liquid epoxy, show great potential in power dependent non linear resistive behaviour. This is mainly caused by the fact that particles are coated, were a high filler volume, over the theoretical percolation threshold, will not lead to percolation, but a very close packing of particles is preserved.
• Measurements are very qualitative in form. Qualitative non linear behaviour has been shown, but the system is still very undefined. Tunneling is probably the most important conduction mechanism, but this can only be verified when the actual path with a certain amount of filler particles, over which the voltage is applied, is quantified. In such a system, the conductive response could be controlled better. Still, the measured system with composite on microparticles has shown to be a setup very useful to analyse this non linear behaviour.
Chapter 5

Microwave characterization

In this chapter, various microwave measurements on the samples made from the composite material of silver nanoparticles in an epoxy resin matrix are outlined. First, 'coaxial' measurements have been carried out. In a coaxial sampleholder setup connected to a two-port network analyzer the frequency depending reflection and transmission response for a range of samples with varying ratios of silver particles is determined. Software calculations have been carried out to determine the material parameters of the samples.

Next, 'X-band' measurements have been carried out. Herefore, new samples of varying filler ratio have been constructed with X-band waveguide dimensions. First, the frequency dependent reflective and transmissive behaviour of these samples is measured in a two-port network analyzer setup. Subsequently, a Thales Matlab model for calculating the reflection and transmission response in a waveguide setup is fitted to these measurements, resulting in material parameters for comparison with the coaxial measurements.

Last, the X-band waveguide setup is measured in a 'high power' setup, in which the frequency depending reflection coefficients of the X-band samples for a range of power output is determined.

5.1 Coaxial measurements

The first microwave measurements on the composite material of epoxy resin filled with a varying ratio of silver nanoparticles are carried out in a coaxial network analyzer setup. With this setup, the dielectric constant, or permittivity $\varepsilon_r$ and the permeability $\mu_r$ of the composite material can be determined. This section will outline the preparation of the samples, the experimental setup that is been used and the measurements that have been carried out. Subsequently, the material parameters calculated from these measurements, are outlined and discussed.
5.1.1 Sample preparation and experimental setup

To carry out the coaxial microwave measurements, samples have to be constructed that fit the experimental setup. The experimental setup requires samples with very accurate dimensions. Samples need to be cylindrically shaped, with an inner diameter of 3.03mm and an outer diameter of 7.01mm. The thickness of the sample may vary, but has to be at least 1mm. These dimensions have to be precise, since the samples has to fit in the measurement setup as tightly as possible. This because leakage will influence the material parameter calculations, as will be discussed in section 5.1.4.

To create samples with these dimensions as accurate as possible, teflon sample holders, displayed in figure 5.1, are created with the use of a lathe.

![Figure 5.1: Schematical representation of the teflon mold in which the coaxial samples are made.](image)

These molds are filled with the liquid composite with varying silver filler ratio. Subsequently, a teflon 'lid' is tightened on top of the mold. Then, the filled molds are put in a vacuum, to remove excessive air which could lead to air holes. Next, all the molds are put in a plastic cup which is attached to a stirrer, inside an oven. Hereby, the samples are cured, while tumbling around, which prevents particles from sinking.

When removed from the mold, samples look smooth and homogenous, but small air bubbles are present. The influence of these bubbles on measurements will be discussed in section 5.1.2.

A schematic overview of the measurement setup is displayed in figure 5.2. A copper hollow cylinder is put into the hole in the sample. Then, the sample is placed in a cylindrical cutout in a piece of copper, with a diameter of about 7mm, as can be seen in figure 5.2(a). A copper 'lid' with the same cutout is then placed on top, fixing the sample in place. Two connectors are screwed on each side of the sampleholder.

These connectors are connected to two ports of a network analyser, as can be seen in figure 5.2(b), which is set to an output power of 10dBm. In this way, a so-called scatter matrix or S-matrix is obtained. A scatter matrix contains the reflection and transmission coefficients over a frequency span, on the two ports of the network analyser. This sweep runs from 100MHz to 18.2GHz with 100MHz steps, covering various microwave frequency bands.

For a two-port setup, this S-matrix will contain four parameters, \( \begin{pmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{pmatrix} \), where x and y corresponds with respectively port one and port two of the network analyzer. Hence,
5.1. COAXIAL MEASUREMENTS

Figure 5.2: A schematic representation of the sample holder and the experimental setup for the coaxial measurements is shown. Figure 5.2(a) shows the sample holder, with the silver/epoxy sample shown in grey. Figure 5.2(b) shows this Device Under Test (DUT) connected to a two port Network Analyzer (NA).

$S_{11}$ and $S_{22}$ correspond to the reflective signal of respectively port one and two, were $S_{12}$ and $S_{21}$ correspond to the transmitted signal between port one and two [20].

The value of the coefficients indicates the ratio between the outgoing signal to the incoming signal in decibel (dB). For instance, when $S_{11}$ equals -1dB, the measured reflection, or incoming signal at port one is 1dB weaker then the outputted signal by port 1. Reflective material, such as metals, will obviously show high reflection coefficients. Vice versa is the case for low reflective materials, such as epoxy resins.

To determine the material parameters from the measurements, the dielectric constant or permittivity $\varepsilon_r$ and the permeability $\mu_r$, the network analyser is coupled to software which makes a readout of the network analyzer measurements. Subsequentlty, a fitting algorithm in the software translates the S-matrix data to values for the real and complex part of the permittivity and permeability, $\varepsilon'(\omega)$, $\varepsilon''(\omega)$, $\mu'(\omega)$ and $\mu''(\omega)$, of the composite material. The material parameters depend on parameters such as the thickness of the sample and the ‘fitmargins’ of the sample inside the sample holder in the case of small spacings between sample and holder. To carry out these fitting calculations, these depending fitting parameters need to be defined in the software.

5.1.2 Measurements

A total of eleven samples is measured in the described experimental setup. These eleven samples contain one sample with a zero filler ratio, a sample purely constructed of epoxy resin. The other ten samples are divided in two samples per filler ratio. The used ratios are 5%, 10%, 15%, 20% and 25% volume percentage silver nanoparticles. In table 5.1, the dimensions of the samples are outlined. These dimensions are of critical value in the calculations of the material parameters, as will be discussed later on.

First, as can be seen in figure 5.3, the reflection and transmission scattermatrix measurements on all samples is shown. From the upper left to the lower right, the four graphs
show respectively the $S_{11}$, $S_{12}$, $S_{21}$ and $S_{22}$ coefficients of the various samples.

Table 5.1: The various constructed coaxial samples with their filler ratio and dimensions. Error margin for all measurements is estimated to be ±0.05mm and is discussed in section 5.1.4.

<table>
<thead>
<tr>
<th>Volume percentage silver particles (%)</th>
<th>Outer diameter (mm)</th>
<th>Inner diameter (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>5 (1st)</td>
<td>6.9</td>
<td>3.2</td>
<td>3.1</td>
</tr>
<tr>
<td>5 (2nd)</td>
<td>6.9</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>10 (1st)</td>
<td>7.0</td>
<td>3.2</td>
<td>2.8</td>
</tr>
<tr>
<td>10 (2nd)</td>
<td>7.0</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>15 (1st)</td>
<td>7.0</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>15 (2nd)</td>
<td>7.0</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>20 (1st)</td>
<td>7.0</td>
<td>3.1</td>
<td>3.0</td>
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<td>20 (2nd)</td>
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</tr>
<tr>
<td>25 (1st)</td>
<td>7.0</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>25 (2nd)</td>
<td>7.0</td>
<td>3.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The reflection $S_{11}$ and $S_{22}$ parameters show more or less the same qualitative behaviour. At lower frequencies, the composite material is very non-reflective. When low lossiness of the samples is assumed, i.e. the sample dissipates very minimal energy, this behaviour is obviously linked to a higher transmission coefficient at lower frequencies, as can be seen from the $S_{12}$ and $S_{21}$ coefficients.

The influence of different filler ratios is best seen in the values for the transmission coefficients. The transmission $S_{12}$ and $S_{21}$ coefficients clearly show an increase in transmission at lower filler ratio, as can be expected. With a higher filler ratio of silver particles, the material becomes more metallic, hence, more reflective.

Interesting behaviour can be seen when looking at the samples with 20% and 25% volume percent silver. The overall transmission for the 25% sample is in average more or less the same, or even a little bit higher compared to the 20% samples. The reflection of the 20% also seems to be a bit higher compared to the 25% sample. This is rather strange, since one would expect that the 25% sample behaves more metallic, hence, more reflective and less transmissive. The opposite is the case.

Furthermore, the 5% and 10% samples seem to overlap more or less. The 10% sample even has a slightly higher transmission coefficient compared to the two 5% samples, the second 10% sample has a lower transmission coefficient.

Also, for the samples with increasing filler ratio, there seems to be a frequency dependent trend, in which the transmission declines up to 10GHz, after which it increases again. But especially the 20% and 25% samples drop significantly around 10 GHz, which differs from the general trend.

Last, mainly in the transmission measurements, all the measurements show irregularities which are independent from the filler ratio and a general trend, as samples with different filler ratio do not show the same artifacts. These artifacts include a strange drop for the
5.1. COAXIAL MEASUREMENTS

Figure 5.3: The reflection and transmission parameters depending on frequency for all the measured samples.

first 5% sample at 14GHz which is not present in the other samples and the drops in the 20% and 25% samples mentioned above.

Discussion artifacts scatter matrix measurements

The unexpected behaviour in which artifacts occur on irregular basis described above could have more causes. In general, the unexpected artifacts must be a result of the structural intrinsic properties of the sample, since the method of measuring in the network analyzer setup itself is accurate and leads to reproducible measurements. Considering the calibration, a free space measurements and the measurement on the teflon sample, shown in figure 5.4, also indicate a correct calibration. A possible miscalibration of the setup, which would lead to incorrect measurements, would lead to a systematic error, which does not explain the irregularities or inconsistent correlation between filler ratio and reflection/transmission.

Possible forms of structural irregularities are:

- Microscopically, the silver particles are not spread homogenous through the epoxy matrix. Bigger and smaller clusters of silver particles are visible. This results in a 'non symmetric' sample, with different material properties on different areas of the sample.
- Macroscopically, imperfections such as air bubbles and small cracks due to removal from the mold, occur in the sample.
- Also macroscopically, the dimensions of the samples are not 'perfect'. This means
that there are spacings between the edges of the samples with the sample holder. These spacings vary per sample, as shown in table 5.1.

The presence of the first two possible forms is verified after analyzing cuts of each sample with Scanning Electron Microscopy (SEM). Back-Scattered Electron (BSE) and Secondary Electron Imaging (SEI) images were taken, shown in appendix E.1. These images clearly show the irregular presence of small air bubbles. Also it can be seen that on a macroscopic level, the composite material is rather homogeneous, bigger and smaller clusters of silver particles are spread homogeneously. But as said, on a microscopic level, the composite is inhomogeneous, particles are clustered together. The dimensional misfit of the samples is simply determined by measuring the samples with a micrometer. The misfit obviously present, as indicated in table 5.1, were a perfect sample would have a inner diameter of 3.04mm and an outer diameter of 7mm.

Intuitively, the first two types of irregularities mainly effect the ‘smoothness’ of the measurement, and are the reason for the irregularities in the measurement in for instance the 5%, 20% and 25% samples. The drops at 10GHz for the 20% and 25% samples can be seen in both samples, so are not completely irregular. Still the first two causes could be the reason for these drops, since all sample were constructed in the same way. Therefore, a same amount of ‘lack of homogenity’ could be present in both sets of samples.

To verify this cause of micro and macroscopic irregularities leading to a less smooth measurement, a measurement has been carried out on a perfect homogenous sample. It shows a more smooth measurement, as can be seen in figure 5.4. This figure shows the scatter matrix parameters and the dielectric constant and loss tangent. Again, the difference between the composite and teflon is the micro and macroscopic inhomogeneities in the composite, concluding that these types of inhomogeneities are therefore very likely to have caused the irregularities in the measurements.

Discussible is whether the macroscopic air bubbles contribute in the presence of the irregularities. Also the 0% sample has bubbles, but shows a rather smooth measurement. This might indicate that microscopic inhomogeneities in the spread of silver particles are the main cause for the irregularities.

![Figure 5.4: Scatter matrix of a teflon sample plotted left, its permittivity and loss tangent plotted on the right.](image)
5.1. COAXIAL MEASUREMENTS

The third form of imperfection, the dimensional misfit of samples is the most plausible explanation for some samples having an overall higher transmission then expected. If the sample does not fit perfectly in the sample holder, there will be leakage, which causes the transmission coefficients to be a bit higher and the reflection coefficients to be a bit lower. Again, the presence of this misfit is verified by the dimension measurements outlined in table 5.1. Indeed, the 25% samples have a little bit bigger inner diameter, which results in leakage. Furthermore, the first 10% sample is thinner than the second, which obviously also results in a higher transmission coefficient.

Considering the dimensions of the samples, it can be concluded that there is a correlation between the samples dimensions deviating from perfectly fitting in the sample holder, and the resulting scatter matrix coefficients. A worse fit leads to more leakage, resulting in a higher transmission. Still, the difference in size dimensions between the samples is rather small, but the artifacts are rather big, which would imply a large dependence of the transmission and reflection to the matter of fitting of the sample in the sample holder. This dependence will be discussed in the next section. Nonetheless, if this dependence is taken to account, the data qualitatively clearly shows a dependence of the reflection and transmission coefficient on the composite filler ratio.

5.1.3 Permittivity and permeability

From the scatter matrix coefficients the material parameters can be determined. With the used software, the real and complex part of the dielectric constant, or permittivity, \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \), and the real and complex part of the permeability, \( \mu'(\omega) \) and \( \mu''(\omega) \), can be calculated. The relation between the relative permittivity and its real and complex part is \( \varepsilon_r(\omega) = \varepsilon'_r(\omega) + i\varepsilon''_r(\omega) \). A similar relation between the real and complex part of the permeability exists, which gives the relation for the relative permeability.

Stated earlier, the software uses an algorithm to calculate these material parameters from the scatter matrix. A certain parameterset needs to be defined to carried out these calculations, which will have its effect on the resulting outcome for the permittivity and permeability. These parameters include:

- Inner diameter of the sample
- Outer diameter of the sample
- Thickness of the sample
- ‘Model’ of calculation. In the first model, only calculate the permeability, set \( \mu'=1 \) and \( \mu''=0 \). The second model calculates both the permittivity and permeability.

As introduced before, the fitting algorithm needs the dimensions of the sample as input parameters to calculate the material parameters. For instance, when a sample does not fit perfectly, there will be leakage. This results in a higher transmission and lower reflection. If this dimensional misfit is not corrected for in the parameter calculation, this will lead to a lower permittivity than the actual permittivity of the sample. The samples dimensions are simply determined with an ordinary micrometer and are outlined in table 5.1.
Per sample the two calculation 'models' mentioned above have been carried out to determine the material properties.

As shown, in the first the permeability is set to one. These calculations result in values for only the real and complex part of the permittivity. In the second, the permeability is also taken into account, resulting in not only the permittivity, but also values for the real and complex part of the permeability. By comparing these two sets of data, it can be determined whether the samples show magnetization effects.

Figure 5.5 shows the relative permittivity of the various samples with different filler ratios, as a function of frequency.

**Figure 5.5:** 5.5(a) shows the permittivity for the various samples, calculated with the first model, with \( \mu_r \) set to one. In the second model, with the permeability also set as a fit parameter, 5.5(b) shows the permittivity and 5.5(c) shows the permeability of the samples.

When the two plots of the relative permittivity, 5.5(a) and 5.5(b) of the samples are compared globally, average values are more or less the same, which means that the permeability is of little influence on the calculations and has a value more or less around one, as also can be seen in figure 5.5(c).

For higher and lower values of the frequency, the permeability becomes more irregular, which for higher frequencies also can be seen in the permittivity. Apparently, with the
permeability taken into account as an output fitting parameter, for higher frequencies, the fitting algorithm has trouble fitting its model to the scatter matrix values. This is very likely to result in strange effects and values for both permeability and permittivity. In the first model, these artifacts are not present. Therefore it can be concluded, that fitting the measurements with the permeability fixed to one leads to more reliable material parameters. This means that it can be concluded that the samples show very little to no significant magnetization. This is expected in the first place, since silver is a diamagnetic material. Diamagnetic materials show very little magnetization effects, with a relative permeability just slightly smaller than 1. For silver, $\mu_r = 0.999983$. [21]

From the previous it is assumed that the first fit model with only the permittivity as output parameter is more accurate. Therefore, a closer look is taken on these calculations, which still show some interesting artifacts.

- Around 10GHz, the second 20% and 25% samples show a significant decline in value. A less significant but present drop around 10GHz can also be spotted for the first 20% and 25% sample. Also the first 5% sample shows a strange rise and decline at around 14 GHz.
- All the calculations show a 'wavy' character with general increasing and decreasing permittivity. At about 3GHz, all the measurements show an increase, were in subsequently declines at 5GHz. Again an increase is present between 6 and 7GHz and so on.
- A steep rise of the 25% sample at low frequency is present.
- Overall, there is a correlation between the permittivity and the filler ratio, were the permittivity increases with increasing filler ratio, as can be expected. But there is quite a difference between samples of equal filler ratio. All sets of samples differ in value from two to four, which results in for instance the first 5% sample overlapping with the first 10% sample, the first 15% sample overlapping with the second 10% sample and so on, which is not expected. This behaviour was also observed in the scatter matrix measurements, were it is concluded to be caused by the dimensional misfit. But in the calculations, a correction was taken in account for this dimensional misfit. Therefore, the accuracy of the calculations is questionable.

First, this strange behaviour is clearly directly correlated to the behaviour at exact the same points in the scatter matrix measurements as can be seen in figure 5.3. The cause of these artifacts has already been discussed in the previous section and are most likely to be caused by the inhomogeneities of the samples.

Second, since all samples show this behaviour, it must be intrinsic to the composite material, independent of the filler volume and is very likely to be a macroscopic effect caused by the dimensions of the samples which are in average more or less equal. This behaviour seems therefore independent whether on a microscopic scale the composite material is inhomogeneous.

Third, this could be the result of the software having trouble to assign a value during the fitting process, were the transmission coefficients $S_{12}$ and $S_{21}$ of the 25% sample at low frequencies also showed strange behaviour, not limiting to zero. This can be seen in the
CHAPTER 5. MICROWAVE CHARACTERIZATION

$S_{12}$ and $S_{21}$ transmission coefficient measurements shown in figure 5.3.

Fourth, as said, in the calculations of the permittivity a correction for the dimensional misfit is taken into account. But obviously, when measuring the actual dimensions of the sample, a certain error margin in the measurement needs to be taken into account. This error obviously also leads to a error margin in the calculation of the permittivity. Therefore, an analyses on the error margins in the dimensional measurements and the consequence on the error in the permittivity calculations needs to be carried out. This will be discussed in the next section.

5.1.4 Discussion error margins permittivity

As introduced earlier, the dimensions of the sample in the sampleholder are needed as input parameters for the calculation of the material parameter from the scattermatrix measurements. A misfit of a sample in the sample holder will influence the scatter matrix measurements. In the material parameter calculations, this misfit is taken into account and corrected for.

This section will discuss the influence of an error margin in these dimensional input values resulting in an error margin in the calculation of the material parameters. The dimensional input values are:

- The inner diameter of the sample
- The outer diameter of the sample
- The thickness of the sample

The dimensions of the samples, outlined in table 5.1 are simply determined with a micrometer. An average value is taken, since the samples do not have perfect round dimensions. The error in the dimension measurement is therefore estimated to be $\pm 0.05\text{mm}$.

To determine the influence of the error margin of the dimensional input parameters mentioned above on the error in the permittivity calculations, for the first 15% sample, the permittivity is calculated for a range of values for each of the three input parameters above, keeping the other two parameters fixed. The 15% volume filler ratio sample is chosen since this filler volume ratio is the average used silver filler ratio.

It turned out that a change in the inner diameter is most influential on the calculated permittivity. These measurements are shown in figure 5.6. Figure 5.6(a) shows the calculation for the permittivity at fixed value for the outer diameter (7mm) and thickness (3mm). The inner diameter varies from 3.04mm, which is the exact size of the inner tube put through the sample, see figure 5.2(a), to 3.25mm. The lower red line obviously represents the smallest inner diameter, with no leakage, which results in the lowest permittivity. With increasing inner diameter and more leakage, the calculations from the same scatter matrix measurements lead to a higher permittivity.

The values for the second and third set of calculations, in which the outer diameter and the thickness is changed are outlined in table 5.2. These calculations are shown in appendix A.
5.1. COAXIAL MEASUREMENTS

It can be seen that for small variations in size, there is a more or less linear dependence between the difference in permittivity and size. Obviously, the derivative of this dependence is a measure for the error margin in the permittivity calculation. It shows the variation of the permittivity per variation in size. Assuming a more or less linear dependence, the derivation is show in the last column of table 5.2. It shows that, again, a variation in the inner diameter has the most influence on the permittivity.

Table 5.2: Determining the influence of varying dimension parameters on the calculated permittivity of the 15% sample. Subsequently the inner diameter, outer diameter and thickness is changed, with \( |\Delta \varepsilon/\Delta x| \) as error margins, shown in the last column.

| Figure | Inner diameter (mm) | Outer diameter (mm) | Thickness (mm) | step size (mm) | \( |\Delta \varepsilon/\Delta x| \) (mm⁻¹) |
|--------|---------------------|---------------------|---------------|--------------|------------------|
| 5.6/A.1 | 3.04-3.25           | 7.0                 | 3.0           | 0.01         | ~40 |
| A.2    | 3.04                | 6.8-7               | 3.0           | 0.01         | ~10 |
| A.3    | 3.04                | 7.0                 | 2.7-3.3       | 0.5          | ~1.5 |

Stated earlier, due to a lack of perfect dimensions, the error margin in the size of the sample is estimated to be 0.05mm for the thickness, inner and outer diameter. Since the influence of the inner diameter is much bigger than the other dimension parameters, this is the only source of error taken in account. With \( |\Delta \varepsilon/\Delta x| \)=40, and an error of 0.05mm for the size measurement, this leads to an error in the permittivity of ±2 for each measurement value of the permittivity.

Figure 5.6: On the left, the calculated permittivity is shown, for increasing inner diameter of the coaxial sample from perfect fit of 3.04mm to a loose fit of 3.25mm. On the right, the average permittivity is plotted.

It has to be taken in account, that this error margin is based on average rough estimations, which actually leads to an ‘error’ in the error margin. It does give a qualitative indication that the error margins for the permittivity calculations are simply very significant. Also, this error is determined from the 15% sample. A variation in size for a sample with lower filler ratio will turn out less influential on the permittivity. The opposite is the case for a sample with a higher filler ratio. The relative permittivity of the samples without the permeability taken in account is plotted again in figure 5.7(a). Figure 5.7(b) shows the average value for the permittivity per sample, including the error margins.
It now can be seen that although the permittivity for a set of samples with the same filler ratio may differ significantly, the error margins still overlap. Very roughly, a trend is visible, in which the relative permittivity linearly increases with the filler ratio up to 15% to 20%. From this point, the relative permittivity seems to stop increasing, and stays more or less the same value independent of the filler ratio. Samples with a higher filler ratio would be needed to verify this relation.

5.1.5 Loss tangent

Next, the lossiness of the samples is determined. The loss tangent is related to the real and complex permittivity as follows:

\[
\tan\delta(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}
\]  

(5.1)

Since in the calculations the real and complex part of the permittivity is determined both are plotted separately in figure 5.8. The real and complex part are separated with a dashed line. The calculations with \(\mu_r\) set to one show an increasing complex part at increasing filler ratio, which is expected, since the complex part of the permittivity is a measure for loss. This increase is related to the increase in metal particles in the composite material.

In figure 5.9, equation 5.1 is applied, showing the loss tangent for the different samples. The loss of the samples with \(\mu_r\) equal to one is shown in figure 5.9(a). An increase of the loss tangent with increasing filler ratio can be seen. Also, overall, the loss also increases with increasing frequency.

For the calculations with \(\mu_r\) not equal to one, shown in figure 5.9(b), the loss tangent drops below zero around 14GHz. This means that the complex permittivity also drops below zero around that frequency, as can be seen in figure 5.8(b). This is obviously not possible, since a negative loss tangent is trivially impossible. Also from this it can be concluded, that the fit calculations in which \(\mu_r\) is assumed not to be one leads to a less reliable calculated value for the real and complex part of the permittivity.
Also, the value for the loss in the calculations with $\mu_r$ not equal to one is for every sample about the same, for frequencies up to 10GHz, as can be seen in figure 5.9(b). This is not expected, since one would expect an increase in loss with an increase in filler ratio, stated earlier. This is also an indication that the assumption of $\mu_r$ is not equal to one in the fit calculations does not lead to accurate and realistic values for the permittivity.

So assuming the values from figure 5.9(a) being accurate, taking a closer look to the absolute value of the loss tangent, it shows rather high values, when compared to the loss tangent of common dielectric materials used in the microwave industry, shown in appendix C. The loss tangent of the samples at 100MHz is about 0.05 for all samples, at 10GHz on average 0.1, which is about two orders larger compared to these materials.
Figure 5.9: The loss tangent of each sample. The calculation with $\mu_r$ set to one, shown in figure 5.9(a), shows a clear relation between the lossiness and the filler ratio, where $\tan\delta$ increases with increasing filler ratio. The strange rise in the 25% sample for low frequencies is clearly an artifact related to the steep rise in the complex part of the permittivity, the rise in relative permittivity shown in figure 5.5(a) and the non-zero transmission at low frequency shown in figure 5.3, discussed in the previous section. It is not a result of an intrinsic property of this sample, as no other sample shows this behaviour.

5.1.6 Conclusions coax measurements

In a coaxial network analyzer setup, a series of samples with varying silver particle filler ratio is analyzed. These measurements produce a scatter matrix, which gives information about the reflection and transmission behaviour of the samples.

The frequency depending scatter matrix showed a clear filler ratio dependence of transmission and reflection. With increasing filler ratio, reflection increased and transmission decreased. The samples with the highest filler ratio, 20% and 25%, showed strange behaviour, as they showed contradictory behaviour with a lower transmission for the 20% sample. This is very likely to be caused by imperfect dimensions of the sample. This is verified when the samples dimensions were measured. The 25% samples showed less perfect fit, which leads to leakage.

Next, from the scatter matrix measurements, the frequency dependent real and complex part of the permittivity and permeability can be determined. Two types of calculations are carried out, with and without the permeability taken into account. When the permeability is taken into account, the fit led to negative values for the complex permittivity and hence, the loss tangent. Since this is impossible, the calculations with the magnetization, or a permeability fixed to one, led to more credible values for the permittivity. This also means that no significant magnetization occurs in the material as expected, since silver is diamagnetic with a permeability close to one.

Irregularities are present in the scatter matrix measurements, and therefore permittivity calculations, which are likely to be caused by inhomogeneities such as the silver particles not being spread homogeneous on microscopic scale. Macroscopically, there were air bubbles present in the samples, but very likely do not contribute to these irregularities.
Also, values for the permittivity of samples with equal filler ratio were significantly deviating. It has been shown that dimensional misfit of the samples in the sample holder has a significant influence on the calculated value for the permittivity.

For the permittivity calculations, a rough error margin estimation has been carried out. It is concluded that the dimensions of the sample as input parameters for the calculations are of most significant influence on the permittivity. Roughly, the permittivity calculations have an error of about ±2. This is an average, samples with lower filler ratio have a smaller error, with a higher filler ratio a higher error.

A closer look on the average relative permittivity with the error margins taken in account, a clear qualitative relation between the filler ratio and the permittivity can be seen, which increases with increasing filler ratio. Also, the permittivity seems to increase linearly with increasing filler ratio, up to in between 15% and 20%. At higher filler ratio, the permittivity seems to become more or less independent of the filler ratio.

Also, a rough relation between the filler ratio and the lossiness of the samples is present. The loss of the composite increases with increasing filler ratio and is quantitatively very lossy compared to other commonly used materials in the microwave industry.
5.2 Low power X-band measurements

In the previous section, the material properties of the used composite material are determined. This section will outline microwave measurements in an X-band waveguide setup on samples made from the same composite material. The measurements have been carried out, to see how these composites with different filler ratios react in an actual waveguide setup. The microwave X-band covers a frequency span of 8GHz to 12GHz, much smaller than the previous measurements, which were carried out in a span of 100MHz to 18.2GHz. In a network analyzer setup the scatter matrix of various samples is measured over the X-band frequency width.

In the previous section, a software fitting algorithm was used to calculate the relative dielectric constant and permeability of the samples from the scatter matrix data. In this section, a fit is carried using a matlab algorithm, which models an X-band setup. For various input parameters such as the permittivity and the permeability, a scatter matrix is calculated mathematically. This will be outlined more thoroughly later on. By adjusting the initial input parameters of the model such that the calculated scatter matrix fits the measurements, the material parameters are determined and compared to the calculated values in the previous section.

This section first will outline the construction of the various samples to fit an X-band waveguide. This chapter will outline on the sample preparation and the results of the RF measurements.

5.2.1 Sample preparation and experimental setup

To carry out the X-band waveguide measurements, samples with accurate waveguide dimensions need to be constructed. This to prevent leakage on the sides of the sample inside the waveguide. Therefore a mold is constructed. By lasercutting the exact sized holes are cut in the sample holder. The size for X-band measurements is 22.86 x 10.16mm.

![Figure 5.10: Schematic representation of the mold used for constructing the X-band measurement samples.](image)

The holes are subsequently filled with the composite material with different volume ratios
5.2. LOW POWER X-BAND MEASUREMENTS

of silver nanoparticles. Subsequently, the sampleholder is 'sandwiched' between two teflon and two aluminum plates and screwed together thoroughly. To prevent particles from possible sinking, the sampleholder is continuously turned inside the oven. A total of two sets of seven X-band samples are constructed with volume ratios spanning from 0% up to 30% silver filler particles. The two sets are outlined in table 5.3. For the X-band measurements outlined in this chapter, only the first set of samples is used, since the second set of samples was constructed for measurements in the high power X-band setup, outlined in the next chapter.

Table 5.3: Curing parameters of the silver nanoparticles in an epoxy resin composite samples.

<table>
<thead>
<tr>
<th>Low power measurements</th>
<th>High power measurements (section 5.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol.(%)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>25</td>
<td>60</td>
</tr>
</tbody>
</table>

In the table also the curing parameters of the samples are outlined for information. Their influence on the measurements is purely a recommendation for investigation, and will not be investigated in this research. Curing parameters mainly have influence on the speed in which the samples harden and the brittleness or flexibility of the samples. The curing parameters include the curing temperature, the amount of curing accelerator and roughly the curing time in days. As can be seen, difference between the two sets of samples is mainly the curing time and the temperature and amount of curing accelerator at higher volume ratio. The curing process for the samples with a higher silver particle ratio is more difficult, especially due to the setup in which the mold was 'sandwiched' in between two teflon plates, which prevented exposure to the air. Therefore, curing temperature and amount of curing accelerator was increased, to optimize the curing of the samples. The indicated curing time is not the actual time for the samples to harden, but simply the time the sampleholder is placed in the oven.

To carry out measurements on the X-band samples, a network analyser setup is used, using the same network analyser as shown in figure 5.2(b). The coaxial sampleholder is now replaced for an X-band waveguide. A sample is placed in the middle of the waveguide, 'squeezed' in between two pieces of foam. Two transmitter/receiver ports are connected to both sides of the waveguide. These are connected to the two ports of the network analyser. As explained in the previous section, now a reflection and transmission coefficient S-matrix can be measured over a frequency sweep. The frequency span is much smaller than in the previous section, since the in the microwave frequency spectrum, displayed in figure C.1, the X-band covers 8 to 12 GHz.
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Figure 5.11: Schematical representation of the used network analyzer setup. Two ports of the network analyzer are coupled to the Device Under Test (DUT), the X-band waveguide in which the X-band sample is placed.

5.2.2 Measurements

For the seven samples, the frequency depending scatter matrix is determined shown in figure 5.12. For each sample, the figures show the reflection coefficients $S_{11}$ / $S_{22}$ and the transmission coefficients $S_{21}$ / $S_{12}$. It can be seen that for each sample the transmission coefficients $S_{21}$ and $S_{12}$ always overlap, which means that the samples are all symmetrically transmissive.

In general it can be seen that the reflection increases with increasing filler ratio, while the transmission decreases. All measurements show a sine-shaped periodicity in the signal, which is caused by the correlation between the length of the waveguide and the frequency of the microwaves.
Interesting behaviour can be seen for the reflective signal. Especially for the $f = 10\%$, 15\% and 25\% samples, there is a difference of about 2\,dB between $S_{11}$ and $S_{22}$. To analyze whether this asymmetry is caused by the sample itself or by the experimental setup, all samples have been measured four times, considering the symmetry of the waveguide, shown in figure 5.13. These four measurements per sample are shown in appendix B.6.

These measurements show that the waveguide positioned ‘up’ or ‘down’ does not have any influence on the measurements. They also show, that the asymmetry of the reflection is caused by the sample. When the waveguide is turned also $S_{11}$ and $S_{22}$ switch, which excludes a measurement error and or artifact caused by a miscalibration. The cause of this difference in reflection coefficients will be discussed in section 5.2.3.

To compare reflection and transmission of the various samples, the average values $S_{xx}$ and $S_{xy}$ are shown in figure 5.14. The dependence of the reflection and transmission on filler ratio can be seen, as reflection increases and transmission decreases with increasing filler ratio. Maximum reflection is reached for the 20\% and 25\%, as there reflection is almost
equal. The transmission coefficient of the 25% seems to be rather strange, since it is much lower compared to the 20% sample, while the reflection is only slightly higher. One has to take into account that transmission and reflection is expressed in dB. Considering the output power of the network analyzer of 10dBm or 10mW, the reflection of the 20% sample of ∼-2dB and 25% sample of ∼-2.2dBm corresponds with a reflection of respectively 6.3mW and 6mW. For the transmission, -7dB and -12.5dB lead to 0.56mW and 2mW transmission. Hence, also the difference between the transmission is rather small compared to the difference in reflection.

Next, the power conservation of each sample is determined. The power conservation states that $|S_{xx}|^2 + |S_{yx}|^2$ is equal to unity for lossless materials [22]. A deviation from unity implies loss in the material. The power conservation on both ports is shown in figure 5.15. It can be seen that especially for the samples which show varying $S_{11}$ and $S_{22}$ this obviously results in different conservations when both ports are compared.

If the strange behaviour of the 25% is not taken in account it can be seen that the power
conservation for the 0% and 1% is closest to unity, followed by the 5% and 20% samples
with a conservation of about 80%. The 10% and 15% samples show power conservation
of about 60%. This does not immediately mean that these samples are the most lossy.
Considering the following. The samples with low filler ratio are less lossy and highly
transmissive, which results in a power conservation close to unity. For a sample with high
filler ratio, which has a high reflection coefficient, almost all energy is reflected, only a
very small amount of power transmits or ‘penetrates’ in the material and is subjected to
the lossiness of the material. Therefore, also for samples with a high filler ratio, the power
conservation is close to unity.

But for the samples with a filler ratio in between these extremes the amount of transmitted
power is significantly subjected to the possible lossiness of the material, which results in a
power conservation deviating from unity.

The fact that the power conservation for the 10% and 15% samples is significantly deviating
from unity, it can be concluded that the composite material indeed is lossy, which matches
coaxial measurements and calculations. Again, the fact that the power conservation of
the 20% and 25% samples is closer to unity does not mean that the composite material
at these ratios is not lossy anymore. Simply due to the higher reflective behaviour of the
composite at these ratios, less power is transmitted and subjected to the lossiness of the
material, resulting in a power conservation closer to unity. This limits in for instance a
piece of metal perfectly fitting in the waveguide were $|S_{xx}|$ is unity and $|S_{yx}|$ zero, resulting
in a power conservation equal to unity.

### 5.2.3 Theoretical waveguide model fit to measurements

To determine material parameters from the scatter matrix data Thales developed a code
for calculating the scatter matrix for a waveguide setup with certain dimensions and a
layer composition inside the waveguide with certain material parameters. The parameters
for this fit model are outlined in table 5.4.

**Table 5.4:** Input parameters for the X-band waveguide model developed by Thales to calculate the re-

duction and transmission scatter matrix of an X-band waveguide setup.

<table>
<thead>
<tr>
<th>Parameters fitmodel</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waveguide dimensions BxH (mm)</td>
<td>22.86mm x 10.16mm</td>
</tr>
<tr>
<td>Frequency (GHz)</td>
<td>8-12GHz, 26 points</td>
</tr>
<tr>
<td>Layer composition</td>
<td>layers (mm)</td>
</tr>
<tr>
<td>Relative permittivity per layer ($\varepsilon_r$)</td>
<td>($\varepsilon_r$) per layer</td>
</tr>
<tr>
<td>Loss tangent per layer ($\tan\delta$)</td>
<td>($\tan\delta$) per layer</td>
</tr>
<tr>
<td>Relative permeability per layer ($\mu_r$)</td>
<td>($\mu_r$) per layer</td>
</tr>
</tbody>
</table>

Non coinciding $S_{11}$ and $S_{22}$ coefficients due to varying loss

In the previous section the scatter matrix measurements were discussed, were some samples
showed non coinciding reflection coefficients. Calculations have shown that a waveguide
setup filled with various layers with varying material parameters will have different $S_{11}$ and $S_{22}$ reflection coefficients. It has shown that mostly a difference in lossiness of the layers is the main cause of this non coinciding. But obviously, in the case of the used composite, a higher loss indicates a higher filler ratio of silver particles, which also leads to a higher dielectric value of this layer.

An example of non coinciding reflection parameters caused by layers with varying loss coefficients is given below. In the example the setup that has been used for the measurements is modelled. This includes the waveguide setup with the dimensions mentioned in table 5.4. Length of the waveguide is 206mm. Inside the waveguide a sample with a thickness of 1mm is placed, 'squeezed' in between two pieces of foam. The permittivity $\varepsilon_r$ of the foam is 1.08, the loss tangent $\tan\delta$ of the foam is 0.0025, negligible compared to the loss of the sample. The 1mm thick sample is modelled as two layers with a thickness of 0.5mm.

Two situations are modelled. In both cases the permittivity $\varepsilon_r$ is assumed to be 4. In the first case, the loss tangent $\tan\delta$ of both layers is 0.01, in the second case, the loss tangent of the first layer is 0.01, the second layer is much higher, 0.5. Again, these values do not represent a realistic setup, since a layer with a higher loss will also have a higher permittivity, but these values are chosen to show the influence of a difference in only the loss of the two layers. Figure 5.16 shows a schematic example of this waveguide setup filled with two layers of dielectric material between two pieces of foam. The model assumes a perfect fit of the layer material without any leakage.

![Figure 5.16](image.png)

**Figure 5.16:** Schematical representation of the X-band waveguide setup, in which the 1mm thick composite sample is modeled as two layers, which equal and different loss tangent.

The calculation results of the two situations are shown in figure 5.17. Figure 5.17(a) shows the situation in which both layers have the same loss tangent, which means that the two layers in fact form one dielectric layer with a thickness of 1mm. As expected the two reflection and transmission coefficients coincide. Figure 5.17(b) shows the calculations in the second situation, in which both layers vary in loss, respectively 0.01 and 0.5. It can be seen that the transmission coefficients overlap, but there is a small difference in reflection coefficients. Similarities can be seen when these results are compared with the X-band measurements shown in figure 5.12.

The position of the sample could also obviously influence this discrepancy. This is also investigated with the model. It showed that since the sample is very thin (1mm) compared
5.2. LOW POWER X-BAND MEASUREMENTS

Figure 5.17: Calculated reflection and transmission coefficients for both models. On the left, both layers have the same loss tangent, resulting in coinciding reflection coefficients. On the right, the 1mm thick sample is modeled in two layers with a loss tangent of 0.01 and 0.5. Clearly, there is a separation between the two reflection coefficients.

(a) Identical layers, $\tan \delta = 0.01$

(b) Different layers, $\tan \delta = 0.01$ and 0.5

to the length of the waveguide (206mm) and the error in the exact position in the middle of the waveguide is quite small, about 2mm at most, this variation hardly had any influence on the spacing between the $S_{11}$ and $S_{22}$ parameters.

It can be concluded, that a system, containing multiple layers with varying thickness, loss and permittivity is the cause of a discrepancy between the $S_{11}$ and $S_{22}$ reflections coefficients.

This is verified when sections of the 10%, 20% and 25% X-band samples are analyzed with Scanning Electron Microscopy (SEM). Images are made using Back Scatter Electron (BSE) imaging, which gives information about the element distribution based on the atomic number. Contrast in the images will be caused by a difference in atomic number, were silver particles obviously have a much higher atomic number then the organic material. All images are shown in appendix E.2.

Figure 5.18: BSE on the 10% sample at 100x zoom (left) and 1000x zoom(right). Clearly visible is a thin layer with an increased density of silver filler particles.

Figure 5.18 shows two BSE images at different zoom levels, were clearly a thin layer is visible with an increased density of silver filler particles. In appendix E.2 it can be seen that also the 25% sample shows this thin layer of increased density. The 20% sample also shows a (thicker) layered structure, but these layers have more or less the same density.
which will not lead to noncoinciding reflection coefficients, as can be seen in the scatter matrix measurements in figure 5.12.

These layers are very likely not caused by sinking of particles, since the gradient between the layers would be more smooth. It is caused by the method of fabrication, were the samples were created in two steps. After filling and curing the samples inside the mold, air-holes were present in the samples. These holes were filled again with an amount of composite, resulting in a thin layer on top of the sample, were no holes were present. The reason for the increased density of silver particles in this layer is unclear. Likely the remaining composite was not stirred well enough, before applying in the sample in the mold.

Fitting the model to the X-band measurements

Next, to determine the material parameters from the scatter matrix measurements quantitatively, the Thales model is fitted to the X-band measurements. For an initial set of parameter values mentioned earlier, the difference between the model and the measurement calculated. Then, this difference is limited to zero by changing the initial parameters of the fit model. This results in a material parameter set that fits best to the measured reflection and transmission coefficients.

In the fitmodel four parameters can be adjusted, the relative permittivity $\varepsilon_r$, permeability $\mu_r$, the loss tangent $\tan\delta$ and the position of the sample. The permeability and the position of the sample are kept at a fixed value. The coaxial measurements showed that the permeability can be assumed to be one, for the position it is determined that it is of very little influence, which is set to zero. This means that the sample is modeled as being positioned in the middle of the waveguide.

As shown earlier, one of the parameters in the model is the amount of layers. It has shown in the previous section, that some samples are in fact 'multilayered', causing the reflection parameters to not coincide. Therefore, in the first fit calculations, the input parameters were set such that the sample was modelled in multiple layers. Since the actual sample consists of two layers, a thick and very thin layer, with different permittivity and loss, it was analyzed whether the model would also show this layered structure in the calculated parameters per layer. For example, when the sample is modeled in ten equally thick layers, it could be expected, that nine layers would more or less have the same values, were one outer layer would show higher permittivity and loss.

But these models resulted in unreliable data, as the model would quickly assign extreme boundary values to the multiple layers, to 'split' $S_{11}$ and $S_{22}$. The model would assign minimal values to the first nine layers and extreme values for the tenth layer. This indicates that the perfect model has trouble to 'explain' the non-coinciding reflection coefficients.

A trivial explanation would be that the layer model does not describe the actual system, where more parameters have an influence on the measurements. For instance, the model assumes perfect layers, where layer characteristics are equal in the height and width direction of the setup. A difference in the loss tangent of the sample could not only occur in this thickness direction, but in more directions, which is likely to be the case.
Theref ore the waveguide setup is modeled more simply as just one layer in between foam, which results in more plausible calculated values. The fits to the measured reflection and transmission coefficients per sample are shown in figure 5.19.

Since the setup is modeled with a one layer sample between two pieces of foam in a fixed position, $S_{11}$ and $S_{22}$ calculated by the model obviously coincide, as explained earlier. Therefore, the model is fitted to the sum of the measured $S_{11}$ and $S_{22}$, which will lead to an average fit in between the $S_{11}$ and $S_{22}$ measurements.

Figure 5.19: The reflection and transmission coefficients per sample as shown in figure 5.12. Indicated with $\times$ and $\circ$ are the fit calculations to the average of respectively the $S_{11}$ and $S_{22}$ reflection and $S_{21}$ and $S_{12}$ transmission of each sample.

It can be seen that the calculations especially for the higher filler ratio fit the measurements
perfectly. For the samples with non-coinciding $S_{11}$ and $S_{22}$ the fit averages the values perfectly. For samples with a lower filler ratio, the model does not fit perfectly, especially for the rather low values for the reflection. This because the model assumes a perfect setup. For very low intensities it is likely that the accuracy of the receiving port varies resulting in less accurate measurements.

All fit calculations in the four symmetry directions of the 5% to 25% samples are shown in appendix B.6.

The calculated permittivity and loss tangent values per filler ratio are plotted in figure 5.20. The permittivity increases with increasing filler ratio, as expected from the previous coaxial measurements, shown in figure 5.20(a). Only the 25% sample shows strange behaviour compared to the value for the permittivity of the 25% sample determined in the coaxial measurements. Where the coaxial measurements show a rather constant permittivity for the 20% and 25% samples, the waveguide measurements show a permittivity value for the 25% of about 26, which is almost double the value of the 20% sample.

![Figure 5.20](a)

Figure 5.20: On the left, the frequency dependent permittivity calculated with the fit model is shown for each sample. Clearly remarkable is the much higher permittivity of the 25% sample. On the right, the frequency dependent loss tangent for each sample is shown. No correlation is present between the filler ratio and the loss, as the 10%, 15% and 25% have very high losses, compared to the other samples. This indicates difficulty for the 'perfect' model to fit to the measurements.

The loss tangent calculations shown in figure 5.20(b) qualitatively show interesting behaviour. The 5% and 20% sample show a low loss of about 0.05-0.1, while the 10%, 15% and 25% samples show a very high loss of about 0.5 (the 0% and 1% samples obviously show very low loss). This in contrast with the coaxial measurements which showed an average increase in the loss with increasing filler ratio. The samples with high loss calculations are also the samples were the reflection coefficients have the biggest separation between $S_{11}$ and $S_{22}$. This is related to the presence of the thin layer with high loss, causing the reflection coefficients to not coincide and an overall higher loss of the sample.

Whether quantitatively these calculated values are reliable is very questionable. Especially the high values are not very reliable, as the values are extremely high compared to the loss tangent of commonly used materials shown in table C.2. The low loss samples have a value which is more or less the same as the coax measurements. Again, this loss tangent data has to be interpreted more qualitatively. The samples with non-coinciding reflection
parameters have a highly lossy thin layer, measured with SEM, which in the fit model leads to a high overall loss. The average reflection, to which is fitted, is lower, resulting in the model to a higher loss.

Since the permittivity more or less has an constant value, as can be seen in figure 5.20(a), the average value is plotted together with the average permittivity values from the coaxial measurements for comparison, both shown in figure 5.21. It can be seen that for lower filler ratio, the measurements perfectly fit the coaxial measurements. Only the 25% sample does not match with the coaxial measurement.

![Figure 5.21: The average permittivity plotted against the filler ratio for both the coaxial as the x-band measurements. An overlap is clearly visible for the lower filler ratio.](image)

### 5.2.4 Conclusions: Low Power X-band Measurements

In an X-band network analyser setup RF microwave measurements have been carried out on a set of samples made from the composite material containing varying ratio’s of silver particles embedded in an epoxy resin. Standard two-port scatter matrix data was obtained containing reflection parameters $S_{11}$ and $S_{22}$ and transmission coefficients $S_{21}$ and $S_{12}$, measured in four directions. Overall an increase in reflectivity and decrease in transmission with increasing filler ratio was observed. Three samples showed strange behaviour, as the reflection coefficients do not coincide, inherent to the sample. Furthermore, transmission in the highest filler ratio sample was deviating from the average decreasing trend in the transmission.

A waveguide model has been developed by Thales to calculate theoretically the scatter-matrix coefficients depending on waveguide dimensions, frequency span, layer composition inside the waveguide, thickness, permittivity, permeability and loss tangent of each layer. It is shown, that the main cause for non coinciding reflection coefficients is a difference in loss tangent of various layers. This would indicate that the sample lacks homogeneity in the thickness direction. This is verified by SEM images of section of the samples. The
samples with noncoinciding reflection coefficients showed a \( \sim 10\mu m \) thin layer on the side of the sample with an increased density of filler particles, very likely to be caused by the fabrication method.

The theoretical model is used to determine the permittivity and loss tangent of the various samples by fitting the model to the measurements. The model assumes a 1mm layer in between two pieces of foam with a fixed permeability of one, concluded from the coaxial measurements. The resulting permittivity more or less agreed the coaxial measurements except for the 25% sample. The value for the loss tangent of the samples with non coinciding reflection parameters is very high and not very plausible, but is a qualitative indication and verification that an extra very loss layer is present, which causes the overall loss to increase. Values for the loss for the samples with coinciding reflection coefficients match the values in from the coaxial measurements.

It was attempted to model the 1mm thick samples in multiple layers, since again, these multiple layers are physically present, but this led to extreme and non-plausible output values, which shows the difficulty for the 'perfect' model to assign values in a less perfect system. Also, the model is based on a minimization between a waveguide model and the measurements. Including more parameters introduces more possible local minima. More research on initial parameter values would be necessary to determine whether this multilayer extensive model can actually be applied on such a system.
5.3 High power X-band measurements

All the previous microwave measurements on the composite material samples have been carried out at constant 'low' output power of 10dBm, or 10mW. One of the main research goals is to examine the power dependence of the reflective behaviour of these composite materials. Therefore, a setup is constructed in which the X-band waveguide setup described above is used, in which it is possible to measure the reflectivity of the composite material samples inside the waveguide in a range of output power.

This section will outline these measurements. Different from the previous measurements, instead of a two-port scatter matrix, only the reflective behaviour of the X-band samples is measured. First, the experimental setup and the samples used is outlined in sections 5.3.1 and 5.3.2. Next, the measurements and results will be outlined in sections 5.3.3, 5.3.4 and 5.3.5. Last, the measurements will be compared with the low power measurements from the previous section to lead to the conclusions, outlined in section 5.3.6.

5.3.1 Experimental setup

To carry out measurements in a high microwave power range, a different setup needs to be constructed, as the network analyser setup produces a limited power with a maximum output of 25dBm or about 300mw.

![Figure 5.22: Schematic representation of the setup used for measuring the reflectivity of samples with varying composition at a high power range. In this setup, the power meter is connected to the 1st DC to measure reflectivity. When connected to the 2nd DC, the transmission line power is measured.](image)

Therefore, a new setup is constructed, schematically shown in figure 5.22. The most important part of the setup is the travelling wave tube (TWT) amplifier. This device amplifies any input microwave signal up to a maximum of 56dB or 400W. In the setup, this input signal is generated by a signal generator. This device is able to generate a continuous wave (CW) or pulsed wave, at varying frequency and power. While the TWT amplifier simply amplifies this wave by a certain amount of dBm, the output power of the signal can be controlled by the signal generator. This makes it possible to measure over a range of power controlled by the signal generator with a maximum of 56dB, the maximum output of the TWT.
The signal from the TWT will first pass through a circulator. This is a three port non-reciprocal device. This means that microwave power that is entering any port is transmitted to the next port only. The circulator is placed in such a way, that reflected microwave power will be led into the connected load, instead of returning back into the TWT, which could damage the amplifier.

Next, the microwaves pass through an X-band waveguide setup. This setup exists of two directional couplers (DC), placed opposite from each other. Although this report will not go into the theory on which this coupling mechanism is based, in short, inside a directional coupler, two transmission lines are constructed close together. Due to the interaction of the electromagnetic fields of each line, power can be coupled between the lines [1]. In other words, a part of the power in the transmission line will be coupled to a different line connected to another output port.

These directional couplers make it possible to measure the power through the transmission line in both directions. The direction coupler used in this setup, weakens the power by ~20dBm. This means that the signal measured with the power meter at the coupled port, also connected to a power tap that weakens the signal with 10dB, is always ~30dBm lower than the actual power through the transmission line. This weakening of the signal is necessary, since the power sensor has a measurement range up to ~30dBm. Higher power could damage the power sensor.

Connected to these directional couplers is the X-band waveguide which holds the X-band sample, the so-called Device Under Test or DUT. After the DUT, a load is placed, to dissipate the power that passes through the sample.

![Figure 5.23: Actual experimental high power setup.](image-url)
5.3. **HIGH POWER X-BAND MEASUREMENTS**

Table 5.5: Curing parameters silver nano particles/epoxy composite samples. A line is put through the samples which were lost in the calibration measurements and are not used for the measurements.

<table>
<thead>
<tr>
<th>Samples low power measurements</th>
<th>Samples high power measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vol. (%)</strong></td>
<td><strong>T (°C)</strong></td>
</tr>
<tr>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
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<tr>
<td>10</td>
<td>60</td>
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<td>45</td>
<td>60</td>
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<tr>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>25</td>
<td>60</td>
</tr>
</tbody>
</table>

5.3.2 **Samples**

As outlined in section 5.2.1, two sets of X-band waveguide samples, varying in silver particle filler ratio, have been constructed to carry out the X-band microwave measurements. These two sets of samples are shown again in table 5.5. The first set of samples which is used for the low power measurements outlined in the previous section was partially lost in the test and calibration measurements outlined in the next section. Due to heat dissipation some of the samples disintegrated. Only the 10%, 20% and 25% sample 'survived' the test measurements. Therefore, a full second set of samples was constructed. Although curing parameters differ, which is discussed in the previous section, the samples were constructed in an identical way. This set of samples will be referred to as 'high power samples,' were the three surviving samples from the low power measurements will be referred to as 'low power samples.'

5.3.3 **Calibration measurements**

First, test and calibration measurements were carried out to determine the limits of the measurement parameters, frequency range and RF power. For these measurements, the 'low power samples' were used. As stated earlier, it is possible to create a continuous or pulsed wave, depending on the type of signal from the signal generator. In the first tests, the signal was set to a continuous wave. As shown, the samples are quite lossy and dissipate a lot of heat, obviously especially at higher power. The amount of dissipated heat caused irreversible damage to the sample. Even the foam, ‘sandwiching’ the sample in the waveguide was burned due to the heat dissipation of the sample. As this foam obviously worsens the cooling of the sample, the foam was not used anymore in the actual measurements. Also, all the subsequent measurements are carried out with a pulsed microwave signal, since this will drastically reduce the amount of energy dissipated by the sample. A pulsed signal with a pulsewidth of 100µs and a period of 100ms was used. This means that per second, the sample is irradiated by microwaves for only 1ms, which leads to a reduction by a factor of 1000 of the amount of output power on the sample or a ‘duty cycle’ of 0.1%. With these settings, the setup could be set to its maximum peak output power of about 56dBm or 400W, without causing damage to the sample.
CHAPTER 5. MICROWAVE CHARACTERIZATION

As said before, the signal generator generates a microwave signal that is amplified by the TWT amplifier. Therefore, the first step is to measure the actual power that is flowing through transmission line. For this measurement, the power meter is connected to the second directional coupler, shown in figure 5.22. In this way, a part of the microwave signal that is flowing through the transmission line is measured, as explained in section 5.3.1. By setting the power meter to an offset value of 20dBm, correcting for the weakened signal of the directional coupler of 20dBm, the actual transmission power is measured. With the use of labview, the measurement is automated by controlling the signal generator and reading out the power meter automatically. Basically, two loops for the output power and frequency are set. The signal generator output power sweeps from -25dBm to 14dBm with steps of 3dB. At every value for the output power, a frequency sweep is carried out from 8GHz to 10GHz, with steps of 10MHz, resulting in 200 measurement points for each value for the output power. After every step, the program makes a readout of the powermeter. The transmission line output power against frequency for various output powers of the signal generator is shown in figure 5.24. At lower input power, the TWT amplifies the signal by about 50dB. At higher power, this linear relation is lost, as the amplification reaches its maximum value.

Due to the circulator, the signal starts to cut off for higher frequencies. Especially at frequencies higher then 10GHz, there is almost no transmission line power anymore, therefore the range of 8GHz to 10GHz is chosen for the measurements. Still, the transmission line output power slightly declines at higher frequencies. Also, at higher input power, the signal oscillates slightly at lower frequencies. These artifacts will obviously also occur in the reflected signal. Since the \( S_{11} \) reflection parameter is expressed as the difference between the input signal and the reflected signal, and its unit will become dimensionless, these artifacts obviously cancel out.
5.3. **HIGH POWER X-BAND MEASUREMENTS**

5.3.4 **High power samples measurements**

The samples were measured 'two-way'. After each measurement, the waveguide was turned around and the same measurement was carried out once again. In this way, reflection parameters $S_{11}$ and $S_{22}$ of each sample are determined. For the reflective measurements, the same labview program is used that is used to measure the transmission line output. Only obviously, to measure the reflectivity, the power meter is now connected to the first directional coupler, shown in figure 5.22. By running the labview program a dataset is now obtained with which the power dependence of the samples reflective character over a frequency range of 8GHz to 10GHz is characterized.

![Figure 5.25: The reflection $S_{11}$ (a) and $S_{22}$ (b) parameters of the second set of samples are shown as a function of frequency and transmission line output power.](image)

In figure 5.25 the $S_{11}$ and $S_{22}$ reflection measurements are plotted. Clearly visible are seven 'planes' indicating the measurements per sample. Roughly it is already visible that there is no significant power or frequency dependent behaviour, as all planes show no significant gradient.

Therefore, for clarification, the 3D plots are simplified. First, the average $S_{11}$ and $S_{22}$ reflectivity over each frequency sweep is plotted against the average transmission line output power over that frequency sweep. These plots are shown in figure 5.26.

![Figure 5.26: The average value of the reflectivity for each frequency sweep is plotted against the average output power of that same frequency sweep. Clearly, there is no significant power dependence in the reflective behaviour of the samples.](image)
This way of plotting will cancel out reflective behaviour that is frequency dependent, but it will show reflective behaviour that is dependent on the transmission line output power.

This graphs clearly shows a lack of power dependence of the reflective behaviour of the samples. On average, reflectivity $S_{11}$ has the same value for varying output power. Only the sample with a volume ratio of 15% silver shows a small increase at the highest output-power, but this is probably an artifact.

Besides the average reflectivity against average output power, also the average reflectivity over each output power sweep is plotted against frequency, shown in figure 5.27.

![Figure 5.27: Average reflectivity $S_{11}$ (left) and $S_{22}$ (right) over the transmission line power plotted against frequency. Sample with filler ratio of 15% shows a strange decline in reflectivity at higher frequency. This is probably due to an inhomogenous artifact in the sample, not caused by the intrinsic behaviour of the homogenous composite material.](image)

This figure shows reflective behaviour that has a frequency dependence, independent of the transmission line output power. Especially at higher filler ratios, the reflections show oscillations. This oscillation is caused by the experimental setup, by the length of the waveguide in particular. The frequency spacing of the oscillation is a measure for the length of the waveguide as following. Interference of microwaves resulting in maxima in the reflection will occur when $2d = n\lambda$, with $d$ the length of the waveguide and $\lambda$ the wavelength. Substituting $f = \frac{c}{\lambda}$, where $f$ equals the frequency, gives $2d = n\frac{c}{f}$. The difference between two maxima in the oscillation $f_{n+1} - f_n = f_{n=1}$ gives:

$$f_{n+1} - f_n = \frac{(n + 1)c}{2d} - \frac{nc}{2d} = \frac{c}{2d} \tag{5.2}$$

The measurements indicate difference between oscillation maxima of about 100MHz, resulting in a waveguide length $d$ of about 1.5m, which matches the actual setup. This relation obviously also shows that with a longer waveguide setup this oscillation will become smaller. The oscillations are more present at higher filler ratio since the reflected microwave radiation has a higher intensity due to the higher reflectivity. This leads to higher interference effects.

Furthermore the 15% sample shows interesting behaviour. A clear decline in reflectivity at higher frequencies can be seen for both $S_{11}$ an $S_{22}$ reflection parameters. It seems that this behaviour is caused by a macroscopic artifact of this sample in particular, as it occurs
5.3. **HIGH POWER X-BAND MEASUREMENTS**

independent from the output power. It is not likely that the behaviour is related to a property of the composite material, as the behaviour does not occur at the other samples. Furthermore, when removed, this particular sample showed some spots with a change in colour. This could indicate a change in the composite material, caused by for instance local heating on the sample which alters the structure of the sample and herewith the response of the sample to an applied microwave signal.

Other notable behaviour is shown by the sample with the filler volume ratio of 1%. It shows a dip in the signal at around 9000Hz. This could also be an artifact of a non perfect homogenous composite material.

### 5.3.5 ‘Low power samples’ measurements

Beside the new 'high power' set of x-band waveguide samples, also high power measurements were carried out on three samples remaining from the 'low power samples', shown in table 5.5. As said earlier, only three samples remained from this set, due to first test measurements in which the samples were lost. The measurements are shown in figure 5.28. The reflection coefficients $\text{S}_{11}$ and $\text{S}_{22}$ are plotted against frequency and transmission line output power.

**Figure 5.28:** Reflectivity coefficients $\text{S}_{11}$ (left) and $\text{S}_{22}$ (right) plotted against transmission line output power and frequency. There seems to be a power dependence in the $\text{S}_{11}$ reflection of the 10% sample. The $\text{S}_{22}$ parameter does not show this non linear behaviour.

Immediately, strange behaviour can be seen, as one would expect more or less the same behaviour in both plots. This is not the case, as the 10% filler ratio sample seems to have a much higher reflection coefficient $\text{S}_{22}$ than $\text{S}_{11}$. Also, there seems to be a power dependence in the $\text{S}_{11}$ parameter.

This is more clarified in figure 5.29, in which the average $\text{S}_{11}$ and $\text{S}_{22}$ coefficients over the frequency sweep are plotted against the average transmission line output power per frequency sweep. The $\text{S}_{11}$ measurements on the 10% sample clearly shows a power dependence of the reflectivity independent of the frequency. At about 50dBm the reflectivity of the 10% sample rises significantly to about -3dB. The sample becomes as reflective as the 20% sample.

The question obviously rises whether this behaviour can be reproduced and is reversible and makes this behaviour intrinsic to the material. If this is the case, one would expect
the same behaviour to be visible in the $S_{22}$ measurement. But in this measurement, this non linear behaviour does not occur. The reflectivity is roughly the same value as the value at high power in the $S_{11}$ measurement.

Since the $S_{22}$ measurement has been carried out subsequent to the $S_{11}$, this means that the sample intrinsically is altered due to the measurement. The reflectivity went up during the $S_{11}$ measurement, and remained high in the $S_{22}$ measurement.

Apparently the composite material is changed in such a way that it behaves more metallic and reflective. A most likely explanation would be the influence of heating of the sample.

It has already been shown that in this 10% sample a macroscopic inhomogeneity is present, as shown in the low power measurements. The sample shows non coinciding reflection coefficients explained by the presence of a thin lossy layer on top of the sample, discussed in section 5.2.3. Therefore it is very assumable, that especially this sample will be very dissipative in this layer and that during measuring, the sample was heated, altering the composite material in such a way to become more metallic and reflective. The heating could have caused the breaking down of the insulating resin and coating of the nano particles which would lead to percolation paths between the silver particles, and therefore, more metallic and reflective behaviour.

This structural change is also verified when the sample is removed from the waveguide after the $S_{22}$ measurement. The sample showed some spots with a change in colour, see appendix D.1, which is probably caused by heating. This heating could be the result of the higher lossiness of the sample, caused by the layered structure.

A subsequent $S_{11}$ measurement needs to be carried out for exclusion that indeed the sample is irreversibly has changed, but this has not been carried out in this research.

Furthermore, also interesting is the behaviour shown by the 25% sample were the reflection coefficients do not coincide. But this is obviously consistent with the low power network analyzer measurements, in which there also was a difference between the $S_{11}$ and $S_{22}$

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**Figure 5.29:** Average reflectivity $S_{11}(a)$ and $S_{22}(b)$ against the average output power. A remarkable jump in the reflectivity can be seen for the 10% sample. The $S_{22}$ parameter does not show this behaviour which strongly indicates that this behaviour is nonreversible. The sample seems to have changed in its characteristics, making it more reflective. This is probably caused by heating of the sample which possibly has led to a dielectric breakdown in the sample, making the sample more metallic and conducting.
5.3. **HIGH POWER X-BAND MEASUREMENTS**

parameter as can be seen in figure 5.12. As already discussed in the previous section, this is explained by the thin lossy layer present on the sample verified by SEM measurements shown in appendix E.2.

The rise in reflective behaviour of the 10% sample can also be seen in figure 5.30 which shows the average reflectivity over the power sweep is plotted against the frequency. The $S_{22}$ parameter is clearly much higher than the $S_{11}$ parameter. Overall, the oscillation caused by the length of the waveguide setup can be seen in all measurements. The 25% sample here also shows strange behaviour, as the reflectivity overall declines at higher frequency.

Figure 5.30: Average reflectivity against frequency. Clearly visible is the higher $S_{22}$ of the 10% sample (left), compared to the $S_{11}$ value (right).

### 5.3.6 Reflection coefficients of both sets of samples

It is shown in the previous measurements, that there is no significant power or frequency dependence of the reflective behaviour of the samples, which is reproducible, and therefore intrinsic to the composite material characteristics. Therefore, it is possible to compare the reflective behaviour of the first set of samples, measured in the low power setup, with the average reflection parameters of the second set of samples. Hereby the reproducibility of the data is checked, and the consistency of behaviour in more or less identical samples.

This comparison is shown in figure 5.31. Here an interesting relation can be seen. For lower volume ratios, there seems to be a linear dependence between filler ratio and reflective behaviour in dB, or otherwise, an exponential dependence between the filler ratio and reflection expressed as $I_R$. Although per volume ratio filler, the samples differ about 1dB to 2dB, and some samples show non coinciding $S_{11}$ and $S_{22}$ reflection coefficients caused by the layered structure, all the samples do match a general trend, in which there seems to be a saturation point for the 20% sample and up.

At higher volume ratio, reflectivity does not change much anymore. From this rough fit, it can also be concluded that a certain average saturation appears at a filler ratio of about in between 15% and 20%. It seems that the saturation value for these samples does not limit to 0dB, but a little lower, which means that the composite material never fully reflects. This is very likely to be caused by the thin nonconducting shell, that surrounds the particles, which prevents the material from becoming fully metallic and conducting.
Nonetheless it is likely, that in the case of very high filler ratio, eventually, the material becomes fully reflective were for samples with a filler ratio of 20% and up, there is a slow increase in reflection with increasing filler ratio. But this slope obviously is much less steep then the slope for samples with low filler ratio.

![Graph showing reflection vs. ratio for different power levels](image)

**Figure 5.31:** Average $S_{11}$ and $S_{22}$ parameters for both sets of samples plotted against the silver particle volume ratio. The average $S_{11}$ and $S_{22}$ parameters from the first set is obtained from the low power measurements, outlined in the previous chapter. The average $S_{11}$ and $S_{22}$ parameters of the second set is obtained from the high power measurements, outlined in this section. Both sets match a rough relation between the reflection parameter of the composite material, and the filler ratio of silver particles. There seems to be a saturation value around 18%, after which the reflection just slightly increases with increasing filler ratio.

### 5.3.7 Conclusions high power measurements

To analyse the possible power dependence of the reflection of the X-band samples, a 'high power' setup is constructed, in which a TWT makes it possible to output microwaves at varying power up to 56dBm, or 400W. In a range of power, frequency sweeps from 8GHz to 10GHz have been carried out. The nature of the setup only allows to measure reflectivity by simply turning around the waveguide, the $S_{11}$ and $S_{22}$ reflection coefficients are determined.

No clear reversible power dependence was observed. Only one 10% filler ratio sample showed a steep increase, which was not reversible. Investigation of the sample showed heat dissipation marks, which intrinsically altered the sample to become more reflective. This is interesting, as although this behaviour was not reversible, this does mean, that the composite material changed by local heating. For instance, a percolating path could have been formed due to dielectric breakdown effects in the composite material.

As in the coaxial and low power measurements, also the high power measurements showed
the relation of increasing reflection with increasing filler ratio. When compared to the average reflection values from the low power measurements, a rough linear relation is present between the reflection and the filler ratio up to about 17%/18%. Samples with a higher filler ratio show more or less equal reflection values. This implies an exponential dependence between the actual reflection expressed as $\frac{I_r}{I_i}$ and filler ratio, since reflection is expressed in decibel.

Although no quantitative data is obtained about the loss in these measurements, it was shown that the samples do dissipate energy. A continuous output wave caused the samples to burn completely. Subsequent measurements were therefore carried out at pulsed wave. Also, remaining samples from the low power measurements which were calculated to have high loss, showed coloured burn marks after measuring in the high power setup.
5.4 Comparison of the microwave measurements

Three types of microwave measurements have been carried out on various composite material samples, resulting in reflective and transmissive information about the samples. For the coaxial measurements a software algorithm was used to calculate the permittivity and loss of the various samples. For the low power x-band measurements, a Thales waveguide model was fitted to the measurements to calculate the permittivity and loss of the samples. In the high power measurements, only the reflectivity of the samples was determined. Hence, the Thales model cannot be used, since the output of this model is a full two-port scatter matrix. Also transmission information is needed, to fit the model to the measurements and obtain the material parameters.

Therefore, to determine the permittivity from the high power measurements, and compare the three different measurements, relation 2.3 outlined in the theory is used to calculate the value for the relative permittivity from solely the reflection data in the high power setup. The loss parameter $\tan\delta$ is assumed to be 0.1, about the average loss determined in the coaxial measurements.

So for comparison, the values for the relative permittivity determined in the coaxial, low power and high power measurements are now plotted together in figure 5.32.

![Figure 5.32](image)

**Figure 5.32**: Permittivity against silver nano particle filler volume ratio. Up to 15-20% the relation between the permittivity and the filler ratio is roughly linear. At higher filler ratio the permittivity increases drastically.

For the high power measurements these values are indicated in black. The theoretical relation 2.3 is also applied on the low power measurements to calculate the permittivity, indicated in blue. The values for the permittivity from the low power setup calculated with the fit model are indicated in red. In green, the permittivity calculations from the coaxial measurements are shown.
5.4. COMPARISON OF THE MICROWAVE MEASUREMENTS

It is tried to fit the measurements to the various proposed theoretical relations between the permittivity and filler ratio, introduced in the theory in section 2.3. It turned out that the measurements are best fitted by relation 2.8, also shown below:

$$\left(\varepsilon^*\right)^\alpha = \frac{(1 - \Phi)(\varepsilon_m^*)^\alpha}{(1 - \frac{\Phi}{\Phi_C})} \quad (5.3)$$

For $\alpha = 0.3\pm 0.01$ and $\Phi_C = 0.42\pm 0.01$ this relation fits the measurements best. $\varepsilon_m^*$, which represents the complex permittivity of the embedding medium is expressed as $\varepsilon_m^* = \varepsilon_m' - j\varepsilon_m''$ or $\varepsilon_m^* = \varepsilon_m' - j\tan\delta\varepsilon_m'$, with $\varepsilon_m' = 3$ and $\tan\delta = 0.003$.

Figure 5.33 shows the measurement in log scale. At $\Phi_C$ of 42% the fit obviously becomes an asymptote.

Mainly two types of interesting behaviour are observed:

- The fit shows a percolation filler ratio of 42%, much higher then a theoretical expected value of about 15-20%
- Up to 15% filler ratio values for the permittivity per sample are roughly in the same order. For values with higher filler ratio, values start to differ.

First, this is very likely to be explained by the coating of the particles. The mathematical expression assumes a percolation threshold, the point were particles make actual contact. This simply does not occur in the first place, since neighbouring particles will never percolate. Therefore, the actual percolation threshold from the fit is very doubtful, though the expression for low filler ratio is assumed to be very accurate.

Second, for high filler ratio, it can be seen that values per sample start to differ. Specifically,
for the 20% and 25% samples the coaxial measurements and the reflection measurements lead to lower values compared to the other measurements. For the coaxial measurements, this could be explained by the great influence of a non perfect fit, leading to leakage and less reflection, discussed in section 5.1.4. Although the calculations are corrected for this misfit, especially for high reflective samples, error margins are likely to be much larger than discussed. A slight misfit for a high dielectric sample could lead to much more leakage and lower reflection than can be corrected for in the calculation. Concerning the reflection measurements, the assumption of tanδ to be 0.1 is discussable, since the coaxial measurements showed higher losses. This would lead to higher permittivity values.

Overall it can be concluded that for low filler ratio values, measurements are more reliable. For higher filler ratio, imperfections seem to influence measurements greatly, leading to a wider spread in values.

This can be correlated to the theoretical relation between the permittivity and the reflection, shown in figure 2.4. It can be seen that for a reflection up to -2dB a rough linear relation between the permittivity and reflection is present. Qualitatively, since these materials have a low reflection coefficient, this makes them dielectric materials by definition. For materials that have a reflectivity higher than -2dB, permittivity increases drastically. It actually becomes an asymptote dependent on the frequency, as the model cannot calculate the permittivity for reflection up to a certain value.

This high reflection is caused by the material becoming more metallic and less dielectric. The model has trouble describing the material as a dielectric and assigning a value for the permittivity.

When comparing figure 5.31 and 2.4 it is shown that samples with a reflection coefficient higher then this -2dB correspond to samples with a filler ratio of ~20% and higher. So considering the theoretical relation, permittivity increases drastically for samples with a higher filler ratio and therefore higher reflectivity.

This significant change in permittivity for a change in reflectivity at high filler ratio samples also explains the wider spread between the measurements. Imperfections have a greater influence on the reflectivity. For highly reflective samples, this results more significant changes in the values for the permittivity.

It can be concluded, that the composite material experiences a transition from more dielectric to more metallic behaviour in between 15% and 20% filler particles. Below this percentage, the material can very well be described as a dielectric material with a dielectric value. Various measurements and samples led to consistent permittivity values. Above this percentage, the material becomes highly reflective and has lost its dielectric properties.
5.5 Conclusions RF microwave measurements

This chapter outlines the sample preparation and the RF microwave measurements that have been carried out on various composite samples. The following research questions were stated for investigation:

- What are the dielectric properties of this composite material, in relation to the ratio of filler particles and epoxy resin?
- What are the loss properties of these composite materials?
- What is the reflective behaviour of the composite materials as a function of the power of the microwave radiation?

Three different setups have been used:

- A coaxial network analyser setup,
- An X-band network analyser setup
- An X-band high power setup

For these different setups, samples with varying volume ratio silver nanoparticles were constructed, to measure the microwave response at varying filler ratio.

In the network analyzer setups, frequency dependent reflection and transmission response was obtained, which showed a clear filler ratio dependence, in both coaxial and X-band measurements. Also in the high power X-band measurements, in which only the reflection coefficients were determined, this filler ratio dependence was present.

For the X-band samples, the scatter matrix measurements showed strange behaviour, as for some samples, their reflection coefficients did not coincide. It is shown that the non-coinciding reflection coefficients can only be caused by a gradient in loss. This indicates an inhomogeneity in the samples caused by the construction method. This gradient resulting in non coinciding reflection coefficients is most influential on the sample with the highest loss in general.

To determine the material parameters from these scatter matrix coefficients, in the coaxial measurements, permittivity and loss were determined with a software algorithm. It is shown that in these calculations the fit of the sample in the sample holder is of great influence, resulting in high error margins in the calculated permittivity. To calculate the material parameters from the X-band network analyser measurements, a Thales waveguide model was fitted to the scatter matrix measurements. The permittivity from these reflection measurements was determined by applying the theoretical relation between the reflection of a perpendicular wave in a two interface system and the permittivity.

The permittivity calculations from each measurement were compared and fitted with a theoretical proposed model. This model showed a perfect fit, when a percolation threshold of 42% volume ratio filler was chosen. This is much higher than values the percolation threshold described in literature of in between 10-20%. This is explained by the coating of the particles, were actual percolation will never occur in the first place in this composite. Therefore, the actual value for the percolation threshold in this fit is very doubtful, though
CHAPTER 5. MICROWAVE CHARACTERIZATION

this expression to describe the relation between the permittivity and the filler ratio for low values of the filler ratio is assumed to be very accurate.

So for samples up to 20% there is a well defined relation between filler ratio and permittivity from \( \varepsilon_r \sim 2 \) to \( \varepsilon_r \sim 8 \) for 0% to 15%. Permittivity calculations for samples with higher filler ratio become less accurate, as different measurements lead to different values. This implies a difficulty in describing the material as a dielectric. This uncorrelated behaviour is verified by the theoretical relation between reflection and permittivity. In this relation, for a reflection above \( \sim -2\text{dB} \), permittivity increases drastically. Therefore, macroscopic inhomogeneities such as less perfect fit have a more significant influence on the permittivity calculations, as a slight change in reflection and transmission will lead to significant different values for the material parameters. According to the reflection measurements, this -2dB reflection and higher corresponds with a filler ratio in between 15% and 20% and higher. This seems to be the breakpoint between a composite material that can be described as a dielectric, and a more metallic, highly reflective material.

Although the loss calculations from the coaxial and X-band setup are more or less contradictory, calculations do indicate a relation, where the lossiness increases for samples with a filler ratio up to this ‘transition volume ratio’ of 15-20% with an average loss \( \tan\delta \) of about 0.1. It is likely, that samples above this breakpoint have even higher losses, but because of their high reflective character, microwaves simply hardly penetrate the material, power is conserved, which in models will lead to low loss values.

Considering the research goals of possible power dependent reflective behaviour, this behaviour has not been observed. Though, one of the samples showed a non reversible drastic increase in reflectivity during a high power measurement. This indicates an intrinsic change in the composite material. Although it turned out not to be reversible, this still indicates that microwaves interact with the composite material. Very likely, due to dissipation, a breakdown has occurred, making the composite material more reflective. This behaviour is very interesting for further investigation.
Chapter 6

Conclusions and discussion

This research describes the electrical and microwave characterization of coated silver nanoparticles composite material. Main focus has been the investigation of the presence of non linear resistive and reflective behaviour. This behaviour is most likely to occur in composites with a filler ratio near the percolation threshold. This in mind, it is chosen to fabricate and characterize composite material in which silver nanoparticles are used, which are coated with a thin insulating shell. The following research goals were formulated:

- The fabrication of a composite material of coated silver nanoparticles in a insulating epoxy resin. Analyzing particles for their composition and presence of a coating in the first place, then creating homogeneous composite material with a defined varying filler ratio.

- Electrical characterization of this composite material. This includes resistance measurements and field dependence measurements, to investigate possible non linear field dependent resistive behaviour.

- The microwave characterization of this composite material at varying conductive filler ratio. This includes measuring the power dependent reflective and transmissive behaviour of these composite materials, to investigate a possible power dependence in the reflective behaviour of the composite material. From these measurements the calculation of the material parameters, relative permittivity $\varepsilon_r$, relative permeability $\mu_r$ and loss tangent $\tan\delta$.

Composite material

TEM, SEM and XPS measurements have been carried out for the characterization of the silver nanoparticles and composite of nanoparticles in epoxy resin. Were the use of microparticles shows difficulty to create a homogeneous spread through epoxy resin, this research focusses on commercially available silver nanoparticles and epoxy resin, which resulted in a macroscopic homogeneous spread of particles through the samples. The presence of a thin 1-3nm thick coating is verified and ensures no percolation occurs, even though at microscopic level, particles do tend to cluster.
Electrical characterization

Electrical characterization on composite material with a filler ratio of 25%, above the theoretical percolation threshold in the macroscopic and microscopic measurements showed that the material is fully insulating at low voltage. A unique measurement setup for electrical characterization is constructed. Composite material is deposited on a substrate with microscopically small contacts. In this way, a more defined system is characterized were potential is applied over a distinct amount of silver particles. In this setup, two-point measurements have been carried out.

These measurements show a reversible non linear behaviour in the resistance of the composite material. In a voltage sweep, with increasing voltage, resistance dropped almost three orders of magnitude. This effect, considering literature, is very likely the result of tunnel effects between particles close together. It is therefore shown, that a rather simply fabrication method, were simply nanoparticles are stirred in liquid epoxy, show great potential in power dependent non linear resistive behaviour. This is mainly caused by the fact that particles are coated, and although the filler ratio is higher then the theoretical percolation threshold, particles will not percolate.

Microwave characterization

For the microwave characterization of the composite material, samples with varying filler ratio have been created. Three different setups were used. In a low power coaxial and X-band waveguide setup, reflection and transmission of the various samples is determined. In a high power setup, the reflection as function of the microwave power is measured. Overall, with increasing filler ratio, reflection increases were transmission decreases.

Some samples showed non coinciding reflection parameters with a spacing up to 2db. It has shown that this is caused by a layer structured of the sample with varying loss, as is verified in SEM images. The existence of this multilayered structure is an artifact in the fabrication, but is interesting, since it makes sample very asymmetric in reflection.

To calculate the material parameters, for the coaxial measurements, a software algorithm is used. The low power X-band measurements are fitted to a Thales waveguide model. To determine the material parameters from the high power reflection measurements, the theoretical expression describing a two interface system is used.

For samples up to 20% there is a well defined relation between filler ratio and permittivity from $\varepsilon_r \sim 2$ to $\varepsilon_r \sim 8$. The calculated values perfectly match the proposed model. For higher filler ratio permittivity calculations become less accurate, as different measurements lead to different values. This implies a difficulty in describing the material as a dielectric. This seems to be the breakpoint between a composite material that can be described as a dielectric, and a more metallic, highly reflective material.

Considering the research goal of possible power dependent reflective behaviour, this behaviour has not been observed. Though, one of the samples showed a non reversible drastic increase in reflectivity during a high power measurement. This indicates an intrinsic change in the composite material. Although it turned out not to be reversible, this still indicates
that microwaves interact with the composite material. Very likely, due to dissipation, a breakdown has occurred, making the composite material more reflective. This behaviour is very interesting for further investigation.

**Recommendation**

Macroscopic imperfections influence the various measurements. The samples did not show perfect dimensions and air bubbles were occasionally present due to the method of fabrication. These imperfections are likely the cause of irregularities in the measurements. More practical research should be carried out on the method of fabrication to prevent these macroscopic imperfections.

This research has shown the potential of composite material with coated silver nanoparticles to show non linear resistive behaviour. But measurements that showed this behaviour only qualitatively. The system is not very defined. Tunneling is probably the most important conduction mechanism, but this can only be verified when the actual path with a certain amount of filler particles, over which the voltage is applied, is quantified. In such a system, the conductive response could be controlled better and tunable. For instance, the spacing between the particles obviously influence the response in resistivity on applied field. Resistivity will drop at lower voltage, when particles are closer together. Still, the used setup with composite on microcontacts has shown to be very useful to analyse this non linear behaviour. Research on depositing composite material on the contact more accurately would be of interest.

Although reversible power dependence in reflective behaviour in the composite with varying filler ratio is not observed, an irreversible increase in reflectivity for increasing power has been observed. This is likely due to heat dissipation, obviously correlated to the lossy character of the material. It could be interesting to investigate the response of a multilayered structure of layers of composite material with different filler ratio, resulting in different material parameters. This results in asymmetric reflective response, as has been showed, but could have potential in showing power dependent behaviour. A layered structure with for instance a thin, highly lossy layer could cause a breakdown in the whole structure due to heat dissipation, at a certain microwave power.
Bibliography


Appendix A

Calculations coaxial measurements

Figure A.1: $\varepsilon_r(\omega)$ at increasing inner diameter of sample (left). Average $\varepsilon_r$ against inner diameter of sample (right).

Figure A.2: $\varepsilon_r(\omega)$ at decreasing outer diameter of sample (left). Average $\varepsilon_r$ against outer diameter of sample (right).

Figure A.3: $\varepsilon_r(\omega)$ at decreasing thickness of sample (left). Average $\varepsilon_r$ against thickness of sample (right).
Appendix B

Low power measurements

Figure B.1: Four symmetry directions of a X-band waveguide.

Figure B.2: $f = 5\%$ sample.
Figure B.3: $f = 10\%$ sample.

Figure B.4: $f = 15\%$ sample.
Figure B.5: $f = 20\%$ sample.

Figure B.6: $f = 25\%$ sample.
Appendix C
Microwave properties

Table C.1: Specific frequency bands in the microwave spectrum

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>L band</td>
<td>1 to 2 GHz</td>
</tr>
<tr>
<td>S band</td>
<td>2 to 4 GHz</td>
</tr>
<tr>
<td>C band</td>
<td>4 to 8 GHz</td>
</tr>
<tr>
<td>X band</td>
<td>8 to 12 GHz</td>
</tr>
<tr>
<td>Ku band</td>
<td>12 to 18 GHz</td>
</tr>
<tr>
<td>K band</td>
<td>18 to 26.5 GHz</td>
</tr>
<tr>
<td>Ka band</td>
<td>26.5 to 40 GHz</td>
</tr>
<tr>
<td>Q band</td>
<td>30 to 50 GHz</td>
</tr>
<tr>
<td>U band</td>
<td>40 to 60 GHz</td>
</tr>
<tr>
<td>V band</td>
<td>50 to 75 GHz</td>
</tr>
<tr>
<td>E band</td>
<td>60 to 90 GHz</td>
</tr>
<tr>
<td>W band</td>
<td>75 to 110 GHz</td>
</tr>
<tr>
<td>F band</td>
<td>90 to 140 GHz</td>
</tr>
<tr>
<td>D band</td>
<td>110 to 170 GHz</td>
</tr>
</tbody>
</table>

Table C.2: The loss tangent of some material commonly used in the microwave industry, at two different frequencies.

<table>
<thead>
<tr>
<th>Material</th>
<th>tanδ (100MHz)</th>
<th>tanδ (10GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PTFE (Teflon)</td>
<td>0.0002</td>
<td>0.00015</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0.0002</td>
<td>0.00031</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.0001</td>
<td>0.0007</td>
</tr>
<tr>
<td>FR-4</td>
<td>0.021</td>
<td>0.021</td>
</tr>
<tr>
<td>Rogers Ro4003C</td>
<td>0.0027</td>
<td></td>
</tr>
<tr>
<td>Coax samples</td>
<td>~0.05</td>
<td>~0.05 &lt;εr&lt; ~0.2</td>
</tr>
</tbody>
</table>
Appendix D

Discoloration X-band sample

Figure D.1: A coloured spot on the 10% sample likely to be caused by heating is visible in the middle of the sample.
Appendix E

SEM images

Sem images on the coaxial measurements samples and remaining 10%, 20% and 25% X-band low power samples. Back-scattered electrons (BSE) and secondary electron imaging (SEI) images are shown.

E.1 Coax samples

Figure E.1: Sample with 5% volume ratio filler
Figure E.2: Sample with 10% volume ratio filler

Figure E.3: Sample with 15% volume ratio filler
E.1. **COAX SAMPLES**

Figure E.4: Sample with 20% volume ratio filler

Figure E.5: Sample with 25% volume ratio filler
E.2 X-band low power samples

Figure E.6: BSE 10 % sample, 100x (left), 1000x (right)

Figure E.7: BSE 20 % sample, 25x, 70x, 200x magnification (from left to right)

Figure E.8: BSE 25 % sample, 25x, 70x, 400x magnification (from left to right)