ADVANCED 0–3 CERAMIC POLYMER COMPOSITES FOR HIGH FREQUENCY APPLICATIONS
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MERJA TEIRIKANGAS

ADVANCED 0–3 CERAMIC POLYMER COMPOSITES FOR HIGH FREQUENCY APPLICATIONS

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Oulu, Finland

Abstract

The main object of this thesis was to research injection mouldable 0–3 type ceramic polymer composites and their dielectric and magnetic properties in the GHz frequency region.

The work has been divided into three sections. In the first section, two–phase ceramic polymer composites containing dielectric and magnetic fillers have been investigated and their characteristics analysed by reference to pre–existing mixing rules. The exploitation of these composites in miniaturizing devices, such as antennae, is presented and discussed. The second part describes three phase composites containing different nanosize additives (silver, silicon and alumina fibres) towards improving their dielectric properties. In the third part, some periodical and multilayer structures for ceramic polymer composite layers are proposed.

In the case of two–phase ceramic polymer composites, with 37 vol.% of dielectric filler (Barium Strontium Titanate, BST) embedded into a thermoplastic polymer (ER140) matrix, the highest measured relative permittivity was 15 with a dielectric loss value of 0.008 at 1 GHz. With 43 vol.% of magnetic filler (hexaferrite, CO2Z) in ER182 matrix, the highest achieved relative permeability was 1.8 with a magnetic loss value of 0.077 at 1 GHz. Composites with CO2Z filler provide a 77% size reduction, and could thus be used advantageously in antennae.

It was found that a 2–6 vol.% nanoaddition in BST–ER140 composites enhanced the relative permittivity drastically with only a minor effect on the dielectric losses. In particular, with only 2 vol.% addition of nanosize silver particles into the BST–ER140 composite, a 52% increase in the relative permittivity was obtained, with no significant change in the dielectric losses (\(\tan \delta_\varepsilon = 0.004\)).

Vertically and horizontally periodical dielectric composite structures comprising layers of different dielectric properties have been fabricated as well as multilayered structures containing dielectric and magnetic layers. The measurement results indicate that such multilayer structures are good candidates for components with reduced dielectric and magnetic losses.

Keywords: 0–3 ceramic polymer composite, electrical properties, high frequency properties, injection moulding, interphase, layered structures
Väitöstön tavoitteena oli tutkia ruiskuvallattavien 0–3-litiäärinen keraami-polymeerikomposiittien ominaisuuksia erityisesti niiden GHz-taajuusalueen dielektristen ja magneettisten ominaisuuksien kannalta.


Kaksikomponenttisten keraami-polymeerikomposiittien tapauksessa suurin permittiivisyyden arvo 15 dielektristen häviöiden ollessa 0.008 (mittaustaajuus 1 GHz) saatiin komposiitille, jossa dielektristä täytemateriaalia (Barium Strontium Titanattii, BST) oli 37 tilavuus-% termoplastisessa polymeerimatriisissa (ER140). Korkein saavutettu permeabiliteetin arvo 1.8 magneettisten häviöiden ollessa 0.077 (mittaustaajuus 1 GHz) saatii n komposiitille, jossa magneettista täyteaineetta (hexaferriitti, Co2Z) oli 43 tilavuus-% ER182-matriisissa. Tämä täyteaine mahdollistaa nykyistä jopa 77 % pienempien antennielementtien kehittämisen.

Tukimuksessa todettiin 2–6 tilavuus-% nanomateriaalin lisäyksen BST-ER140-komposiiteihin kasvattavan permittiivisyyttä merkittävästi juurikaan vaikuttamatta dielektrisiin häviöihin. Erityisesti 2 tilavuus-% hopean nanopartikkeleiden lisäsä BST-ER140-komposiiteihin kasvattaa permittiivisyyttä 52 % dielektristen häviöiden (tan δe = 0.004) kasvamatta. Työssä on myös tutkittu periodisesti (vertikaali ja horisontali) koostettuja dielektrisiä komposiittirakenteita, jossa eri kerroksissa on erilaiset dielektriset ominaisuudet sekä monikerrosrakenteita, joissa vuorotteluvat dielektriset ja magneettiset kerrokset. Mittaukset osoittivat, että monimateriaaliset monikerrosrakenteet ovat hyviä kandidaatteja komponentteihin, jotka vaativat pieniä dielektrisiä ja magneettisiä häviöitä.

\textit{Asiasanat:} 0–3 keraamilipomeerikomposiitti, korkean taajuuden ominaisuudet, monikerrosrakenteet, rajapinta, ruiskuvalu, sähköiset ominaisuudet
"What one man can invent another can discover"

Sir Arthur Conan Doyle
Acknowledgements

First of all, I wish to thank my supervisor Professor Heli Jantunen who gave me the opportunity and resources to perform this research. I am most grateful for her encouragement, constant support and believing and trusting in me even on my stubborn days. I wish also to acknowledge Dr. Jari Juuti for pushing me on and for all the guidance on the way.

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Special thanks to all my friends for reminding me of the truly important things in life. My sincere gratitude goes to my parents whom have always encouraged and support me in all my endeavours. Finally, my deepest gratitude is dedicated to my better half and husband ”Ukko” Juhani, for his understanding, patience and love; vi sitter i samma bil. I know I demanded a lot.

Oulu, September 2011

Merja Teirikangas
**List of abbreviations and symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space</td>
</tr>
<tr>
<td>$\varepsilon'$</td>
<td>Real part of complex permittivity</td>
</tr>
<tr>
<td>$\varepsilon''$</td>
<td>Imaginary part of complex permittivity</td>
</tr>
<tr>
<td>$\varepsilon_{\text{com}}$</td>
<td>Permittivity of composite</td>
</tr>
<tr>
<td>$\varepsilon_f$</td>
<td>Permittivity of filler</td>
</tr>
<tr>
<td>$\varepsilon_m$</td>
<td>Permittivity of matrix</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative permittivity</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Impedance in vacuum</td>
</tr>
<tr>
<td>$\eta_m$</td>
<td>Characteristic impedance in material</td>
</tr>
<tr>
<td>$\tan\delta_e$</td>
<td>Dielectric loss tangent</td>
</tr>
<tr>
<td>$\tan\delta_\mu$</td>
<td>Magnetic loss tangent</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>Wavelength in vacuum</td>
</tr>
<tr>
<td>$\lambda_c$</td>
<td>Wavelength in material</td>
</tr>
<tr>
<td>$\mu'$</td>
<td>Real part of complex permeability</td>
</tr>
<tr>
<td>$\mu''$</td>
<td>Imaginary part of complex permeability</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Permeability of free space</td>
</tr>
<tr>
<td>$\mu_{\text{com}}$</td>
<td>Permeability of composite</td>
</tr>
<tr>
<td>$\mu_r$</td>
<td>Relative permeability</td>
</tr>
<tr>
<td>BST</td>
<td>Barium strontium titanate, $\text{Ba}<em>{0.55}\text{Sr}</em>{0.45}\text{Ti}_{1.01}\text{O}_3$</td>
</tr>
<tr>
<td>CLNT</td>
<td>CaLiNbTiO</td>
</tr>
<tr>
<td>COC</td>
<td>Cyclo–olefin copolymer</td>
</tr>
<tr>
<td>Co$_2$Z</td>
<td>Z-type hexaferrite, $\text{Ba}<em>5\text{Co}<em>2\text{Fe}</em>{24}\text{O}</em>{41}$</td>
</tr>
<tr>
<td>ER140</td>
<td>Polypropylene – <em>graft</em> – poly(styrene – <em>stat</em> – divelbenzene)</td>
</tr>
<tr>
<td>ER182</td>
<td>Polypropylene – <em>graft</em> – poly(styrene – <em>stat</em> – divelbenzene)</td>
</tr>
<tr>
<td>f</td>
<td>Filler fraction</td>
</tr>
<tr>
<td>F</td>
<td>Frequency</td>
</tr>
<tr>
<td>FEGSEM</td>
<td>Field emission gun scanning electron microscope</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field-emitted scanning electron microscope</td>
</tr>
<tr>
<td>GdIG</td>
<td>Gadolinium iron garnet</td>
</tr>
<tr>
<td>HexaZ</td>
<td>Z-type hexaferrite, $\text{Ba}<em>3\text{Co}</em>{1.4}\text{Cu}<em>{0.6}\text{Fe}</em>{24}\text{O}_{41}$</td>
</tr>
<tr>
<td>nAg</td>
<td>Nanosize silver</td>
</tr>
<tr>
<td>nAl$_2$O$_3$</td>
<td>Nanosize alumina fiber</td>
</tr>
<tr>
<td>nSi</td>
<td>Nanosize silicon</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>POE</td>
<td>Polyolefin elastomer</td>
</tr>
<tr>
<td>PPS</td>
<td>Polyphenylene sulphide</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>PWB</td>
<td>Printed wiring board</td>
</tr>
<tr>
<td>Q</td>
<td>Quality factor</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>vol.%</td>
<td>Loading in volume percents</td>
</tr>
<tr>
<td>YIG</td>
<td>Yttrium iron garnet, Y$<em>{2.94}$Cu$</em>{0.15}$Fe$<em>{5}$O$</em>{12}$</td>
</tr>
<tr>
<td>$Z_m$</td>
<td>Impedance in material</td>
</tr>
<tr>
<td>$Z_{\text{diff}}$</td>
<td>Difference in characteristic impedance</td>
</tr>
</tbody>
</table>
List of original papers

This thesis is based on the following 5 original papers, which are cited in the text by the given roman numerals.


In Papers I & II, injection mouldable two-phase composites with 0–3 connectivity are introduced, and their dielectric and magnetic properties, within the frequency range from 1 MHz to 1 GHz, are presented. In Paper I, BST thermoplastic polymer composites with different matrix polymers and ceramic filler loadings are studied. In Paper II, magnetic and dielectric properties of 0–3 type ceramic polymer composites are investigated, and their utility for miniaturizing antennae discussed.

In Paper III, the effect of nanoadditives on the high frequency dielectric properties of ceramic polymer composites are researched.

Papers IV and V introduce periodical composite structures constructed from two-phase ceramic polymer composites. In Paper IV the two different periodical structures, horizontal and vertical, are developed. In Paper V, a multilayered structure consisting altering dielectric and magnetic layers is presented.

In Paper I, the main idea was developed in association with the co-authors, and the material fabrication, experiments and measurements were done with the kind help of the co-authors. The author’s contributions to Paper II were the development of the main idea, the material fabrication and experimental measurements. The main ideas in Papers III–V and the writing of the manuscripts were done by the author with the kind assistance of the co-authors. The experiments and measurements for the Papers III–V were done by the author.
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1 Introduction

The rapid development of the electronics industry requires inexpensive electronic components offering higher performance yet smaller size. In this regard, ceramic polymer composites with 0–3 connectivity are especially attractive for various applications due to their ease of fabrication, and they have thus been widely studied over the last few decades. In these composites, the 0–3 connectivity is formed by suspending 0–dimensional ceramic particles within a 3–dimensional continuative polymer matrix. For low-frequency applications, composite materials have already been developed for hydrophones operating under 40 kHz, ultrasonic transducers for medical diagnosis applications, sonars and piezoelectric transducers (1–10 MHz). [1–3] Additionally, these composite materials have been investigated for telecommunication applications [4–9].

The main advantages of 0–3 ceramic polymer composites, especially when thermoplastic polymers are used as the matrix, are flexibility, ductility and compatibility with printed wiring board (PWB). In addition, they enable easy fabrication into various shapes, including three–dimensional structures [10, 12]. The ability to make a composite of a particular, bespoke permittivity and permeability (albeit within certain limits) provides useful degrees of freedom in applications design. Such flexibility in the fabrication of inductive and capacitive circuit elements would be hugely advantageous in telecommunication applications. [4–9, 10, 13]

Additionally, 0–3 composites provide opportunities to develop materials with the combined magnetic and dielectric properties desired for multifunctional components [10]. The principal advantage to be had here is the downsizing of telecommunication devices. For instance, the miniaturisation of antennae can be done using materials having higher permittivity or permeability or, as proposed, by utilising materials having combined performance [11].

Towards cost-efficient utilisation in advanced devices, a deeper, more quantitative understanding of the high frequency magnetic and dielectric properties of these 0–3 ceramic polymer composites is required.

1.1 0–3 ceramic polymer composites for high frequency applications

Polymer ceramic composites with relatively high permittivity (10–15) are good candidates to meet requirements set by e.g. embedded capacitors, capacitively
coupled electrical solutions and integrated RF devices. Composites exhibiting both inductive and capacitive properties are also a solution to the fabrication of miniature filters and antennas, control of electromagnetic interference (EMI), etc.

Investigations relating to the tailoring of the dielectric and magnetic properties of high frequency polymer based composites have recently created some interesting results [13–16]. The electrical properties of these materials are affected by the composing phases and microstructure. In addition to the electrical properties of the matrix material and filler, the particle size, distribution and shape of the filler particles are also important, as well as their loading level in the composite [17].

To meet the requirements of multifunctional components, much work hitherto has been performed to synthesize ceramic–ceramic composite materials offering advantageous dielectric and magnetic properties. In these composites, the shrinkage mismatch and diffusion between phases during firing can drastically influence the properties/performance of the final material. [18–21] Though the permittivities and permeabilities of polymer–based composites cannot be made to be as high as those afforded by ceramic–ceramic composites, they do not in compensation suffer from these challenges during fabrication.

The size reduction of e.g. an antenna is inversely proportional to the square root of the relative permeability and permittivity of the material out of which it is made – commonly achieved using solely high permittivity materials [22–24]. However, with regard to size reduction and minimising the free energy trapped within the substrate, the most efficient approach is to have equal and enhanced permittivity and permeability values [25]. This also affords improved impedance matching between the medium and free space, thus increasing the reflection coefficient of the antenna [11]. However, the fabrication of such materials is a challenging task, especially taking into account the requirements for low magnetic losses and a drastic decrease of permeability at high frequencies. [18, 19] Magneto–dielectric composite materials have the potential to overcome these challenges.

The permittivity of a composite is a nonlinear function of the ceramic loading and typically high volume fractions are required to obtain a significant increase in the permittivity, especially at higher frequencies. As a consequence, the mechanical properties are reduced as a function of ceramic loading introducing brittleness and inhibiting flexural characteristics. Multilayered and periodical structures of different polymer based composites might overcome these
difficulties as indicated by earlier studies concentrated on ceramic–ceramic composites or structures with pure polymer and ceramic layers [26–29].

1.2 Scope and outline of the thesis

The main objective of this thesis is to study high frequency properties of 0–3 type ceramic polymer composites with thermoplastic polymer as a matrix material combined with dielectric or magnetic fillers. In addition, methods to improve the electrical performance of these materials by adding nanosize materials were investigated. Periodical and multilayered structures utilising composite materials were also investigated for these purposes. Furthermore the research focuses in possibilities to predict the attainable high frequency properties before actual fabrication of composites. It should however be noticed that in this work the functionalising, coating, drying and particle size distribution of filler materials is not in the scope of this research, even though it is well-known and proven to be an effective method [30–32]. Also neither the mechanical nor thermal nor thermomechanical properties of the composite materials are discussed within this research. The content of this thesis is summarized as follows:

Chapter 2 introduces the basics, and then describes the state of the art and existing mixing equations of composites. Fabrication and electrical characterization methods used in this thesis are presented as well as those for microstructure analysis of the fabricated composites and structures.

Chapter 3 presents the high frequency dielectric and magnetic properties of fabricated two-phase composites in the frequency range from 1 MHz to 1 GHz. The correspondence of measurement results to the presented mixing equations and their usage is discussed. The miniaturisation properties of the fabricated composites are presented and discussed.

In Chapter 4, the effect of nanoadditives towards improving the high frequency properties of ceramic polymer composites are presented. Also, the effect of these nanoadditives on interfacial properties is discussed briefly. Three different nanosize materials are tested. Also the feasibility of the mixing equations is discussed.

In Chapter 5, the fabrication and properties of periodic composite structures are introduced. Two different types of structure are researched; one with different dielectric layers and another with periodically altering dielectric and magnetic composite layers.
2 Developed composites and structures with adjustable properties

By combining high-permittivity ceramic powders with ductile polymers, composites with good dielectric properties can be developed. Such composites offer low losses in the GHz region and are thus candidates for applications in electronics and telecommunications. Thermosetting polymers like epoxy have been used for decades as matrix materials [33–34]. Lately, thermoplastic polymers such as COC (cyclo–olefin copolymer), PE (polyethylene), PPS (polyphenylene sulphide), POE (polyolefin elastomer), and PVDF (polyvinylidene fluoride), PMMA (Poly(methyl methacrylate)) have also been investigated for more advanced applications. The motivation here is that thermoplastic polymers can be re-melted and remoulded repeatedly. 0–3 type composites based on thermoplastic polymers have gained particular attention [4–9, 12, 35–37].

In general, the properties achievable with composites depend of the initial matrix and filler properties. With 0–3 type composites, their dielectric and magnetic properties are dominated by the matrix material. The permittivity and permeability of such composites are greatly reduced, as compared to their corresponding sintered bulk ceramics, due to the significantly lower permittivity/permeability of the polymer. Obtaining high permittivity or permeability and low losses is especial challenging at high frequencies. In the case of permittivity, an additional decrement as a function of frequency is caused by dielectric relaxation [38–40]. On the other hand, because of magnetic resonance, typical to all magnetic materials, permeability values decrease dramatically above a certain cut-off frequency. [10–12]

2.1 Basis and theory of functional composites

To facilitate the utilization of the 0–3 composites, various different mixing rules, e.g. Lichtenecker [4, 5, 19, 30, 31, 41], Maxwell–Garnett and Bruggeman [6, 8, 9, 10, 12, 15, 22, 41–45] to predict the dielectric ($\varepsilon_{\text{com}}$) or magnetic ($\mu_{\text{com}}$) properties of composites comprising different sorts of matrix and filler materials and different sorts of matrix-filler geometries have been used. The simplest of these is the logarithmic Lichtenecker equation (Eq. 1) and its modified version (Eq. 2):

$$\log \varepsilon_{\text{com}} = (1-f) \log \varepsilon_{m} + f \log \varepsilon_{f} ,$$

(1)
\[
\log \varepsilon_{\text{com}} = \log \varepsilon_m + f (1-k) \log \left( \frac{\varepsilon_f}{\varepsilon_m} \right),
\]
(2)

where \( f \) is the volume fraction of matrix and filler, and \( \varepsilon_m \) and \( \varepsilon_f \) are the relative permittivities of pure polymer and ceramic and \( k \) is a fitting factor of the composite, respectively. Most commonly used of these mixing rules are the Maxwell–Garnett equation (Eq. 3) and Bruggeman’s (Eq. 4) effective medium theory:

\[
\varepsilon_{\text{com}} = \varepsilon_m \left[ 1 + \frac{3f \left( \varepsilon_f - \varepsilon_m \right)}{1 - f \left( \varepsilon_f - \varepsilon_m \right) \left( \varepsilon_f + 2\varepsilon_m \right)} \right],
\]
(3)

\[
\varepsilon_{\text{com}} = \frac{f \left( \varepsilon_f - \varepsilon_m \right)}{\varepsilon_f \varepsilon_{\text{com}} + \frac{1}{3} \left( \varepsilon_f - \varepsilon_{\text{com}} \right)}.
\]
(4)

The Maxwell–Garnett equation is especially suitable for low filler loading levels below percolation, where it gives good correspondence with measured results. The Bruggeman theory, on the other hand, is more relevant at higher loading levels. A differential mixing equation (Eq. 5) recently introduced by Jylhä & Sihvola combines the aforementioned mixing rules. It has the characteristics of the Maxwell–Garnett equation at low filling ratios yet approaches the Bruggeman equation as the filler loading increases [45]

\[
\frac{d\varepsilon_{\text{com}}}{d\varepsilon_f} = \frac{3\varepsilon_m \left( \varepsilon_f - \varepsilon_{\text{com}} \right)}{\varepsilon_f + 2\varepsilon_{\text{com}} - f \varepsilon_{\text{com}}}.
\]
(5)

The solution for the inverse function \( df / d\varepsilon_{\text{com}} \) of the differential equation, when \( \varepsilon_m < \varepsilon_{\text{com}} < \varepsilon_f \) is

\[
f = 1 - \frac{1}{3} \frac{\varepsilon_f - \varepsilon_{\text{com}}}{\varepsilon_f - \varepsilon_m} \left( 2 + \left( \frac{\varepsilon_f - \varepsilon_{\text{com}}}{\varepsilon_f - \varepsilon_m} \right)^{\varepsilon_f^{1/2} - 1} \right).
\]
(6)

The inverse function can be used to solve the corresponding volume fraction by giving a value for the permittivity of composite. [45]

Same equations can also be used to calculate the effective permeability of composite materials, in which case the permittivity is replaced with permeability.
These mixing rules can be used to analyse the complex electrical properties of composites subject to certain restrictions. If the predominant loss mechanism is the same for bulk material as it is for small particles, then the same mixing rule can be used to predict the composite’s losses (imaginary part), as well as its reactance (real part), with a complex value for the relevant electrical property inserted [46].

In addition, several other mixing rules and simulation-based methods to predict electrical properties of 0–3 composites have been proposed. Some of these rules/methods may be applied to estimate the thermomechanical properties of composites [7, 40] as well.

2.2 Fabrication of composites and samples

Various composite materials were fabricated and studied as a function of filler loading and frequency in each case. Thermoplastic polymers used in matrix, dielectric and magnetic fillers and nanoadditive materials were all commercial materials, except for two magnetic compositions synthesised by the oxide mixing method.

2.2.1 Materials used

Matrix materials

The basic properties of the thermoplastic polymers used in this research are presented in Table 1. Reason to select PPS as one matrix candidate is its high melting temperature (280 °C) enabling solder joints onto the composite substrate. Traditionally COC has been used in optic applications where glass-like clarity is needed such as medical devices, but it was selected due to its low losses (0.0006 at 1 GHz).
Table 1. Main properties of used thermoplastic matrix materials.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Manufacturer</th>
<th>Melting temperature [°C]**</th>
<th>Density [g/cm³]**</th>
<th>ε’ [GHz]**</th>
<th>tan δ [GHz]**</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPS (Fortron 9205C4)</td>
<td>Ticona GmbH, Germany</td>
<td>280</td>
<td>1.35</td>
<td>3.2</td>
<td>0.001</td>
</tr>
<tr>
<td>COC (Topas 8007S–04)</td>
<td>Ticona GmbH, Germany</td>
<td>190</td>
<td>1.02</td>
<td>2.4</td>
<td>0.0006</td>
</tr>
<tr>
<td>ER182</td>
<td>NOF Co, Japan</td>
<td>170</td>
<td>0.93</td>
<td>2.4</td>
<td>0.0002</td>
</tr>
<tr>
<td>ER140</td>
<td>NOF Co., Japan</td>
<td>170</td>
<td>0.93</td>
<td>2.4</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

* Manufacturer, ** Measured

Additionally in order to reach high filler loading levels modified polypropylenes ER182 and ER140 (polypropylene–graft–poly(styrene–stat–divenylbenzene)), with longer polymer chains were selected. These polymers exhibit also extremely low dielectric losses (0.0002) at 1 GHz

**Filler materials**

Commercial Ba₀.₅₀Sr₀.₄₅Ti₁.₀₁O₃ powders (BST₁, BST₂, BST₂) in paraelectric state at room temperature have been used as dielectric filler in composites. The subscript indicating different manufacturers as denoted in Table 2. The BST was selected as filler due to its high relative permittivity with moderately low losses (BST₂ ε’ > 2000 tan δ ~ 0.0005 at 1 MHz).

As magnetic fillers two commercially available materials, MnZn ferrite and Z-type hexaferrite (Co₂Z, Ba₁Co₀.₆₆Fe₂₀O₄₁), were selected. Additionally two magnetic materials, Z-type hexaferrite (HexaZ, Ba₃Co₁.₄Cu₀.₆Fe₂₀O₄₁) and yttrium iron garnet (YIG, Y₂.₉Cu₀.₁₅Fe₅O₁₂), were synthesized. Hexagonal ferrites (Co₂Z, HexaZ) exhibits lower losses (~0.04 and 0.06 at 1 GHz, respectively) due to their higher crystal anisotropy compared to cubic crystal system (spinel ferrites) [25]. YIG was selected due to its long history in MHz applications.
Table 2. Main properties of used ceramic filler materials.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Manufacturer</th>
<th>Particle size (µm)*</th>
<th>Density (g/cm³)**</th>
<th>ε'/µ' [Hz]</th>
<th>tan δε/µ [Hz]</th>
<th>cut-off frequency *</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSTF1</td>
<td>Filtronic Comtek Ltd., UK</td>
<td>~1</td>
<td>5.43</td>
<td>2740 (3.6 G)**</td>
<td>0.001 (100 k)*</td>
<td>–</td>
</tr>
<tr>
<td>BSTP</td>
<td>Praxair Specialty Ceramics, USA</td>
<td>1.23</td>
<td>5.34</td>
<td>2110 (100 k)*</td>
<td>0.002 (100 k)*</td>
<td>–</td>
</tr>
<tr>
<td>BSTF2</td>
<td>Ferro, USA</td>
<td>1.42</td>
<td>5.88</td>
<td>2080 (1 M)**</td>
<td>0.0005 (1 M)**</td>
<td>–</td>
</tr>
<tr>
<td>MnZn</td>
<td>Toda Kogyo, Japan</td>
<td>1.7</td>
<td>4.66</td>
<td>30/33 (1 M)**</td>
<td>0.2/0.03 (1 M)**</td>
<td>~20–30 MHz</td>
</tr>
<tr>
<td>Co2Z</td>
<td>TransTech, USA</td>
<td>4.67</td>
<td>4.54</td>
<td>10/12 (1 G)**</td>
<td>0.5/0.04 (1 G)**</td>
<td>~900 MHz</td>
</tr>
<tr>
<td>HexaZ</td>
<td>–</td>
<td>5.26*</td>
<td>24/2.6 (1 G)*</td>
<td>0.05/0.06 (1 GHz)*</td>
<td>~800 MHz</td>
<td></td>
</tr>
<tr>
<td>YIG</td>
<td>–</td>
<td>5.39*</td>
<td>29/1.5 (1 G)*</td>
<td>0.14/1.6 (1 G)</td>
<td>~300 MHz</td>
<td></td>
</tr>
</tbody>
</table>

* Measured, ** Manufacturer

YIG and HexaZ were synthesized with oxide mixing method using Y₂O₃, Fe₂O₃, CuO, BaCO₃, Co₃O₄ from Alfa Aesar and Aldrich Chemical Co. as explained elsewhere [47, 48]. Bulk samples from the commercial and synthesized powders were dry pressed in order to measure their properties presented in Table 2. The measured porosities of the YIG and HexaZ bulk samples were 37% and 44%, respectively [Paper V].

The natural resonance frequencies of different hexaferrites reported by Nakamura & Hatakeyama are at 0.5–1.5 GHz depending e.g. on their chemical compositions. This is also the so-called cut-off frequency beyond which the permeability dramatically decreases. [49] The observed cut-off frequencies of the bulk samples of the used magnetic fillers are presented in Table 2.

Nanoadditives

To achieve higher permittivity or permeability in ceramic–polymer composites one option is to increasing the filler content. This action however decreases processability and ruggedness. Earlier in low frequency piezoelectric composites the conductivity of the matrix, in order to facilitate the poling, was controlled by adding small amounts of semiconducting filler such as carbon, germanium or silicon [2]. Murugaraj et al. discovered that the enhancement of permittivity was in correlation with surface area of the nanoparticles used as fillers [50]. In this research the efficiency of nanoadditives to enhance the dielectric properties of high frequency composites was investigated. This was performed with small addition (1–6 vol.%) of nanosize silver (nAg) and silicon (nSi) particles and
alumina (nAl₂O₃) fibres with general properties shown in Table 3. Silver and silicon nanoadditives were expected to modify the conductivity of the matrix as in the earlier studies by Sa-Gong et al. [2]. Alumina fibres were selected due to their large specific surface area (~630 m²/g) to evaluate their effect on dielectric properties via interphase modification.

Table 3. Used nanosize additive materials and their properties provided by manufactures.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Manufacturer</th>
<th>SSA m²/g</th>
<th>density (g/cm³)</th>
<th>particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nAg</td>
<td>NanoDynamics Inc., USA</td>
<td>11.02</td>
<td>2.70</td>
<td>41</td>
</tr>
<tr>
<td>nSi</td>
<td>Hefei Kaier Co., China</td>
<td>80</td>
<td>2.3</td>
<td>60</td>
</tr>
<tr>
<td>nAl₂O₃</td>
<td>Argonide Corp., USA</td>
<td>~630</td>
<td>3.9 Ø 2–4, 100 (rule length)</td>
<td></td>
</tr>
</tbody>
</table>

2.2.2 Fabrication methods

The 0–3 type composite materials with ceramic loadings varying from 6–44vol.% were fabricated using Haake Minilab twin-screw mixing extruder (Thermo, Electron Corporation, Germany) with mixing temperatures between 170–310 °C depending on the melting temperature of the polymer used and the level of filler loading. In the extrusion process, the thermoplastic polymer in granular form was fed to the mixing extruder with slow addition of ceramic filler into the melt. In composites with nanoadditives, the nanosize materials were firstly dry mixed with BST powder after which the mixture was used as filler.

The processing temperature was increased with increasing filler loadings as ceramic content was absorbing part of the heat. By increasing the processing temperature, the melting of the polymer was kept as rapid as possible, which facilitated the compounding. This was done to prevent the filler material forming rigid agglomerates between the mixing screws and thus blocking the extruder. To achieve homogeneous dispersion of the fillers throughout the composite materials, the processing time was increased with increasing filler loading so that the components were mixed up to 30 min.

After compounding, the extruded composite materials were injection moulded into circular (Ø18 × 0.3 mm³) or square shapes (18 × 18 × 1 mm³). In the injection moulding process, the cylinder and the mould temperatures were 200–220 °C and 80–100 °C, respectively, and the injection pressure was 65 MPa with 70 MPa post-pressure for 15 s. The periodical and multilayer structures using composites with different fillers and filler loading [Paper IV, V] were
constructed with injection moulded sheets and discs by hot lamination at 90 °C temperature with 12 MPa pressure for 30 minutes.

During the mixing and extrusion procedure, some of the filler material is lost. The actual volume fraction of filler for each fabricated composite material was thus determined by measuring its density using the Archimedes method [51] with a pycnometer (Gay-Lussac BlauBrand®, Brand GmbH + Co KG, Germany). Average filler loss in the compounding process was between 10–20% of the input amount.

For the high frequency dielectric measurements, 250 nm thick Ag electrodes were deposited onto the carefully ground and polished samples by RF-sputtering with PVD system (Torr International, New Windsor, NY). The electrodes enable higher measurement accuracy especially in the case of dielectric loss values.

### 2.3 Microstructure characterization of composites

Microstructures of the fabricated high frequency composites and their interfaces were studied with different types of scanning electron microscopes; SEM (Jeol JSM-6400, Jeol LTD., Japan), field-emitted SEM (FESEM, Zeiss Ultra Plus FESEM (Carl Zeiss SMT AG, Germany) and high resolution field emission gun SEM (FEGSEM, LEO Gemini 1525 FEGSEM, Carl Zeiss NTS GmbH). For composites containing thermoplastic polymer matrix, it is important to keep the accelerating voltage as low as possible since the thermoplastics are sensitive to heat and, with high acceleration voltage, might cause the material to degrade. This makes the FEGSEM the most advantageous equipment. Microstructure studies were done in order to create better understanding of the achieved high frequency properties, for example to detect voids or agglomerates which can influence the composite’s electrical properties (as functions of frequency).

Figure 1 presents the microstructures of BSTF1–PPS composites with different ceramic filler loadings. Results show that the ceramic filler is distributed close to homogeneously in the polymer matrix regardless of the loading level in composites. This was also noticeable in all other ceramic–polymer composites investigated in this research, regardless of the matrix polymer or filler ceramic used.
In almost all of the composite materials, though large voids were absent, some micron scale voids ($\mu$ void) within the polymer matrix, as well as nanoscale voids (n void) between ceramic–polymer interfaces were observed. The images shown in Figure 2 below are typical.

In general, the nanoadditives did not appear to affect the particle distribution in composite materials. However with a greater than 4 vol.% addition of nAl$_2$O$_3$, the nanofibres formed clusters with diameter of 0.5–2 $\mu$m (Figure 3). This causes some porosity due to air trapped between the loosely joined fibres. In this case, there seems to be a clear need for functionalisation of the fibres before addition so as to improve their dispersion and wetting by the polymer matrix.
In the multilayered structures (Figure 4) with alternating dielectric and magnetic layers no de-laminations or air gaps were observed between the layers. However, in some cases a thin layer of pure polymer (<5 µm, Figure 4c) was observed. This layer was segregated from the composites during the lamination process when the polymer was melted and flowed easily [Paper V]. Although this segregated layer was on 0.5% of the thickness of one composite layer thus supposed to have minimal effect to electrical properties, the microstructure shows that the lamination temperature could be somewhat further optimised. Anyway, it should be noted that similar pure polymer areas could not be observed in the periodic structures.
2.4 High frequency characteristics of composites

Dielectric properties

The complex permittivity ($\varepsilon’$-je$’’$) of materials is related to a variety of physical phenomena. In lower frequencies (< 100 MHz), the imaginary part of permittivity, $\varepsilon’’$, is dominated by the influence of ion conductivity. The variations in complex permittivity at microwave range are mainly caused by dipolar relaxation and, in the infrared region, mainly due to atomic and electronic polarizations. [52]

The dielectric characteristics of disc-shaped composite samples and structures at high frequencies were investigated as a function of frequency from 1 MHz to 1 GHz with an Agilent E4991A RF Impedance/Material Analyzer (Agilent Technologies Inc., USA) using a 16453A dielectric material test fixture at room temperature. In this apparatus, the measurement accuracy according to the manufacturer depends on the sample thickness, the permittivity of the material and the measurement frequency. The accuracy decreases at both ends of the frequency range (below 10 MHz and close to 1 GHz). The measurement accuracy is lower at low frequencies for low permittivity materials and lower at high frequencies for high permittivity ($\varepsilon’$ > 100) materials. To increase measurement accuracy at both ends of the frequency range, silver electrodes were applied onto the samples. To exclude measurement errors, samples were measured several times with inconsistencies resolved. In the results, all the presented permittivity and loss tangent values at 1 GHz nominal are (for technical reasons associated with the apparatus) averaged from measurements taken between 970 MHz and 1 GHz.

Magnetic properties

The frequency dependency of magnetic materials is rather complex. In the low frequency range (< 1 MHz), magnetic properties do not vary within frequency. At high frequencies (up to 100 MHz), the real part of the permeability ($\mu’$) decreases and imaginary part ($\mu’’$) increases rapidly. Between 100 MHz and 10 GHz ferromagnetic resonance usually occurs. [52]

The magnetic properties of samples were measured as a function of frequency with an Agilent E4991A RF Impedance/Material analyzer (Agilent Technologies, Palo Alto, CA). Composite samples were modified in shape from as-moulded solid disks to cylindrical toroids. Samples were measured with a coil structured
16454A magnetic material test fixture. The measurement accuracy depends on the sample thickness, surface quality, toroid size and permeability of the material. The error in measured magnetic loss tangent decreases within increasing material permeability and measurement frequency.

In consequence of the relatively poor measurement accuracy for low permeability materials below 10 MHz, the measurement frequency was limited from 10 MHz to 1 GHz. To improve accuracy (at least with respect to comparisons between different samples), the measured samples were consistently polished and their dimensions were kept constant. Gross errors were eliminated by measuring each sample several times.

**Miniaturisation properties**

The length of an electromagnetic wave propagating inside a material is given by (Eq. 7), where $\lambda_c$, $\lambda_0$, $\varepsilon_r$ and $\mu_r$ are the wavelength in the material, the wavelength in a vacuum, the relative permittivity and the relative permeability of materials, respectively [11]

$$\lambda_c = \frac{\lambda_0}{\sqrt{\varepsilon_r \mu_r}}. \quad (7)$$

Hence the size reduction of electromagnetic waves in materials can be controlled by the permittivity and permeability of the material. The miniaturisation factor can be described by (Eq. 8) [53–55]

$$\text{Miniaturisation factor} = \frac{1}{\sqrt{\varepsilon_r \mu_r}}. \quad (8)$$

As regards miniaturisation, it should thus be noticed that, instead of using materials with just a high permittivity, it is more advantageous materials with moderate values of permittivity and permeability combined. Furthermore, the impedance ($Z_m$) of the material is given by (Eq. 9) [11]

$$Z_m = \eta_0 \sqrt{\frac{\mu_r}{\varepsilon_r}}. \quad (9)$$

where $\eta_0 = \mu_0/\varepsilon_0$ is the impedance of free space, $\mu_0$ and $\varepsilon_0$ are the permeability and permittivity in a vacuum, respectively. So, if the ratio between $\varepsilon_r$ and $\mu_r$ becomes 1, the matching between two intrinsic impedances is reached thus increasing the
antenna efficiency as a consequence of the disappearance of reflections and surface waves [56]. With almost equal values of permittivity and permeability, improvements of antenna properties can also be expected. Hence the characteristic impedance of the material is described (Eq. 10)

$$\eta_m = \sqrt{\mu_\mu / \varepsilon_\varepsilon_0}.$$ \hspace{1cm} (10)

Zero difference in characteristic impedance ($\eta_0 = \eta_m$) indicates perfect impedance matching, hence the difference in characteristic impedance from free space becomes (Eq. 11.) [53, 55]

$$Z_{\text{diff}} = 1 - \left( \sqrt{\frac{\mu_\mu_0 / \varepsilon_\varepsilon_0}{\mu_0 / \varepsilon_0}} \right).$$ \hspace{1cm} (11)
3 Two-phase composites

3.1 Dielectric properties

Throughout the measured frequency range from 1 MHz to 1 GHz, the behaviour of the permittivity and the loss tangent for BST-polymer composites was remarkably stable. Minor wobbles were noticeable in some cases at lower frequencies (< 10 MHz), but these were artefacts associated with the greater inaccuracy of the apparatus in this frequency range as stated earlier.

Dielectric properties (\(\varepsilon_{\text{com}}, \tan \delta_e\)) of BST–ER140 with varying filler loadings (19–37 vol.%) measured from 10 MHz to 1 GHz are presented in Figure 5 [Paper III]. The results show that the measured samples exhibited very low frequency dispersion in relative permittivity and dielectric losses. The permittivity and dielectric loss tangent of composites are increasing with filler loading, which is in line with other studies of BST-polymer composites [4, 5, 57]. In SrTiO\(_3\)–POE composites with 40 vol.% filler loading, relative permittivity of 11 and dielectric loss of 0.01 at 900 MHz have been reported [6]. For BST–PPS composites with 70 vol.% loading, a relative permittivity of 13.5 and dielectric losses of 0.0025 at 1 GHz have been obtained [5]. In Bi\(_2\)O\(_3\)–ZnO–Nb\(_2\)O\(_5\)–PTFE composites with 60 vol.% filler loading, a permittivity of 12.5 and dielectric losses of 0.001 at 800 MHz were obtained [8]. Thus, the achieved permittivity (\(\varepsilon_{\text{com}} = 15\)) and dissipation factor (\(\tan \delta_e = 0.008\)) at 1 GHz region for BST–ER140 composites with 37 vol.% filler loading proved to be competitive.
The relative permittivities of the BST_{F}–COC and BST_{F}–PPS with different volume fractions of the ceramic at 1 GHz are shown in Figure 6. Differences observed in permittivities can be explained by higher intrinsic permittivity of PPS.

The permittivities of the composites ($\varepsilon_{\text{com}}$) for different polymers and loadings were calculated using the modified Lichtenecker equation (Eq. 2). For the fitting factor $k$ a value of 0.3 has been reported for well dispersed polymer–ceramic composite [40] and for BST–COC and BST–PPS composites 0.43 and 0.37, respectively [4, 5]. In the calculations $\varepsilon_{\text{com}}$ was matched with the measurement results by fitting the constant $k$ (Figure 6). As the filler loading is increased the variation of the predicted results increases between minimum and maximum values for the fitting factor $k$. At maximum filler loading in the BST_{F1}–PPS and BST_{F1}–COC composites, the variation of measured values reaches 33% and 18%, respectively, while at minimum filler loading the variations are 7% and 5%, respectively. [Paper I]
In previous studies by Xiang et al. [6], it was observed that the experimentally measured properties of SrTiO$_3$–POE composites were in good agreement with Bruggeman’s model. In BZN–PTFE composites, the experimental data was fitted to a modified Bruggeman equation where the phenomenon of percolation was taken into account [8]. It was found by George and Sebastian that the Maxwell–Garnet model matched well with experimental values in CLNT (CaLiNbTiO)–epoxy composites [58]. As the differential equation combines the small filler loading properties of the Maxwell–Garnett equation and the percolation properties of Brugeman equation, the percolation threshold of the composites can be a priori unknown. Figure 7 presents the calculated predictions of relative permittivity as a function of filler loading using equations 3 (Maxwell–Garnett), 4 (Bruggeman) and 5 (Differential) composites with measured values of each composites with varying loading levels at 1 GHz. With all measured composites, the differential equation (Eq. 3) showed the best correspondence with the measured values. [Paper V]
3.2 Magnetic properties

Measured real ($\mu'$) and imaginary parts ($\mu''$) of the permeability and magnetic loss tangent ($\tan\delta\mu$) of MnZn–ER182 and Co$_2$Z–ER182 composites with different ceramic volume fractions are shown in Figure 8. The $\mu'$ shows slightly declining behaviour for MnZn ferrite composites together with greatly smoothened features compared to the characteristics of the corresponding bulk material. In the case of Co$_2$Z (Figure 8 b), the results are not as obvious due to the already stable $\mu'$ of Co$_2$Z bulk material within the available frequency bandwidth, and therefore further research is required.

The behaviour with Co$_2$Z composites is expected to be analogous with MnZn ferrite counterparts. Lower magnetic losses were obtained with Co$_2$Z–ER182 composites as $\tan\delta\mu$ values of 0.06 and 0.009 at 100 MHz were measured for bulk Co$_2$Z and the composite with the highest loading. Co$_2$Z–ER182 composites with 36% and 43% by volume of ceramic exhibited only small differences in Figure 8 b), though large discrepancies should be expected near the percolation threshold.

As there is no detectable peak in the imaginary part of the permeability of the composites (Figure 8), it indicates that magnetic resonances are shifted to significantly higher frequencies compared to the bulk properties of filler materials. Li et al. [10] have also noted in their studies of Co$_2$Z–PVDF composites that the resonance frequency of the two-phase composite shifts to much higher frequencies (beyond 1.1 GHz) compared to the bulk (900 MHz).

To verify this conclusion, a wider frequency bandwidth would be required as the increase of the values near 1 GHz is due to the proximity of a resonance in the apparatus (i.e. in the test fixture), which obscures the real behaviour of the
material in this region. Nevertheless, the measured properties reveal a decline of \( \mu' \) towards higher frequencies as compared with bulk samples and at the same time lower magnetic losses can be obtained.

![Fig. 8. Real and imaginary parts of relative permeability and magnetic loss tangent of (a) MnZn–ER182 and (b) Co2Z–ER182 composites with different ceramic volume fractions [II, published by permission of John Wiley & Sons, Inc.].](image)

The achieved relative permeability (\( \mu' \)) and magnetic loss factor (\( \tan \delta_\mu \)) of Co2Z ferrite–ER182 polymer composites with 36 vol.% were at 500 MHz 1.5 and 0.02, respectively. These are in the same level as the properties achieved with Co2Z–PVSDF composites with filler loading of 60 vol.% by Li et al. [10], where the achieved relative permeability was ~3.5 with a quality factor Q ~5 (Q = 1/\( \tan \delta_\mu \)), giving a magnetic loss factor of ~0.2.

For two-phase composites with thermoplastic piezoelectric polymer PVDF matrix and magnetic Co2Z inclusions the measured initial permeabilities are in good agreement with the calculations by using the Maxwell–Garnet formula over the whole volume fraction range [10]. In previous studies by Yang et al. [22], it was found that the Maxwell–Garnet formula was applicable to the measured
magnetic properties of composites comprising dielectric (SrTiO$_3$) and magnetic (NiZn ferrite) particles embedded within a thermoplastic (POE) matrix.

The measured relative permeabilities of HexaZ–ER182 and YIG–ER182 composites and their corresponding calculated values using the aforementioned mixing rules (Eq. 3, 4, 5) are presented in Figure 9. Due to the high porosity of the fabricated bulk samples, the calculated values for the composites deviate significantly from the measured values, especially in the case of YIG–ER182 composites. This might also be due to the higher bulk permeability of YIG below the cut-off frequency compared to HexaZ. For HexaZ–ER182 composites, the relative permeabilities are calculated also using a permeability of 6, as measured by Zhang et al. [48]. [Paper V]

![Fig. 9. Measured and calculated magnetic properties of a) YIG–ER182, b) HexaZ–ER182 composites at 1 GHz using different mixing equations [V, published by permission of Elsevier Ltd.].](image)

3.3 Miniaturisation effect

The miniaturisation factor (Eq. 8) and the difference in characteristic impedance from free space (Eq. 11) of MnZn–ER182 and Co$_2$Z–ER182 composites are calculated and presented in Figure 10 as a function of ceramic loading. As shown in the figure the miniaturisation factor decreases as a function of loading level. It can be explained by the enhanced permittivity and permeability which produce a decreased velocity of electromagnetic waves and a shorter wavelength at a given frequency. Correspondingly, the miniaturisation factor increases as a function of frequency due to decreased $\varepsilon'$ and $\mu'$. On the other hand, the difference in characteristic impedance increases as a function of ceramic loading, decreasing the antenna efficiency. This is caused by the increasing difference between $\varepsilon'$ and $

38
as the increase in permittivity is more pronounced as a function of ceramic loading. Thus these two characteristics are opposite to each other and compromises must be made between miniaturisation and efficiency [Paper III]. Optimum miniaturising properties and impedance matching would be achieved with equal values of permittivity and permeability. Due to the intrinsic properties of the used matrix materials (\(\mu'<\varepsilon'\)) in all fabricated ceramic–polymer composites, it is not possible to achieve the situation where \(\mu' = \varepsilon'\). The same problem was noted earlier by Do and Halloran with Co\(_2\)Z–polyethylene composites [59].

![Fig. 10. Miniaturising factor and difference of characteristic impedances from that of free space of a) MnZn–ER182 and b) Co\(_2\)Z–ER182 composites with different frequencies and ceramic loadings [II, published by permission of John Wiley & Sons, Inc.].](image)

Miniaturising properties of the MnZn–ER182 and Co\(_2\)Z–ER182 composites and ER182 polymer at 1 GHz are presented in Table 4. MnZn–ER182 composite offered the highest miniaturisation factor of 90% with 44.7 vol.% ceramic loading. Evidently lower miniaturisation factors were obtained with Co\(_2\)Z–ER182 reaching a maximum of 77% in size reduction as a consequence of the lower permeability and permittivity at 1 GHz. The magnetic losses are nevertheless significantly lower in Co\(_2\)Z–Er182 composites (Figure 8) compared to MnZn–ER182 composites with no significant differences in characteristic impedance.

Measured values show improved miniaturisation factors, impedance matching to free space and ratio of \(\varepsilon'\) and \(\mu'\) especially in the 1 GHz region compared to previous results for Yttrium Iron Garnet (YIG), Gadolinium Iron Garnet (GdIG) and their ceramic–ceramic composites reported by Fechine et al. [54]
Table 4. Ratio of $\varepsilon'$ and $\mu'$, miniaturising factor, characteristic impedance difference and antenna size reduction at 1 GHz of ER182 polymer, MnZn–ER182 and Co2Z–ER182 composites (II, published by permission of John Wiley & Sons, Inc.).

<table>
<thead>
<tr>
<th>Material</th>
<th>Ceramic loading [vol.%]</th>
<th>$\varepsilon'/\mu$</th>
<th>$\sqrt{\mu/\varepsilon}$</th>
<th>$Z_{\text{eff}}$</th>
<th>size reduction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnZn–ER182</td>
<td>18.1</td>
<td>2.72</td>
<td>0.29</td>
<td>0.39</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>26.3</td>
<td>3.45</td>
<td>0.19</td>
<td>0.46</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>37.8</td>
<td>4.68</td>
<td>0.13</td>
<td>0.54</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>44.7</td>
<td>7.05</td>
<td>0.09</td>
<td>0.62</td>
<td>90</td>
</tr>
<tr>
<td>Co2Z–ER182</td>
<td>20.6</td>
<td>3.43</td>
<td>0.34</td>
<td>0.46</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>28.2</td>
<td>4.00</td>
<td>0.30</td>
<td>0.50</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>35.7</td>
<td>4.74</td>
<td>0.26</td>
<td>0.54</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>43.0</td>
<td>6.09</td>
<td>0.23</td>
<td>0.59</td>
<td>77</td>
</tr>
<tr>
<td>ER182</td>
<td>0</td>
<td>2.41</td>
<td>0.63</td>
<td>0.34</td>
<td>37</td>
</tr>
</tbody>
</table>
To overcome the challenges in achieving the high dielectric and magnetic properties without increasing filler content and thus jeopardizing the mechanical properties, a third phase was added into the composites. In this research, various amounts of nanosize conductive (nAg), semiconductive (nSi) and dielectric (nAl2O3) were added into BST-polymer composites. Previously, an increase in relative permittivity had been gained at the cost of increased dielectric losses by utilizing BST nanoparticles [4]. More recently, a small amount of silver was used to enhance the dielectric properties of ceramic–metal (BST+BCB–Ag) composites, where changing the volume fraction of silver from 0 to 0.14 yielded an increase in the relative permittivity from 50 to 450 [60]. In ceramic–polymer composites, the effect of silver particle additions has been studied in CLNT–epoxy composites, where 5 vol.% silver addition increased the relative permittivity from 8 to 11 at 1 MHz [58]. A 1 vol.% addition of multiwall carbon nanotubes into BaTiO3–PVDF composites with 20 vol.% filler loading improved the relative permittivity without affecting the loss factor at low frequencies (1 kHz) [61].

The calculated average particle–particle distance [62] for BST particles in BST–ER140 composites with additive materials was ~700 nm (Figure 3) being far from tunnelling distances. This for instance, in CNT–epoxy composites, is 1.8 nm [63]. On the other hand, inclusions with higher conductivity than that of the matrix will cause interfacial or Maxwell–Wagner–Sillars polarization, which has a major influence in the acoustic frequency regime, i.e. 10 Hz – 1 MHz. Thus, it is not expected to have a major effect on high frequency properties. [39, 40]

Hence is expected that the nanoadditives with large specific surface area, will lead to an exceptionally large interfacial area (Figure 11), so increasing the permittivity of composites. [64] Accordingly, a large area of the polymer matrix has altered properties. [50, 65] In such cases, nanoparticles will introduce a two-fold enhancement: There is a primary effect due to the higher permittivity of the additive materials entering the matrix. But there is also a secondary enhancement through improved coupling of the matrix and primary particles. Furthermore, even at the low volume fractions of the nanoadditives (2–6 vol.%), nearly the entire matrix can actually be interfacial region. [66]
4.1 Dielectric properties

The frequency behaviour of the BST$_p$–ER140 composites with nanoadditives had good correspondence with the reference composite, regardless of the type and volume fraction of the nanoadditives (Figure 12). It was noticeable how even small amounts of nanosized materials produced higher relative permittivity with only a slight increase in the dielectric losses in all cases, as had been observed previously with low frequency composites with carbon black addition [2]. For example, samples with 2 vol.% of nSi and nAg additions exhibited dielectric losses at the same level compared to the reference sample while the relative permittivity was increased by 44–52%. Porosity caused by the air trapped between loosely joined fibres leads to somewhat decreased dielectric properties as can be seen in Figure 12.
4.2 Comparison with two-phase composites

The net permittivity of two-phase composites can be approximated with classical dielectric mixing rules, i.e. Maxwell–Garnett and Bruggeman or with the differential mixing equation, as discussed earlier. In previous studies of three-phase composites, or composites with two fillers with different properties embedded in a PVDF matrix, the mixing rules has been used as for two-phase composites but with the matrix material being itself two-phase composite. In other words, one filler loading was set constant, while the loading of the other was modified. [11, 12] In this study, it was attempted to keep the amount of BST loading a constant. Upon measuring the final filler loadings of fabricated composites (Table 5), it was found that the loss of filler within each composite was varying.
Table 5. Measured filler loadings and dielectric properties at 1 GHz of BST–ER140 reference composites and with nanoparticle additions. [III, reproduced courtesy of The Electromagnetics Academy].

<table>
<thead>
<tr>
<th>Composite</th>
<th>Additive</th>
<th>Add loading[vol.%]</th>
<th>Meas BST loading [vol.%]</th>
<th>Total filler loading [Vol.%]</th>
<th>$\varepsilon'$</th>
<th>tan $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BST–ER140</td>
<td>nSi</td>
<td>2 17.6</td>
<td>19.6</td>
<td>11.59</td>
<td>0.0044</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 15.0</td>
<td>19</td>
<td>12.61</td>
<td>0.0063</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6 16.4</td>
<td>22.5</td>
<td>13.06</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td></td>
<td>nAg</td>
<td>2 21.5</td>
<td>23.5</td>
<td>12.24</td>
<td>0.0042</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 22.6</td>
<td>26.6</td>
<td>15.38</td>
<td>0.0063</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6 20.8</td>
<td>26.8</td>
<td>14.60</td>
<td>0.0063</td>
<td></td>
</tr>
<tr>
<td></td>
<td>nAl$_2$O$_3$</td>
<td>2 22.2</td>
<td>24.2</td>
<td>13.56</td>
<td>0.0072</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 18.7</td>
<td>22.7</td>
<td>12.71</td>
<td>0.0090</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6 16.9</td>
<td>22.9</td>
<td>14.13</td>
<td>0.122</td>
<td></td>
</tr>
<tr>
<td>BST–ER140</td>
<td></td>
<td>18.7</td>
<td>18.7</td>
<td>5.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.9</td>
<td>22.9</td>
<td>8.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.0</td>
<td>28.0</td>
<td>9.65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As can be seen in Figure 13, the BST–ER140 reference samples without nanoparticle additions are within good and fair correspondence with the Differential and Maxwell–Garnet mixing equations, respectively. Thus, in this case, the three phase composites were treated as two-phase BST–ER140 composites and to evaluate the effect of nanoadditives the measured values were fitted by varying the permittivity of the polymer in the mixing equations.
Fitting the approximations into the measurement results of the composites with nanoadditions is done by increasing the initial permittivity of matrix from 2.35 to as high as needed. Perfect fit is achieved using matrix permittivity of 6.50 in the calculations, as can be seen in Figure 13. To affirm the effect of nanoadditive loadings itself, nSi–ER140 and nAl₂O₃–ER140 composites were fabricated. With 6 vol.% of nSi the relative permeability increases from 2.35 to 2.59 and with 10 vol.% loading of nAl₂O₃ and relative permittivity of 2.90 is achieved [Paper III]. This confirms the assumption that the nanoadditives create large areas of interface and so increase the net permittivity of composites.
5 Periodic composite structures

Layered dielectric/ferromagnetic materials have been explored for microwave applications. In these materials, the large saturation magnetization of ferromagnetic material is combined with the low losses of dielectrics [67]. Other layered composites have been studied including piezoelectric–piezomagnetic [68] and piezoelectric–magnetostrictive [69] materials. [Papers IV, V]

5.1 Layered composite structures with dielectric properties

In Paper IV, two different periodic structures (vertical and horizontal, Figure 14) were constructed from the BSTp–COC composite materials (Table 6).

<table>
<thead>
<tr>
<th>Layer</th>
<th>BSTp loading [vol.%]</th>
<th>ε'</th>
<th>tan δ,</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2.4</td>
<td>0.0002</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>2.9</td>
<td>0.0016</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>3.5</td>
<td>0.0016</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>7.3</td>
<td>0.0014</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
<td>8.1</td>
<td>0.0017</td>
</tr>
<tr>
<td>5</td>
<td>37</td>
<td>18.3</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Layers with high filler loading and thus higher permittivity but decreased mechanical properties are combined with rigid layers having a lower filler loading and permittivity. Thus structures with spatially modulated permittivities, losses and mechanical properties are created. The dielectric properties in the frequency range from 1 MHz to 1 GHz of each layer and periodically layered structures were investigated. The vertical structures can also be considered as a “2–2 type” composite (Figure 14, samples A–D), in which case the layers are perpendicular to the electric field. The horizontal can be treated as a 1–3 type composite (Figure 14, samples E–G) where layers are parallel to the electric field [Paper IV]. Sputtered electrodes were put onto the horizontal structures covering entirely the bottom and top surfaces, such that the applied electric field was distributed evenly across all layers.
In Table 7, the average loading levels of the structures and also the relative permittivity and dielectric losses at 1 GHz are presented. The results show that the structures B and E are closely matching in average ceramic loading, but in the horizontal structure E the relative permittivity is 40% higher than in the vertical structure B. The comparison between the structures C and F shows that although the average loading level of the vertical structure C is higher, its relative permittivity is only one third of the value for the horizontal structure F. On the other hand the dielectric losses in the horizontal structure F are ~5 times higher compared to the vertical structure C. This indicates that, for horizontal structures, the high permittivity layers dominate a structure’s overall relative permittivity and dielectric losses. In the case of vertical structures, due to a non-uniform electric field distribution within the structure as proposed by Sherman et al. [70], similar behaviour cannot be obtained.

Table 7. Main properties of the periodical dielectric structures at 1 GHz [IV, published by permission of Taylor & Francis Ltd.].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Average ceramic loading [vol.%]</th>
<th>ε_r</th>
<th>tan δ,</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>21.2</td>
<td>4.83</td>
<td>0.0026</td>
</tr>
<tr>
<td>B</td>
<td>17.8</td>
<td>6.54</td>
<td>0.0031</td>
</tr>
<tr>
<td>C</td>
<td>28.4</td>
<td>6.35</td>
<td>0.0026</td>
</tr>
<tr>
<td>D</td>
<td>21.2</td>
<td>4.65</td>
<td>0.0026</td>
</tr>
<tr>
<td>Horizontal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>16.9</td>
<td>10.60</td>
<td>0.0062</td>
</tr>
<tr>
<td>F</td>
<td>26.9</td>
<td>16.95</td>
<td>0.014</td>
</tr>
<tr>
<td>G</td>
<td>15.1</td>
<td>10.11</td>
<td>0.0053</td>
</tr>
</tbody>
</table>
The relative permittivity and dielectric losses of the periodically layered structures are presented in Figure 15. Almost frequency independent behaviour of relative permittivity was obtained for both structures. In the E and G structures, there is only one composite layer with high loading, which can be addressed as lower losses and more stable frequency behaviour in Figure 15 b), while the F sample has two layers with the highest filler loading.

![Fig. 15. Dielectric properties of a) vertical and b) horizontal periodic structures [IV, published by permission of Taylor & Francis Ltd.].](image)

The expected reason for the difference in relative permittivity is that, in the horizontal structure, the distribution of the electric field is homogeneous along the surfaces whereas in vertical structures the interfaces between layers break the continuity of the electric field. Nevertheless, the field is still homogeneous inside each single layer. [70]

### 5.2 Multilayer structure with dielectric and magnetic properties

Low loss multilayered 2–2 type composite structures were fabricated and their complex permittivities and permeabilities measured in the frequency range from 10 MHz to 1 GHz. The performance of these composites was estimated using Maxwell–Garnet, Bruggeman and differential mixing theories (Eq. 3–5) [Paper V]. Periodic structures are utilized (Figure 16) consisting of alternated layers with independent permittivity and permeability for each layer (Table 8).
Fig. 16. Schematic of layered structure and realized multilayered structures with dielectric and magnetic layers [V, published by permission of Elsevier Ltd].

Table 8. Magnetic and dielectric properties of individual layers used in multilayered structure [V, published by permission of Elsevier Ltd].

<table>
<thead>
<tr>
<th>Material</th>
<th>Filler loading [vol.%]</th>
<th>(\varepsilon')</th>
<th>(\tan \delta_{\varepsilon})</th>
<th>(\mu')</th>
<th>(\tan \delta_{\mu})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BST–ER182</td>
<td>26</td>
<td>8.8</td>
<td>0.003</td>
<td>1.1</td>
<td>0.007</td>
</tr>
<tr>
<td>HexaZ–ER182</td>
<td>30</td>
<td>4.7</td>
<td>0.008</td>
<td>1.4</td>
<td>0.025</td>
</tr>
<tr>
<td>YIG–ER182</td>
<td>28</td>
<td>4.2</td>
<td>0.012</td>
<td>1.5</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The dielectric properties of the multilayer structures were measured in two ways: Either the dielectric layer or the magnetic layer against the positive electrode of the measurement fixture. Alignment of the multilayer structure was also tested in the measurement of the magnetic properties.

The dielectric and magnetic properties of periodic dielectric-magnetic multilayers as a function of frequency are presented in Figure 17. Stable behaviour of dielectric properties and relative permeability was observed for both multilayer structures, while the magnetic properties of the YIG–BST showed significantly increasing losses towards higher frequencies. In both of the structures, higher permittivities and lower losses were obtained when the dielectric side of the structure was towards the positive electrode, but no noticeable corresponding effect was observed in the magnetic properties.
When the electric field is parallel and the magnetic field is perpendicular to the lamination planes, the effective permittivity for the whole multilayer composite structure can be calculated with Eq. 12

\[
\varepsilon_{\text{com}} = \frac{1}{\sum h_i \varepsilon_i},
\]

where \( i = 1, 2, 3 \), is the number of layers (Figure 16 a), \( h_i = d_i/d \), \( d = \sum d_i \) and \( d_i \) is the thickness of \( i \):th layer [71–73]. The same equation can be used to calculate the effective magnetic permeability of a layered structure, in which case \( \varepsilon \) is replaced with \( \mu \). The structure presented contains periodic layers (Figure 16 b) with the same thickness and in which \( \varepsilon_1 = \varepsilon_3, \mu_1 = \mu_3 \) and \( \varepsilon_2 = \varepsilon_4, \mu_2 = \mu_4 \). Thus (Eq. 12) can be written as

\[
\varepsilon_{\text{com}} = \frac{2(\varepsilon_1 + \varepsilon_2)}{\varepsilon_1 \varepsilon_2}.
\]

By using Eq. (5) and Eq. (13) the effective properties of multilayer composite material consisting of layers of two phase composites can be calculated [Paper V].
Taking into account the thin polymer layer observed (Fig. 4c) in microstructure analysis, Eq. (12) becomes as follows:

\[
\varepsilon_{\text{com}} = \frac{\varepsilon_r \varepsilon_m}{2h_{\text{com}} \varepsilon_m (\varepsilon_1 + \varepsilon_2) + \varepsilon_r \varepsilon_2},
\]

where \( \varepsilon_m \) is the permittivity of the thin matrix polymer layer, \( h_{\text{com}} \) and \( h_m \) are the relative thicknesses of the composite and polymer layers to the complete structure, respectively. In this case the \( h_{\text{com}} \) is 0.25 and the \( h_m \) is 0.001.

The measured effective permittivities and dielectric losses of the multilayered structures are nicely in line with the values calculated with the different equations (Table 9). Regarding their magnetic properties, however, the calculations gave values that were too positive, i.e. higher permeability and significantly lower losses, compared to measured values. This might be due to a demagnetization effect of the randomly orientated particles and further research is required in this area. [Paper V]

| HexaZ–BST–ER | | | | |
|--------------|----------------|----------|----------------|
| Measured     | 6.4            | 0.005    | 1.18           | 0.049          |
| Eq. 13       | 6.1            | 0.004    | 1.22           | 0.11           |
| Eq. 14       | 6.1            | 0.004    | 1.22           | 0.01           |

| YIG–BST–ER   | | | | |
|--------------|----------------|----------|----------------|
| Measured     | 6.4            | 0.005    | 1.25           | 0.24           |
| Eq. 13       | 5.7            | 0.005    | 1.28           | 0.014          |
| Eq. 14       | 5.7            | 0.005    | 1.28           | 0.013          |

Good correspondence (discrepancy below 10%) with measured results, excluding magnetic losses, was exhibited by utilizing Eqs. 13 and 14. The observed thin polymer layers had only very minor influence on the results as indicated by the calculations.
6 Conclusion

The primary goal of this thesis has been to develop and study the high frequency properties of two-phase ceramic polymer composites based on thermoplastic polymer matrices with dielectric or magnetic fillers, to benefit the fabrication and optimization of advanced mass-producible RF and microwave components. The study focuses on their high frequency dielectric and magnetic properties and how they might be enhanced through the inclusion of nanoadditives or by the layering of different composite material together in periodic heterostructures.

In the first part of the thesis, the fabrication methods used for making two-phase 0–3 connectivity composites as well as relevant measurement techniques were described. The fabrication of periodical composite structures was also presented. Composites over ranges of filler loadings (from 0 to 47 vol.%) were studied and the applicability of different mixing equations discussed. It should be noted that, in this work, the functionalising, coating, drying and particle size distribution of filler materials were not performed, since the main scope was to investigate the effect on the pure phases of mixing them, and subsequently of layering different composites.

The microstructure analysis showed that, in the case of two-phase composites, the ceramic filler homogeneously distributed into the polymer matrix regardless to the filler loading and matrix polymer used. Neither large voids nor agglomerates were detected. In composites with nanoadditions, especially in the case of nAl₂O₃ fibres, clusters with diameter of 0.5–2 µm were observed, which worsened their dielectric properties. In the multilayered structure comprising alternate dielectric and magnetic layers, the layers were found to be well attached to each other with no delaminations or air gaps. However, a thin layer of pure polymer was observed between the middle layers of some fabricated structures. This layer was segregated from the composite material during the lamination process when the polymer was molten (or at least softened) and could thus easily flow. The effect of this thin pure polymer layer into the electrical properties was shown to be minimum.

Throughout the measured frequency range of 1 MHz to 1 GHz, the behaviour of dielectric properties, relative permittivity and loss tangent of BST–polymer composites were remarkably stable. The relative permittivity and dielectric loss tangent increased with filler loading. Utilising the Lichtenecker’s equation, variations of the fitting factor \( k \) were investigated over the sample range. More importantly, large differences in the fitting factor were noticed between different
polymer matrices even though the ceramic filler was the same. Also effective–
medium theories, Maxwell–Garnet, Bruggemann and Differential equations were
used to analyse the measurement results. For BST–ER182, HexaZ–ER182 and
YIG–ER182 composites, the differential mixing equation showed the best
correspondence with the measured dielectric values.

Composites with 0–3 connectivity had greatly decreased $\varepsilon'_r$ and $\mu'_r$ compared
to their bulk ceramic counterparts, though this was wholly expected. Promising
levels of miniaturisation could nevertheless still be obtained with the MnZn–
ER182 and Co$_2$Z–ER182 composites, especially at higher frequencies near 1 GHz.
Furthermore, it was observed that the miniaturisation and impedance matching to
free space in the composites exhibited opposite trends.

The dielectric properties of 0–3 type BST–ER140 thermoplastic ceramic–
polymer composites with nanoadditive materials (nSi, nAg, nAl$_2$O$_3$) showed
significant increases of relative permittivity with all additives while the dielectric
losses and frequency dispersion were at levels similar to those of samples without
additives. Especially nanosilver addition was observed to be extremely effective
at improving the dielectric properties of the composites. Only a 2 vol.% addition
could boost the relative permittivity from $\varepsilon_r = 8.1$ to $\varepsilon_r = 12.2$ (an increase of 52%)
without increasing the dielectric losses (the latter property, as measured, went
from $\tan \delta_e = 0.0047$ for no nAg to $\tan \delta_e = 0.0042$ at 2 vol.% nAg).

Periodically layered BST–COC composite structures could, by interleaving
ductile layers of low–permittivity with relatively more brittle layers of high
permittivity, provide materials that are, overall, advantageous. Measurements
showed that the dielectric properties in horizontally multilayer structures are more
efficient than in vertical ones. With dielectric–magnetic multilayer structures, a
flat frequency response of their magnetic and dielectric properties from 10 MHz
to 1 GHz was observed. The results show also that structures with low loss can be
achieved by dielectric–magnetic composites even though the initial filler material
shows significant loss values.

The advantages and the most important results are:

1. Materials with relatively high permittivity with low losses can be fabricated.
2. Significant reductions of filler loading by the utilization of Si and Ag
   nanoparticles, and thus improved mechanical properties, can be expected.
3. Polymer ceramic composites with magnetic properties can be used over much
   wider frequency ranges than pure bulk ceramic ones.
4. Magnetic polymer ceramic composites offer significant antenna size reduction with good impedance matching for free space.

5. The measured properties in composites and their structures were close to the calculated ones, thus facilitating the design of materials and enabling the exploitation of additional degrees of freedom by structural designing.

6. Composites materials with good high frequency properties yet without compromised mechanical properties can be achieved with periodical structures.

The research results of the ceramic polymer composites and their structures have demonstrated their potential advances in high frequency application, such as in antenna miniaturisation. More work still needs to be done to obtain the miniaturisation advantages of dielectric–magnetic composites in an antenna demonstrator. And after the properties of basic two-phase composites have been fully characterised, the three phase composites and composites using modified fillers (drying, surface coatings, etc.) requires further investigation. Also, the true possibilities of periodical and multilayered structures can be proven only with actual devices.
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